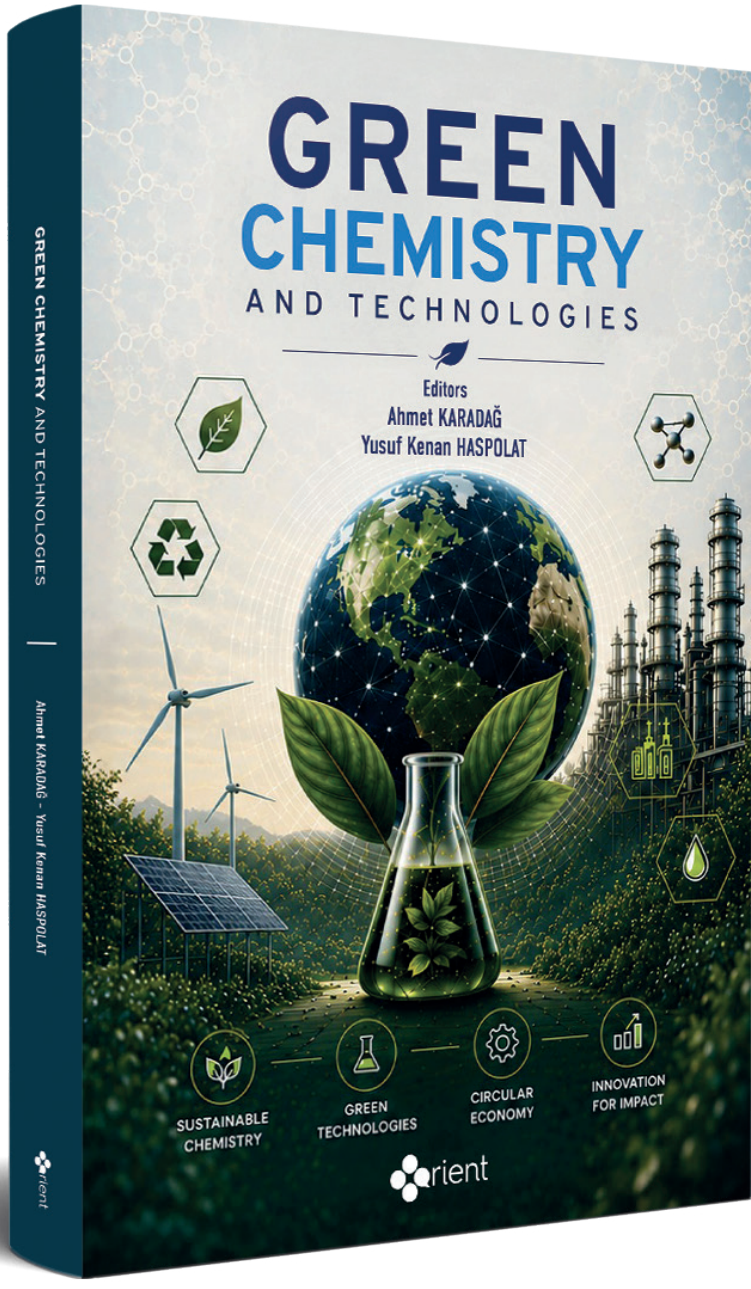
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Editors
Ahmet KARADAĞ
Yusuf Kenan HASPOLAT

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PREFACE

The global chemical enterprise is currently undergoing its most profound transformation since the Industrial Revolution. As planet-wide ecological boundaries are pushed to their critical limits, the traditional mandate of chemistry is shifting from a narrow focus on molecular synthesis efficiency toward a systemic integration of socio-ecological responsibility, digital intelligence, and long-term planetary resilience. This e-book, titled *"Green Chemistry and Technologies,"* emerges at this very historical juncture, serving not merely as a compilation of scientific literature, but as a comprehensive blueprint for designing a sustainable, climate-compatible, and equitable future civilization.

As the editors of this volume, our primary objective was to assemble a multi-disciplinary framework that bridges the historical gap between microscopic molecular engineering and macroscopic sustainability policies. Throughout the chapters of this book, esteemed researchers explore cutting-edge paradigms that extend far beyond the classical Twelve Principles of Green Chemistry. From the integration of cyber-physical platforms, machine learning, and digital twins to advanced single-atom catalysis, renewable carbon management, and circular bioeconomy architectures, this work offers actionable technological pathways to decouple industrial growth from environmental degradation and fossil-fuel reliance.

An academic endeavor of this magnitude is inherently a collective triumph. First and foremost, we extend our deepest gratitude and profound appreciation to the contributing authors. Your scholarly rigor, visionary research, and unwavering dedication to **global environmental stewardship** have formed the backbone of this treatise. Each chapter reflects a unique intellectual commitment to redefining how human intellect and chemical systems intelligently interact with ecological processes and societal well-being.

Furthermore, a special and distinguished token of appreciation is reserved for **Orient Publishing (Orient Yayınevi)** and its esteemed editorial and publication board. Their visionary support, meticulous attention to structural quality, and belief in the global necessity of this project have been indispensable in transforming this conceptual manuscript into a state-of-the-art digital reality.

Ultimately, we present this e-book to the scientific community, policymakers, and future generations of chemical innovators. It is our sincere hope that the paradigms proposed herein will inspire deeper interdisciplinary collaborations, ignite educational reforms, and serve as a foundational catalyst for global environmental stewardship. The transition toward regenerative chemical technologies is no longer an optional trajectory; it is the defining responsibility of modern science in the twenty-first century.

Editors
Ahmet KARADAĞ
Yusuf Kenan HASPOLAT

ÖNSÖZ

Küresel kimya sektörü, Sanayi Devrimi'nden bu yana en köklü dönüşümünü yaşamaktadır. Gezegen ölçeğindeki ekolojik sınırlar kritik limitlerine dayanırken, kimyanın geleneksel misyonu da dar bir moleküler sentez verimliliği odağından; sosyo-ekolojik sorumluluğun, dijital zekanın ve uzun vadeli gezegensel dayanıklılığın bütünleşik bir sistemine doğru evrilmektedir. "*Green Chemistry and Technologies*" (Yeşil Kimya ve Teknolojileri) başlıklı bu e-kitap, tam da bu tarihi dönüm noktasında ortaya çıkmakta; yalnızca bilimsel literatürün bir derlemesi olarak değil, sürdürülebilir, iklimle uyumlu ve adil bir geleceğin inşası için kapsamlı bir rehber olarak hizmet etmektedir.

Bu eserin editörleri olarak temel amacımız; mikroskobik moleküler mühendislik ile makroskobik sürdürülebilirlik politikaları arasındaki tarihsel boşluğu kapatan çok disiplinli bir çerçeve bir araya getirmekti. Kitabın bölümleri boyunca değerli araştırmacılar, Yeşil Kimyanın klasik On İki İlkesinin çok ötesine geçen son teknoloji paradigmaları incelemektedir. Siber-fiziksel platformların, makine öğreniminin ve dijital ikizlerin entegrasyonundan; gelişmiş tek atomlu katalizörlere, yenilenebilir karbon yönetimine ve döngüsel biyoelektrik mimarilerine kadar bu çalışma, endüstriyel büyümeyi çevresel tahribattan ve fosil yakıt bağımlılığından ayırmak (decoupling) için uygulanabilir teknolojik yollar sunmaktadır.

Bu büyüklükteki bir akademik çaba, tabiatı gereği kolektif bir başarıdır. İlk ve en önemli olarak, kitaba katkı sağlayan tüm değerli yazarlarımıza en derin şükranlarımızı ve takdirlerimizi sunarız. Akademik titizliğiniz, vizyoner araştırmalarınız ve küresel çevre yönetimine (stewardship) olan sarsılmaz bağlılığınız bu eserin omurgasını oluşturmuştur. Her bir bölüm, insan zekasının ve kimyasal sistemlerin ekolojik süreçlerle ve toplumsal refahla nasıl akıllıca etkileşim kurabileceğini yeniden tanımlamaya yönelik benzersiz bir entelektüel adanmışlığı yansıtmaktadır.

Ayrıca, Orient Yayınevi'ne ve onun saygın yayın ile yayın danışma kuruluna özel ve ayrıcalıklı bir teşekkürü borç biliriz. Onların vizyoner desteği, yapısal kaliteye gösterdikleri titiz özen ve bu projenin küresel gerekliliğine olan inançları, bu kavramsal taslağın modern bir dijital gerçekliğe dönüşmesinde vazgeçilmez bir rol oynamıştır.

Nihayetinde bu e-kitabı bilim camiasına, politika yapıcılara ve geleceğin kimyasal yenilikçilerine sunuyoruz. Burada önerilen paradigmaların daha derin disiplinler arası iş birliklerine ilham vermesini, eğitim reformlarını ateşlemesini ve küresel çevre yönetiminde temel bir katalizör görevi görmesini içtenlikle umuyoruz. Rejeneratif (yenileyici) kimyasal teknolojilere geçiş artık isteğe bağlı bir tercih değil; yirmi birinci yüzyılda modern bilimin üstlenmesi gereken en belirleyici sorumluluktur.

Editörler
Ahmet KARADAĞ
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BEYOND THE TWELVE PRINCIPLES OF GREEN CHEMISTRY: FROM FOUNDATIONAL CONCEPTS TO FUTURE CHEMICAL SYSTEMS

AHMET KARADAĞ*
FATMA ALTIN**

ABSTRACT

The Twelve Principles of Green Chemistry have served for nearly three decades as a foundational framework for designing safer, more efficient, and environmentally benign chemical processes. However, the accelerating challenges of the climate crisis, severe resource depletion, chemical pollution, and unprecedented technological complexity necessitate a critical re-examination of these principles beyond their original, reaction-centered scope. This chapter presents a forward-looking paradigm shift in green chemistry, moving from a rigid principle-based checklist toward an integrated, systems-oriented framework for next-generation chemical technologies. Rather than reiterating the established principles individually, we critically reassess their collective meaning within the context of modern cyber-physical and chemical ecosystems. Particular emphasis is placed on how digitalization (artificial intelligence, machine learning, and digital twins), catalysis-driven process intensification (single-atom, bio-, and electrocatalysis), renewable carbon management, and circular material flows are redefining prevention, efficiency, safety, and sustainability. By replacing traditional metrics with holistic frameworks like the carbon and function economies, life cycle assessment (LCA), and inherently resilient process safety, this chapter bridges foundational concepts with emerging scientific frontiers. Ultimately, this contribution establishes a unifying, adaptive conceptual framework that aligns future chemical systems with global planetary boundaries and societal needs, serving as a comprehensive guiding reference for the thematic chapters that follow in this book.

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1. INTRODUCTION: WHY REVISIT THE TWELVE PRINCIPLES OF GREEN CHEMISTRY TODAY?

In 1998 Paul Anastas and John Warner developed a guiding statement for chemical science and industry to reduce their detrimental impacts on the environment: The Twelve Principles of Green Chemistry (Anastas & Warner, 2000). These principles which were illustrated in Figure 1, offered a general framework for molecular-level design, from waste prevention and energy efficiency to the utilization of renewable feedstocks and the design of safer compounds. This radical and creative approach for the time, caused a paradigm change in chemical literature. But today, as we stand on the threshold of leaving behind the first half of the 21st century, we must address a vital question: Are the formulas of 1998 sufficient to solve the complex issues of today and tomorrow? This introduction section has been produced not to discard the 12 Principles, but to reintegrate, deepen, and "reframe" them in the realities of the present world.

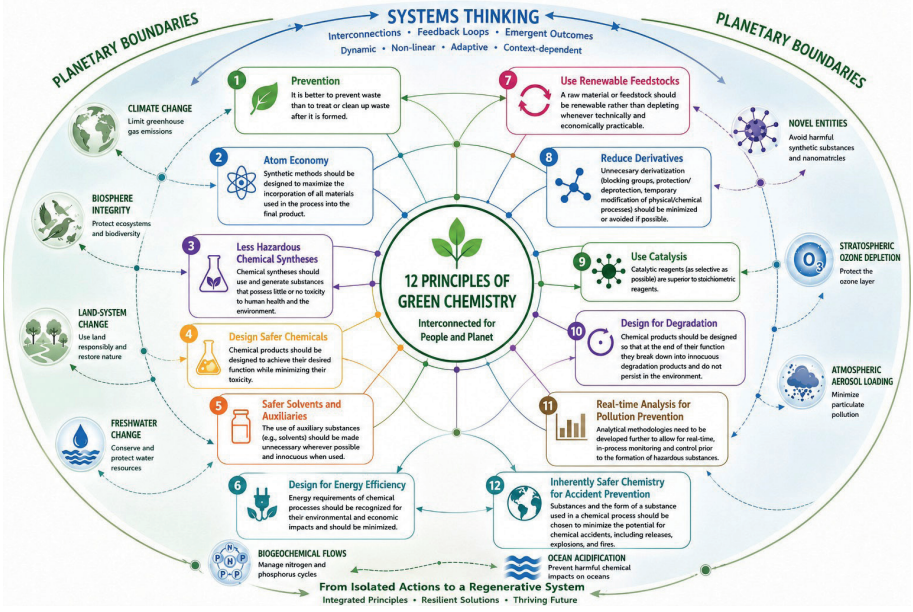

Figure 1. *The foundational Twelve Principles of Green Chemistry as established by Anastas and Warner (1998). While initially developed as a linear blueprint for laboratory-scale hazard reduction and waste prevention, these core tenets are critically reframed within this chapter as a deeply interconnected, dynamic ecosystem that interfaces with modern digitalization, advanced catalysis, and global planetary boundaries.*

1.1. The Changing Relationship Between Chemistry, Society, And The Environment Since 1998

The scope of green chemistry by the late 1990s was largely reactive and localized goals, namely, the reduction of end-of-pipe pollution and reduction of laborato-

ry-scale waste (Sheldon, 2016). The chemical industry is often viewed as a separate world: it is perceived as detrimental to the environment, yet it is necessary for modern society. In the modern period, the interaction between chemistry, society and the environment has transformed from a linear model to a complete circular and comprehensive representation. In 1998 the concept of a "safe" chemical was largely limited to occupational health and acute toxicity hazard regulations. But modern civilization examines the carbon footprint of a product, microplastic emissions and bioaccumulable environmental impacts including those related to "forever chemicals" (PFAS) (Brooks, 2019). Chemistry is no longer limited to the laboratory. It is now an integral part of a vast global network, encompassing raw material extraction, such as mining and agriculture, and end-of-life product management. Figure 2 presents the evolution of green chemistry from 1998 to the present.

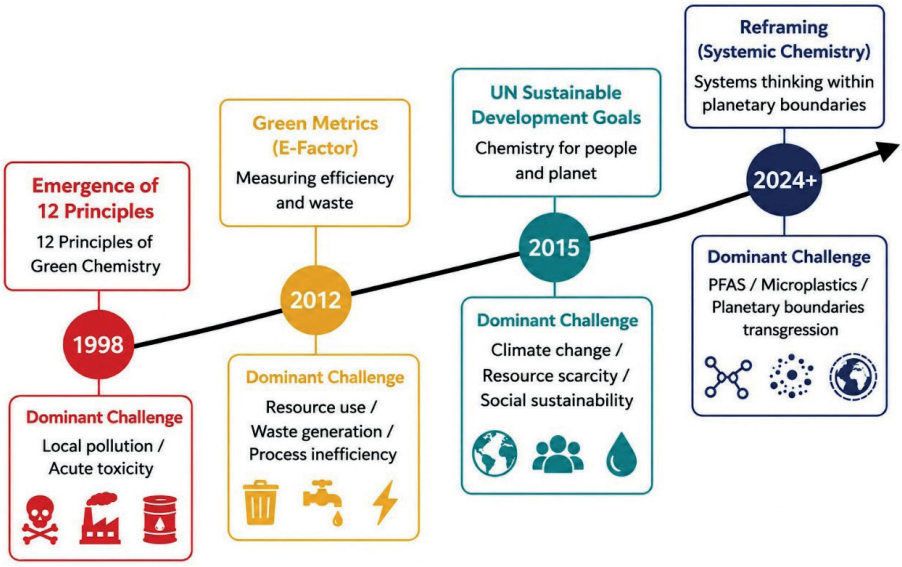

Figure 2. *A Descriptive Timeline of Key Milestones in Green Chemistry: From Theory and Metrics to Global Sustainability and Systemic Reconfiguration. This timeline highlights the evolution of green chemistry from the establishment of its foundational principles in 1998 to its current systems-based approach, marked by advances in green metrics, integration with the SDGs, and a growing focus on sustainability across environmental, social, and economic dimensions.*

Therefore, the connection between chemistry and the environment is not only about regional solutions like the rehabilitation of a regional river, but also about the comprehensive protection of the global biosphere.

1.2. Climate Crisis, Resource Scarcity and Systemic Risks

Climate change was just a theoretical issue back in 1998; now it is a hard reality impacting our everyday lives. This transition has profoundly altered the context in which the 12 Principles are applied. The crises that we face today are not singular events but deeply connected. The shortage of water is a consequence

of the climate crisis and has a significant effect on agricultural productivity and therefore biomass-based green feedstock, influencing global supply chains. Thus, the chemical industry must not only be 'clean', but also proactively build resilience to these systemic hazards. At the time of the publication of the 12 Principles, the petroleum-centric economy was at its peak, and renewable resources were regarded just as an option. The shortage of essential raw materials and growing geopolitical problems are forcing a change in chemistry from a Linear Economy (take-make-dispose) to a Circular Economy (recover-reuse) at present (Ncube et al., 2023).

1.3. Why a 'Reframing' is Needed, Not an 'Update'?

A simple "update" that changes the articles of the 12 Principles word by word won't fix the structural problems we have now. We have to 'reframe' the philosophy of these ideas in a contemporary worldview. Table 1 provides a comparison between the 1998 approach and the reframing approach.

Reframing doesn't mean discarding or destroying the fundamentals. On the other hand, it means building on the solid foundation established in 1998 and broadening its vision through the integration of digitalisation (molecular design with artificial intelligence and machine learning), green energy (green hydrogen and electrification), circular economy and principles of a just transition. Today's re-examination of the 12 Principles of Green Chemistry is not a criticism of the past but a vital step towards the future. Chemical research must be transformed from an industry that 'minimises harm' to a restorative force that 'heals' the earth and humanity. The purpose of this section is to provide the conceptual and practical framework for this change.

Table 1. *1998 and Present: Comparative Analysis. This table describes the paradigm shift from the traditional approach to green chemistry when it was first established in 1998 to the current "Reframing" perspective, in four main categories*

Category	1998 Approach	Reframing Approach
Focus Area	Local Pollution Prevention	Global Planetary Boundaries (Rockström et al., 2009)
Supply Chain	Linear	Circular
Risk Definition	Acute Toxicity	Systemic and Persistent Risks (PFAS, Microplastics)
Energy Source	Efficieny-Focused (Fossil)	Electrification and Green Hydrogen

2. FROM PRINCIPLES TO SYSTEMS: GREEN CHEMISTRY IN A COMPLEX WORLD

The Twelve Principles were reductionist and linear in nature (introduced in 1998). The emphasis was largely on a single chemical reaction, a single laboratory flask, or a single industrial line. Improving the atom economy of a reaction or choosing a less hazardous solvent was considered a success in itself. However, the complex and highly related issues of 21st century have shown that chemistry does not take place in

isolation. Now green chemistry must move from the 'implement individual principles' phase to the 'management of complex systems' phase (Matlin et al., 2016).

2.1. Transition From Linear Principles to a Systems Approach

Traditionally, green chemistry is viewed as improving inputs and outputs along a linear pathway: raw material A is processed with technique B to produce product C with minimal waste. Systems thinking, however, disrupts this linear progression and views the process as an integral part of a large network. Expanding Boundaries in a systems approach requires more than simply measuring the "greenness" of a process based on its laboratory efficiency (Eichwald et al., 2025). Principle 7: Use of Renewable Feedstocks." Initially, the use of a renewable bio-based raw material for a process may seem ideal. But if the production of that biomass requires large amounts of fertilizer application, leads to eutrophication in aquatic systems, and competes with food production, then that chemical process can't be considered "green" at a systemic level (Felicioni et al., 2023; Tufvesson et al., 2013). This fundamental conflict between surface-level renewability and systemic sustainability is conceptualized as the Biomass and CO_2 Flow Paradox (see Figure 3). This diagram illustrates how unmonitored socio-ecological trade-offs act as critical barriers between raw feedstocks and true green chemical manufacturing.

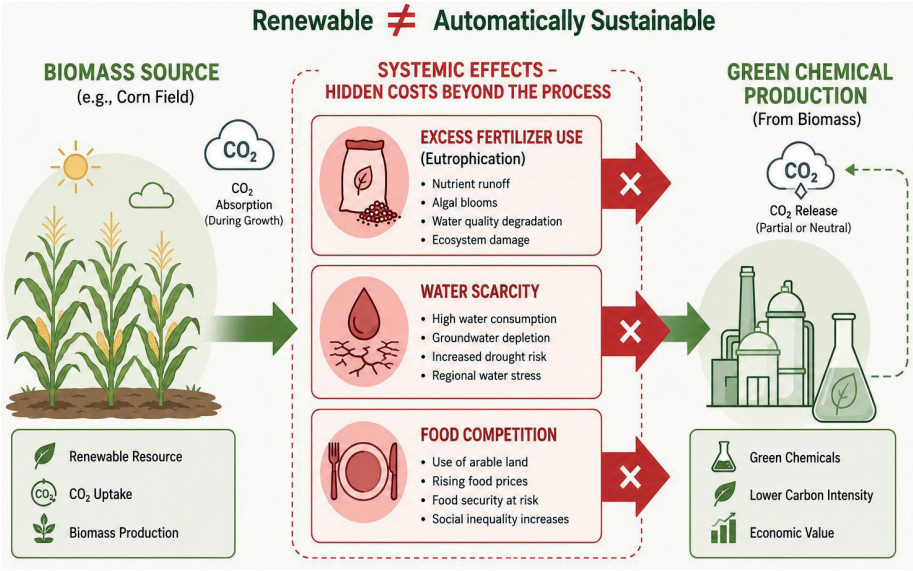

Figure 3. *The Biomass and CO_2 Flow Paradox illustrating the critical concept that "Renewable ≠ Automatically Sustainable." The diagram maps the hidden systemic socio-ecological costs that occur beyond the immediate chemical process boundaries. While bio-based feedstocks offer lower carbon intensity and renewable pathways, their macro-scale production introduces hidden friction points—such as eutrophication from excessive fertilizer runoff, regional water scarcity via groundwater depletion, and food competition over arable land—acting as barriers (red indicators) that must be comprehensively evaluated through Life Cycle Assessment (LCA) to achieve true sustainability.*

Life Cycle Assessment (LCA) is the most definitive, robust and pragmatic tool for implementing systems thinking in green chemistry and sustainability. LCA is a systematic approach for assessing the environmental impacts of a product, service or process throughout its entire life cycle- from raw material extraction and acquisition, through manufacture, transport and use, to end-of-life phases such as disposal or recycling. This is often called a "cradle-to-grave" assessment. Traditional environmental assessments usually look only at the direct emissions of a plant or the amount of trash created. Life Cycle Assessment (LCA) considers the entire system. This step is necessary to avoid shifting of environmental costs between different life-cycle stages, e.g. from production to raw material extraction. LCA considers several environmental impact categories, e.g., global warming potential, water footprint, depletion of fossil resources, eutrophication, and human toxicity. It offers comprehensive, data-driven insights for designers, engineers and decision makers to enhance products and processes at the systemic level and to improve their sustainability (Felicioni et al., 2023; Tufvesson et al., 2013).

2.2. Aligning Green Chemistry with Planetary Boundaries

The expanding boundaries of systems thinking in green chemistry must ultimately converge with the macro-scale ecological thresholds that govern the stability of the Earth system. Introduced by Johan Rockström and colleagues (2009) and later updated by Steffen et al. (2015) and Richardson et al. (2023), the Planetary Boundaries framework defines nine critical biophysical thresholds within which humanity can safely operate and develop. Emerging green chemistry paradigms are increasingly shifting away from simply maximizing laboratory reaction yields toward explicitly preventing the transgression of these global boundaries. When viewed through this systemic macro-lens, the Twelve Principles of Green Chemistry cease to be mere operational metrics for synthetic efficiency; instead, they serve as essential technological interventions required to keep human industrial activities within the "safe operating space" of the planet.

The most direct and critical intersection between green chemistry and the planetary boundaries lies within the domain of novel entities (chemical pollution, plastics, and synthetic materials). In 2022, a seminal assessment concluded that the planetary boundary for novel entities had already been heavily transgressed, driven by the sheer volume of synthetic chemicals introduced into the biosphere without adequate life-cycle predictability (Persson et al., 2022). Traditional environmental engineering operates reactively via end-of-pipe remediation. Conversely, next-generation green chemistry targets this boundary proactively. By integrating molecular design platforms such as advanced quantitative structure-activity relationship (QSAR) machine learning models and predictive ecotoxicity screening (Eichwald et al., 2025), green chemists can engineer novel molecular networks that are inherently benign, non-persistent, and fully degradable. This shift from reactive treatment to safe-by-design structural molecular planning is paramount to halting the irreversible accumulation of hazardous synthetic materials in global ecosystems.

Beyond chemical pollution, the systemic deployment of green chemistry directly mitigates the transgression of several other tightly interconnected planetary boundaries:

Climate Change and Stratospheric Ozone Depletion: The transition toward a circular bioeconomy—relying on renewable biomass, closed-loop carbon capture, and carbon-negative synthetic pathways—fundamentally de-links chemical manufacturing from fossil fuel extraction. Concurrently, replacing hazardous volatile organic solvents with benign designer matrices like advanced bio-derived deep eutectic solvents and non-ozone-depleting ionic liquids protects atmospheric integrity while minimizing cumulative greenhouse gas (GHG) footprints.

Biogeochemical Flows (Nitrogen and Phosphorus Cycles): Industrial agriculture and bulk chemical production have heavily disrupted global nitrogen and phosphorus cycles, leading to widespread aquatic eutrophication. Green chemistry interventions address this bottleneck by developing highly selective, slow-release green fertilizers and bio-based nutrient recovery catalysts that minimize agricultural runoff and promote circular nutrient recycling.

Biosphere Integrity and Freshwater Change: Traditional chemical processing demands vast, intensive volumetric consumption of high-purity water, often returning polluted effluents to aquatic reservoirs. By enforcing process intensification strategies—such as solvent-free synthesis, multi-step telescopic reactions, and highly selective electrocatalytic systems operating close to theoretical thermodynamic limits (Yang et al., 2013)—green engineering heavily minimizes the freshwater withdrawal footprint and safeguards biological habitats from chemical stress.

Ultimately, mapping green chemistry onto the Planetary Boundaries framework elevates the discipline from a localized industrial methodology to a foundational planetary stewardship science. By reconciling the molecular mechanics of catalysis with the macro-dynamics of global biogeochemical flows, this integrated framework guarantees that technological advancements actively contribute to regenerative planetary resilience rather than ecological destabilization.

2.3. Integration of Chemical Processes with Ecosystems, The Economy and Society

The integration of chemical processes with ecosystems, the economy and society is one of the most important and complex networks that supports the functioning of the modern world. Chemistry is not a laboratory discipline; it is a fundamental basis, built in to nature, that drives economic mechanisms and shapes social dynamics. We can think of this integration as a triple helix, a way of expressing the interconnection of different dynamics.

It is a hybrid model that integrates principles from Green Chemistry and Industrial Ecology, that is, the combination of chemical processes and ecology. This approach expands the traditional product-oriented view and provides a systems-based framework to improve the environmental sustainability of chemical production.

Integration is at three main levels with the application of Green Chemistry principles at the individual product level to develop cleaner methods of production, with improved selectivity and better utilization of raw materials and reduction of waste formation. Ecological considerations increase dramatically at the level of the product food web as the scope of the system expands. In a chemical park, vertical and horizontal integration of enterprises allows the waste or by-products of one enterprise to be used as raw materials by other enterprises. At the infrastructure sharing level, resource efficiency is improved by sharing common utilities such as energy systems, water supply and wastewater treatment facilities, under an eco-industrial development framework. This integration is important because Green Chemistry alone can still lead to high waste generation, particularly in the case of multi-step syntheses with high E-factors. By integrating Industrial Ecology concepts, these wastes can be reintroduced into an industrial ecosystem instead of being treated as disposable, greatly improving the overall material efficiency (Hao et al., 2017).

The integration of chemical processes into the economy and society is based on a systematic approach linking cost effectiveness, social good and long-term sustainability. The integration is primarily driven by cost minimization and competitive advantage. Reducing waste at the source; rather than after generation, reduces operational costs and improves efficiency of raw materials. Lower E-factors mean that less material is input, there is less cost to deal with waste, less energy is required and production capacity is better used. This shows that green chemistry is not only good for the environment but also for the economy. In addition, catalysis and biocatalysis are of great importance for the resource efficiency by reducing the use of scarce or expensive metals, reducing the reaction pathways, and reducing energy consumption. The internalization of external costs is a key factor for the achievement of full integration, being necessary to incorporate the environmental degradation and resource depletion within the industrial economics through new sustainability-oriented indicators (Sheldon, 2016).

The integration is based on the principle of "benign by design" which prioritises human health and environmental safety by minimising exposure to toxic compounds for both workers and end consumers, as was the case with historical dangerous chemicals such as DDT. It emphasizes the ethical use of resources in the transition to a bio-based economy with a preference for agricultural residues over food-based biomass, which minimizes competition with the food supply and addresses social responsibility issues. Moreover, the replacement of fossil fuels with renewable biomass helps reduce climate change by reducing the concentration of CO_2 in the atmosphere, while the shift from a linear "take-make-dispose" model to a circular economy ensures resource conservation for future generations through recycling and sustainable product design. The integration transforms chemical manufacturing from a purely technical activity into an integrated system that balances economic profit with social responsibility and environmental sustainability (Sheldon, 2016).

2.4. The Interdisciplinary Evolution of Green Chemistry

The concepts of green chemistry have evolved greatly within the last 30 years from the initial focus on the environmental implications and human health to a more expansive perspective. Such transformation requires chemical practice to be addressed at the laboratory level as well as in a systems, life cycle and interdisciplinary manner (Constable, 2021). Systems thinking for green (sustainable) chemistry is illustrated in Figure 4.

Green Chemistry has evolved outside the field of chemistry since its inception, and has become an interdisciplinary subject that incorporates many fields such as chemical engineering, industrial ecology, toxicology, and biology. In the early years the discipline was mostly restricted to pollution prevention (P2) and the synthesis of new processes, but it has expanded quite a bit over the years to encompass a much larger set of areas including nanotechnology, renewable energy and education. Reflecting the shift towards holistic systems thinking, the 12 Principles of Green Chemistry have increasingly been seen not as independent principles but as an integrated system. This evolutionary process has been supported by collaboration between academic and industrial partners. Thus, Green Chemistry has gradually established its own character, becoming an important, active and integrated scientific movement for the attainment of the Sustainable Development Goals (Marques & Machado, 2021).

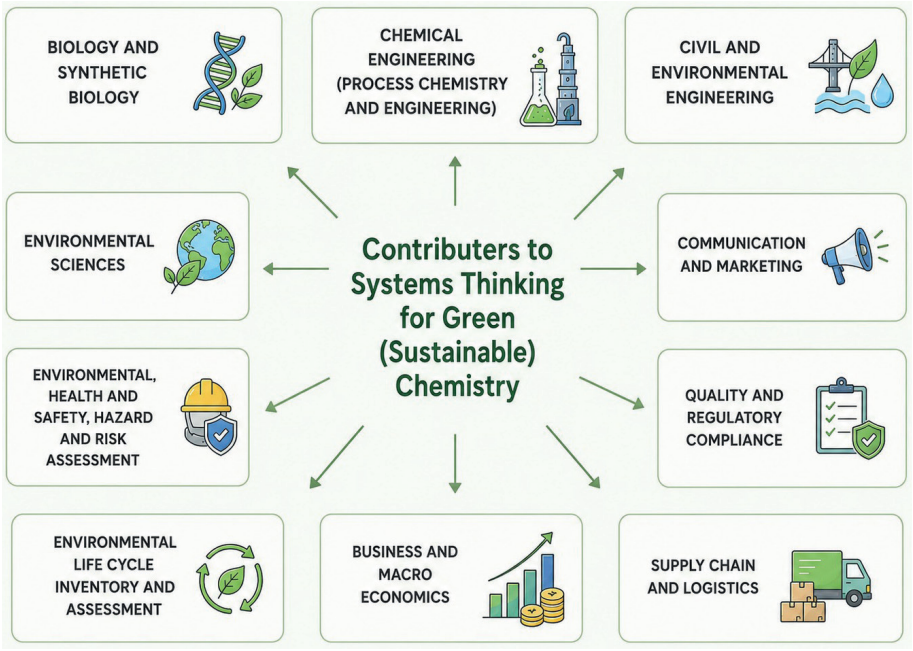

Figure 4. *Contributors to systems thinking for green (sustainable) chemistry. The figure shows the interdisciplinary collaborative network needed for the successful implementation of green (sustainable) chemistry. It demonstrates the integration of different areas of expertise: chemistry and process engineering, environmental risk assessment, supply chain management and macroeconomic factors, in the overall framework of systems thinking in the search for sustainability.*

3. RETHINKING WASTE, EFFICIENCY, AND PREVENTION

The first two principles of Green Chemistry, Waste Prevention and Atom Economy, were developed by Paul Anastas and John Warner in 1998, and are key principles of industrial chemistry. But the climate crisis, the depletion of resources and the increased sustainability demands of the 2020s have pushed these concepts beyond their traditional boundaries. Efficiency today is not only defined by the output in a reaction vessel, but also by its overall global impact on ecological, economic and societal aspects.

3.1. Redefining the Concept of "Waste"

The definition of waste is being redefined, in accordance with the principles of the circular economy and green chemistry, from the classical view of "a problem to be disposed of" to a promise of product innovation and value creation. This new paradigm breaks with the linear "extract–produce–use–dispose" model, turning material life cycles into circular systems, where items are designed from the outset for recovery, reuse and recycling. In this context, products traditionally considered as waste (e.g. biomass residues, wastewater, food waste) are increasingly recognized as important resources and high-potential by-products. Wastewater can be regarded as a source of energy and nutrients and metal contaminated soils can be regarded as a resource for metal recovery. This has led to waste being viewed as a strategic feedstock that can be turned into high-value products using advanced technologies like biotechnology and biorefineries, decreasing reliance on virgin natural resources and environmental degradation (Gutiérrez & Palos, 2023).

3.2. Circular Economy and Prevention at the Molecular Level

The circular economy is a strategic model of sustainable development, aimed at balancing economic growth, sustainability of resources and environmental protection, through the substitution of the traditional linear "take-make-use-dispose" model. It is about closing the loops of renewable materials and optimizing the systems by applying 5R practices (redesign, reduction, recovery, recycling and reuse) to improve the efficiency of resources and energy. Prevention at the molecular level is essential to achieve this circularity, a core principle of the Green Chemistry Principles (GCP) which highlights the reduction or prevention of pollution at its source before it is created. By studying the ways to avoid pollution at a molecular level it is possible to design safer compounds and more effective techniques, such as the use of catalysts instead of stoichiometric reagents, to reduce the use of dangerous substances during the lifetime of a chemical. The integration of molecular level prevention with the circular economy model ensures non-toxicity and sustainability of the materials within the system, thereby enabling safer workplaces, minimizing environmental impacts and efficient reclamation of resources (T. L. Chen et al., 2020). In Figure 5, relation between circular economy and green chemistry principles have been illustrated.

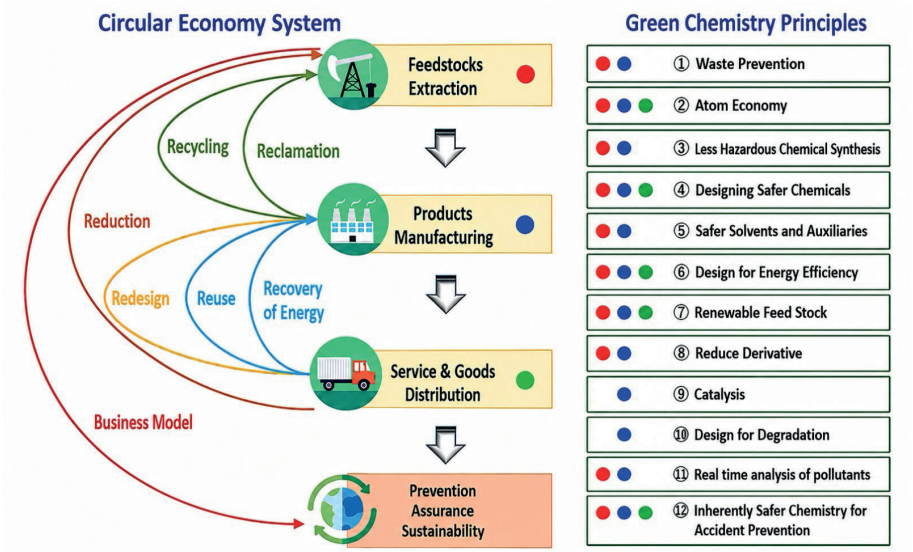

Figure 5. *The structural framework integrating the Twelve Principles of Green Chemistry with circular economy dimensions across the entire product life cycle. While fundamentally adapted from the holistic lifecycle mapping of T. L. Chen et al. (2020), this enhanced visualization explicitly accentuates the synergistic feedback loops between molecular-level design and macro-scale material recirculation. It illustrates how strategic interventions—ranging from sustainable feedstock sourcing to zero-waste end-of-life management—converge to minimize systemic environmental footprints, shifting the paradigm from linear chemical production to closed-loop industrial ecology.*

3.3. From Atom Economy to Carbon and Function Economy

Atom economy is a measure of how well the atoms in the reactants are used and included in the final product in a chemical process (Li et al., 2022). This metric evaluates how efficiently atoms are utilized in synthesis processes and how effectively waste generation is minimized by expressing the ratio of the molecular weight of the desired main product to the total molecular weight of all reactants involved in the reaction:

$$\text{Atom Economy } (\%) = \left(\frac{\text{Formula Mass of the Target Product}}{\text{Total Formula Mass of All Reagents}} \right) \times 100$$

This metric is useful for molecular weight and atom use; however, it is not sufficient by itself in the context of today's ecological and economic conditions. This limitation has resulted in a major paradigm shift in the chemical sector.

For centuries traditional chemistry has revolved around one question: "How do I synthesize this substance in the lab with the highest yield and lowest cost?" But climate change, resource depletion and environmental pollution have demonstrated that a "efficient" response is not necessarily "sustainable" for the earth. The focus is shifting from Atom Economy, which primarily looks at atom usage within chem-

ical equations, to more holistic frameworks like Carbon Economy and Function Economy that incorporate wider ecological and economic systems into sustainability assessments (Moser & Jakl, 2015).

The Carbon Economy expands on the conventional notion of atom economy to encompass not only the efficiency of the incorporation of carbon atoms into goods but also the source of those carbon atoms and their flow through the larger system. In conventional atom economy, carbon from fossil sources and carbon from renewable biological sources are treated as equivalent if they contribute equivalently to the final output. Conversely, the carbon economy focuses on the replacement of fossil-based feedstocks (petroleum, coal, and natural gas) by renewable and circular carbon sources. These include biomass, agricultural wastes and recovered carbon dioxide that could be captured and used as a feedstock for chemical synthesis. This approach is focused on the source, consumption and recirculation of carbon to reduce dependency on scarce fossil resources, reduce greenhouse gas emissions and support a transition towards a more sustainable and circular chemical industry. Function Economy (also known as Chemical Leasing in the chemical industry) is a shift from selling chemical products to selling the functions or services of the products. The traditional industrial chemistry business model is that the more chemicals you sell, the more profitable the business i.e. increased consumption generally means increased revenue. This approach can lead to increased levels of resource use and waste generation. The function-based model focuses on the desired performance or outcome, rather than a specific quantity of a chemical ingredient. However, the producer is still responsible for the chemical, and thus is strongly motivated to minimize the amount of material used, maximize process efficiency, recover and recycle chemicals whenever possible, and use technologies that minimize waste production. Thus, value is created by delivering a function efficiently, not by selling more chemicals. This aligns economic objectives with environmental sustainability and resource efficiency (Moser & Jakl, 2015).

4. SAFER BY DESIGN: HAZARD REDUCTION IN THE ERA OF MOLECULAR ENGINEERING

Traditionally, industrial chemistry has been production and performance oriented, often treating the negative effects of chemical compounds on the environment and human health as problems to be tackled later through waste management and control measures. But the advent of nanotechnology and molecular engineering in the twenty-first century has made this paradigm less and less acceptable.

The third principle of Green Chemistry, Less Hazardous Chemical Syntheses, and the fourth principle, Designing Safer Chemicals, attempt to eliminate hazards at the source by considering hazards during the molecular design stage (Anastas & Warner, 2000). The "Safer by Design" approach is intended to prevent the emergence of hazardous properties in chemical products and processes. Safety in molecular engineering is not a constraint on chemical innovation, but rather a powerful strategy to enable the development of next-generation intelligent, sustainable, and environmentally friendly materials.

4.1. A Functional Safety Approach Instead of Toxicity-Based Design

Earlier methods depended on ongoing use of dangerous substances and focused on minimizing exposure through protective gear or filtering apparatus. "On the other hand, the functional safety approach aims at destroying the threat (toxicity). Functional safety aims at molecular changes to eliminate unwanted biochemical interactions with live beings leading to toxicity, including endocrine-disrupting properties, while preserving the desired commercial or technical efficacy of a molecule. This method aims to maximize the effectiveness of the chemical product, but also to improve human health and the health of the environment, not just focusing on traditional notions of toxicity. During the design phase, the function and the toxicity prevention are evaluated simultaneously. The preventative design approach shifts the focus from dealing with toxicity after the fact to the rational design of chemicals to achieve inherent safety at a structural level. This implies the selection of molecular features at the design stage, to reduce biological and environmental interactions (Mellor et al., 2018).

4.2. Molecular Design, QSAR, and Artificial Intelligence

Green Toxicology is a sustainable approach to reduce or avoid possible toxicity of chemical substances during the developing phase. The "safety by design" approach focuses on preventing toxicity at the source, through structural changes at the design stage of molecules, rather than controlling hazardous chemicals after they enter the marketplace.



Figure 6. *Structural workflow of the DETOX-QSAR computational toxicity prediction framework, systematically mapping the Pre-Modeling, Modeling, Post-Modeling, and In-Modeling stages. While theoretically conceptualized from the methodology of Çelik and Doğan (2026), this entirely redesigned and enhanced visualization clarifies the high-fidelity data integration nodes and iterative validation feedback loops. It illustrates how green molecular design utilizes modern computer-aided toxicity screening to screen out hazardous candidates at the in-silico stage, thereby saving material resources and aligning chemical design with predictive prevention principles.*

Modern risk assessment is now characterized by AI-empowered QSAR (Figure 6) (Quantitative Structure-Activity Relationship) models that allow for fast, humane and cost-effective evaluation of the toxicity profiles of compounds. These in silico technologies solve toxicity issues instantaneously through optimization of molecular descriptors, unlike the traditional trial-and-error strategies. This therefore allows the inclusion of green toxicological principles into the molecular design process and encourages a more sustainable chemical manufacturing (Çelik & Doğan, 2026).

4.3. Regulation-Science Interaction (REACH, Green Deal)

Science at the molecular level is strongly connected to world-wide laws and policies. Scientists influences and shapes regulation and regulatory frameworks force scientists to arrive at safer answers.

The European Union REACH law is based on the principle of "no data, no market". The chemical industry must show the toxicity profiles of the products it manufactures. This requirement forced firms to spend resources on QSAR rather than animal testing (EUR-Lex - 02006R1907-20260511 - EN - EUR-Lex, n.d.).

The European Green Deal and the Chemicals Strategy for Sustainability target a toxic-free environment in the EU. This work has included the establishment of "safe and sustainable by design" (SSbD) as an official policy approach. Today

a chemical needs to be considered not only 'safe' but also sustainable through its entire life cycle from manufacture to disposal and in line with the principles of circular economy (Apel et al., 2026).

5. CATALYSIS, SELECTIVITY, AND PROCESS INTENSIFICATION

Green Chemistry Principle 9 (Catalysis) advocates for the utilization of catalysts that remain unconsumed during the reaction, as opposed to stoichiometric reagents typically employed in conventional chemical processes, which frequently result in waste post-reaction (Anastas & Warner, 2000). In the contemporary age of molecular engineering, catalysis has transcended its role as a mere technical instrument that "accelerates" reactions. Currently, it is central to process intensification, atom economy, energy efficiency, and selectivity, rendering it one of the most pivotal instruments for sustainability.

5.1. Catalysis as a Tool for Sustainability, Not Only for Acceleration

One of the 12 principles of green chemistry is catalysis. Unlike stoichiometric reactions, catalytic transformations reduce waste at source, maximize atom economy and improve the yield of useful products in a shorter time and with a lower energy cost. Moreover, catalysts from waste materials can enhance the energy and atom efficiency of conventional chemical processes. Catalysis gives access to high-value products via shorter synthetic pathways and novel designs. This in turn decreases the overall carbon footprint of chemical manufacturing. Catalysts allow reactions to proceed under milder conditions (i.e., lower temperature and pressure) thereby reducing energy consumption and greenhouse gas emissions (Habib et al., 2023).

In summary, the sources portray catalysis not just as a technical element to accelerate reactions, but as a strategic tool for sustainability, which helps to reduce waste generation, save energy and lower environmental risks.

5.2. Selectivity-Energy-Resource Relationship

Energy efficiency and purification are intrinsically linked by the key principle of selectivity. High selectivity means that only the desired product is formed, drastically reducing the formation of unwanted by-products. This means that the separation and purification steps, which are usually one of the most energy and costly parts of chemical manufacture, are minimized or even eliminated altogether. This leads to a large reduction in the overall energy demand of the process. Catalytic strategies enhance resource efficiency by lowering waste generation at the source. Atom economy maximization leads to better selectivity, i.e. a larger proportion of the atoms of the starting materials are taken up by the end product, and reduces the need for auxiliary reagents. This not only improves material efficiency but also promotes more sustainable use of resources. Figure 7 shows the diagram of sustainable catalysis criteria.



Figure 7. *Multi-criteria sustainability assessment matrix for advanced catalytic systems. The radar chart maps six interconnected operational and ecological vectors: Selectivity, Energy Efficiency, Environmental Impact, Cost-Effectiveness, Stability, and Reusability. This multi-dimensional profile demonstrates that optimizing a sustainable catalyst requires a balanced trade-off analysis, ensuring that high chemical performance (selectivity and stability) directly aligns with low life-cycle impacts and industrial economic viability.*

From an economic point of view, the interaction of selectivity, energy consumption and resource use is equally important. Improved selectivity helps in the creation of useful products with less raw material consumption, shorter reaction times and lower energy consumption, which reduces overall production costs. It also provides the possibility to design more efficient and "intelligent" synthetic pathways, that greatly reduce the carbon footprint of chemical production. Sustainable catalytic systems often enable reactions to occur under mild conditions, e.g. ambient temperature and pressure, instead of requiring high temperature and pressure. Such moderate conditions not only increase energy efficiency but also decrease stress on equipment and slow down material degradation. As a consequence, high selectivity is central to sustainable chemical design, because it reduces energy consumption by

minimizing the need for purification, and it prevents resource waste by avoiding the formation of by-products (Habib et al., 2023).

5.3. Single-Atom Catalysis, Biocatalysis, Electrocatalysis

The rise of single-atom catalysts (SACs) has ushered in a new era of heterogeneous catalysis, in perfect accordance with the principles of green chemistry. Researchers say that by downsizing metal particles to the atomic scale, metal utilization efficiency can be improved, with better selectivity and activity than traditional nanostructured catalysts. In conventional nanoparticle catalysts, reactions occur only on surface atoms, while metal atoms in the core are mostly inactive, limiting overall efficiency. In contrast, each metal atom is an active site in single atom catalysts, and the atomic utilization efficiency can approach 100%. In addition, the ability to precisely tune the coordinating environment around each atom provides the opportunity to generate highly uniform and tunable active sites. This structure combines the robustness of heterogeneous catalysts with the high selectivity typical of homogeneous catalysts, thus allowing a more controlled and precise catalysis (Yang et al., 2013).

Biocatalysts are becoming more important tools in synthetic chemistry, opening the way for industrial chemical production towards more sustainable methodologies. This modification has important environmental and economic advantages, since biocatalysts are highly selective and efficient in the synthesis of high-value chemicals. They produce less waste and are more cost-effective than traditional chemical methods and thus are more attractive for industrial applications. Moreover, enzyme engineering and directed evolution have enabled the fine-tuning of protein structures, thus improving the synthesis of specific targeted products. Biocatalytic approaches have advantages in purification, as they allow for simpler and more efficient separation processes compared to conventional transition-metal-based catalysts, although the transformation of silicon-containing compounds is mainly an underexplored domain (Yang et al., 2013).

Electrocatalysts are materials that can harness electrical energy, preferably from renewable sources such as wind and sunlight, to directly drive chemical reactions in place of using heat from fossil fuels. Hydrogen is a clean energy carrier with high energy density, which is generated by water electrolysis via hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Although Pt-based catalysts for hydrogen evolution reaction (HER) and Ru/Ir-based catalysts for oxygen evolution reaction (OER) show excellent activity, their high cost and limited availability hinder their broad application. The study therefore focuses on earth-abundant replacements, increasing performance by optimizing the electronic structure, increasing the active surface area and improving conductivity. Green chemistry concepts are very important in designing catalysts to minimize the use of dangerous chemicals. Some synthetic routes (e.g. metal phosphides) release toxic PH_3 gas, but eco-friendly alternatives such as microwave-assisted synthesis, bio-based phosphorus sources and PH_3-free technologies are being developed (Jamesh et al., 2022).

To map the distinct operational landscapes of these cutting-edge synthetic drivers, a multi-dimensional comparison is structured. The performance trade-offs across critical operational parameters are visually aggregated in Figure 8, while their respective core mechanisms and primary advantages are systematically summarized in Table 2.

Table 2. *Comparative Analysis of the Operating Principles and Advantages of Different Catalyst Types*

	Core Mechanism	Primary Advantage
Single-Atom (SACs)	Downsizing metal particles to the atomic scale.	100% metal utilization efficiency and precisely tunable active site.
Biocatalysis	Use of enzymes and protein structures for synthesis.	High selectivity and sustainable, cost-effective industrial production.
Electrocatalysis	Using renewable electrical energy instead of fossil fuel head.	Production of clean energy (hydrogen) and reduction of dependence on fossil fuels.

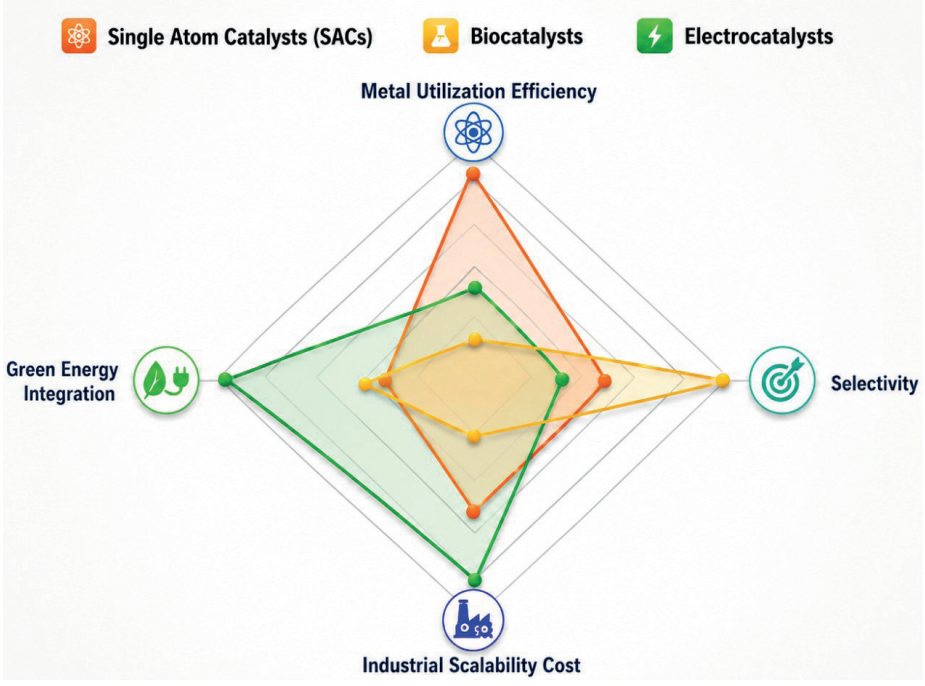

Figure 8. *Catalyst Types Performance Matrix evaluating Single-Atom Catalysts (SACs), Biocatalysts, and Electrocatalysts across four sustainability and operational axes: Metal Utilization Efficiency, Selectivity, Green Energy Integration, and Industrial Scalability Cost. The radar chart illustrates how each catalytic class occupies a distinct strategic niche: SACs maximize atom efficiency near the 100% threshold, biocatalysts exhibit unmatched molecular selectivity, and electrocatalysts excel at direct coupling with renewable power grids, thereby highlighting the necessity of a tailored selection framework in modern chemical process intensification.*

6. ENERGY AND TIME AS GREEN CHEMISTRY PARAMETERS

The sixth principle of Green Chemistry (design for energy efficiency) states that energy needs must be recognized and minimized in the design of chemical processes, to maintain environmental and economic impacts (Anastas & Warner, 2000). In the traditional paradigm this idea is often reduced to a fundamental rule for the conduct of reactions whenever possible at ambient temperature and standard pressure. Energy and time aspects are now treated in a much more dynamic and integrated way in the field of green chemistry and sustainable engineering. In modern molecular engineering, energy efficiency is not only about reducing temperature, but also about optimizing time, mass, reactor design, and the quality of the energy source.

6.1. Energy Efficiency ≠ Low Temperature

Energy management and reduction of energy input are considered major benefits of flow chemistry (continuous-flow chemistry), especially for cost-sensitive industrial applications. Flow chemistry is energy-efficient due to lower temperature operation and extensive process optimization, unlike traditional batch reactors. Flow reactors allow reactions at high temperatures by fast mixing and accurate residence time control, without excessive cooling and with a large reduction in energy consumption, while conventional batch systems often require cryogenic conditions (-78 °C or lower) to avoid decomposition. Microreactors have a high surface area-to-volume ratio allowing for efficient heat transfer to rapidly dissipate heat generated in exothermic reactions and reduce dependence on energy intensive cooling systems. Furthermore, process intensification enables a shortening of the reaction times from hours to seconds thereby lessening the total energy demand per unit of product. The restricted temperature profile and increased control limit side reactions, thus reducing the need for downstream purification and therefore lessening additional energy needs (Plutschack et al., 2017).

6.2. Reaction Time, Process Intensification

In green chemistry, time is not simply a measure of duration but a direct factor impacting volumetric efficiency and the carbon footprint. Time compression is an important aspect of process intensification. Batch reactors have traditionally been the predominant technology in fine chemical production and have been the main industrial method for a long time because they can produce a wide range of products in the same configuration at a relatively low cost and high profitability. However, the transition to continuous flow systems represents a pivotal axis of technological transformation; while demanding more complex and time-consuming engineering design, continuous architectures offer unparalleled advantages in micro-scale mass and heat transfer parameters (Figure 9) (Bukhtiyarova et al., 2023).

Flow reactors offer important advantages such as better mixing, improved mass and heat transfer, lower operating costs, efficient control of side products formation, higher process safety and easier scale-up. They have smaller reactor volumes so they

can exchange heat much more efficiently and so reduce energy costs. Furthermore, the reactions take place at a limited volume under continuous flow, preventing the generation of intermediates and allowing the rapid removal of by-products from the system and therefore increasing the process safety. From a scalability point of view, a batch process may seem easier to scale-up, but flow processes can provide better control, reproducibility and robustness for industrial applications with proper planning, kinetic information and modeling tools (Bukhtiyarova et al., 2023).

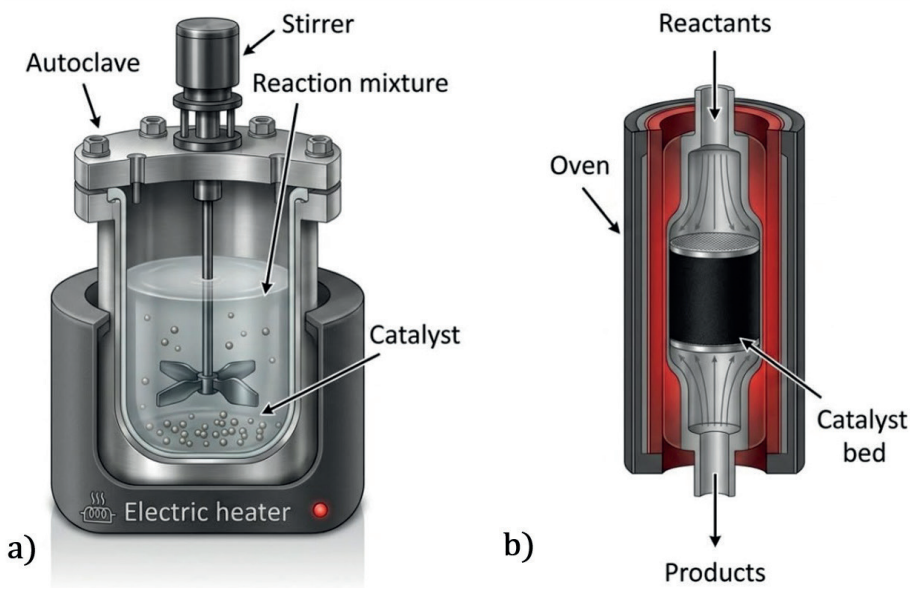

Figure 9. *Operational configuration of batch (***a***) versus continuous flow (***b***) reactors. The schematic illustrates how continuous flow systems optimize reaction trajectories through spatial process intensification, offering high mass/heat transfer coefficients and precise reaction duration management compared to conventional, macro-scale batch processing.*

6.3. Renewable Energy Integration

Green chemistry together with renewable energy technologies is the basis of the environmentally sustainable development. Principles of green chemistry, such as use of renewable feedstocks and design for energy efficiency, are aimed at reducing the raw material and energy consumption in chemical processes. Also, the use of renewable sources of energy such as solar, wind, hydro and biomass is necessary for pollution prevention. The hydrogen production from renewable energy sources and its conversion to electricity by means of fuel cells constitutes a fully sustainable energy cycle with no emission of pollutants. By combining these two areas, we not only decrease waste in industrial processes, but also encourage economic innovation and efficiency, while safeguarding human health and the environment (Kaygusuz, 2019).

6.4. Socio-Ecological Dimensions: Environmental Justice and Chemical Equity

The structural transition from a fossil-dependent industrial baseline toward a circular bioeconomy driven by advanced biomass valorization and biorefineries cannot be evaluated solely through the lenses of thermodynamic efficiency, carbon accounting, or macroeconomic viability. As green chemistry matures from an isolated laboratory methodology into a macro-systemic infrastructure, its socio-ecological footprints demand critical cross-examination. Scurrilous historical precedents within bulk chemical manufacturing demonstrate that industrial pollution and toxic chemical exposures are disproportionately concentrated within marginalized populations, low-income communities, and the Global South—a systemic imbalance widely recognized as environmental racism (Bullard, 2000; Mohai et al., 2009). Consequently, next-generation green engineering paradigms must actively expand their boundaries to internalize environmental justice and chemical equity as core operational mandates (Anastas & Warner, 2000). A chemical process cannot be considered truly "green" if its global supply chain, raw material extraction, or regional processing stages exacerbate localized socioeconomic vulnerabilities or perpetuate chemical colonialism (Bastos Lima, 2022).

A profound socio-ecological bottleneck within this paradigm lies in the concept of a Just Transition, which emphasizes that sustainability transitions must be not only environmentally effective but also socially equitable, ensuring that the benefits and burdens of technological change are distributed fairly across society (Newell & Mulvaney, 2013; Wang et al., 2022). The shift away from petrochemical refineries toward large-scale integrated biorefineries fundamentally reconfigures regional labor markets, land-use patterns, and resource distributions. From a technological perspective, replacing fossil-derived feedstocks with agricultural residues or dedicated energy crops can substantially reduce greenhouse gas emissions and alleviate several environmental pressures associated with conventional petrochemical production. However, the sustainability gains associated with biomass-based systems cannot be evaluated solely through environmental metrics. If biomass cultivation contributes to land-grabbing, the displacement of indigenous or smallholder farming communities, unequal access to natural resources, or other forms of socio-economic exclusion, the legitimacy of the transition itself becomes questionable (Bastos Lima, 2022). Similarly, when large-scale biomass production competes with food systems, intensifies pressure on agricultural land, or exacerbates regional food insecurity, the environmental benefits achieved through decarbonization may be offset by significant social costs (Ahmed et al., 2021). Green chemical systems engineering must therefore move beyond conventional environmental life cycle assessment (LCA) and incorporate socio-ecological life cycle assessment (S-LCA) frameworks capable of evaluating social justice, labor conditions, land governance, food security, and community well-being alongside environmental performance (Wang et al., 2022; Bastos Lima, 2022). Such an integrated assessment framework can help ensure that biomass sourcing strategies respect local land rights, uphold fair labor standards,

and encourage decentralized, community-oriented biorefinery models that distribute economic benefits more equitably among rural and marginalized populations, thereby aligning green chemistry with the broader objectives of sustainable and just development (Newell & Mulvaney, 2013; Bastos Lima, 2022).

Concomitantly, the principle of chemical equity mandates universal, non-discriminatory access to non-toxic consumer products, advanced green technologies, and clean manufacturing environments (Mohai et al., 2009). Historically, hazardous industrial chemical facilities and poorly regulated waste treatment plants have been disproportionately located near politically marginalized communities, contributing to persistent public health disparities, elevated cancer risks, and chronic toxicological burdens (Mohai et al., 2009). By enforcing the foundational principles of inherent safety, non-persistent molecular design, and non-volatile alternative solvents, such as bio-derived deep eutectic solvents and tailored ionic liquids, green chemistry provides a structural pathway toward environmental justice and public health protection (Anastas & Warner, 2000). Eliminating hazardous volatile organic compounds (VOCs) and persistent organic pollutants (POPs) at the molecular design stage systematically reduces chemical exposures that have historically affected fence-line communities (Anastas & Warner, 2000; Stockholm Convention, 2001).

Finally, ensuring chemical equity requires democratizing access to advanced green engineering platforms. The deployment of digitalization tools, machine-learning pipelines such as DETOX-QSAR, and Model Predictive Control (MPC) integrated with Digital Twins should not remain confined to well-resourced institutions in the Global North. If manufacturing sectors in developing countries are excluded from green technology transfer because of financial limitations, inadequate institutional capacity, or barriers to technology access, hazardous production may increasingly shift toward jurisdictions with weaker environmental governance, reinforcing patterns of environmental dumping and global environmental injustice (UNEP, 2023). Overcoming this inequity requires strengthened international cooperation, transparent chemicals governance, capacity building, and equitable technology transfer to narrow regulatory disparities among nations and enable the sound management of chemicals throughout their life cycle (UNEP, 2023).

7. SOLVENTS, AUXILIARIES, AND REACTION MEDIA: FROM SUBSTITUTION TO ELIMINATION

Principle 5 of Green Chemistry, Safer Solvents and Auxiliaries, states that the use of solvents and separation agents should be minimized wherever possible and, when their use is unavoidable, they should be innocuous (Anastas & Warner, 2000). In the conventional chemical industry solvents are regarded as necessary for mass transfer, heat transfer and homogenization. Volatile organic compounds (VOCs) account for almost 80% of the environmental impact of chemical processes due to their toxicity, flammability and waste burden. There is a significant paradigm shift in modern green chemistry, from replacing harmful solvents with less toxic alternatives to removing solvents from the system altogether.

7.1. Solvent-Free Systems Instead of Solvent Selection

Organic solvents are used in traditional chemistry laboratories and materials production, and they are generally hazardous to the environment and human health; organic solvents contribute to air pollution and ozone depletion and can be carcinogenic, neurotoxic and reproductive toxic. This has led to an increasing demand for green chemistry approaches to reduce or eliminate the use of hazardous solvents altogether. Solvent-free reaction methods offer important advantages in industrial processes concerning pollution reduction, cost-effectiveness, improved simplicity of operation and decreased reaction times, apart from the removal or time and energy cost of solvent recovery. The use of techniques such as mechanochemistry, microwave-assisted synthesis, sonochemistry and photochemical reactions enables faster and more efficient reactions in the absence of solvents, offering robust alternatives for sustainable chemistry. When the complete removal of solvent is not feasible, more environmentally friendly options such as water, ionic liquids, supercritical fluids and deep eutectic solvents are used to decrease the impact on the environment. Modern green chemistry emphasizes the reduction of the use of solvents for safer, more efficient and sustainable chemical synthesis (Younis & Said, 2023).

7.2. Water, Ionic Liquids, Deep Eutectic Solvents

Water is the most common naturally occurring solvent on the earth and is considered as one of the most eco-friendly alternatives in green chemistry due to its non-flammability, non-explosive nature, non-toxic nature and low-cost. Besides its physical properties, water is extraordinary for its advantageous impact on chemical reactions; the hydrophobic effect can boost specific organic transformations and enhance selectivity. The great practical advantage for the reduction of extraction procedures is provided by the easy phase separation of the water-insoluble organic compounds after the reaction. However, water does have some limitations. The disposal of wastewater polluted with hazardous compounds is a serious environmental concern and the use of supercritical or subcritical water requires high temperature and pressure conditions, which pose technical problems. Nevertheless, water is considered to be the most environmentally friendly solvent because of its availability, safety and low impact on the environment (Zhou et al., 2019).

Ionic liquids (ILs) are considered as a new category of green solvents, which have low vapor pressure, high thermal stability and excellent solubility for substrates, and have attracted great attention in academia and industry. There are many possible combinations of different cations and anions, and these structures can be tuned greatly to the needs of a particular reaction. Enzymes often show improved stability and sometimes even enhanced activity in these media, making ionic liquids attractive for biocatalytic systems, but their high cost, complex production, and possible toxicity hinder their widespread application (Nian & Li, 2022).

In this context, Deep Eutectic Solvents (DESs) are a more cost-effective, safer and sustainable alternative to ionic liquids. These systems are typically obtained by interaction between a hydrogen bond donor and acceptor (Figure 10). They have sim-

ilar advantages like ionic liquids such as low vapor pressure and thermal stability but also have better advantages such as low cost, easier preparation, biodegradability and safety. Deep eutectic solvents (DESs) are divided into four types (I-IV) and Type III systems with choline chloride are the most studied due to their low cost, while natural deep eutectic solvents (NADESs) composed solely of natural metabolites represent a safer alternative. DESs dissolve biopolymers that are normally hard to solubilize, such as starch and lignin, which enhances the efficiency of biomass conversion. They also help in maintaining the structure of the enzymes and in some cases enhance the enzyme activity in biocatalytic processes. High viscosity is a major constraint but can be compensated by adding small amounts of water (Nian & Li, 2022).

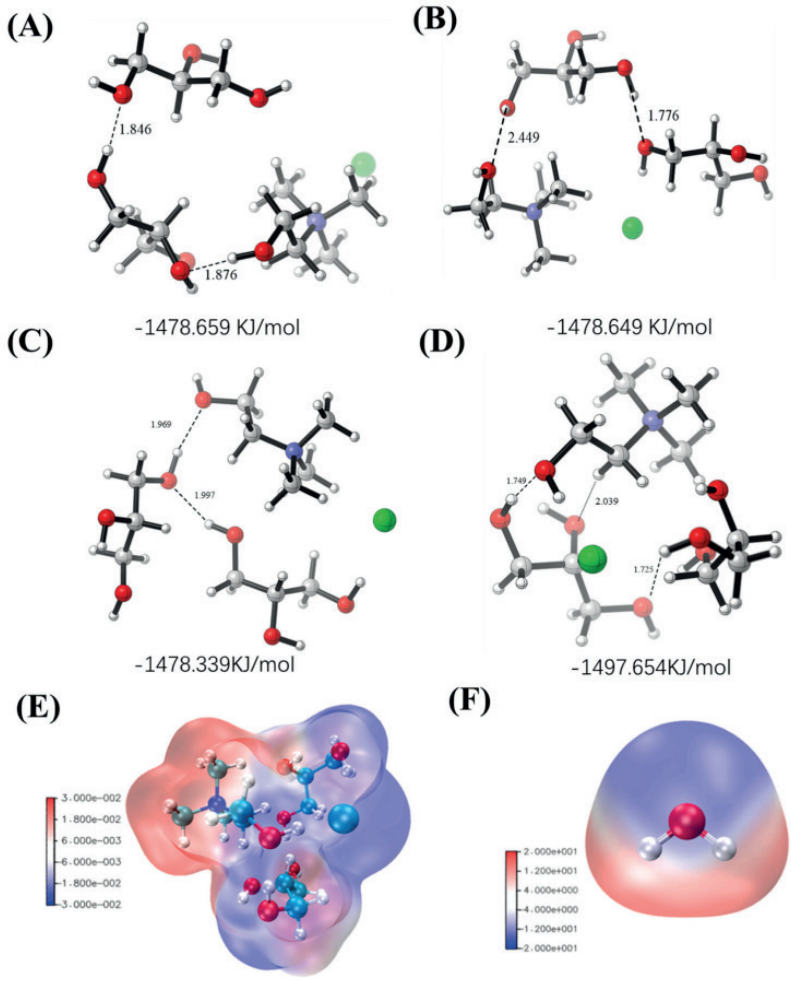

Figure 10. *Quantum chemical optimization configurations and electrostatic topologies of deep eutectic solvent (DES) or ionic liquid constituents. Panels (A–D) detail the optimized geometries, hydrogen-bond distances (Å), and computed binding energies (kJ mol^{-1}) of the stabilizing intermolecular networks, while panels (e) and (f) map the corresponding molecular electrostatic potential (MEP) surfaces to visualize nucleophilic and electrophilic charge distributions (reproduced with permission from Nian & Li, 2022).*

7.3. Active Role of The Reaction Medium

In traditional chemistry the solvent was seen as a "passive spectator" which only allowed the reactants to meet and did not influence the reaction itself. In modern green chemistry, the reaction medium is an active participant in the efficiency, speed and selectivity of the process. Deep eutectic solvents (DES) and ionic liquids (ILs) are an integral part of metal-catalyzed reactions in that they are used not only as inert reaction media but also as multifunctional systems actively influencing the catalytic process. Modern solvents, especially in metal nanoparticle systems, stabilize the catalyst by preventing aggregation and sustaining active species for extended periods. Simultaneously, modification of the chemical composition of the solvent allows one to fine-tune reaction rate and selectivity, which is especially important for improving the yield of products in cross-coupling processes. Moreover, the solvents are characterized by low volatility and appropriate physical properties, which facilitate the easy separation and reuse of the catalyst from the reaction medium, thus improving sustainability and economic feasibility. In some instances, they may serve not only as the medium of reaction but as active catalytic agents themselves. Furthermore, the ionic nature of the solvent enhances solubility of gases like hydrogen and consequently promotes reactivity in hydrogenation reactions. The solvent-catalyst synergistic interactions result in higher efficiency than conventional organic media (Gracia-Barberán et al., 2022).

8. RENEWABLE CARBON AND FEEDSTOCK CIRCULARITY

The 7th Principle of Green Chemistry says that whenever practicable, raw materials that are renewable are preferred to raw materials that are non-renewable (Anastas & Warner, 2000). Within the current circular economy paradigm, this idea has a broader, systemic meaning than the simple substitution of fossil fuels by biomass. This section discusses the notion of renewable carbon, feedstock circularity and the overall impact of carbon sources on ecosystems.

8.1. Renewable ≠ Automatically Sustainable

Although renewable energy and sustainable development are sometimes used interchangeably, using renewable resources does not always result in a sustainable society. The relation between these two concepts is much more complex and it involves several issues that have to be resolved. There are still many technological limitations of renewable energy technologies that are not sufficiently addressed and sometimes their environmental or societal impacts can be greater than expected from the beginning. There are significant technical and environmental limitations that hamper the effective collection, transmission and exploitation of renewable resources.

Renewable energy sources are critical elements for a sustainable future. But the fact that an energy source is renewable does not necessarily mean it is sustainable. True sustainability means looking at not only where an energy resource originates, but what its effects are throughout production, transmission, use and disposal. As

discussed in Section 2.1 and illustrated in the Biomass and CO_2 Flow Paradox (see Figure 3), the socio-ecological footprint of feedstock cultivation must be integrated into the process design. While renewable energy options may reduce environmental impacts when compared to fossil fuels, there are some technical, environmental and social issues that may arise during resource extraction, infrastructure construction, energy storage and power transmission. Furthermore, sustainability is not only a change in the energy source, but also holistic approaches like waste minimization, adoption of circular economy principles, recovery of critical raw materials and improvement of resource efficiency. The transition to renewable energy is in the long run unavoidable, but it must be planned and managed carefully, taking into account its environmental, economic and social dimensions (Ray, 2019).

8.2. Biomass, CO_2, and Waste Carbon Flows

Biomass flows are the backbone of the bio-based economy. They encompass raw materials, intermediate goods, final products and byproducts that move across various sectors nationally and internationally (imports and exports). Properly defining biomass flows is important for policy makers who wish to embed the bioeconomy in many sectors. This is a hard job because the instructions and amounts of these flows are often opaque and can vary from year to year. If biomass is taken away from its intended use and used for other purposes, such as generating energy, then this can directly or indirectly change existing biomass flows and increase demand for more biomass resources to make up for supply shortfalls in the original sectors. The tracking of flows of internationally traded sustainable and certified biomass is of critical importance for global climate policies, especially for greenhouse gas (GHG) emission accounting which requires differentiation of biomass certified under sustainability schemes. Many countries are increasing their ambitions to improve the efficiency of biomass utilization, which has created new demands for biomass resources. Biodiesel, bioethanol and wood pellets now represent the lion's share of the world's biomass trade flows. However, biomass supply chains are sometimes characterized by a lack of transparency, as enterprises generally keep trade information (quantities, sources and destinations) confidential for economic reasons. Moreover, the trade classification systems used by customs authorities do not always clearly distinguish between materials for energy production and raw materials, which further complicates the tracking and control of the flow of biomass (Goh et al., 2014).

In the terrestrial carbon cycle, transfers of CO_2 are typically differentiated between biotic (biological) and abiotic (non-biological) processes. The transient components are the biotic flows. They are mainly driven by photosynthesis, which takes CO_2 from the atmosphere and respiration, which returns it. In contrast, abiotic flows, which are sometimes omitted from ecosystem-scale analyses, may have a significant effect on short-term CO_2 exchange, particularly in carbonate-rich environments. These include geochemical weathering processes such as calcite dissolution (which removes CO_2 from the atmosphere) and calcite precipitation (which releases CO_2 into the atmosphere), and subsurface ventilation mechanisms

including caves, fractures, and macropores that serve as subterranean CO_2 reservoirs. The exchange of air between these underground spaces and the atmosphere may strongly influence the emissions of CO_2 at the surface (Serrano-Ortiz et al., 2010).

Several environmental conditions influence the volume and direction of CO_2 emissions. Large CO_2 emissions from carbonated soils can occur especially after arid periods as percolating water can dissolve and transport CO_2 or activate pH-dependent release mechanisms. Temperature differences between underground voids and the atmosphere and wind-induced ventilation drive CO_2 exchange, while soil CO_2 concentrations due to root respiration and microbial activity can be 10 to 100 times higher than atmospheric levels, promoting downward carbon flux. Because of the short time scales involved, processes such as carbonate dissolution and precipitation can strongly affect local ecosystem carbon balances but are generally thought to cancel each other out over geologic time scales. Yet the global subsurface CO_2 reservoir is expected to be sufficiently large so that the potential ventilation flux might be on the order of 60% of the annual atmospheric carbon sink. This highlights the need to understand abiotic CO_2 flows, especially in desert and karst ecosystems where they could account for the "missing carbon sink" (Serrano-Ortiz et al., 2010).

Carbon in urban waste streams can be classified into two main groups according to source. Degradable organic carbon (DOC) is derived from biological matter, such as food waste, paper, wood and textiles; fossil carbon (FoC) is derived from petroleum-based materials, such as plastics and rubber. These carbon fractions can be converted to carbon dioxide (CO_2) and methane (CH_4) in the course of waste management, both of which contribute to the global carbon cycle.

Much of the climatic impact of these emissions depends on their source. Fossil derived CO_2 and methane emissions are considered net greenhouse gas emissions because they add new carbon to the atmosphere. Conversely, CO_2 that is released from biogenic carbon is generally considered to be climate-neutral as it is part of the natural carbon cycle. The fate of carbon will depend on the waste treatment process employed. Garbage decomposition in landfills produces both CO_2 and CH_4 but some of the carbon is sequestrated as a long-term carbon reservoir to resist degradation. Most of the carbon content is quickly burned to CO_2. But the total climate impact is highly dependent on what fraction of the trash is fossil carbon. Composting uses biological degradation mechanisms to turn biodegradable carbon into CO_2. The evolution of carbon dynamics in waste systems is governed by three key elements. The increment effect refers to the increase of waste generation and total carbon emissions resulting from urbanization and economic growth. The compositional effect refers to changes in the composition of waste, including increases in carbon-intensive products such as plastics and paper as living standards increase. The management effect is related to the influence of the waste treatment options (source separation, recycling, landfilling and incineration) on the emission profiles and carbon recovery rates. The main goal of a circular economy is to integrate waste separation, material recycling and energy recovery into a closed loop system. The goal of this technique is to maximize the recycling of carbon, minimize the net emissions of greenhouse gases and ensure the safe management of the carbon stored in existing landfill sites (Zhang et al., 2024).

8.3. Integrated Biorefinery and Carbon Cycle

The integration of biorefineries is required for the transition of modern industrial systems from linear fossil fuel-based production models to a circular bioeconomy based on renewable biomass resources. These facilities are multifunctional systems, not single output plants, that convert agricultural and industrial byproducts such as wheat straw, rice husks and sugarcane bagasse into a diverse set of products including biofuels, platform chemicals and high-value materials. The successful development of biorefineries depends on the ability to pair the specific characteristics of the biomass feedstocks (e.g., ash content, lignin composition, moisture content, etc.) with the most suitable conversion technology. For thermochemical processes, like pyrolysis, biomass with a moisture content below 20% is preferred, but for biochemical processes, like fermentation, the biomass should have a moisture content above 50%, avoiding the costly drying procedures. Figure 11 summarizes the engineering and optimization approach used in the production of biofuels and biochemicals from biomass, which seeks to answer the question: "Based on the structural characteristics of the available feedstock, which target product can be produced using the most efficient and cost-effective conversion pathway?"

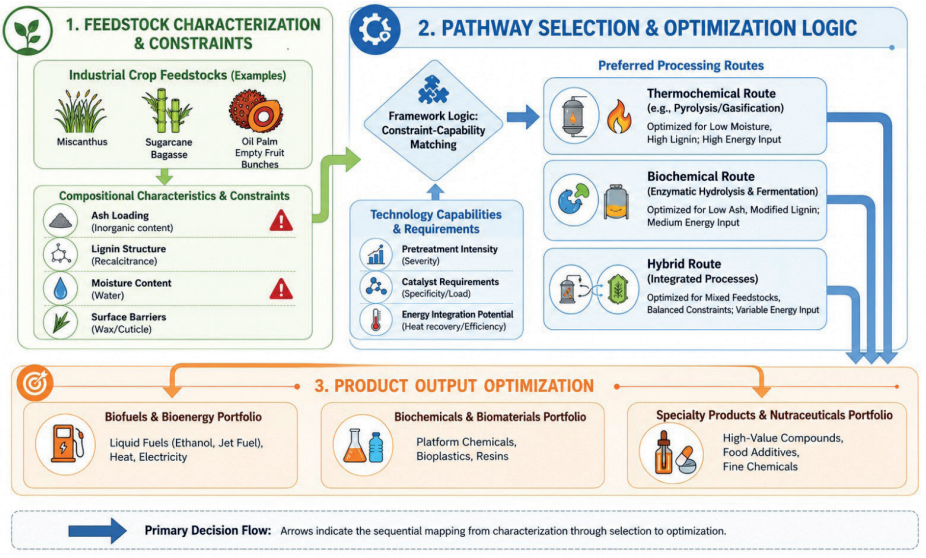

Figure 11. *Multi-pathway decision-making architecture in integrated biorefineries for circular biomass valorization. The framework maps the strategic transformation of diverse agricultural and industrial residues into optimized portfolios of bio-based chemicals, materials, and energy carriers. By matching specific feedstock constraints with technological capabilities, the diagram delineates thermochemical, biochemical, and hybrid conversion routes alongside real-time optimization nodes (adapted with structural modifications from Sun & Wang, 2026). This holistic mapping highlights how expanding process boundaries prevents upstream resource fragmentation.*

This integrated approach leads to recovery and reintegration into the economy of over 92% of resources. Integrated biorefineries have a positive impact on the carbon cycle with a reduction of net greenhouse gas emissions of 62-78% under optimum

conditions compared to fossil-based systems. The reductions are primarily due to the substitution of fossil fuels by biofuels/biochemicals, the sequestration of atmospheric carbon during biomass growth, and the application of process residues as fertilizers, avoiding emissions related to the manufacturing of synthetic fertilizer. Furthermore, biorefineries can contribute to reducing greenhouse gas emissions and air pollution from the burning or uncontrolled decomposition of agricultural residues while generating new cash flows for rural communities from the valorization of waste materials. Furthermore, these systems help to conserve soil organic carbon and, as a result, improve overall ecosystem services. The economic and regulatory frameworks, particularly the integration of carbon pricing as a fundamental design feature, heavily influence the commercial implementation of biorefineries. Carbon prices of USD 50-75 per tonne can make many biorefinery pathways economically attractive relative to fossil-based alternatives. Further, durable and stable policy instruments such as blending mandates and green public procurement programs are important to move technologies from pilot demonstrations to commercial viability. Technological progress in biorefineries, together with appropriate regulatory frameworks, can shift from environmental initiatives to building blocks of a sustainable industrial framework that is economically feasible and aligned with global climate targets (Sun & Wang, 2026).

9. DURABILITY, DEGRADABILITY, AND END-OF-LIFE DESIGN

Industrial design has for more than a century mostly functioned in a linear economic model, based on a "take–make–dispose" premise. The biggest disadvantage of this approach is planned obsolescence, where products are intentionally made to have a limited lifespan. However, the limitation of planetary resources and the growing problem of waste have made it necessary to adopt the concepts of Green Chemistry and Sustainable Engineering. Principle 10: Design for Durability, Degradability and End of Life Management is important because it attempts to establish at the design stage how materials will re-enter nature or industrial cycles at the end of their commercial life. This section examines the redefinition of the life of products, the complex balance between stability of functioning and controlled degradation, and the crises of microplastics and persistent chemicals progressively putting at risk the contemporary world.

9.1. Redefinition of The Product Lifetime Concept

In the context of Life Cycle Assessment (LCA), the idea of 'product lifetime' has been re-conceptualized by integrating the various definitions previously found in the literature, thereby changing its nature from a simple temporal duration to a complex analytical variable. This methodology clearly separates product lifespan from the notion of "obsolescence" which describes the causes leading to product termination and thus provides a more consistent modeling framework. Figure 12 demonstrates that product lifetimes differ based on the product's characteristics, and these variations are crucial for the precise description and analysis of product lifespan within a systematic framework.

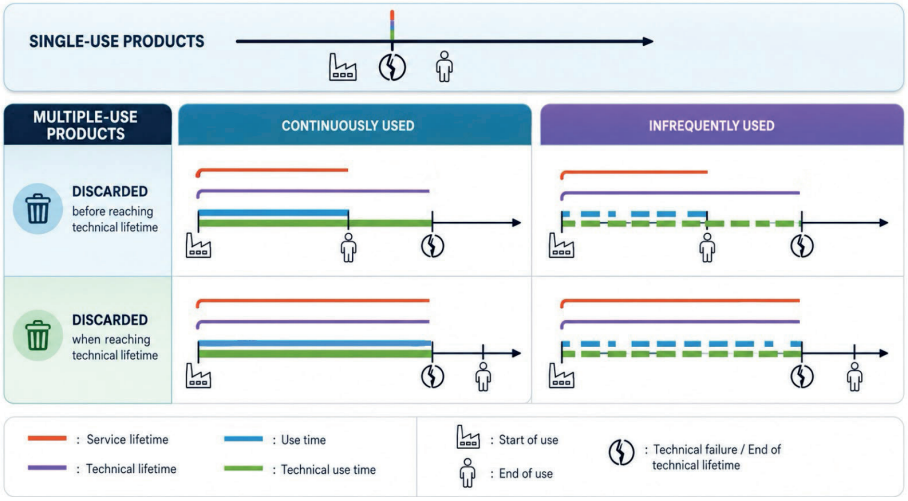

Figure 12. *Life cycle scenarios mapping the temporal relationship between service lifetime and technical lifetime across single-use and multi-use product paradigms. The comparative matrix delineates the waste transition dynamics for continuous versus infrequent utilization profiles, illustrating how sub-optimal product management triggers premature disposal (early waste) prior to actual technical failure (adapted with structural modifications from Jerome & Ljunggren, 2025). This distinction highlights the necessity of decoupling functional durability from linear consumption behaviors within circular economies.*

In this case, the product lifetime consists of four elements: service lifetime, technical lifetime, usage time, and technical usage time. Service life is the total time that a product is used, including the time it is not in use. Technical lifetime is the ability of a product to perform until it deteriorates or breaks down due to structural or material limitations. The time used is only the time of active use, not including maintenance, repair and idle time. The technical use time is the active use time until the product reaches its physical limits. This distinction explains the common confusion in the literature where the terms "lifetime" and "lifespan" are used interchangeably and loosely. It emphasizes the need for a systematic modeling framework including definitions, incorporation into equations and sensitivity analysis (Jerome & Ljunggren, 2025).

9.2. Controlled Degradation and Functional Stability

The controlled degradation and functional stability approach is based on the principle that materials within a device can be designed to undergo controlled breakdown through physical, chemical, or biological processes under specific conditions, while simultaneously performing designated functions. Within this strategy, materials are engineered to exhibit programmed degradation behavior in response to environmental triggers such as temperature, humidity, or pH, enabling sequential transformation processes without the need for external energy input. Degradation mechanisms are categorized into three main types: physical (melting, dissolution), chemical (corrosion, oxidation), and biological (enzymatic or microbial breakdown). In contrast, the functional stability of the system is ensured by dividing device components into two main categories. Substrate components maintain high stability throughout the operational period, providing mechanical support and energy storage functions, while responsive components are initially stable but rapidly degrade upon exposure to specific environmental conditions, thereby triggering system transformation. The design process carefully balances long-term stability under non-target conditions with accelerated degradation under target conditions, ensuring that materials remain durable during storage but deactivate in a controlled manner in their operational environment. Performance monitoring is carried out using metrics such as relative tensile strength, where functional transformation occurs once a defined threshold is reached. This approach enables the development of self-regulating systems that operate autonomously and completely degrade after completing their function, particularly in applications such as ecological restoration where external intervention is limited (Lu et al., 2024).

9.3. Microplastics and Persistent Chemicals Context

The global problem of plastic pollution is largely accounted for by the high persistence of compounds like per- and polyfluoroalkyl substances (PFAS). These compounds are not degraded because of their high persistence and remain in the environment for a long time, causing accumulation and global environmental concern. Current regulatory frameworks, especially in the European Union, are increasingly assessing microplastics and PFAS based solely on persistence criteria, suggesting that persistence in the environment over time is being recognized as a risk factor per se, independent of toxicity. As shown in Figure 13, microplastics are generated from different sources and transported to different environmental compartments and can finally be bioaccumulated in living organisms via bioaccumulation processes (Sivakumar et al., 2026).

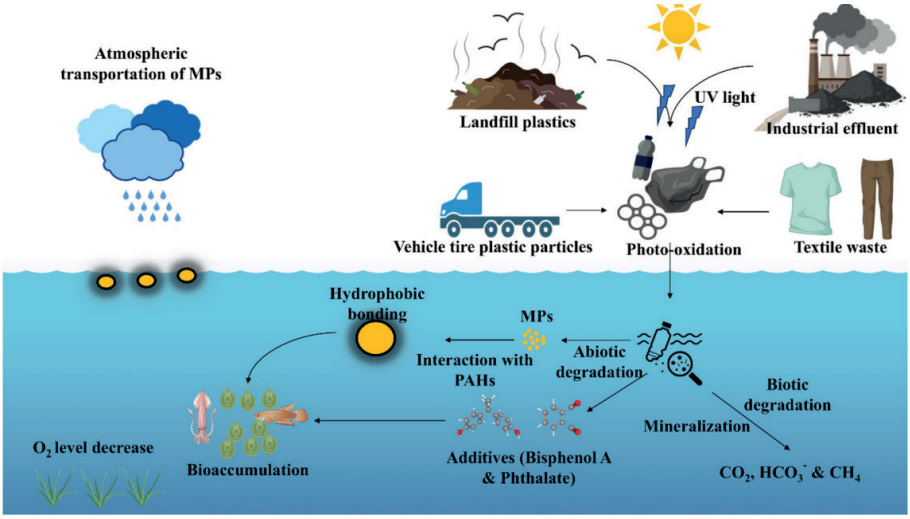

Figure 13. *Comprehensive environmental life cycle and transport dynamics of microplastics (MPs) across terrestrial, atmospheric, and aquatic interfaces. The pathway maps how MPs from industrial, transportation, and agricultural runoffs enter marine ecosystems, where they undergo UV-induced photo-oxidation and adsorb persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs). The framework details the subsequent biotic and abiotic fragmentation, trophic bioaccumulation, and ultimate chemical mineralization vectors (reproduced with permission from Sivakumar et al., 2026).*

What this means is that plastics are now considered "novel entities" (along with synthetic organic chemicals and engineered nanomaterials), defined as substances that are not naturally occurring and require specific regulation in the environment. Persistent pollutants can affect in many ways. Some chemicals have toxicological effects or deplete the ozone layer, whereas plastics mainly cause physical damage, in particular microplastics. The ability of these compounds to accumulate in environmental compartments (water, soil, sediments) is what makes them a worldwide threat with long-lasting and hard-to-reverse ecological consequences (Scheringer et al., 2022).

10. REAL-TIME MONITORING, DIGITALIZATION, AND PREDICTIVE CONTROL

Principle 11, from traditional definitions of Green Chemistry and Sustainable Engineering, refers to the design of analytical methodologies that allow for real-time in-process monitoring and control to avoid the generation of hazardous substances. In the traditional paradigm, this principle was mostly limited to simple sensors deployed in the facilities to prevent major incidents, such as leaks or explosions.

Today, when digitization, artificial intelligence and advanced analytics are combined, Principle 11 has gone from a reactive safety principle to a proactive sustainability principle. Principle 11 incorporates digital technologies into chemical and process engineering to eliminate raw material waste, improve energy efficiency in real time and actively reduce the carbon impact.

10.1. In Situ / Operando Analysis

In Situ Analysis: This is the observation of chemical changes in real time, right in the reactor, and without the need to take samples out of the reaction mixture. It is carried out with probes and sensors inserted into the reactor such as FTIR, Raman or UV-Vis spectroscopies. This procedure checks the molecular state of the reaction in its present state without any interference of material transfer or change in temperature. Table 3 provides a short comparison of operational conditions and instrumentation of in situ and operando analytical methods.

Table 3. *Comparison of in situ and operando analysis*

Criterion	In Situ Analysis	Operando Analysis
Measurement Environment	Inside the reactor (real-time, no sampling)	Inside the reactor (real-time, no sampling)
Process Conditions	Present/static state of the reaction	Actual operating conditions (High pressure, extreme temperature)
Catalyst Status	Molecular-level monitoring	Monitored during active catalyst operation
Instrumentation	FTIR, Raman, or UV-Vis probes	Condition-adapted spectroscopy
Common Advantages	Pinpoints the exact onset of by-product (waste) formation. Detects the exact moment of catalyst deactivation.Enables real-time optimization or shutdown to reduce environmental damage (Prajapati et al., 2025).	

Operando Analysis: In addition to in situ analysis, operando approaches follow chemical transformations under actual reaction and operational conditions, for example, under high pressure, at extreme temperature, or during active catalyst operation, by spectroscopic methods. Both methods enable us to determine the exact moment of the beginning of formation of by-products (waste) or the beginning of catalyst deactivation. This allows for real time shut down or optimization of operation, reducing environmental damage and improving overall efficiency (Prajapati et al., 2025).

10.2. Digital Twins and Artificial İntelligence

The core to reach efficiency, precision and adaptability in autonomous manufacturing is the combination of Digital Twins with Artificial Intelligence (AI/ML). A Digital Twin is a virtual replica of a physical system, used to monitor, improve the model, predict and make decisions in real-time. The integration of artificial intelligence enables the formulation of proactive control techniques in industrial processes. Therefore, it helps to make real-time decisions when there are operational changes and uncertainties. In the case of additive manufacturing in particular, faults can be predicted and avoided before they occur, thus improving the quality

of the product. Deep learning methods are used to capture complex and nonlinear manufacturing systems. Multivariate models such as TiDE (Time-Series Dense Encoder) are surrogate models in digital twins, which allow for fast prediction of future system behavior and accelerate decision-making. Traditional PID control strategies only react to the presence of an error. On the other hand, digital twin systems with AI capabilities apply Model Predictive Control (MPC) to forecast future states and optimize the operation of multivariable processes. It is expected that this link will migrate from part-level production to more complex decision problems such as scheduling using time series applications. In this context, artificial intelligence serves as an important catalyst which improves the prediction and optimization functions of digital twins and thus achieves the goal of fully autonomous and flawless manufacturing (Y. P. Chen et al., 2025).

10.3. Preventive Control Strategies

Model Predictive Control (MPC) differs from traditional controllers in that it is not reactive but predictive. It uses a process model to predict future system behavior and anticipate deviation before it happens. The prediction feature helps the system to stick to the reference value and improves stability in general. An important feature of MPC is its ability to incorporate hard constraints instantaneously. This does not exceed the physical limits of the actuators and keeps the system within safe operational limits. Furthermore, integration of advanced neural networks allows the MPC framework to dynamically adjust feed rates and thermal profiles under fluctuating industrial conditions. This predictive agility ensures that the chemical reactor operates at peak thermodynamic efficiency while strictly avoiding the degradation of heat-sensitive products. Furthermore, MPC is widely used in manufacturing technologies to reduce adverse phenomena such as noise in milling processes and to avoid collisions in robotic applications, thereby increasing the overall process safety. In effect, these characteristics allow MPC to act as a prospective control strategy that anticipates possible hazards and prevents negative outcomes before they happen, in addition to being a control mode for the current states of a system. To illustrate these practical advantages of cyber-physical process intensification, Figure 14 delineates the comparative performance profiles of traditional PID controllers and advanced MPC-Digital Twin architectures regarding systemic stability, waste minimization, and carbon footprint reduction (Schwenzer et al., 2021).

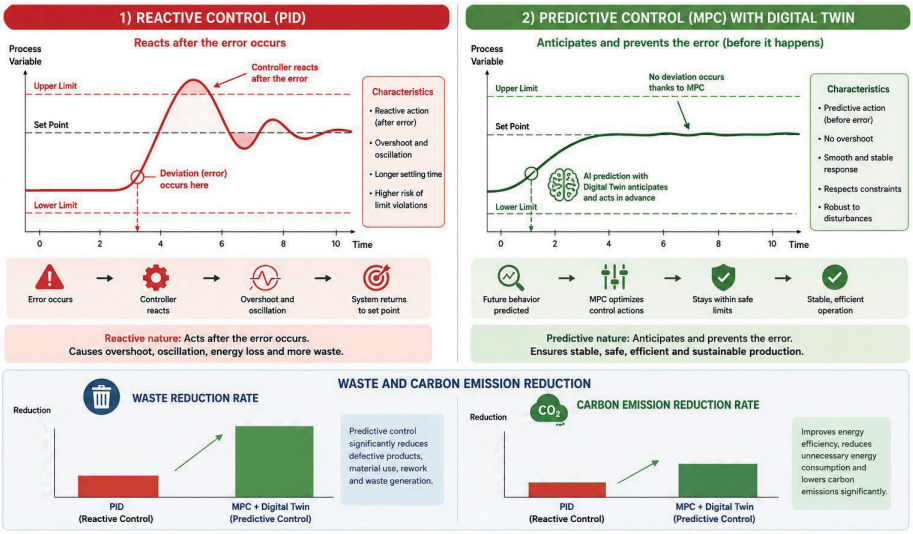

Figure 14. *Comparative operational matrix of reactive PID control versus proactive MPC integrated with Digital Twin architectures. The time-series graphs illustrate that traditional PID mechanisms exhibit lagging oscillatory corrections after a process deviation occurs, whereas the AI-driven MPC-Digital Twin framework achieves real-time predictive mitigation along a smooth, optimal trajectory. The lower bar charts quantify the resulting environmental dividends, showcasing significant reductions in cumulative waste and greenhouse gas (GHG) emissions through high-fidelity process control.*

Preventive control solutions reduce waste generation by avoiding deviations from optimal conditions and reducing the production of off-spec or defective items. They also reduce energy losses and associate carbon emissions by ensuring that plants are running at their best performance level all the time. In addition, predictive maintenance allows anticipating equipment breakdowns, preventing uncontrolled spills and reducing environmental risks. This approach enhances the safety, efficiency and sustainability of processes and allows zero waste and low emissions.

11. SAFETY, RISK, AND RESILIENCE IN CHEMICAL SYSTEMS

Principle 12 of Green Chemistry and Sustainable Engineering Inherently Safer Chemistry for Accident Prevention: Substances and the Form of a Substance Used in a Chemical Process Should Be Chosen to Minimize the Potential for Chemical Accidents, Including Releases, Explosions and Fires. The current industrial ecosystem is facing severe weather events due to climate change, cyber attacks, supply chain fragility and increasingly complex human-machine interfaces.

This situation has resulted in an extension of Principle 12 from the classical accident prevention to the concept of system resilience. Principle 12, in its modern understanding, emphasizes not only the elimination of risks at source, but also the assessment of systems' flexibility to unforeseen shocks, quick recovery and the maintenance of safe interactions in the human-machine-environment interface.

11.1. Accident Prevention → System Resilience

The connection between accident prevention and system resilience plays an important role in today's safety management. In this context, resilience is understood as a concept that reveals aspects that are not easily addressed by traditional safety engineering and management tools like the standard audits and is defined as the ability of a system to recognize internal deviations and "slippery slopes" before an accident occurs. The technological and human barriers, such as software interlocks, alarms and operator controls, form the basis of accident prevention, but resilience emphasizes the importance of the operational effectiveness of the barriers within an overall organizational safety system. It explores how firms develop and strengthen these barriers under complex and dynamic settings such as pressures of production and market demands. From this point of view, system resilience is a technique used in "the art of avoiding normal accidents" in high-reliability organizations, emphasizing the importance of maintaining a continuous awareness of fragility and capacity to adapt to complexity. To evaluate resilience, it is necessary to combine the question "what happens during times of inactivity?" including the understanding of normal operations, with an analysis of the organizational basis of past events and accidents. It is a way to assess the real level of resilience in practical operational contexts and not only based on theoretical or procedural assessments (Le Coze et al., 2006).

In this context, accident prevention is not confined to the implementation of technical barriers, but more significantly, the organizational resilience mechanisms that maintain and reinforce these barriers in time are the key factors that influences the safety performance.

11.2. Process Safety and The Relationship With Green Chemistry

Process safety and green chemistry are inherently connected fields that come together in a synergistic manner, resulting in great benefits. Green chemistry is built on twelve principles that focus on the design of chemical products and processes to reduce or eliminate the use or generation of hazardous substances through waste reduction and increased efficiency. These principles focus heavily on hazard elimination at the design stage, thereby providing an important foundation for process safety. One of the principles, Inherently Safer Chemistry for Accident Prevention, links the prevention of chemical accidents, explosions, and hazardous releases directly to the design of the process itself. Moreover, green chemistry is closely aligned with the hierarchy of controls used in occupational health and safety. It goes a long way to improving process safety performance by focusing on hazard removal and substitution, the top levels of the hierarchy. Prevention via Design (PtD) is the idea of removing hazards at the molecular level through process and equipment design. It is the same preventive attitude that is the basis of green chemistry. The close relationship between green chemistry principles and occupational safety practices is particularly apparent in their alignment with the hierarchy of controls as portrayed in Figure 15.

A method described as "green" does not necessarily mean that it is safe. The use of biomass instead of fossil feedstocks may open new routes of exposure to a variety of worker groups. Similarly, substituting hazardous solvents with water may involve increased temperatures and pressures, and thus other pressure and heat hazards. Steps to reduce pollution by keeping waste in a plant may increase worker exposure and increase risks of fire and explosion. Therefore, sustainable chemical production should combine environmental targets with process safety issues rather than address them as separate objectives. Integration of green chemistry principles with occupational health and safety measures can optimise health benefits, environmental performance and economic efficiency in chemical manufacturing systems (Schulte et al., 2013).

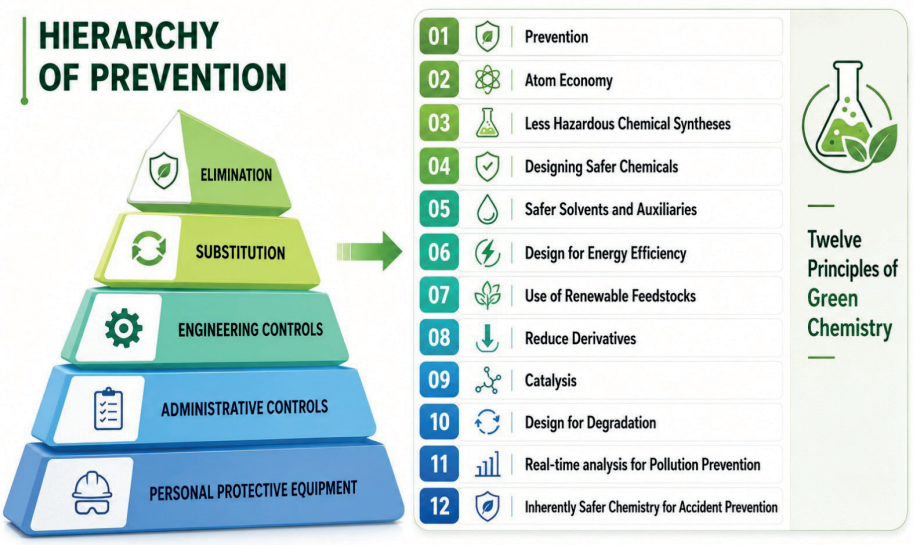

Figure 15. *Conceptual integration framework mapping the Twelve Principles of Green Chemistry alongside the traditional Hierarchy of Prevention in occupational health and safety (OHS). This synergistic model illustrates how molecular-level design rules—such as utilizing benign solvents, inherently safer chemistry, and hazard prevention—directly align with upstream industrial safety tiers (Elimination and Substitution). By embedding chemical risk mitigation at the synthesis stage, the framework demonstrates a proactive paradigm shift from reactive end-of-pipe engineering controls toward inherently resilient, sustainable laboratory and manufacturing ecosystems.*

11.3. Human-Machine-Environment Interaction

A significant problem in modern industrial systems is the interaction between humans, machines and the environment. This problem concerns the mutual influence of operators, intelligent machines and their environment and the optimization of these interactions. The human operator is central to this connection, with real time recording of stress levels, fatigue, physiological state and body movements through biometric markers such as Electrocardiogram (ECG) and Electrodermal Activity (EDA) signals. These physiological data are key inputs for adaptive industrial systems.

Here, the machines are collaborative industrial robots and robotic manipulators that are able to collaborate with people. These systems have self-adaptive features that enable them to change their operating speed, task allocation and operating parameters as per the physiological state and performance of the operatör (Antão et al., 2018).

The contact occurs in industrial production and communal physical work environments where people and robots work together. Sensors, cloud infrastructures and cyber-physical technologies allow continuous communication among all the components of the system, thus improving collaborative environments. The main architecture to control this interaction is the Cyber-Physical Production Systems (CPPS), which enables the machines to identify the human states, like fatigue or stress, measured by Electrocardiogram (ECG) and Electrodermal Activity (EDA) measurements, and to adjust their behaviour according to the environmental requests and the human performance. Consequently, human-machine-environment interaction can lead to a human-centered automation that focuses on operator health and safety while improving productivity, adaptability and overall effectiveness of the system (Antão et al., 2018).

12. EDUCATION, POLICY, AND THE FUTURE OF GREEN CHEMISTRY

The 12 Principles of Green Chemistry and Sustainable Engineering have sparked a technical revolution, from synthesis methods at the lab scale to industrial production processes. But sustainable transformation of society and economy from these scientific angles is not possible just by changing the chemical compositions and production processes. Real change will require the alignment of attitudes, regulatory frameworks and international investment patterns around a shared vision.

12.1. Transformation of Green Chemistry Education

Green chemistry education has undergone a significant transformation over the past 25 years, and structured strategies have been proposed for the next 25 years. This development is primarily driven by the need to improve laboratory safety, overcome infrastructural limitations such as inadequate ventilation, and modernize outdated chemistry curricula. Traditional laboratory practices were increasingly perceived as hazardous and disconnected from contemporary scientific and societal needs, which acted as a key catalyst for change. Curriculum reform strategies have played a central role in this transformation, particularly through instructor-centered design approaches. These strategies include replacing traditional content with safer alternatives, promoting the widespread sharing of educational resources, establishing networks among educators, and leveraging existing drivers of change. In parallel, capacity building has been strengthened through strategic partnerships and educator networks such as the Green Chemistry Education Network, while platforms like GEMs (Greener Educational Materials) have facilitated access to teaching resources through searchable databases (Haack & Hutchison, 2016).

Over time, green chemistry education has expanded beyond chemistry departments and become increasingly interdisciplinary, integrating fields such as business, design, and public policy. For instance, case studies have been developed to help MBA students understand the value proposition of green chemistry. Despite these advances, gaps in the curriculum still remain, and a dedicated Green Chemistry Education Roadmap has been proposed to coordinate future innovations. This roadmap aims to incorporate emerging concepts such as toxicology-informed molecular design and systems thinking into education frameworks (Haack & Hutchison, 2016).

12.2. Science-Policy-Industry Interaction

The importance of science, policy and industry relationship is discussed at length as a critical framework in sustainability research and is identified as one of the two critical issues explored in the literature. This interaction points to the need for better cooperation between science, policy and industry to co-create information and solutions successfully for sustainability. The main aim is to reduce the constant difference between these three bodies, and to form a more integrated collaborative structure.

This association is often studied in the light of the "Triple Helix" model of Etzkowitz (Figure 16), adapted to the context of sustainable development. In this approach, science (universities), policy (government) and industry are seen as the main actors driving sustainability. Each actor plays a distinct role: politics provides the environmental rules and constraints; research identifies socio-ecological potentials and brokers between actors; and industry proposes socio-economic solutions within achievable limits. Effective contact is more than cooperation; it requires a condition of "consonance" that is, common ideals, common ends, and mutual comprehension. The authors emphasize that systems thinking is a useful tool to facilitate communication and engagement among various stakeholders, with common language and concepts. This link is touted as a key lever for achieving sustainability goals based on a systems-thinking approach to increase coordination and effectiveness among stakeholders (Saviano et al., 2019).



Figure 16. *Comprehensive macro-systemic framework illustrating the dynamic interdependencies among society, environment, and economy within the sustainable development paradigm. This original conceptual model delineates the pivotal, collaborative roles of science (knowledge generation), industry (technological execution), and policy (regulatory governance) in driving structural sustainability. By mapping the operational interface specifically socio-ecological opportunities, socio-economic solutions, and rigorous environmental requirements—the diagram provides an integrated roadmap for transitioning from fragmented sectoral operations toward cohesive, planetary-scale sustainable development.*

12.3. Roadmap for Sustainable Chemical Technologies

Sustainable chemical production technologies are concerned with novel approaches to improve production sustainability. In catalysis, organocatalysts that reduce energy requirements and minimize waste are important, as are chiral catalysts that improve efficiency in pharmaceutical synthesis. In biotechnology applications, specific enzymes, bacteria or cultures of algae are used for chemical processing, and the advantage is that they work at ambient pressure and at low temperature settings. Continuous flow chemistry and microreactors provide better control of parameters such as temperature and mixing, which result in better resource and energy efficiency. Recent separation methods include membrane technologies which reduce energy consumption, reactive distillation and extraction processes. New methods of energy input such as plasma, ultrasound and microwave are also used to modify reactions and improve yields. We expect the energy transition and electrification segment to move away from fossil fuels. Electrification means using renewable power to

replace natural gas, for example, electrically heated steam cracker furnaces. Green hydrogen made from water electrolysis is used as a substitute to natural gas in high temperature industrial processes (Steinhäuser & Große Ophoff, 2025).

The focus of circularity and recycling technologies is to shift from linear to circular production processes. Mechanical recycling depends on enhanced sorting and collection logistics to enhance quality while chemical recycling involves conversion of non-recyclable polymers into feedstocks through processes such as pyrolysis, gasification and solvolysis. Three main fossil-free methods are marked out by alternative feedstock technologies. Carbon Capture and Utilization (CCU) is a green hydrogen application that converts CO_2 from emission sources or direct air capture into basic compounds such as methanol or hydrocarbons. The bioeconomy strategy converts biomass and biological waste into chemical feedstocks using biosynthetic pathways or Fischer-Tropsch synthesis. In this framework, the transformation is based on the development of Safe and Sustainable by Design (SSbD) products and on the reduction of the overall material throughput (sufficiency strategy) (Steinhäuser & Große Ophoff, 2025).

12.4. Mapping Green Chemistry onto United Nations Sustainable Development Goals (SDGs)

The ultimate translation of sustainable technological roadmaps (Section 12.3) and Triple Helix collaborative models (Section 12.2) into a functional global reality relies on their capacity to align with the United Nations Sustainable Development Goals (SDGs). While green chemistry education reformulates the academic mindset and institutional consonance harmonizes stakeholder interactions, the SDGs provide the universal, macro-scale metrics toward which these coordinated efforts must converge (Matlin et al., 2015). Next-generation green chemistry transcends the boundaries of localized laboratory efficiency or isolated commercial optimization; it functions as a primary technological and political vector for addressing systemic global crises. By converting the technical pathways established in current roadmaps—encompassing carbon capture, electrification, sufficiency strategies, and Safe and Sustainable by Design (SSbD) protocols—into scalable policy interventions, the microscopic mechanics of molecular design are explicitly mapped onto the macroscopic targets of global sustainability (Steinhäuser & Große Ophoff, 2025). This systematic alignment, illustrating how strategic chemical architectures drive the realization of key United Nations sustainability thresholds, is comprehensively detailed in Figure 17.

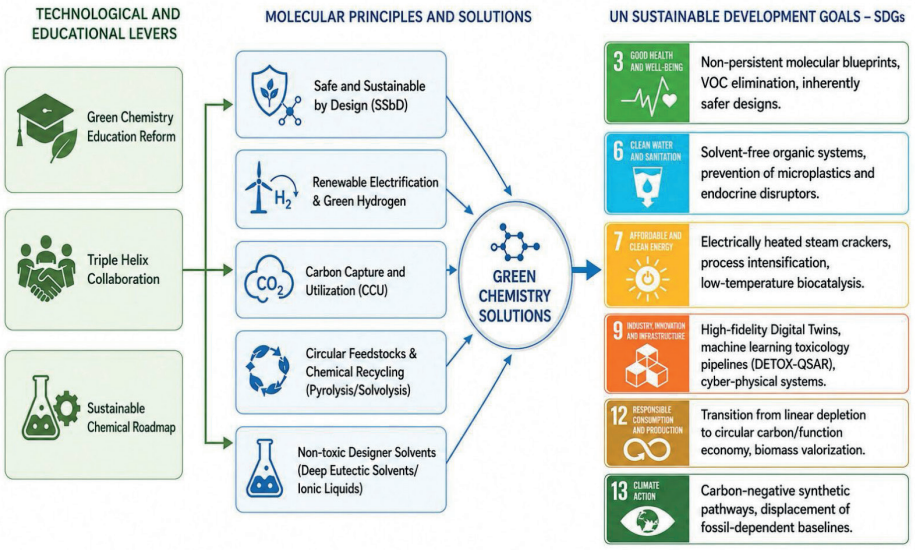

Figure 17. *Conceptual mapping of green chemistry workflows onto the United Nations Sustainable Development Goals (SDGs). The framework illustrates the macro-systemic trajectory originating from foundational drivers (education reform, Triple Helix dynamics, and technology roadmaps), translating through core molecular strategies (inherent safety, circular feedstocks, and industrial electrification), and ultimately converging onto target socio-ecological SDG thresholds (SDGs 3, 6, 7, 9, 12, and 13).*

As delineated in Figure 17, the most direct and immediate socio-ecological impact of advanced green engineering occurs at the nexus of public health and ecosystem preservation, heavily advancing SDG 3 (Good Health and Well-being) and SDG 6 (Clean Water and Sanitation). Traditional chemical manufacturing structures have historically generated persistent, bioaccumulative, and toxic substances that systematically degrade aquatic reservoirs and impose chronic toxicological burdens on vulnerable fence-line communities. By institutionalizing instructor-centered green curricula and adopting rigorous SSbD design protocols, the discipline proactively dismantles these hazards at the blueprint stage. Eliminating volatile organic solvents, utilizing non-persistent alternatives, and deploying highly selective catalytic recovery systems directly prevent the release of microplastics and endocrine disruptors into the biosphere, thereby securing global access to untainted freshwater networks and mitigating environmental health disparities.

Concurrently, the operational synchronization of alternative feedstock technologies and circularity platforms serves as a foundational engine for industrial modernization and resource circularity, directly underpinning SDG 7 (Affordable and Clean Energy), SDG 9 (Industry, Innovation, and Infrastructure), and SDG 12 (Responsible Consumption and Production). The integration of cyber-physical platforms—such as high-fidelity Digital Twins, machine learning toxicology frameworks, and real-time Model Predictive Control (MPC)—allows modern chemical infrastructures to operate close to their theoretical thermodynamic limits. This technological transformation heavily reduces cumulative volumetric energy

consumption and facilitates the systemic adoption of renewable electrocatalysis, green hydrogen loops, and electrically heated steam crackers. By transitioning away from linear fossil fuel extraction toward a circular bioeconomy fueled by biomass valorization, chemical recycling (pyrolysis, solvolysis), and CCU methodologies, the molecular frameworks of the discipline are re-mapped into an integrated matrix that bridges institutional chemistry with global sustainability goals and educational paradigms (da Silva Júnior et al., 2024).

Ultimately, this macro-systemic integration provides the critical technical architecture required for comprehensive SDG 13 (Climate Action). Replacing energy-intensive thermal crackings with low-temperature biocatalytic networks, upgrading to electrified industrial processes, and pioneering carbon-negative synthetic pathways address the anthropogenic drivers of climate change at their molecular source. However, achieving these targets demands that the science-policy-industry interface actively mitigates global imbalances between the Global North and Global South. Ensuring equitable technology transfers, democratizing open-access computational tools, and harmonizing international regulatory frameworks are mandatory steps to prevent chemical colonialism and environmental dumping, thereby rethinking the role of chemical processes for a permanently sustainable world (Kümmerer et al., 2020). By unifying the microscopic precision of catalysis with the macroscopic imperatives of global governance, the mapping of green chemistry onto the SDGs transforms the discipline from a technical methodology into an indispensable instrument for global equity, regenerative environmental democracy, and long-term planetary resilience.

CONCLUSION AND FUTURE PERSPECTIVES

The central argument of this chapter is that green chemistry must evolve beyond its traditional reaction-centered foundations toward a cyber-physical and systems-oriented paradigm capable of integrating molecular design, circular resource management, artificial intelligence, and real-time process optimization.

The evolution of green chemistry—from its foundational conceptual inception in the late twentieth century to its contemporary recognition as a cornerstone of global industrial strategy—represents one of the most significant paradigm shifts in modern scientific history. Yet, the environmental and societal challenges of the twenty-first century reveal that sustainability can no longer be achieved through isolated technological improvements or incremental process modifications alone. Climate change, biodiversity loss, resource depletion, pollution, and the proliferation of novel entities collectively demonstrate that future chemical innovation must operate within the ecological limits defined by planetary boundaries. Consequently, green chemistry must expand from a discipline focused primarily on minimizing environmental harm to a systems-oriented framework actively designed to contribute to the long-term resilience of coupled human–environment systems.

Within this broader perspective, the Twelve Principles of Green Chemistry should no longer be regarded as a static checklist of operational recommendations. Rather, they must be understood as an adaptive and interconnected framework capable of guiding decision-making across molecular, process, industrial, and societal scales. Through the lens of systems thinking, waste prevention, safer synthesis, renewable feedstocks, catalysis, energy efficiency, and end-of-life design become mutually reinforcing components of a larger sustainability architecture. Such an approach enables a transition from conventional hazard reduction toward the generation of measurable ecological, economic, and social value throughout the entire life cycle of chemical products and technologies.

The future trajectory of green chemistry will be increasingly shaped by the convergence of molecular science and digital intelligence. Predictive artificial intelligence, machine learning-assisted toxicity assessment, quantum chemical simulations, digital twins, and advanced process analytics provide unprecedented opportunities to design safer molecules, optimize reaction pathways, and prevent environmental burdens before they emerge. In this emerging cyber-physical ecosystem, sustainability becomes a predictive rather than reactive objective, allowing environmental performance, safety, and resource efficiency to be optimized simultaneously from the earliest stages of innovation.

Equally important is the recognition that technological sustainability cannot be separated from social sustainability. The successful implementation of green chemistry requires not only environmentally benign processes but also equitable access to sustainable technologies, responsible resource governance, protection of public health, and the creation of resilient industrial systems that generate societal benefits alongside economic value. The transition toward sustainable chemical manufacturing

must therefore be guided by principles of environmental justice, circular resource stewardship, and intergenerational responsibility, ensuring that technological progress contributes to both ecological integrity and human well-being.

The strategic deployment of advanced catalytic systems—including single-atom catalysis, biocatalysis, and electrocatalysis—together with process intensification strategies and predictive control architectures, offers a pathway toward operating increasingly close to theoretical efficiency limits. Simultaneously, integrated biorefineries, renewable carbon management, carbon circularity, and comprehensive life cycle assessment frameworks provide practical mechanisms for decoupling industrial growth from resource depletion and greenhouse gas emissions. These approaches collectively establish a direct connection between molecular-scale decisions and global sustainability outcomes.

Importantly, the principles and technologies discussed throughout this chapter directly support several United Nations Sustainable Development Goals (SDGs), including Good Health and Well-Being (SDG 3), Clean Water and Sanitation (SDG 6), Affordable and Clean Energy (SDG 7), Industry, Innovation and Infrastructure (SDG 9), Responsible Consumption and Production (SDG 12), and Climate Action (SDG 13). By transforming technical pathways—such as carbon capture, electrification, and sufficiency strategies—into scalable pedagogical and policy interventions, the discipline bridges the historical gap between microscopic engineering and global socio-economic priorities. Green chemistry therefore emerges not merely as an isolated laboratory methodology but as a strategic enabler of sustainable development and international regulatory alignment.

Ultimately, this chapter proposes a transition from conventional green chemistry toward an integrated sustainability paradigm that unites chemistry, engineering, digital technologies, industrial ecology, and societal responsibility within a single conceptual framework. By embracing planetary boundaries, circular carbon systems, renewable resource management, digitalized manufacturing, and life-cycle thinking, the next generation of chemical innovation can move beyond minimizing harm and begin actively rethinking chemical processes for a permanently sustainable world.

The future of chemistry will not be defined solely by how efficiently molecules are synthesized, but by how intelligently chemical systems interact with ecological processes, economic structures, and human societies. In this new paradigm, green chemistry becomes more than a methodology for cleaner production; it becomes a foundational framework for designing a resilient, equitable, and climate-compatible civilization. The transition toward this vision is no longer optional. It is an ecological necessity, a technological opportunity, and one of the defining responsibilities of modern science in the twenty-first century.

SONUÇ VE GELECEK PERSPEKTİFLERİ

Bu bölümün temel argümanı; yeşil kimyanın, geleneksel reaksiyon odaklı temellerinin ötesine geçerek moleküler tasarımı, döngüsel kaynak yönetimini, yapay zekayı ve gerçek zamanlı süreç optimizasyonunu entegre edebilen siber-fiziksel ve sistem yönelimli bir paradigma yönünde evrilmesi gerektiğidir.

Yeşil kimyanın yirminci yüzyılın sonlarındaki kavramsal doğuşundan, günümüzde küresel endüstriyel stratejinin temel taşı olarak kabul edilmesine kadar uzanan dönüşümü, modern bilim tarihinin en önemli paradigma değişimlerinden birini temsil etmektedir. Ancak, yirmi birinci yüzyılın çevresel ve toplumsal zorlukları, sürdürülebilirliğin artık yalnızca izole teknolojik gelişmeler veya kademeli süreç modifikasyonları ile tek başına sağlanamayacağını göstermektedir. İklim değişikliği, biyoçeşitlilik kaybı, kaynak tükenmesi, kirlilik ve yeni kimyasal unsurların hızla yayılması, gelecekteki kimyasal inovasyonun gezegen sınırları tarafından tanımlanan ekolojik limitler dahilinde işlemesi gerektiğini kolektif olarak kanıtlamaktadır. Sonuç olarak yeşil kimya, yalnızca çevresel zararı en aza indirmeye odaklanan bir disiplinden, insan-çevre sistemlerinin uzun vadeli dayanıklılığına aktif olarak katkıda bulunmak üzere tasarlanmış sistem yönelimli bir çerçeveye doğru genişlemelidir.

Bu daha geniş perspektif içinde, Yeşil Kimyanın On İki İlkesi artık statik bir operasyonel öneriler kontrol listesi olarak görülmemelidir. Aksine, moleküler, süreç, endüstriyel ve toplumsal ölçeklerde karar alma süreçlerine rehberlik edebilecek esnek ve birbiriyle bağlantılı bir çerçeve olarak anlaşılmalıdır. Sistem düşüncesi merceğinden bakıldığında; atık önleme, daha güvenli sentez, yenilenebilir hammaddeler, kataliz, enerji verimliliği ve ömür sonu tasarımı, daha büyük bir sürdürülebilirlik mimarisinin birbirini karşılıklı olarak güçlendiren bileşenleri haline gelir. Böyle bir yaklaşım, geleneksel tehlike azaltma anlayışından, kimyasal ürünlerin ve teknolojilerin tüm yaşam döngüsü boyunca ölçülebilir ekolojik, ekonomik ve toplumsal değerler üretilmesine doğru bir geçişi mümkün kılar.

Yeşil kimyanın gelecekteki yörüngesi, moleküler bilim ile dijital zekanın yakınsamasıyla giderek daha fazla şekillenecektir. Öngörücü yapay zeka, makine öğrenimi destekli toksisite değerlendirmesi, kuantum kimyasal simülasyonları, dijital ikizler ve gelişmiş süreç analitiği; daha güvenli moleküller tasarlamak, reaksiyon yollarını optimize etmek ve çevresel yükleri daha ortaya çıkmadan önlemek için benzeri görülmemiş fırsatlar sunmaktadır. Gelişmekte olan bu siber-fiziksel ekosistemde sürdürülebilirlik, reaktif (tepki veren) bir hedef olmaktan çıkıp prediktif (öngörücü) bir amaca dönüşmekte; böylece çevresel performans, güvenlik ve kaynak verimliliğinin inovasyonun en erken aşamalarından itibaren eşzamanlı olarak optimize edilmesine olanak tanımaktadır.

Teknolojik sürdürülebilirliğin toplumsal sürdürülebilirlikten ayrılamayacağının kabul edilmesi de aynı derecede önemlidir. Yeşil kimyanın başarılı bir şekilde uygulanması, yalnızca çevreye zararsız süreçleri değil, aynı zamanda sürdürülebilir teknolojilere adil erişimi, sorumlu kaynak yönetişimini, halk sağlığının korunmasını ve ekonomik değerin yanı sıra toplumsal fayda da üreten dayanıklı endüstriyel sis-

temlerin kurulmasını gerektirir. Sürdürülebilir kimyasal üretime geçiş, bu nedenle çevresel adalet, döngüsel kaynak yönetimi ve nesiller arası sorumluluk ilkeleriyle yönlendirilmeli; teknolojik ilerlemenin hem ekolojik bütünlüğe hem de insan refahına katkıda bulunması sağlanmalıdır.

Tek atomlu kataliz, biyokataliz ve elektrokataliz dahil olmak üzere gelişmiş katalitik sistemlerin, süreç yoğunlaştırma stratejileri ve öngörücü kontrol mimarileriyle birlikte stratejik olarak konuşlandırılması, teorik verimlilik sınırlarına giderek daha yakın çalışılmasına yönelik bir yol sunmaktadır. Eşzamanlı olarak, entegre biorafineler, yenilenebilir karbon yönetimi, karbon döngüselliği ve kapsamlı yaşam döngüsü değerlendirme (LCA) çerçeveleri, endüstriyel büyümeyi kaynak tükenmesinden ve sera gazı emisyonlarından ayırmak (decoupling) için pratik mekanizmalar sağlamaktadır. Bu yaklaşımlar, moleküler ölçekteki kararlar ile küresel sürdürülebilirlik çıktıları arasında doğrudan bir bağlantı kurmaktadır.

Daha da önemlisi, bu bölüm boyunca tartışılan ilkeler ve teknolojiler, Birleşmiş Milletler Sürdürülebilir Kalkınma Amaçları'ndan (SDG'ler) birçoğunu doğrudan desteklemektedir; bunlar arasında Sağlık ve Kaliteli Yaşam (SDG 3), Temiz Su ve Sanitasyon (SDG 6), Erişilebilir ve Temiz Enerji (SDG 7), Sanayi, Yenilikçilik ve Altyapı (SDG 9), Sorumlu Tüketim ve Üretim (SDG 12) ve İklim Eylemi (SDG 13) yer almaktadır. Karbon yakalama, elektrifikasyon ve yeterlilik stratejileri gibi teknik yolları ölçeklendirilebilir pedagojik ve politik müdahalelere dönüştürerek bu disiplin, mikroskobik mühendislik ile küresel sosyo-ekonomik öncelikler arasındaki tarihsel boşluğu kapatmaktadır. Bu nedenle yeşil kimya, yalnızca izole bir laboratuvar metodolojisi olarak değil, sürdürülebilir kalkınmanın ve uluslararası mevzuat uyumunun stratejik bir kolaylaştırıcısı olarak ortaya çıkmaktadır.

Nihayetinde bu bölüm, geleneksel yeşil kimyadan; kimya, mühendislik, dijital teknolojiler, endüstriyel ekoloji ve toplumsal sorumluluğu tek bir kavramsal çerçevede birleştiren bütünleşik bir sürdürülebilirlik paradigmasına geçişi önermektedir. Gezegen sınırlarının gözetildiği, döngüsel karbon sistemlerinin benimsendiği, yenilenebilir kaynak yönetiminin desteklendiği, dijitalleşmiş üretim altyapılarının kullanıldığı ve yaşam döngüsü düşüncesinin merkeze alındığı bu yeni yaklaşım, sonraki nesil kimyasal inovasyonun yalnızca zararı en aza indirmekle kalmayıp, çevresel ve toplumsal değeri aktif olarak yeniden üretmeye (rejenerasyon) başlamasını sağlayacaktır.

Kimyanın geleceği yalnızca moleküllerin ne kadar verimli sentezlendiği ile değil, kimyasal sistemlerin ekolojik süreçler, ekonomik yapılar ve insan toplumlarıyla ne kadar akıllıca etkileşim kurabildiği ile tanımlanacaktır. Bu yeni paradigmada yeşil kimya, temiz üretim yöntemlerinin ötesine geçerek dayanıklı, adil ve iklimle uyumlu bir medeniyetin tasarımı için temel bir çerçeveye dönüşmektedir. Bu vizyona doğru geçiş artık isteğe bağlı bir tercih değildir. Bu, ekolojik bir zorunluluk, teknolojik bir fırsat ve yirmi birinci yüzyıl modern biliminin üstlenmesi gereken en belirleyici sorumluluklardan biridir.

REFERENCES

1. Ahmed, S., Warne, T., Smith, E., Goemann, H., Linse, G., Greenwood, M., Kedziora, J., Sapp, M., Kraner, D., Roemer, K., Haggerty, J. H., Jarchow, M., Swanson, D., Poulter, B., & Stoy, P. C. (2021). Systematic review on effects of bioenergy from edible versus inedible feedstocks on food security. npj Science of Food, 5(1), Article 9. https://doi.org/10.1038/s41538-021-00091-6
2. Anastas, P. T., & Warner, J. C. (2000). Green Chemistry. Oxford University PressOxford. https://doi.org/10.1093/oso/9780198506980.001.0001
3. Apel, C., Kümmerer, K., Mendoza, G., Cerrillo, C., Ormazabal, G., Colin, C., Walter, L., Nam, A., Denisenko, R., Meeus, M., Petrovykh, D. Y., Batel, A., Aguirre, I. G., & Soeteman-Hernández, L. G. (2026). Safe and Sustainable by Design (SSbD) landscape: Mapping state of the art approaches along the innovation process and developing good practices. Sustainable Chemistry and Pharmacy, 50, 102355. https://doi.org/10.1016/j.scp.2026.102355
4. Bastos Lima, M. G. (2022). Just transition towards a bioeconomy: Four dimensions in Brazil, India and Indonesia. Forest Policy and Economics, 136, Article 102684. https://doi.org/10.1016/j.forpol.2021.102684
5. Brooks, B. W. (2019). Greening chemistry and ecotoxicology towards sustainable environmental quality. Green Chemistry, 21(10), 2575–2582. https://doi.org/10.1039/C8GC03893G
6. Bukhtiyarova, M. V., Nuzhdin, A. L., & Bukhtiyarova, G. A. (2023). Comparative Study of Batch and Continuous Flow Reactors in Selective Hydrogenation of Functional Groups in Organic Compounds: What Is More Effective? In International Journal of Molecular Sciences (Vol. 24, Number 18). Multidisciplinary Digital Publishing Institute (MDPI). https://doi.org/10.3390/ijms241814136
7. Bullard, R. D. (2018). Dumping in Dixie: Race, class, and environmental quality. Routledge. ISBN 13: 978-0-8133-6792-7
8. Antão, L., Pinto, R., Reis, J., Gonçalves, G., & Pereira, F. L. (2018, June). Cooperative human-machine interaction in industrial environments. In 2018 13th APCA International Conference on Automatic Control and Soft Computing (CONTROLO) (pp. 430-435). IEEE. ISBN: 9781538653463
9. Çelik, F. K., & Doğan, S. (2026). Safe-by-redesign guidance for toxic industrial chemicals using explainable artificial intelligence: Introducing the DETOX-QSAR model. Scientific Reports, 16(1), 18072. https://doi.org/10.1038/s41598-026-48176-0
10. Chen, T. L., Kim, H., Pan, S. Y., Tseng, P. C., Lin, Y. P., & Chiang, P. C. (2020). Implementation of green chemistry principles in circular economy system towards sustainable development goals: Challenges and perspectives. Science of The Total Environment, 716, 136998. https://doi.org/10.1016/J.SCITOTENV.2020.136998
11. Chen, Y. P., Karkaria, V., Tsai, Y. K., Rolark, F., Quispe, D., Gao, R. X., Cao, J., & Chen, W. (2025). Real-time decision-making for Digital Twin in additive manufacturing with Model Predictive Control using time-series deep neural networks. Journal of Manufacturing Systems, 80, 412–424. https://doi.org/10.1016/j.jmsy.2025.03.009
12. Constable, D. J. (2021). Green and sustainable chemistry–The case for a systems-based, interdisciplinary approach. IScience, 24(12). https://doi.org/10.1016/j.isci.2021.103489

13. da Silva Júnior, C. A., Morais, C., de Jesus, D. P., & Girotto Júnior, G. (2024). The role of the periodic table of the elements of green and sustainable chemistry in a high school educational context. Sustainability, 16(6), Article 2504. https://doi.org/10.3390/su16062504

14. Eichwald, S., Ostovari, H., Minten, H., Meyer-Waßewitz, J., Förtsch, D., & von der Assen, N. (2025). Assessing mass intensity as a green chemistry metric: why expanding system boundaries is not enough. Green Chemistry, 27(34), 10153–10168. https://doi.org/10.1039/D5GC02994E

15. EUR-Lex - 02006R1907-20260511 - EN - EUR-Lex. (n.d.). Retrieved June 25, 2026, from https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A02006R1907-20260511

16. Felicioni, L., Gaspari, J., Veselka, J., & Malík, Z. (2023). A comparative cradle-to-grave life cycle approach for addressing construction design choices: An applicative case study for a residential tower in Aalborg, Denmark. Energy and Buildings, 298, 113557. https://doi.org/10.1016/j.enbuild.2023.113557

17. Goh, C. S., Junginger, M., & Faaij, A. (2014). Monitoring sustainable biomass flows: General methodology development. Biofuels, Bioproducts and Biorefining, 8(1), 83–102. https://doi.org/10.1002/bbb.1445

18. Gracia-Barberán, S., Leal-Duaso, A., & Pires, E. (2022). Are deep eutectic solvents a real alternative to ionic liquids in metal-catalysed reactions? In Current Opinion in Green and Sustainable Chemistry (Vol. 35). Elsevier B.V. https://doi.org/10.1016/j.cogsc.2022.100610

19. Gutiérrez, A., & Palos, R. (2023). Green Chemistry: From Wastes to Value-Added Products. In Processes (Vol. 11, Number 7). Multidisciplinary Digital Publishing Institute (MDPI). https://doi.org/10.3390/pr11072131

20. Haack, J. A., & Hutchison, J. E. (2016). Green chemistry education: 25 years of progress and 25 years ahead. ACS Sustainable Chemistry and Engineering, 4(11), 5889–5896. https://doi.org/10.1021/acssuschemeng.6b02069

21. Habib, U., Ahmad, F., Awais, M., Naz, N., Aslam, M., Urooj, M., Moqeem, A., Tahseen, H., Waqar, A., Sajid, M., & Shabbir, M. J. (2023). Sustainable Catalysis: Navigating Challenges and Embracing Opportunities for a Greener Future. Journal of Chemistry and Environment, 2(2), 14–53. https://doi.org/10.56946/jce.v2i2.205

22. Hao, Q., Tian, J., Li, X., & Chen, L. (2017). Using a hybrid of green chemistry and industrial ecology to make chemical production greener. Resources, Conservation and Recycling, 122, 106–113. https://doi.org/10.1016/j.resconrec.2017.02.001

23. Healy, N., & Barry, J. (2017). Politicizing energy justice and energy system transitions: Fossil fuel divestment and a "just transition". Energy Policy, 108, 451–459. https://doi.org/10.1016/j.enpol.2017.06.014

24. Jamesh, M. I., Akila, A., Sudha, D., Gnana Priya, K., Sivaprakash, V., & Revathi, A. (2022). Fabrication of Earth-Abundant Electrocatalysts Based on Green-Chemistry Approaches to Achieve Efficient Alkaline Water Splitting—A Review. In Sustainability (Switzerland) (Vol. 14, Number 24). MDPI. https://doi.org/10.3390/su142416359

25. Jerome, A., & Ljunggren, M. (2025). Product lifetime in life cycle assessments of circular economy strategies — A review and consolidation of methodology. In International Journal of Life Cycle Assessment (Vol. 30, Number 10, pp. 2162–2189). Springer. https://doi.org/10.1007/s11367-025-02470-7

26. Kaygusuz, K. (2019). Green chemistry and green energy technologies for environmental friendly sustainable development. Journal of Engineering Research and Applied Science, 8(1), 1013–1024. https://www.journaleras.com/index.php/jeras/article/view/148/138

27. Kümmerer, K., Clark, J. H., & Zuin, V. G. (2020). Rethinking chemistry for a permanent sustainable world. Science, 367(6476), 369–370. https://doi.org/10.1126/science.aba4979

28. Le Coze, J.-C., Dupre, M., Christophe Le Coze, J., & Dupré, M. (2006). How to prevent a normal accident in a high reliable organisation ? The art of resilience, a case study in the chemical industry How to prevent a Normal Accident in a High Reliable Organisation? The art of resilience, a case study in the chemical industry. 181–190. https://hal-ineris.archives-ouvertes.fr/ineris-00973243

29. Li, J., Yang, R., Xu, S., Zhou, C., Xiao, Y., Hu, C., & Tsang, D. C. W. (2022). Biomass-derived polyols valorization towards glycolic acid production with high atom-economy. Applied Catalysis B: Environmental, 317, 121785. https://doi.org/10.1016/J.APCATB.2022.121785

30. Lu, Q., Yi, S., Gan, M., Huang, J., Zhang, X., Yang, Y., Shen, C., & Yao, L. (2024, October 13). Degrade to Function: Towards Eco-friendly Morphing Devices that Function Through Programmed Sequential Degradation. UIST 2024 - Proceedings of the 37th Annual ACM Symposium on User Interface Software and Technology. https://doi.org/10.1145/3654777.3676464

31. Marques, C. A., & Machado, A. A. S. C. (2021). An integrated vision of the Green Chemistry evolution along 25 years. Foundations of Chemistry, 23(3), 299–328. https://doi.org/10.1007/s10698-021-09396-6

32. Matlin, S. A., Mehta, G., Hopf, H., & Krief, A. (2016). One-world chemistry and systems thinking. Nature Chemistry, 8(5), 393–398. https://doi.org/10.1038/nchem.2498

33. Mellor, K. E., Coish, P., Brooks, B. W., Gallagher, E. P., Mills, M., Kavanagh, T. J., Simcox, N., Lasker, G. A., Botta, D., Voutchkova-Kostal, A., Kostal, J., Mullins, M. L., Nesmith, S. M., Corrales, J., Kristofco, L., Saari, G., Steele, W. B., Melnikov, F., Zimmerman, J. B., & Anastas, P. T. (2018). The safer chemical design game. Gamification of green chemistry and safer chemical design concepts for high school and undergraduate students. Green Chemistry Letters and Reviews, 11(2), 103–110. https://doi.org/10.1080/17518253.2018.1434566

34. Mohai, P., Pellow, D. N., & Roberts, J. T. (2009). Environmental justice. Annual Review of Environment and Resources, 34, 405–430. https://doi.org/10.1146/annurev-environ-082508-094348

35. Moser, F., & Jakl, T. (2014). Chemical leasing—a review of implementation in the past decade. Environmental Science and Pollution Research 2014 22:8, 22(8), 6325–6348. https://doi.org/10.1007/S11356-014-3879-3

36. Ncube, A., Mtetwa, S., Bukhari, M., Fiorentino, G., & Passaro, R. (2023). Circular Economy and Green Chemistry: The Need for Radical Innovative Approaches in the Design for New Products. Energies, 16(4), 1752. https://doi.org/10.3390/en16041752

37. Newell, P., & Mulvaney, D. (2013). The political economy of the "just transition". The Geographical Journal, 179(2), 132–140. https://doi.org/10.1111/geoj.12008

38. Nian, B., & Li, X. (2022). Can deep eutectic solvents be the best alternatives to ionic liquids and organic solvents: A perspective in enzyme catalytic reactions. In International Journal of Biological Macromolecules (Vol. 217, pp. 255–269). Elsevier B.V. https://doi.org/10.1016/j.ijbiomac.2022.07.044

39. Persson, L., Almroth, B. M. C., Collins, C. D., Cornell, S., de Wit, C. A., Diamond, M. L., Fantke, P., Thomsen, M., Carriker, M. W. O., Sørensen, J. A., Backhaus, T., Christensen, F. M., Fauser, P., MacLeod, M., Cousins, I. T., Posthuma, L., van de Meent, D., Rauscher, H., Salieri, B., ... & Hauschild, M. Z. (2022). Outside the safe operating space of the planetary boundary for novel entities. Environmental Science & Technology, 56(3), 1510–1521. https://doi.org/10.1021/acs.est.1c04158

40. Plutschack, M. B., Pieber, B., Gilmore, K., & Seeberger, P. H. (2017). The Hitchhiker's Guide to Flow Chemistry â¥. In Chemical Reviews (Vol. 117, Number 18, pp. 11796–11893). American Chemical Society. https://doi.org/10.1021/acs.chemrev.7b00183

41. Prajapati, A., Hahn, C., Weidinger, I. M., Shi, Y., Lee, Y., Alexandrova, A. N., Thompson, D., Bare, S. R., Chen, S., Yan, S., & Kornienko, N. (2025). Best practices for in-situ and operando techniques within electrocatalytic systems. Nature Communications, 16(1). https://doi.org/10.1038/s41467-025-57563-6

42. Ray, P. (2019). Renewable energy and sustainability. In Clean Technologies and Environmental Policy (Vol. 21, Number 8, pp. 1517–1533). Springer Verlag. https://doi.org/10.1007/s10098-019-01739-4

43. Richardson, K., Steffen, W., Lucht, W., Bendtsen, J., Cornell, S. E., Donges, J. F., Fetzer, I., Karandage, S. J., Forbes, V., Heinke, J., Hewitt, K., Jaramillo, F., Jin, W. X., Kim, D. H., Kittel, T. G. F., Kummu, M., Lane, S. E., Lewis, K., Lenton, T. M., ... & Rockström, J. (2023). Earth beyond six of nine planetary boundaries. Science Advances, 9(37), eadh2458. https://doi.org/10.1126/sciadv.adh2458

44. Rockström, J., Steffen, W., Noone, K., Persson, Å., Chapin, F. S., Lambin, E. F., Lenton, T. M., Scheffer, M., Folke, C., Schellnhuber, H. J., Nykvist, B., de Wit, C. A., Hughes, T., van der Leeuw, S., Rodhe, H., Sörlin, S., Snyder, P. K., Costanza, R., Svedin, U., ... & Foley, J. A. (2009). A safe operating space for humanity. Nature, 461(7263), 472–475. https://doi.org/10.1038/461472a

45. Saviano, M., Barile, S., Farioli, F., & Orecchini, F. (2019). Strengthening the science–policy–industry interface for progressing toward sustainability: a systems thinking view. Sustainability Science, 14(6), 1549–1564. https://doi.org/10.1007/s11625-019-00668-x

46. Scheringer, M., Johansson, J. H., Salter, M. E., Sha, B., & Cousins, I. T. (2022). Stories of Global Chemical Pollution: Will We Ever Understand Environmental Persistence? In Environmental Science and Technology (Vol. 56, Number 24, pp. 17498–17501). American Chemical Society. https://doi.org/10.1021/acs.est.2c06611

47. Schulte, P. A., Mckernan, L. T., Heidel, D. S., Okun, A. H., Dotson, G. S., Lentz, T. J., Geraci, C. L., Heckel, P. E., & Branche, C. M. (2013). Occupational safety and health, green chemistry, and sustainability: a review of areas of convergence. http://www.ehjournal.net/content/12/1/31

48. Schwenzer, M., Ay, M., Bergs, T., & Abel, D. (2021). Review on model predictive control: an engineering perspective. In International Journal of Advanced Manufacturing Technology (Vol. 117, Numbers 5–6, pp. 1327–1349). Springer Science and Business Media Deutschland GmbH. https://doi.org/10.1007/s00170-021-07682-3

49. Serrano-Ortiz, P., Roland, M., Sanchez-Moral, S., Janssens, I. A., Domingo, F., Goddéris, Y., & Kowalski, A. S. (2010). Hidden, abiotic CO2 flows and gaseous reservoirs in the terrestrial carbon cycle: Review and perspectives. In Agricultural and Forest Meteorology (Vol. 150, Number 3, pp. 321–329). https://doi.org/10.1016/j.agrformet.2010.01.002

50. Sheldon, R. A. (2016). Green chemistry and resource efficiency: towards a green economy. Green Chemistry, 18(11), 3180–3183. https://doi.org/10.1039/C6GC90040B

51. Sivakumar, L., Rajamohan, R., Asaithambi, A. T., Elumalai, P., Kumar, A. S., Cui, J., Gao, X., Parthipan, P., Kim, W., & Govarthanan, M. (2026). Persistence of Polycyclic Aromatic Hydrocarbons and Microplastics: A Serious Alarm to Human Health and Ecosystems. In Chemical Record. John Wiley and Sons Inc. https://doi.org/10.1002/tcr.202500206

52. Steffen, W., Richardson, K., Rockström, J., Cornell, S. E., Fetzer, I., Bennett, E. M., Biggs, R., Carpenter, S. R., de Vries, W., de Wit, C. A., Folke, C., Gerten, D., Heinke, J., Mace, G. M., Persson, Å., Ramanathan, V., Reyers, B., & Sörlin, S. (2015). Planetary boundaries: Guiding human development on a changing planet. Science, 347(6223), 1259855. https://doi.org/10.1126/science.1259855

53. Steinhäuser, K. G., & Große Ophoff, M. (2025). The Need for Change: A Roadmap for the Sustainable Transformation of the Chemical Industry. In Sustainable Chemistry (Vol. 6, Number 2). Multidisciplinary Digital Publishing Institute (MDPI). https://doi.org/10.3390/suschem6020016

54. Stockholm Convention on Persistent Organic Pollutants. (2001). Stockholm Convention on Persistent Organic Pollutants: Text and annexes. United Nations Environment Programme. https://chm.pops.int

55. Sun, X., & Wang, Z. (2026). Advancing sustainable bioeconomy: Integrative biorefinery pathways for circular valorization of agro-industrial residues. Industrial Crops and Products, 243. https://doi.org/10.1016/j.indcrop.2026.123038

56. Tufvesson, L. M., Tufvesson, P., Woodley, J. M., & Börjesson, P. (2013). Life cycle assessment in green chemistry: overview of key parameters and methodological concerns. The International Journal of Life Cycle Assessment, 18(2), 431–444. https://doi.org/10.1007/s11367-012-0500-1

57. United Nations Environment Programme (UNEP). (2023). Global framework on chemicals: For a planet free of harm from chemicals and waste. United Nations Environment Programme. https://www.unep.org/global-framework-chemicals

58. Wang, X., Lo, K., Guan, J., & Liu, Y. (2022). Just transition: A conceptual review. Energy Research & Social Science, 92, Article 102809. https://doi.org/10.1016/j.erss.2022.102809

59. Yang, X. F., Wang, A., Qiao, B., Li, J., Liu, J., & Zhang, T. (2013). Single-atom catalysts: A new frontier in heterogeneous catalysis. Accounts of Chemical Research, 46(8), 1740–1748. https://doi.org/10.1021/ar300361m

60. Younis, A., & Said, A. O. (2023). Solvent-free Organic Reaction Techniques as an Approach for Green Chemistry. In Journal of the Turkish Chemical Society, Section A: Chemistry (Vol. 10, Number 2, pp. 549–576). Turkish Chemical Society. https://doi.org/10.18596/jotcsa.1188983

61. Zhang, J., Du, H., Wang, T., Xiao, P., Lu, S., Zhao, G., Zhao, J., & Li, G. (2024). Tracking the carbon flows in municipal waste management in China. Scientific Reports, 14(1). https://doi.org/10.1038/s41598-024-51698-0

62. Zhou, F., Hearne, Z., & Li, C. J. (2019). Water—the greenest solvent overall. In Current Opinion in Green and Sustainable Chemistry (Vol. 18, pp. 118–123). Elsevier B.V. https://doi.org/10.1016/j.cogsc.2019.05.004

GREEN CHEMISTRY–BASED DESIGN AND PROCESS APPROACHES FOR POLLUTION PREVENTION AT SOURCE

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ABSTRACT

Industrial production has become a major source of environmental pollution alongside its contributions to economic and technological development. The increasing complexity of chemical production systems and growing energy and resource demands have revealed the limitations of approaches that focus solely on controlling pollution after it is generated. Consequently, greater attention has been directed toward preventive strategies that seek to reduce environmental impacts at their source. Green Chemistry addresses these challenges by promoting the design of chemical products and processes that minimize pollution, waste generation, and resource consumption from the outset. This chapter examines source-oriented pollution prevention from a Green Chemistry perspective, focusing on the influence of process design, raw material selection, energy use, reaction pathways, and technological choices on environmental performance. Approaches used to evaluate pollution prevention performance and limitations are also discussed, highlighting the importance of integrating preventive principles into production systems to support sustainable development.

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1. INTRODUCTION

Industrial production activities play a central role in the economic and technological development of modern societies, while at the same time constituting one of the major sources of environmental pollution. The increasing complexity of chemical products and processes, high production volumes, and the widespread use of energy-intensive technologies have revealed the limitations of approaches that rely solely on controlling environmental impacts at the final stages. This situation has made it necessary for environmental protection practices to shift from methods focused on remediating pollution after it has occurred toward preventive approaches that aim to reduce environmental impacts during the design and process development stages. Source-oriented pollution prevention focuses on reducing the environmental impacts of chemical products and processes at the earliest possible stage. This includes strategies aimed at minimizing waste generation, promoting the use of safer chemicals and reaction pathways, and improving energy and resource efficiency. Within this perspective, Green Chemistry provides an important framework for integrating environmental considerations into design and process-related decisions (Anastas & Warner, 2000).

The rapid expansion of industrial production and the increasing use of chemical products have made environmental pollution problems more complex and multidimensional. Recent assessments suggest that addressing chemical risks and environmental impacts only through specific substances or isolated processes is often insufficient for the effective management of pollution-related problems. In particular, process design, energy use, raw material selection, and technological choices interact closely with one another and strongly influence the mechanisms through which pollution is generated. For this reason, strategies aimed at reducing environmental impacts should consider not only the properties of chemical products themselves, but also the broader design and operation of production processes. International assessment reports emphasize that the wider adoption of preventive approaches is essential both for reducing environmental risks and for supporting sustainable production objectives (UNEP, 2019).

Green Chemistry is increasingly viewed not only as an approach for reducing environmental impacts at the process level, but also as a broader design strategy that supports sustainability objectives. From this perspective, the relationship between Green Chemistry principles and the United Nations Sustainable Development Goals offers a useful framework for understanding how pollution prevention strategies can contribute to wider sustainability efforts (**Figure 1**).



Figure 1. *Relationship Between Green Chemistry Principles and the United Nations Sustainable Development Goals (Kurul et al., 2025)*

Source-based pollution prevention does not regard regulatory measures or end-of-pipe control technologies alone as sufficient for managing environmental problems. Instead, it emphasizes that decisions related to chemical product and process design should be evaluated together with raw material selection, reaction pathways, process conditions, and operational strategies. Within this approach, pollution is treated not simply as an outcome to be controlled after production, but as an issue that can be addressed during product and process development stages. Previous studies suggest that preventive strategies of this kind can provide more durable improvements in environmental performance, particularly when they are incorporated into design and process selection at early stages (Veleva & Ellenbecker, 2001).

Source-based prevention strategies highlight the strong relationship between environmental impacts and the design and operational decisions made throughout production processes. Factors such as process conditions, raw material selection, and the technologies employed all influence how pollution is generated and the extent of its environmental effects. International assessment reports similarly emphasize that the effectiveness of pollution prevention strategies depends largely on whether environmental considerations are integrated into these decisions from the beginning. In this respect, Green Chemistry–based design and process approaches offer a useful framework for incorporating environmental objectives into production systems at earlier stages and supporting source-oriented pollution prevention (UNEP, 2013).

2. POLLUTION PREVENTION: CONCEPTUAL FRAMEWORK

2.1. Definition of the pollution prevention approach

Pollution prevention refers to an approach that aims to reduce or eliminate the activities that give rise to environmental impacts, rather than controlling those impacts after the completion of the production process. The primary objective of this approach is to prevent the generation of wastes, emissions, and hazardous by-products as much as possible, instead of managing them once they have already been produced. Environmental impacts are therefore not treated as issues addressed at the end of the process, but as results that are directly shaped by the way production systems are designed (Anastas & Warner, 2000).

The pollution prevention approach is based on the recognition that managing wastes and emissions after they have been generated provides limited environmental and economic benefits. The treatment or disposal of wastes generated during production often requires additional energy and resource inputs and, in many cases, does not fully eliminate associated environmental impacts. From this perspective, pollution prevention emphasizes that effective environmental improvement depends on reconsidering the processes that lead to pollution generation, rather than focusing solely on post-production control measures (OECD, 2011).

Beyond improving environmental performance, pollution prevention also seeks to enhance the efficiency and safety of production processes. Practices such as reducing raw material consumption, selecting more selective reaction pathways, and improving process operating conditions can simultaneously limit pollution generation and increase production efficiency. In this sense, pollution prevention establishes a direct link between environmental objectives and production performance (Veleva & Ellenbecker, 2001).

In the literature, pollution prevention is addressed not merely as a set of environmental management practices, but as an integral component of production and design decision-making. The effectiveness of this approach depends on the consideration of environmental impacts during process development and design stages. Accordingly, pollution prevention represents a perspective that prioritizes limiting the conditions that give rise to environmental problems from the outset, rather than intervening after such problems have emerged (UNEP, 2019).

2.2. Comparison with end-of-pipe approaches

End-of-pipe approaches are based on controlling environmental pollution after the completion of the production process. These approaches focus on the treatment, capture, or disposal of wastes and emissions before their release into the environment. Filtration systems, flue gas treatment units, and wastewater treatment plants are among the most common applications of this approach. In these approaches, pollution is generally regarded as a natural consequence of the production process, and environmental intervention is implemented at the final stages of operation (Freeman, 1995).

Although end-of-pipe measures can contribute to reducing environmental impacts under certain conditions, they do not directly modify the processes that give rise to pollution. The treatment of wastes and emissions often requires additional energy, chemical inputs, and infrastructure, which may result in the transfer of environmental impacts to other stages of the system or to different environmental areas. As a result, these approaches tend to focus on managing the effects of pollution rather than reducing the amount of pollution generated (Allen & Rosselot, 1994).

In contrast, the pollution prevention approach is based on the recognition that environmental impacts are largely determined by decisions made at the early stages of the production process. By modifying factors such as raw material selection, reaction conditions, and process design, pollution generation can be limited before it occurs. Environmental improvement is achieved through the restructuring of production processes, rather than through technical interventions applied after pollution has been generated (U.S. EPA, 1990).

Comparative assessments reported in the literature indicate that strategies based on pollution prevention provide more durable environmental and operational benefits in the long term. While end-of-pipe approaches play an important role in meeting regulatory requirements, they remain limited in their ability to reduce pollution generation when applied on their own. For this reason, environmental management practices increasingly emphasize the combined consideration of end-of-pipe measures and preventive approaches to achieve more effective outcomes (European Commission, 2000). The key differences between end-of-pipe approaches and pollution prevention are summarized in **Table 1** (Allen & Rosselot, 1994; Freeman, 1995).

2.3. Position within the philosophy of Green Chemistry

The pollution prevention approach is directly linked to the fundamental principles of Green Chemistry. Green Chemistry emphasizes the consideration of environmental and human health impacts during the design of chemical products and processes, rather than relying on the control of wastes and hazardous substances after they have been generated. From this perspective, pollution prevention can be regarded as a natural extension of the design-oriented philosophy of Green Chemistry (Anastas & Warner, 2000).

The design principles developed within Green Chemistry focus on reducing waste generation, selecting safer substances and reaction pathways, and improving energy and raw material efficiency. Pollution prevention enables the practical application of these principles by ensuring that environmental objectives are taken into account during chemical design and process development stages. This perspective highlights Green Chemistry as a design-driven approach that actively shapes production processes. In this sense, pollution prevention can be regarded as one of the key principles guiding design and process development decisions within Green Chemistry (Clark & Macquarrie, 2002).

Table 1. *Comparison of end-of-pipe and Pollution Prevention Approaches*

Comparison criterion	End-of-pipe approaches	Pollution prevention
Stage of intervention	After completion of the production process	During the design and planning stages of the production process
Primary focus	Treatment or disposal of generated wastes and emissions	Reduction of waste and emissions generation at the source
View of pollution	Considered an unavoidable outcome of production	Considered a consequence of design and process decisions
Typical methods	Filtration systems, flue gas treatment, wastewater treatment systems	Raw material selection, improved reaction conditions, process design
Energy and resource requirements	Often require additional energy and auxiliary materials	Aim to reduce energy and resource consumption
Environmental impact profile	Risk of transferring pollution to other environmental areas	Pollution is limited before it is generated
Long-term implications	Focused on compliance with regulatory requirements	Focused on providing more durable environmental and operational benefits

3. GREEN CHEMISTRY PRINCIPLES AND POLLUTION PREVENTION

Green Chemistry provides a broad framework for reducing environmental impacts through the design of chemical products and processes. Its principles address different aspects of sustainability, including waste minimization, safer chemical selection, energy efficiency, and resource conservation. Among these principles, waste prevention, safer chemical design, and the reduction of hazardous by-products are particularly relevant to source-oriented pollution prevention and are therefore discussed in the following sections.

3.1. Prevention of waste generation

The prevention of waste generation is regarded as one of the fundamental approaches to reducing environmental impacts in chemical production processes. Wastes arising in industrial systems are closely linked to process design, the organization of material flows, and the technical choices made during production. For this reason, waste management should not be viewed as the control of wastes after generation, but as an issue d irectly associated with decisions taken at the early stages of the production process. Research in industrial ecology shows that reducing waste generation can be achieved through the design of more efficient and less resource-intensive systems (Graedel & Allenby, 2010).

Applications aimed at preventing waste generation primarily focus on simplifying production processes, eliminating unnecessary processing steps, and improving the efficiency of raw material use. Cleaner production and eco-efficiency approaches have shown that process-level improvements and design modifications can significantly

reduce the amount of waste generated. Such approaches challenge the assumption that waste is an inevitable outcome of production processes and demonstrate that preventive measures are technically and economically feasible (Van Berkel, 2007).

Waste prevention approaches are closely associated with the principles of the circular economy. In circular systems, materials are kept within the system for as long as possible, with the aim of minimizing the generation of waste. From this perspective, waste prevention is not limited to the production stage, but extends across product design, manufacturing, and post-use phases. Several studies have shown that reducing waste generation at the source can significantly improve resource efficiency while also lowering environmental pressures (Ghisellini et al., 2016).

3.2. Safer chemicals and reaction pathways

The development of safer chemicals plays an important role in approaches aimed at preventing pollution at its source. The impacts of chemical substances on human health and the environment are shaped not only during use, but throughout the entire production process. For this reason, directing chemical design toward substances with lower hazard potential—while maintaining functional performance—contributes to limiting environmental risks at an early stage. The literature shows that considering hazard characteristics during the design phase leads to more effective outcomes than relying on the control of risks after they have arisen (Zimmerman et al., 2020).

The selection of reaction pathways directly influences pollution generation by complementing the use of safer chemicals. Choosing reactions with higher selectivity helps reduce the formation of by-products and limits the presence of hazardous intermediates, thereby lowering the environmental load of production. Developing alternative synthesis routes and employing less hazardous reaction conditions make it possible to reduce both waste generation and process-related risks. Such approaches have been shown to significantly improve the environmental performance of reaction design, particularly in the pharmaceutical industry (Kar et al., 2022).

Applications related to safer chemicals and reaction pathways are not limited to improving individual substances or isolated reaction steps. When the performance of chemical products, their potential for exposure, and the impacts that may arise over their entire service life are considered together, the environmental implications of design decisions become clearer. Such considerations allow for the comparison of chemical alternatives and the identification of options with lower risk profiles. Studies indicate that this approach supports decision-making processes aimed at preventing pollution at its source (Tickner et al., 2015).

3.3. Reduction of by-products and hazardous substances

The formation of by-products and hazardous substances is among the main sources of environmental and health risks in chemical production processes. Undesired by-products generated during production increase the amount of waste and give rise to additional separation, treatment, and disposal requirements, thereby

increasing the overall environmental load of the process. For this reason, pollution prevention approaches emphasize design choices that enhance selectivity toward the desired product while limiting unwanted reaction pathways. Reducing the formation of by-products is therefore viewed not as a means of controlling environmental impacts after they occur, but as an approach aimed at preventing such impacts during the production process (Constable et al., 2002).

The formation and use of hazardous substances are among the key factors shaping environmental and human health risks in chemical production processes. Toxic intermediates or by-products formed during reactions pose challenges not only for waste management, but also for process safety and exposure control. For this reason, pollution prevention approaches focus on design decisions that remove substances with high hazard potential from the process or replace them with alternatives that have lower hazard profiles. The literature shows that reducing hazards at their source leads to more effective and lasting outcomes than attempting to control risks after they have been introduced into the system (Ashford, 2002).

The reduction of by-products and hazardous substances directly reflects the environmental consequences of design and process decisions made in chemical production. Choices related to reaction pathways, chemical inputs, and operating conditions jointly determine both the yield of the desired product and the formation of undesired substances. At the design stage, such choices make it possible to limit process-related risks at earlier points without relying on pollution control measures applied after production. The literature indicates that considering chemical and engineering decisions together plays a decisive role in reducing the formation of by-products and hazardous substances, thereby allowing pollution prevention objectives to be more effectively integrated into production processes (Mulvihill et al., 2011).

4. PROCESS DESIGN AND POLLUTION PREVENTION APPROACHES

4.1. Process strategies for reducing pollution generation

In pollution prevention–oriented approaches, process design plays a central role in shaping the environmental performance of production systems. Pollution arising in chemical manufacturing is closely linked to design choices made throughout the process, as well as to the associated reaction, separation, and energy use steps. The way process flows are structured and how individual production steps interact directly influence the level of environmental impacts. For this reason, pollution prevention requires environmental considerations to be addressed not only during operation, but also at the process design stage (Smith, 2005).

The literature indicates that process strategies aimed at reducing pollution focus on organizing production systems in simpler and less resource-intensive ways. Eliminating unnecessary processing steps, reducing material losses, and considering opportunities for in-process recovery are among the key elements of these strat-

egies. Rather than treating pollution as an output to be managed after it occurs, such approaches view it as an outcome that can be limited at the process design stage. In this way, process design becomes a domain in which pollution prevention objectives can be implemented directly (Stankiewicz & Moulijn, 2000). The effects of key process design decisions on pollution generation are summarized in **Table 2** based on approaches reported in the literature (Klemeš et al., 2013).

Table 2. *Relationship between Key Process Design Decisions and Pollution Generation*

Process design element	Effect on pollution generation	Interpretation from a pollution prevention perspective
Reaction pathway selection	Determines the formation of by-products and hazardous intermediates	Selection of more selective pathways limits pollution at its source
Reaction conditions (temperature, pressure, time)	Influence energy requirements and side reactions	Milder conditions reduce pollution and associated risks
Solvent selection	Determines waste type and toxicity	The use of safer solvents reduces exposure risks
Process integration	Affects energy use and material losses	Integration reduces resource consumption
Separation and recovery strategies	Determines waste quantities and disposal needs	In-process recovery provides preventive benefits

4.2. Optimization of reaction conditions

The optimization of reaction conditions is among the design decisions that directly influence the reduction of pollution generation in chemical production processes. Parameters such as reaction temperature, pressure, residence time, and reaction conditions play a determining role not only in the yield of the target product, but also in the formation of by-products and overall energy requirements. Reactions conducted under milder conditions can limit undesired side reactions and reduce the formation of hazardous intermediates. Careful selection of reaction conditions therefore contributes to limiting environmental loads without relying on pollution control measures applied after production (Lancaster, 2025).

The optimization of reaction conditions is closely linked to solvent use and the choice of reaction environment. Selecting less hazardous solvents and adjusting reaction environments accordingly can reduce both exposure risks and the amount of process-related waste. Such approaches make it possible to improve reaction efficiency while supporting the development of production processes that are more balanced from environmental and safety perspectives. Studies show that evaluating solvents and reaction conditions together strengthens practices aimed at preventing pollution at its source (Henderson et al., 2011). For this reason, the optimization of reaction conditions directly contributes to limiting pollution at the source while improving overall process performance.

4.3. The role of chemical and technological choices

Chemical and technological choices play an important role in determining the level of pollution generation in production processes. The properties of raw materials, the selected reaction systems, and the technologies employed directly influence both process efficiency and environmental outputs. In particular, the use of chemicals with high hazard potential and energy-intensive technologies can structurally increase pollution generation. For this reason, pollution prevention approaches require decisions regarding the selection of chemicals and technologies, in addition to process conditions, to be made with consideration of their environmental implications (Anastas & Eghbali, 2010).

The selection of chemicals with lower hazard profiles and the use of more efficient technologies contribute substantially to limiting pollution at its source. Evaluating alternative technologies makes it possible to restructure processes in ways that generate lower amounts of waste and emissions, while also strengthening the balance between environmental performance and process performance. In this way, chemical and technological choices shape how pollution prevention objectives are translated into production processes and clarify the long-term environmental consequences of design-stage decisions (Klemeš et al., 2013).

5. ENERGY EFFICIENCY IN POLLUTION PREVENTION

5.1. Environmental impacts of energy-intensive processes

Energy-intensive industrial processes are responsible for a substantial share of global environmental impacts and play a critical role particularly in greenhouse gas emissions and resource consumption. The use of high temperatures, pressures, and long processing times in sectors such as chemicals, cement, iron and steel, and refining increases the energy demand of production processes and, consequently, the associated environmental burdens. The strong relationship between energy consumption and emissions in such processes makes it necessary for approaches aimed at reducing environmental impacts to focus not only on end-stage measures but also on process design and operating conditions. In systems characterized by high energy intensity, reducing energy use is therefore regarded as a key factor that directly contributes to lowering emissions and resource consumption (International Energy Agency, 2020).

The environmental impacts of energy-intensive processes are not limited solely to direct energy consumption, but should be assessed together with raw material use, by-product generation, and emissions occurring throughout the life cycle. In industrial production systems, energy use based on fossil fuels leads not only to greenhouse gas emissions but also to increased air pollutants and pressure on natural resources. This situation makes it necessary, particularly in heavy industry sectors, to systematically monitor environmental impacts and to analyze energy use on a process-specific basis. The literature indicates that, in developing strategies to reduce the environmental footprint of energy-intensive industries, production structures and technology choices are as decisive as energy efficiency itself (IPCC, 2022).

In reducing the environmental impacts of energy-intensive processes, focusing solely on lowering energy consumption is often insufficient; the design principles of processes and their operating conditions play a decisive role. In particular, decisions made during the early design stages of processes have long-term effects on energy requirements, emission profiles, and resource use. For this reason, strategies aimed at reducing environmental impacts need to be addressed through design-oriented prevention strategies that take the structural characteristics of processes into account, rather than relying on improvements implemented at later stages. The literature indicates that, in energy-intensive industrial processes, design-based approaches are able to more effectively constrain both energy use and environmental impacts (Allwood et al., 2010).

5.2. Low energy requirement approaches

Low energy requirement approaches are based on principles that aim to minimize energy inputs in the design of chemical reactions and processes. Increasing reaction efficiency, eliminating unnecessary steps, and favoring more selective reaction pathways stand out as key tools for reducing energy consumption. In particular, the development of reaction systems that operate under milder conditions, rather than conventional processes requiring high temperatures and pressures, contributes both to lowering energy use and to limiting the formation of by-products and waste. In this design context, energy efficiency is addressed not as a factor that improves process performance after the fact, but as an integral component of reaction and process design (Sheldon, 2012).

The development of low energy requirement approaches relies heavily on the use of catalysis and the optimization of process conditions. The application of catalytic systems enables reactions to proceed at lower temperatures and pressures, thereby reducing energy requirements while simultaneously increasing reaction selectivity. This contributes to limiting both energy consumption and the formation of by-products and waste. The literature highlights catalysis-based approaches as one of the core strategies for reducing energy use in line with the principles of Green Chemistry (Anastas & Kirchhoff, 2002).

Another important dimension of low energy requirement approaches involves methods aimed at designing chemical processes as more compact, efficient, and integrated systems. Approaches developed within this scope seek to address fundamental operations such as reaction and separation together and to eliminate unnecessary intermediate steps. The restructuring of processes in this manner enables reductions in energy transfers and heat losses, thereby contributing to a decrease in overall energy requirements. The literature indicates that such design-based approaches are effective in reducing energy consumption and provide a basis for the development of low energy requirement processes in alignment with the objectives of Green Chemistry (Stankiewicz & Moulijn, 2000).

5.3. The role of energy conservation in pollution prevention

Energy conservation is one of the key elements that provides direct environmental benefits within source-based pollution prevention approaches. Reducing energy consumption in industrial processes is not limited to lowering indirect greenhouse gas emissions; it also has decisive effects on fuel use, auxiliary chemicals, and waste generation. In this context, energy conservation, unlike approaches aimed at controlling environmental impacts after they occur, contributes to systematically limiting the formation of pollution. The literature indicates that measures aimed at improving energy efficiency function as a preventive mechanism in reducing the environmental burden of production processes and are directly associated with pollution prevention strategies (Worrell et al., 2011).

The role of energy conservation in pollution prevention is directly linked not only to technical improvements but also to the systematic management of energy use. Monitoring, measuring, and managing energy flows in industrial facilities based on continuous improvement enable the reduction of unnecessary energy consumption and associated environmental impacts. Such approaches provide a preventive framework that increases energy efficiency through adjustments in process operating conditions while also limiting emissions and waste generation. The literature emphasizes that the implementation of energy management systems is an important tool for improving environmental performance and supporting strategies aimed at preventing pollution at its source (ISO 50001, 2018).

6. CURRENT APPROACHES FROM AN ENERGY AND PROCESS PERSPECTIVE

6.1. Approaches highlighted in the literature

Recent studies indicate that pollution prevention at source in the Green Chemistry literature extends beyond the selection of chemical substances or reaction pathways and increasingly considers energy use and process design together. Evidence from recent studies suggests that pollution formation largely occurs during energy-intensive stages of processes, indicating that preventive approaches need to place the energy–process relationship at the center. This view expands the scope of application of Green Chemistry principles and points to an approach that addresses prevention not only at the chemical level but also at the system level (Anastas & Kirchhoff, 2002).

Several studies focus on evaluating design strategies that reduce process energy requirements while simultaneously addressing pollution prevention objectives. Strategies such as moderating reaction conditions, restructuring energy-intensive operations, and strengthening process integration contribute both to reducing energy consumption and to limiting the formation of by-products and waste. As a result, energy efficiency in recent studies is no longer treated as a complementary element of pollution prevention, but rather as one of the core components of the preventive approach (Sheldon, 2007).

The literature also features studies in which the relationship between energy efficiency and pollution prevention is addressed in the context of process optimization and integration. These studies propose evaluating the entire process as a whole in terms of energy and material flows, rather than focusing solely on improvements in individual unit operations. Such systematic approaches enable a better understanding of the mutual interactions between energy consumption and environmental outputs and allow pollution prevention objectives to be more effectively considered at the design stage. This trend indicates that Green Chemistry is becoming more strongly integrated with engineering applications (Klemeš et al., 2023).

6.2. Gains achieved in terms of energy efficiency

Approaches that place energy efficiency at the center represent one of the areas where the most tangible gains in preventing pollution at its source are achieved within Green Chemistry. Recent studies emphasize that design- and process-related improvements aimed at reducing energy inputs not only lower energy consumption but also lead to clear improvements in by-product formation, waste generation, and emission loads. This demonstrates that energy efficiency should not be regarded as a secondary objective in terms of environmental benefits, but rather as a direct outcome of the preventive approach (Jeswani et al., 2010).

A substantial share of the gains achieved through energy efficiency arises from design decisions that enable processes to operate with lower energy requirements. Strategies such as moderating reaction conditions, simplifying energy-intensive operations, and increasing heat recovery reduce the environmental footprint of processes while simultaneously improving resource-use efficiency. These approaches demonstrate that improvements in energy use deliver not only performance-related benefits, but also measurable environmental gains (Varbanov & Klemeš, 2011).

At the same time, the benefits provided by energy efficiency–oriented approaches are not limited to short-term energy savings. Reductions in energy consumption improve the long-term environmental performance of processes and strengthen the overall sustainability of the system. In this respect, energy efficiency measures make it possible for pollution prevention strategies to generate measurable and comparable outcomes and serve as an important indicator in the evaluation of preventive approaches (Smith, 2005).

6.3. Monitoring and evaluation of pollution prevention performance

The effectiveness of source-based pollution prevention strategies can be demonstrated not only through implementation, but also through monitoring and evaluation based on measurable indicators. Recent studies show that performance assessment approaches in which energy consumption, resource use, and emission indicators are considered together are widely used to evaluate the success of preventive strategies. In this regard, monitoring and evaluation activities make it possible to express, in quantitative terms, the effects of pollution prevention approaches on environmental performance (ISO 14031, 2021).

The indicators used in the evaluation of pollution prevention performance make the environmental consequences of decisions taken during the design and operation stages of processes visible. Energy intensity, energy consumption per unit product, and the associated emission values are among the indicators commonly used to assess the effectiveness of preventive approaches. Systematic monitoring of such indicators enables the comparison of different process options and allows energy efficiency–based prevention strategies to be supported by technical justification (ISO 14040, 2006).

In addition, monitoring and evaluation processes play a critical role in ensuring the continuity of pollution prevention approaches. Regular tracking of performance indicators makes it possible to identify trends in process performance over time and to determine the necessary improvements. This approach transforms pollution prevention at source from a static practice into a process based on continuous improvement and contributes to more effective management of the relationship between energy use and environmental performance (OECD, 2023).

6.4. Existing limitations

Although the development and implementation of performance indicators for pollution prevention at source have led to significant advances in environmental management systems, the standardization and practical applicability of these indicators still face certain limitations. The literature emphasizes that uncertainties in data collection and measurement for environmental performance indicators affect the outcomes of performance assessments and that a lack of consistent data poses a major challenge, particularly in terms of applicability across different industrial processes and benchmarking. This situation indicates that performance indicators have inherent limitations in terms of real-time monitoring and comparative evaluation (Perotto et al., 2008).

Another limitation relates to the definition and standardization of environmental performance indicators. Various studies report that indicators are defined differently across sectors and organizations, and that this heterogeneity reduces their comparability. Such conditions reflect methodological limitations arising from the selection of indicators used to assess pollution prevention performance and from the lack of standardized data frameworks (Olsthoorn et al., 2001).

In addition, a recent review of the literature on environmental performance indicators shows that some of the existing indicators function only within specific sectors or at certain scales and therefore suffer from limited general applicability. In this respect, the narrow scope of performance indicators and the lack of contextual data constitute significant limitations in the monitoring and evaluation of pollution prevention strategies (Mrak et al., 2025).

7. EVALUATION AND FUTURE PERSPECTIVE

7.1. Overall evaluation of the pollution prevention approach

The pollution prevention at source approach fundamentally differs from traditional end-of-pipe treatment approaches in that it addresses environmental problems at the earliest stages of design and process decision-making, rather than through post-production outcomes. This approach is based on designing chemical products and processes in a manner that minimizes environmental impacts from the outset, aiming to prevent the formation of pollution rather than controlling it after it occurs. Within the framework of Green Chemistry, this preventive view constitutes a core approach that addresses waste reduction, the selection of safer chemicals and reaction pathways, and improvements in energy and raw material use at the design level (Anastas & Warner, 2000).

Another key aspect of pollution prevention is that it is not limited to environmental benefits alone, but also enables a comprehensive evaluation of production process performance. The literature emphasizes that strategies aimed at preventing pollution at its source enhance process efficiency by encouraging the joint evaluation of energy, raw material, and waste flows, and enable environmental performance to be monitored through measurable indicators. In this sense, pollution prevention is treated not merely as an environmental management practice, but as an integral component of production and design decisions, and is regarded as a key evaluation criterion in the transition toward sustainable production (Veleva & Ellenbecker, 2001).

Nevertheless, the success of pollution prevention approaches is closely related to the conditions under which they are assessed and the methods used for their evaluation. The literature notes that methods applied to assess the environmental performance impacts of preventive strategies may yield different outcomes depending on the scope of the study, the reliability of the data used, and the indicators selected. This indicates that pollution prevention practices may not deliver the same level of environmental benefit in all cases and that careful consideration is required when interpreting results based on the chosen evaluation approach. Therefore, in conducting an overall evaluation of the pollution prevention approach, it is important to consider not only the capabilities of the analytical tools employed, but also their limitations (Finnveden et al., 2009).

7.2. The future role of Green Chemistry

The future role of Green Chemistry is linked to the broader and more consistent application of principles focused on systematically reducing environmental and human health risks in the design of chemical products and processes. Within this approach, the development of safer chemicals, reductions in energy and raw material use, the prevention of waste generation, and increased use of renewable resources constitute key objectives. In this regard, Green Chemistry is regarded as an approach that prioritizes consideration of environmental impacts at the design stage rather than relying on their control after the fact, and is therefore expected to play an important role in guiding future chemical production practices (Anastas & Eghbali, 2010).

The growing impact of Green Chemistry is also closely linked to approaches that enable environmental performance to be expressed through quantitative indicators. In particular, in applications aimed at preventing pollution at its source, the ability to evaluate processes in a comparable manner with respect to waste generation and resource efficiency facilitates the practical implementation of Green Chemistry principles. Metric-based approaches developed within this scope contribute to making the environmental impacts of chemical processes more visible and provide a foundation for the more effective use of Green Chemistry in industrial decision-making processes (Sheldon, 2007).

7.3. Outlook for research and practice

From both research and practical perspectives, the future success of approaches aimed at preventing pollution at its source depends on systematic assessments in which energy and material flows are considered together. Particularly in complex industrial systems, analyzing processes as a whole rather than focusing on improvements in individual unit operations enables the simultaneous reduction of energy use, resource consumption, and environmental impacts. Process integration approaches developed along these lines allow preventive strategies to be applied more effectively at the design stage and indicate that future research priorities should increasingly focus on system-level decision-support tools (Klemeš et al., 2013).

Future outlooks for research and practice also require careful consideration of the technical and structural constraints that limit the wider adoption of pollution prevention approaches. In industrial applications, factors such as data availability, process complexity, investment costs, and design constraints of existing facilities can hinder the implementation of preventive strategies. This highlights the need for research efforts to move beyond the development of individual methods and tools and to focus on developing adaptable, flexible, and practically applicable solutions for existing industrial systems. Accordingly, future research priorities are expected to shift toward approaches that take into account not only technical potential, but also implementation conditions and decision-making processes (Varbanov & Klemeš, 2011).

CONCLUSION

Source-based pollution prevention shifts attention from end-of-pipe control measures toward the early stages of process and product design, where environmental impacts are largely determined. Decisions regarding raw material selection, energy requirements, and process conditions directly influence both the quantity and characteristics of pollution generated during production. Therefore, pollution prevention should be regarded not only as an environmental management objective but also as a fundamental component of chemical and process design.

Evaluations focusing on energy consumption and resource efficiency indicate that the effectiveness of pollution prevention strategies is largely dependent on process design and operational practices. Measures aimed at reducing energy demand, improving material-use efficiency, and optimizing process organization can contribute significantly to the reduction of environmental impacts. Nevertheless, the implementation of such strategies on an industrial scale may be constrained by several barriers, including insufficient data availability, limitations of existing infrastructure, and economic considerations.

Overall, Green Chemistry-based design and process approaches provide an important foundation for the development of source-oriented pollution prevention strategies. However, the widespread adoption of these approaches depends not only on their technical feasibility but also on practical considerations associated with industrial implementation and decision-making processes. Future research can make significant contributions to this field by identifying more effective ways to integrate pollution prevention principles into diverse manufacturing systems and by adapting these principles to the specific requirements of different industrial sectors.

In conclusion, achieving sustainable production goals requires the incorporation of source-based pollution prevention approaches as an integral part of process design. In this context, Green Chemistry principles provide a robust framework for reducing environmental impacts, improving resource efficiency, and aligning industrial activities with broader sustainability objectives.

SONUÇ

Kaynağında kirlilik önleme yaklaşımı, dikkati üretim sonrası kontrol önlemlerinden çevresel etkilerin büyük ölçüde belirlendiği proses ve ürün tasarımının erken aşamalarına yönlendirmektedir. Hammadde seçimi, enerji gereksinimi ve proses koşullarına ilişkin kararlar, üretim sırasında oluşan kirliliğin miktarını ve niteliğini doğrudan etkilemektedir. Bu nedenle kirlilik önleme, yalnızca bir çevre yönetimi hedefi olarak değil, aynı zamanda kimyasal ve proses tasarımının temel bir bileşeni olarak değerlendirilmelidir.

Enerji kullanımı ve kaynak verimliliğine odaklanan değerlendirmeler, kirlilik önleme stratejilerinin etkinliğinin büyük ölçüde proses tasarımına ve operasyonel uygulamalara bağlı olduğunu göstermektedir. Enerji talebinin azaltılması, malzeme kullanım verimliliğinin artırılması ve proses organizasyonunun optimize edilmesine yönelik önlemler, çevresel etkilerin önemli ölçüde azaltılmasına katkı sağlayabilmektedir. Bununla birlikte, bu tür stratejilerin endüstriyel ölçekte uygulanması; veri yetersizliği, mevcut altyapı kısıtları ve ekonomik faktörler gibi çeşitli engeller nedeniyle sınırlanabilmektedir.

Genel olarak, Yeşil Kimya temelli tasarım ve proses yaklaşımları, kaynağında kirlilik önleme stratejilerinin geliştirilmesi için önemli bir temel sunmaktadır. Ancak bu yaklaşımların yaygın olarak uygulanabilmesi yalnızca teknik uygulanabilirliğe değil, aynı zamanda endüstriyel uygulamalar ve karar verme süreçleriyle ilgili pratik koşullara da bağlıdır. Gelecekte yapılacak araştırmalar, kirlilik önleme ilkelerinin farklı üretim sistemlerine daha etkin bir şekilde nasıl entegre edilebileceğini ve çeşitli endüstriyel sektörlerin özgün gereksinimlerine nasıl uyarlanabileceğini ortaya koyarak bu alandaki bilgi birikimine önemli katkılar sağlayabilir.

Sonuç olarak, sürdürülebilir üretim hedeflerine ulaşılabilmesi için kirliliğin oluşumunu kaynağında önlemeyi esas alan yaklaşımların, proses tasarımının ayrılmaz bir parçası haline getirilmesi gerekmektedir. Bu kapsamda Yeşil Kimya ilkeleri, çevresel etkilerin azaltılması, kaynakların daha verimli kullanılması ve endüstriyel faaliyetlerin sürdürülebilirlik hedefleriyle uyumlu hale getirilmesi açısından güçlü bir çerçeve sunmaktadır.

REFERENCES

1. Allen, D.T., & Rosselot, K.S. (1994). Pollution prevention at the macro scale: flows of wastes, industrial ecology and life cycle analyses. *Waste Management, 14(3-4)*, 317-328. https://doi.org/10.1016/0956-053X(94)90078-7
2. Allwood, J.M., Cullen, J.M. & Milford, R.L. (2010). Options for achieving a 50% cut in industrial carbon emissions by 2050. *Environmental Science & Technology, 44(6),* 1888-1894. https://doi.org/10.1021/es902909k
3. Anastas, P.T. & Warner, J.C. (2000). Green Chemistry: Theory and Practice. Oxford University Press. Online ISBN: 9780197704059.
4. Anastas, P.T. & Kirchhoff, M.M. (2002). Origins, current status, and future challenges of green chemistry. *Accounts of Chemical Research, 35(9)*, 686-694.
5. Anastas, P.T. & Eghbali, N. (2010). Green chemistry: principles and practice. *Chemical Society Reviews, 39*, 301-312. https://doi.org/10.1039/B918763B
6. Ashford, N.A. (2002). Government and environmental innovation in Europe and North America. *American Behavioral Scientist, 45(9)*, 1417-1434. https://doi.org/10.1177/0002764202045009007
7. Clark, J. & Macquarrie, D. (2002). Handbook of Green Chemistry and Technology. Blackwell Science. ISBN: 0-632-05715-7.
8. Constable, D.J.C., Curzons, A.D. & Cunningham, V.L. (2002). Metrics to 'green' chemistry—Which are the best? *Green Chemistry, 4(6)*, 521-527. https://doi.org/10.1039/B206169B
9. European Commission (2000). Integrated Pollution Prevention and Control (IPPC): Reference Document on the Application of Best Available Techniques to Industrial Cooling Systems. Joint Research Centre, European IPPC Bureau.
10. Finnveden, G., Hauschild, M.Z., Ekvall, T., Guinée, J., Heijungs, R., Hellweg, S., Koehler, A., Pennington, D. & Suh, S. (2009). Recent developments in life cycle assessment. *Journal of Environmental Management, 91(1)*, 1-21. https://doi.org/10.1016/j.jenvman.2009.06.018
11. Freeman, H.M. (1995). Industrial Pollution Prevention Handbook. McGraw-Hill. ISBN: 0-07-022148-0
12. Ghisellini, P., Cialani, C. & Ulgiati, S. (2016). A review on circular economy: the expected transition to a balanced interplay of environmental and economic systems. *Journal of Cleaner Production, 114*, 11-32. https://doi.org/10.1016/j.jclepro.2015.09.007
13. Graedel, T.E.H. & Allenby, B.R. (2010). Industrial Ecology and Sustainable Engineering: International Edition. Pearson. ISBN10: 0138140340
14. Henderson, R.K., Jiménez-González, C., Constable, D.J.C., Alston, S.R., Inglis, G.G.A., Fisher, G., Sherwood, J., Binks, S.P. & Curzons, A.D. (2011). Expanding GSK's solvent selection guide – embedding sustainability into solvent selection starting at medicinal chemistry. *Green Chemistry, 13*, 854-862. https://doi.org/10.1039/c0gc00918k
15. IPCC (2022). Climate Change 2022 Mitigation of climate change – Chapter 11: Industry. Cambridge University Press.
16. International Energy Agency (2020). Energy Technology Perspectives 2020: Special Report on Clean Energy Innovation. IEA Publications.

17. ISO 14040 (2006). Environmental Management — Life cycle assessment — Principles and Framework. International Organization for Standardization.

18. ISO 50001 (2018). Energy Management Systems—Requirements with guidance for use. International Organization for Standardization.

19. ISO 14031 (2021). Environmental Management — Environmental Performance Evaluation — Guidelines. International Organization for Standardization.

20. Jeswani, H.K., Azapagic, A., Schepelmann, P. & Ritthoff, M. (2010). Options for broadening and deepening the LCA approaches. *Journal of Cleaner Production, 18(2)*, 120-127. https://doi.org/10.1016/j.jclepro.2009.09.023

21. Kar, S., Sanderson, H., Roy, K., Benfenati, E. & Leszczynski, J. (2022). Green Chemistry in the Synthesis of Pharmaceuticals. *Chemical Reviews, 122(3)*, 3637-3710. https://doi.org/10.1021/acs.chemrev.1c00631

22. Klemeš, J.J., Varbanov, P.S. & Kravanja, Z. (2013). Recent developments in process integration. *Chemical Engineering Research and Design, 91(10)*, 2037-2053. https://doi.org/10.1016/j.cherd.2013.08.019

23. Klemeš, J.J., Varbanov, P.S., Wan Alwi, S.R., Manan, Z.A., Fan, Y.V. & Chin, H.H. (2023). Sustainable process integration and intensification: saving energy, water and resources (3rd ed.). De Gruyter. https://doi.org/10.1515/9783110782981

24. Kurul, F., Doruk, B. & Topkaya, S.N. (2025). Principles of green chemistry: building a sustainable future. *Discover Chemistry, 2,* 68. https://doi.org/10.1007/s44371-025-00152-9

25. Lancaster, M. (2025). Green Chemistry: An Introductory Text (4th ed.). Royal Society of Chemistry. https://doi.org/10.1039/9781837678037

26. Mulvihill, M.J., Beach, E.S., Zimmerman, J.B. & Anastas, P.T. (2011). Green chemistry and green engineering: a framework for sustainable technology development. *Annual Review of Environment and Resources, 36*, 271-293. https://doi.org/10.1146/annurev-environ-032009-095500

27. Mrak, I., Galjanić, K., Hanak, T. & Marović, I. (2025). An overview of environmental performance indicators in the construction industry. *Applied Sciences, 15(22)*, 12135. https://doi.org/10.3390/app152212135

28. OECD (2011). Towards Green Growth. OECD Publishing. https://doi.org/10.1787/9789264111318-en

29. OECD (2023). OECD Environmental Performance Reviews United States 2023. OECD Publishing.

30. Olsthoorn, X., Tyteca, D., Wehrmeyer, W. & Wagner, M. (2001). Environmental indicators for business: a review of the literature and standardisation methods. *Journal of Cleaner Production, 9(5)*, 453-463. https://doi.org/10.1016/S0959-6526(01)00005-1

31. Perotto, E., Canziani, R., Marchesi, R. & Butelli, P. (2008). Environmental performance, indicators and measurement uncertainty in EMS context: a case study. *Journal of Cleaner Production, 16(4)*, 517-530. https://doi.org/10.1016/j.jclepro.2007.01.004

32. Sheldon, R.A. (2007). The E factor: fifteen years on. *Green Chemistry, 9(12)*, 1273-1283. https://doi.org/10.1039/B713736M

33. Sheldon, R.A. (2012). Fundamentals of green chemistry: efficiency in reaction design. *Chemical Society Reviews, 41(4)*, 1437-1451. https://doi.org/10.1039/C1CS15219J

34. Smith, R. (2005). Chemical Process Design and Integration. John Wiley & Sons Ltd. – ISBN: 0-471-48680-9

35. Stankiewicz, A.I. & Moulijn, J.A. (2000). Process intensification: transforming chemical engineering. *Chemical Engineering Progress, January*, 22-34.

36. Tickner, J.A., Schifano, J.N., Blake, A., Rudisill, C. & Mulvihill, M.J. (2015). Advancing safer alternatives through functional substitution. *Environmental Science & Technology, 49(2)*, 742-749. https://doi.org/10.1021/es503328m

37. UNEP (2013). Global Chemicals Outlook: Towards Sound Management of Chemicals. United Nations Environment Programme.

38. UNEP (2019). Global Chemicals Outlook II: from Legacies to Innovative Solutions.

39. U.S. EPA (1990). Pollution Prevention Act of 1990. Public Law 101-508.

40. Van Berkel, R. (2007). Cleaner production and eco-efficiency initiatives in Western Australia 1996-2004. *Journal of Cleaner Production, 15*, 741-755. https://doi.org/10.1016/j.jclepro.2006.06.012

41. Varbanov, P.S. & Klemeš, J.J. (2011). Integration and management of renewables into total sites. *Computers & Chemical Engineering, 35(9)*, 1815-1826. https://doi.org/10.1016/j.compchemeng.2011.02.009

42. Veleva, V. & Ellenbecker, M. (2001). Indicators of sustainable production: framework and methodology. *Journal of Cleaner Production, 9(6)*, 519-549. https://doi.org/10.1016/S0959-6526(01)00010-5

43. Worrell, E., Bernstein, L., Roy, J., Price, L. & Harnisch, J. (2011). Industrial Energy Efficiency and Climate Change Mitigation. In B. Sørensen (Ed.), Renewable Energy (1st ed.). Routledge. eBook ISBN: 9781315793245

44. Zimmerman, J.B., Anastas, P.T., Erythropel, H.C. & Leitner, W. (2020). Designing for a green chemistry future. *Science, 367(6476)*, 397-400. https://doi.org/10.1126/science.aay3060

GREEN CHEMISTRY–DRIVEN ENGINEERING STRATEGIES FOR REDUCING HAZARDOUS CHEMICALS

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ABSTRACT

This chapter explores how engineering strategies inspired by green chemistry can contribute to the reduction of hazardous chemicals by focusing on prevention rather than end-of-pipe treatment. It discusses the shift from conventional risk management approaches toward the design of inherently safer and less hazardous chemical systems, drawing on principles of green chemistry, systems thinking, and circular design. Particular attention is given to strategies such as safer process design, chemical substitution, process intensification, improved resource and energy efficiency, green catalysis, and the growing role of digital technologies. The chapter also considers how tools such as life cycle assessment and green metrics can support the evaluation of environmental performance and guide decision-making. In addition, practical challenges related to technical implementation, economic feasibility, data availability, and regulatory requirements are discussed. Taken together, these perspectives illustrate the importance of integrating safety, sustainability, and functionality in the design of future chemical production systems.

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1. INTRODUCTION: THE NEED FOR GREEN CHEMISTRY IN HAZARDOUS CHEMICAL REDUCTION

Modern societies are deeply dependent on chemistry, which serves as a foundational component for critical sectors including healthcare, agriculture, materials, energy, and advanced technologies. At the same time, the rapid expansion of global chemical production and consumption has intensified major sustainability challenges, such as climate change, environmental pollution, biodiversity loss, and resource depletion. The increasing material throughput and the expanding diversity of synthetic chemicals have raised significant concerns regarding the long-term environmental and societal consequences of current production and consumption patterns. Recent assessments emphasize that chemistry must play a central role in addressing these planetary-scale challenges by supporting sustainable innovation and responsible resource stewardship (Matlin et al., 2022). Many of these challenges are closely associated with the widespread use and release of hazardous chemicals, which significantly influence environmental quality and human health across global industrial systems.

One of the main structural drivers of these challenges is the long-standing reliance on a linear "take–make–dispose" model, in which finite resources are extracted, transformed into products, and eventually discarded as waste. This linear model leads to large-scale emissions, the accumulation of persistent pollutants, and the inefficient use of finite resources such as fossil fuels. Sustainability frameworks increasingly recognize that maintaining such a model threatens not only environmental integrity but also economic resilience and societal well-being. As a result, the transition toward circular and more sustainable production systems is now widely regarded as essential for long-term sustainability (Matlin et al., 2022). Linear production systems also contribute to the continuous generation and accumulation of hazardous chemicals, highlighting the importance of preventive and design-oriented solutions at the molecular level.

Against this background, reducing hazardous chemicals has become a central engineering challenge rather than a secondary environmental objective. Hazardous substances are not only sources of pollution but also important determinants of process safety, regulatory compliance, and long-term environmental persistence. Minimizing their use and generation therefore requires an integrated approach that connects molecular design, process engineering, and system-level decision-making. Hazardous chemical reduction should consequently be considered a core design criterion—often referred to as "benign by design"—from the earliest stages of chemical and process development.

Beyond their environmental impacts, hazardous chemicals pose substantial risks to human health and ecosystems. Exposure during production, use, and disposal can result in a wide range of acute and chronic effects, including carcinogenicity, endocrine disruption, and neurological disorders. A global synthesis indicates that pollution remains responsible for approximately 9 million premature deaths each year, with chemical pollution continuing to impose significant health and economic

burdens worldwide (Fuller et al., 2022). Furthermore, many hazardous compounds are persistent, bioaccumulative, and toxic, increasing the likelihood of widespread exposure and ecological damage across generations.

Historically, chemical manufacturing has largely prioritized product performance, yield, and cost efficiency, while environmental and health concerns have often been addressed through end-of-pipe control measures. Although such approaches may reduce emissions locally, they rarely eliminate intrinsic hazards and can simply shift pollution from one environmental compartment to another. Auxiliary substances, particularly solvents, account for a substantial fraction—estimated at 80–85%—of the total waste generated in many chemical processes.

This highlights the critical importance of preventive process design and careful solvent selection in reducing both environmental and occupational risks (Brar et al., 2014).

In response to these concerns, green chemistry has emerged as a transformative framework that promotes the design of chemical products and processes that minimize or eliminate hazardous substances from the earliest stages of innovation (Brar et al., 2014; Karagölge & Gür, 2016). Rather than focusing primarily on remediation, green chemistry emphasizes prevention by integrating environmental protection, economic feasibility, and safety considerations into molecular and process design. Over time, the concept has expanded to include life-cycle thinking, resource efficiency, and broader sustainability metrics that address planetary-scale challenges.

Sustainable chemistry has more recently become closely associated with circular economy principles and innovation frameworks that integrate safety and sustainability from the outset. Circular chemistry seeks to retain material value through reuse, recycling, and closed-loop systems, thereby reducing waste generation and dependence on non-renewable resources. Within this broader context, the Safe and Sustainable by Design (SSbD) concept has emerged as a comprehensive framework that integrates hazard reduction, environmental performance, and functionality throughout the development of chemicals and materials (Caldeira et al., 2024). Together, these approaches underscore the importance of simultaneously addressing environmental, economic, and societal dimensions.

Another important development in recent years has been the shift from conventional risk management toward the elimination of intrinsic hazards. While traditional environmental strategies often focus on controlling exposure and treating emissions after they occur, green chemistry promotes the design of molecules and processes that inherently reduce toxicity and persistence. This distinction is vital because risk is a function of both hazard and exposure, whereas hazard is an intrinsic property that can be addressed directly through molecular design. In engineering practice, exposure-control measures may not always remain effective under uncertain operational conditions or over long time scales. Integrating toxicological knowledge into early-stage chemical and process design therefore offers a unique opportunity to prevent the formation of hazardous substances rather than managing their consequences after release (Maertens et al., 2021).

Recognizing this distinction, engineering strategies increasingly focus on eliminating hazards at their source rather than managing exposure scenarios. In practical terms, this involves redesigning chemical pathways, selecting inherently safer substances, and configuring processes to avoid the formation of toxic intermediates and persistent compounds. Such approaches move beyond conventional risk mitigation and embed hazardous chemical reduction directly within the structure of chemical production systems.

Policy and regulatory developments have also accelerated this transition. Recent regulatory frameworks increasingly emphasize the proactive elimination of hazardous substances rather than controlling them after release, aligning policy objectives more closely with the principles of green chemistry. Early initiatives such as the Pollution Prevention Act of 1990 in the United States encouraged preventive innovation in chemical manufacturing, while programs such as the U.S. Presidential Green Chemistry Challenge helped promote the adoption of safer technologies (Brar et al., 2014; Karagölge & Gür, 2016). More recently, international sustainability agendas and regional policies—including the European Green Deal and the Chemicals Strategy for Sustainability—have strengthened expectations for the development of safer, circular, and non-toxic chemical systems. These initiatives encourage the integration of life-cycle assessment, hazard evaluation, and circular economy principles into both research and industrial practice.

For engineers, effective hazard reduction requires a clear understanding of the distinction between hazard and risk. Hazard refers to the intrinsic capacity of a substance to cause adverse effects, whereas risk depends on both hazard and exposure conditions. Consequently, engineering strategies increasingly emphasize intrinsic hazard minimization through molecular design, process intensification, safer solvent selection, and circular resource management. Decisions regarding process routes, operating conditions, solvent systems, and separation technologies therefore play a major role in determining environmental and health outcomes. The integration of green chemistry principles into engineering design supports the development of inherently safer and more sustainable systems (Anastas & Warner, 1998).

Green chemistry–driven engineering strategies are now widely recognized as important enablers of sustainable industrial transformation. By linking molecular design with process intensification, circular resource management, digitalization, and advanced catalysis, these approaches can reduce environmental burdens while improving efficiency and resilience. Figure 1 illustrates the conceptual relationships among global sustainability challenges, green chemistry principles, engineering-based solutions, and sustainable outcomes. The following sections present an integrated perspective on the principles, tools, and applications of green chemistry and sustainable engineering, progressing from foundational concepts to preventive design strategies, safer chemical substitution, and resource-efficient technologies. Emerging digital tools and real-world applications are also discussed, followed by an assessment of current challenges and future research directions.

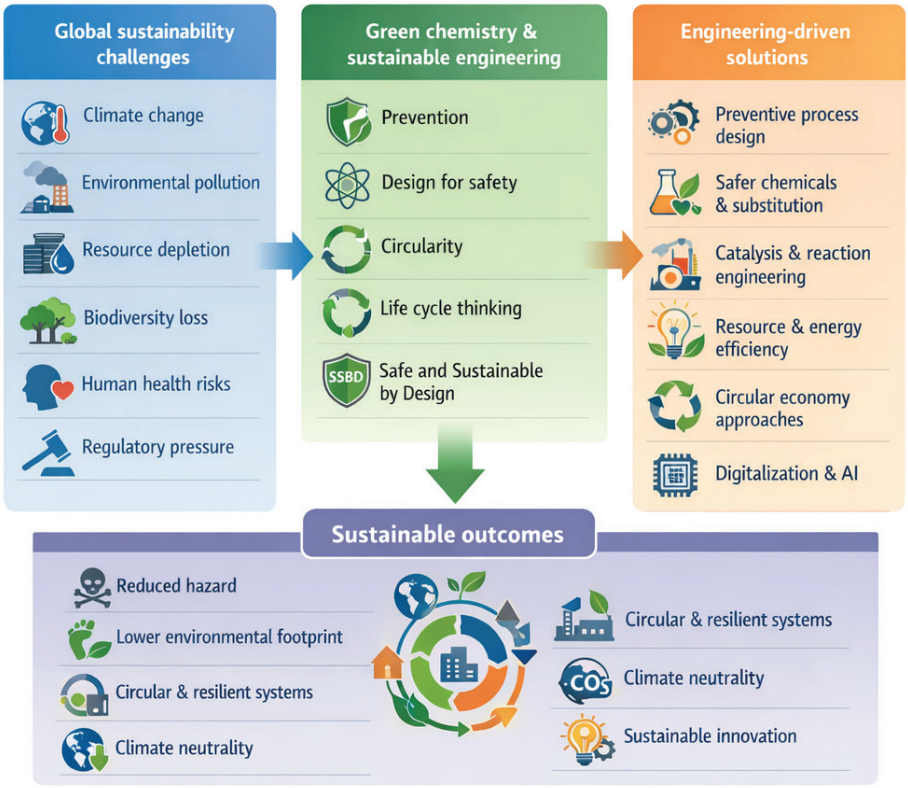

Figure 1. *Integration of green chemistry principles and engineering strategies for reducing hazardous chemicals and achieving circular and sustainable production*

2. FUNDAMENTALS OF HAZARDOUS CHEMICAL REDUCTION

2.1 From Risk Management to Hazard Elimination

The conceptual foundations of green chemistry and sustainable engineering differ fundamentally from traditional environmental protection approaches, which have historically relied on end-of-pipe measures to control pollution after it has been generated. Traditional chemical manufacturing often prioritized product performance and yield, treating environmental and health concerns as secondary issues to be managed via remediation. Green chemistry instead adopts a preventive perspective by considering environmental and health impacts during the design stage of chemicals and processes. By definition, green chemistry involves the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances (Brar et al., 2014). From this perspective, hazardous chemical reduction is not simply the result of improved process control or waste treatment technologies; rather, it is largely determined by decisions made during molecular design, reaction development, and process configuration.

The discipline is guided by the Twelve Principles of Green Chemistry, which provide a practical framework for developing safer and more resource-efficient chemical systems (Anastas & Warner, 1998). These principles address both hazard reduction and the efficiency of chemical transformations. Among them, Atom Economy is particularly important because it evaluates how effectively the atoms of the starting materials are incorporated into the final product, thereby providing a measure of resource efficiency and waste prevention. This concept, formally established by Trost, challenges synthetic chemists to pursue efficiency by maximizing the number of atoms from all raw materials that end up in the desired product. In this framework, the ideal reaction is defined as a simple addition where all starting materials are incorporated into the final product, requiring only catalytic amounts of other reactants (Trost, 1995). By maximizing the incorporation of all reactants into the final product, chemists can pursue pollution prevention at the molecular scale rather than relying on breaking down larger materials, which inherently generates more waste.

A key distinction between conventional environmental management and green chemistry lies in their treatment of risk. Traditional approaches often focus on limiting exposure to hazardous substances through containment, treatment, or control measures. Green chemistry, in contrast, seeks to reduce or eliminate hazards at their source by designing inherently safer chemicals and processes (Maertens et al., 2021). This distinction is vital because risk is a function of both hazard and exposure, whereas hazard is an intrinsic property that can be addressed directly through design. As a result, environmental and health risks can be addressed before they arise rather than being managed after hazardous substances have already been produced. Integrating toxicological knowledge into early-stage design thus offers a unique opportunity to prevent the formation of hazardous substances entirely.

2.2 Green Chemistry Principles in Process Design

As green chemistry has evolved, its principles have increasingly been applied beyond individual molecules and reactions to broader industrial systems and urban infrastructures. An important development in this regard has been the growing integration of green chemistry with Circular Economy concepts, which emphasize not only the reduction of toxicity but also the design of materials for durability, reuse, recycling, and safe degradation. This shift moves the focus from a linear "take-make-dispose" model toward restorative and regenerative systems that maintain the value of resources for as long as possible (Matlin et al., 2022).

This evolution has expanded the role of green chemistry beyond a set of guiding principles. Today, it serves as a practical design framework that informs engineering decisions aimed at reducing hazardous chemicals throughout the life cycle of products and processes. One example of this broader perspective is the Prevention, Assurance, and Sustainability (PAS) framework, which provides quantifiable indicators for evaluating the contribution of chemical processes to global Sustainable Development Goals (SDGs) (Chen et al., 2020). Such approaches help engineers

assess whether a process remains not only technically efficient but also environmentally and socially sustainable within increasingly complex technological systems, including modern smart cities (Oliveira et al., 2024).

The implementation of these principles relies on a range of engineering tools, including process intensification, life-cycle assessment, safer solvent design, and systems-based resource recovery. Together, these approaches support the development of circular production systems that reduce waste generation and resource consumption while minimizing hazardous chemical use. To evaluate progress toward these objectives, quantitative metrics play an important role. Measures such as atom economy and the E-factor provide practical means of assessing how effectively hazardous chemical generation is reduced during process design and operation, aligning molecular-scale efficiency with global environmental protection goals (Sheldon, 2023).

2.3 Systems Thinking and Circular Design

The transition toward a more sustainable chemical industry requires the adoption of systems thinking, which views chemistry as part of interconnected natural and industrial cycles rather than as a collection of isolated processes (Matlin et al., 2022). This perspective is particularly important for hazardous chemical reduction because it helps identify pathways through which hazardous substances may be generated, transformed, or accumulated throughout the life cycle of materials. Within this framework, it is argued that the very concept of "waste" must disappear from design protocols, treating all process outputs as potential feedstocks for other systems (Zimmerman et al., 2020).

A clear example can be found in wastewater treatment and resource management, where the focus has evolved from mere pollutant removal toward the development of integrated resource recovery facilities (Chen et al., 2020; Ghernaout et al., 2021). This transformation involves adopting symbiotic network approaches to reclaim high-value by-products, including catalyst recycling and the recovery of industrial acids or bases (Chen et al., 2020). Furthermore, advanced recovery strategies now facilitate the recuperation of essential nutrients, such as nitrogen and phosphorus, from sewage sludge and livestock manure, transforming potential pollutants into valuable circular feedstocks for global agricultural demands (Ghernaout et al., 2021). By prioritizing such pollution prevention at the source, industrial systems move beyond chemical yield to a paradigm that assigns primary value to waste elimination and the preservation of water circularity (Sheldon, 2023).

Figure 2 illustrates how green chemistry principles, sustainable engineering tools, and circular system thinking interact across molecular, process, and system scales to support hazardous chemical reduction. Together, these concepts form the foundation for the engineering strategies discussed in the following section. Building on this conceptual framework, hazardous chemical reduction is examined through integrated design approaches that operate across multiple scales of chemical production and resource management.



Figure 2. *Conceptual framework linking green chemistry, engineering strategies, and circular systems for hazardous chemical reduction*

3. ENGINEERING STRATEGIES FOR HAZARDOUS CHEMICAL REDUCTION

The reduction of hazardous chemicals requires the integration of engineering strategies that operate across molecular, process, and system levels. Drawing on the concepts discussed in the previous section, this part of the chapter focuses on practical approaches that help minimize hazardous substances at their source. These approaches include preventive process design, safer material substitution, resource-efficient operations, catalytic innovations, and digital optimization tools. Collectively, they illustrate how hazardous chemical reduction can be integrated into the design and operation of chemical systems, shifting the emphasis from downstream control toward prevention and inherently safer production.

3.1 Preventive Process Design and Inherently Safer Systems

Preventive process design is a central element of green engineering, shifting the emphasis from reactive end-of-pipe waste management to the prevention of environmental impacts at their source (Ruiz-Mercado et al., 2016). Unlike conventional remediation approaches that address pollutants after they have been generated, preventive design incorporates environmental and safety considerations during the early stages of process development, including synthesis and scale-up. The integration of green chemistry principles with chemical engineering tools supports

the development of inherently safer production systems in which the reduction or elimination of hazardous substances becomes a primary design objective. By considering these criteria from the outset, engineers can select reaction pathways that reduce environmental impacts while maintaining technical performance and economic feasibility (Morton et al., 2004).

From the perspective of hazardous chemical reduction, preventive process design makes it possible to avoid the formation of hazardous intermediates and by-products rather than controlling them after they have been produced. As a result, both environmental emissions and process-related risks can be reduced at the source. This approach embeds safety and sustainability directly into process design instead of relying primarily on downstream control technologies.

A key aspect of preventive design is the concept of inherently safer systems, which seeks to reduce the intrinsic hazards of a process rather than manage risks through external protective measures (Joshi & Adhikari, 2019). This can be achieved through the substitution of hazardous reagents with less hazardous alternatives and by optimizing operating conditions to reduce temperatures and pressures whenever practical. Solvent selection is particularly important within this strategy because solvent-related waste often represents one of the largest environmental burdens in industrial production. For this reason, green solvents such as water and supercritical CO_2 are frequently promoted as safer alternatives (Anastas & Zimmerman, 2019). Focusing on the intrinsic properties of chemicals and materials allows engineers to develop processes that are inherently more robust and less susceptible to operational failures and long-term environmental impacts.

The advancement of preventive process design is further supported by Process Intensification (PI), which aims to improve process performance while significantly reducing the physical and environmental footprint of manufacturing operations. Process intensification involves the development of innovative equipment and configurations—including technologies such as Spinning Disc Reactors (SDR) and microreactors—that enhance heat and mass transfer and reduce the time reagents remain under potentially hazardous conditions (Ghernaout et al., 2021). These systems can replace conventional unit operations with compact designs, often reducing plant volume by a factor of 100 to 1000, thereby enhancing inherent safety through smaller hazardous material inventories (Baldha & Kolli, 2023).

By increasing reaction selectivity and shortening residence times, process intensification directly contributes to reducing the formation and accumulation of hazardous compounds at the source. These technologies connect molecular-level green chemistry concepts, such as atom efficiency and waste minimization, with industrial-scale process efficiency (Ghernaout et al., 2021). The successful implementation of intensified processes also requires systematic methods for evaluating sustainability performance. Assessment frameworks and tools like SustainPro help identify process bottlenecks, calculate mass and energy indicators, and support the retrofitting of existing industrial systems to improve their sustainability profile (Ruiz-Mercado et al., 2016).

To evaluate progress toward these objectives, quantitative metrics such as atom economy and the E-factor provide objective means for assessing the effectiveness of pollution prevention strategies (Sheldon, 2023). While mass-based metrics provide a practical measure of the environmental footprint, comprehensive sustainability assessment frameworks and Life Cycle Assessments (LCA) are essential to accurately balance ecological performance with economic considerations (Caldeira et al., 2024).

Figure 3 illustrates the integrated workflow of preventive process design, from feedstock selection and inherently safer design to process intensification and sustainability assessment, highlighting the continuous improvement cycle associated with hazardous chemical reduction.

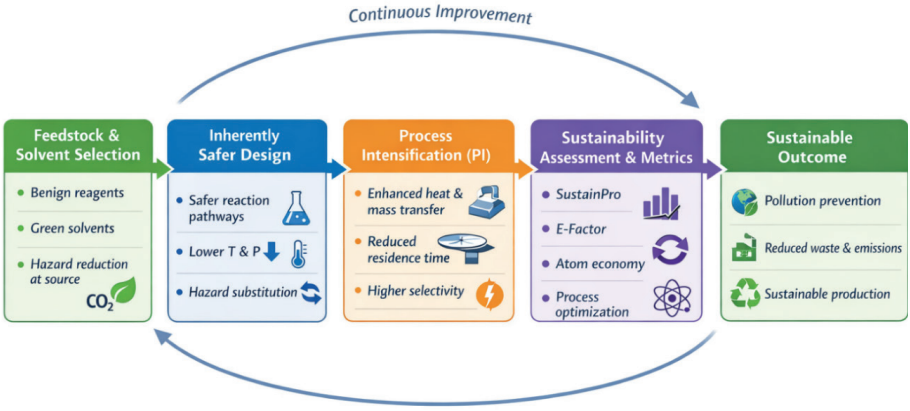

Figure 3. *Integrated workflow for hazardous chemical reduction through preventive design, process intensification, and sustainability assessment*

3.2 Chemical Substitution and Safer Alternatives

Chemical substitution plays a central role in green chemistry by promoting the replacement of hazardous substances with safer alternatives. This involves a "Safer by Design" approach in which toxicity is considered a molecular property that can be modified during early chemical development. Integrating toxicology with synthetic chemistry allows for molecular modifications that reduce biological activity without compromising technical performance (Maertens et al., 2021).

Within the broader objective of hazardous chemical reduction, substitution provides a direct means of removing intrinsic hazards from chemical products and processes. However, the effectiveness of this approach depends on careful evaluation to ensure that hazard reduction is achieved without introducing new environmental or health concerns elsewhere in the product life cycle (Tickner et al., 2018).

The practical application of chemical substitution is evident in several industrial sectors. In the polymer industry, traditional phthalate plasticizers are being replaced with bio-derived esters, such as bio-based succinic acid derivatives, which offer safer profiles and reduced footprints (Zimmerman et al., 2020). Furthermore, the development of Cyrene™ as a bio-based alternative to toxic polar aprotic solvents

like DMF and NMP illustrates how safer molecular design can be combined with renewable feedstocks. Cyrene™ maintains functional performance while providing superior safety and excellent biodegradability (Sheldon, 2023).

Despite its advantages, chemical substitution also presents the risk of "regrettable substitutions". This occurs when a chemical with an unknown hazard replaces a problematic substance, only to later prove harmful, as seen in the transition from Bisphenol A (BPA) to Bisphenol S (BPS) (Maertens et al., 2021). To address this, systematic Alternatives Assessment (AA) frameworks have been developed to support informed decision-making and ensure that replacement chemicals provide net environmental and health benefits (Tickner et al., 2018). These frameworks integrate hazard, performance, and economic viability to guide the transition toward truly sustainable chemical systems.

3.3 Resource and Energy Efficiency for Hazard Reduction

Resource and energy efficiency are fundamental components of green engineering and play an important role in the transition toward more circular and sustainable industrial systems. In this context, resource effectiveness represents a paradigm shift in chemical processing, moving from a focus solely on chemical yield to one that assigns primary value to waste elimination throughout the production cycle (Sheldon, 2023). By utilizing mass-based metrics such as the E-factor, engineers can effectively measure and minimize the amount of waste generated per kilogram of desired product.

Improving resource efficiency contributes directly to hazardous chemical reduction by decreasing the generation of waste streams that may contain toxic or persistent substances. Integrated resource management approaches facilitate this by employing symbiotic network-approaches to reclaim high-value materials (Chen et al., 2020). Practical examples include catalyst recycling, the recovery of industrial acids or bases, and the reclamation of wastewater for reuse within industrial cycles. Such industrial symbiosis, particularly when implemented within Eco-Industrial Parks (EIP), allows for planned materials and energy exchanges that minimize both raw material consumption and the environmental release of hazardous substances (Boix et al., 2012). The environmental benefits of resource recovery have also been demonstrated in pharmaceutical manufacturing, where solvent recovery systems integrating distillation and membrane-based separation technologies enabled the reuse of isopropanol from waste streams and reduced total life-cycle emissions by more than 90% compared with conventional disposal practices (Slater et al., 2012). Water resource management represents another important dimension of resource efficiency in industrial systems. He et al. (2018) developed an optimization framework for chemical industrial parks that simultaneously considers water allocation, wastewater reuse, treatment capacity, and multi-pollutant control under uncertain operating conditions. Their findings demonstrated that integrated water management strategies can improve resource utilization while reducing pollutant discharges, highlighting the role of system-level optimization in supporting sustainable industrial development.

Energy efficiency is equally important in this context. Systematic methodologies such as Process Integration and Pinch Analysis have demonstrated substantial improvements in overall energy performance by designing networks that meet minimum energy requirements (Alwi et al., 2016). Furthermore, Process Intensification (PI) supports these goals by replacing conventional equipment with compact designs that enhance heat and mass transfer, often reducing plant volume by orders of magnitude (Baldha & Kolli, 2023). Lower energy demand and the use of intensified reactors not only reduce emissions but also allow processes to operate under milder conditions, decreasing the likelihood of hazardous by-product formation associated with extreme temperatures and pressures. Together, these strategies ensure that chemical production remains not only technically efficient but also inherently safer.

3.4 Green Catalysis and Reaction Pathway Optimization

Green catalysis improves the efficiency of chemical reactions by lowering activation energy requirements and enhancing reaction selectivity. As a foundational pillar of green chemistry, catalysis contributes to improved atom economy and reduced waste generation by providing alternative pathways with lower activation barriers (Chen et al., 2020). Catalytic systems support hazardous chemical reduction by guiding reaction pathways toward desired products while limiting the formation of toxic intermediates and unwanted side products. A major driver in this field is the shift from stoichiometric reagents to cleaner catalytic alternatives, a paradigm change that assigns primary value to waste elimination throughout the production cycle (Sheldon, 2023).

The use of reusable catalysts further reduces material losses and helps prevent the release of hazardous substances into the environment. Current trends emphasize replacing scarce and precious metal catalysts with Earth-abundant metals, such as iron, copper, and nickel, which offer sustainable and cost-effective alternatives. A wide range of applications demonstrates the value of catalytic design, including the use of reusable magnetic catalysts and advanced systems for biodiesel production (Ghernaout et al., 2021). For example, Naeem et al. (2021) developed a reusable Na-SiO_2@TiO_2 heterogeneous catalyst for biodiesel production from waste cooking oil, achieving biodiesel yields of up to 98% under relatively mild reaction conditions while maintaining significant catalytic activity over five consecutive reuse cycles. This example illustrates how catalyst design can simultaneously support waste valorization, resource efficiency, and the reduction of environmental burdens associated with conventional fuel production. Similarly, Mukundan et al. (2023) demonstrated the potential of magnetically recoverable heterogeneous catalysts in biomass valorization by using an FeOx/C catalyst for the hydrothermal liquefaction of brewer's spent grains into bio-oil. Their study showed that the catalyst improved bio-oil yield and quality, enabled magnetic recovery from solid residues, and maintained catalytic activity over five reaction cycles, highlighting the value of recyclable catalyst systems for circular and resource-efficient bio-based produc-

tion. In this context, heterogeneous cobalt-based catalysts have emerged as highly efficient materials for peroxymonosulfate (PMS) activation, enabling the complete degradation of recalcitrant organic pollutants through the in situ generation of reactive sulfate radicals (Zhao et al., 2023). These sulfate radical-based advanced oxidation processes (AOPs) provide superior oxidation potential and higher selectivity for degrading emerging contaminants compared to traditional hydroxyl radical-based methods, while maintaining effectiveness across a broader pH range (Wang and Wang, 2018). Recent advances in visible-light-driven photocatalysts, including doped semiconductors, graphene-based composites, plasmonic materials, and heterostructured catalytic systems, have further expanded the applicability of photocatalytic technologies for environmental remediation and sustainable chemical production (Wang et al., 2016). Furthermore, emerging technologies such as photocatalysis broaden these opportunities by enabling the use of renewable solar energy to drive chemical transformations, thereby supporting more sustainable and resource-efficient processes.

3.5 Digital Tools for Hazard Reduction and Process Optimization

Digitalization is increasingly influencing the way chemical processes are designed, monitored, and optimized, making it an important component of sustainable engineering technologies such as Artificial Intelligence (AI), Machine Learning (ML), and digital twins provide new opportunities for predictive modeling, real-time process monitoring, and operational optimization. These technologies contribute to hazardous chemical reduction by helping engineers identify conditions that may lead to the formation of hazardous substances and by supporting the selection of inherently safer process configurations (Ali et al., 2026).

Within this framework, ML models such as graph neural networks enable "safety by design" approaches by predicting toxicological properties, bioaccumulation, and endocrine disruption early in the development stage, thus avoiding the synthesis of harmful compounds. In addition, data-driven decision-making can significantly reduce the need for extensive trial-and-error experimental trials, thereby minimizing material consumption and waste generation during process development (Yadav et al., 2026).

Digital tools also enable the evaluation of alternative operating scenarios, the optimization of reaction conditions—such as catalyst loading and residence time—and the maintenance of processes within safe operating limits through real-time monitoring (Ali et al., 2026; Yadav et al., 2026). Digital twins further extend these capabilities by creating dynamic virtual representations of chemical and industrial processes that continuously integrate operational data, process models, and sensor information. In process industries, digital twins have been increasingly recognized as valuable tools for real-time monitoring, predictive maintenance, process optimization, and risk management, enabling more proactive and informed decision-making throughout the process lifecycle. Advanced simulation platforms and digital twin environments further enhance these capabilities by integrating diverse datasets,

uncertainty analysis, and predictive modeling within a unified framework. Such systems allow researchers and engineers to evaluate multiple operational scenarios, quantify risks, and support evidence-based decision making before implementation, thereby reducing both safety risks and resource consumption associated with conventional trial-and-error approaches (Perno et al., 2022). Through these capabilities, digitalization supports more informed and adaptive process management, contributing to both improved environmental performance and safer chemical production.

4. CHALLENGES IN HAZARDOUS CHEMICAL REDUCTION

Although considerable progress has been made in green chemistry and sustainable engineering, reducing hazardous chemicals remains a significant challenge in many industrial applications. The scientific principles and technological tools needed to minimize hazards are increasingly available, yet their implementation is often influenced by process-specific, economic, and organizational constraints. In practice, the adoption of hazardous chemical reduction strategies is affected not only by limitations in process design and the availability of safer alternatives, but also by factors such as economic feasibility, data quality, and regulatory requirements. Addressing these challenges is essential for translating advances in green chemistry into effective and scalable industrial solutions.

4.1 Technical and Process-Level Limitations

Redesigning existing chemical processes remains a major technical challenge because many industrial systems are locked into well-established, carbon-intensive infrastructures with long investment cycles (Chung et al., 2023). Transitioning to inherently safer alternatives often requires substantial changes in reaction mechanisms and overall process configurations, which can be achieved through retrofitting—adapting operating plants to maintain optimal performance under new sustainability criteria. This process is complex and first requires the systematic identification of process bottlenecks related to mass and energy flows (Ruiz-Mercado et al., 2016).

At the same time, emerging technologies such as process intensification (PI), although promising, introduce significant operational challenges. For example, microreactors and intensified configurations require precise control of flow behavior and heat transfer; however, their significantly improved reaction rates often lead to issues in monitoring, as the response periods of instruments become critical compared to the process period (Ghernaout et al., 2021). Furthermore, the scale-up from laboratory studies to industrial applications is hindered by inadequate facilities and a lack of in-depth technical understanding regarding these compact systems (Baldha & Kolli, 2023).

Material compatibility and product performance present additional barriers. Replacing hazardous chemicals with safer alternatives may affect process efficiency or final product quality (Zimmerman et al., 2020). A significant risk in this transition is "regrettable substitution," where a problematic substance is replaced by a

chemical with unknown or unforeseen hazards, such as the transition from BPA to BPS (Maertens et al., 2021). To avoid such failures, substitution must be guided by Alternatives Assessment (AA) frameworks that focus on functional use and the necessity of specific chemical properties rather than simple "drop-in" replacements (Tickner et al., 2018; Maertens et al., 2021).

4.2 Economic and Industrial Constraints

Economic factors strongly influence the adoption of green engineering strategies. Transitioning from established linear "take–make–dispose" production systems to sustainable alternatives involves substantial financial commitments and uncertainty (Matlin et al., 2022). A significant barrier is the high capital expenditure required for energy-intensive facilities, which are typically built for 10 to 30 years, creating a danger of lock-in of carbon-intensive infrastructure and equipment (Chung et al., 2023). Furthermore, current capital investment models often favor incrementalism—which has a clearer risk profile—while disfavoring the large-scale infrastructure changes needed for transformative sustainability (Anastas & Zimmerman, 2019). In this context, assessment tools such as SustainPro can help address these challenges by identifying process bottlenecks and supporting the redesign of existing systems to improve both environmental and economic performance (Ruiz-Mercado et al., 2016).

Research and development (R&D) costs represent another important constraint. The identification and validation of safer alternatives require considerable time and financial resources, as traditional toxicological testing is both slow and expensive (Maertens et al., 2021). These challenges are particularly evident in the pharmaceutical sector, where smaller production volumes and stringent market deadlines often lead to the use of older, inferior stoichiometric technologies instead of cleaner catalytic alternatives (Sheldon, 2023). To justify these transitions, a detailed Techno-Economic Assessment (TEA) is paramount to quantify manufacturing costs and market opportunities upfront (Zimmermann et al., 2020).

Industrial constraints are also shaped by supply chain dependencies. The availability of safer raw materials and green solvents is often limited by the absence of stable and scalable supply networks. Without reliable supply chains, substitution strategies remain uncertain and economically challenging, as reducing hazardous chemicals at an industrial scale requires the internalization of external costs related to resource depletion and environmental pollution (Sheldon, 2023). Consequently, a successful transition depends on developing supporting infrastructure and broader market conditions that enable truly sustainable production practices (Matlin et al., 2022.

4.3 Data, Metrics, and Assessment Challenges

The successful reduction of hazardous chemicals depends heavily on the availability of reliable data and appropriate assessment methods. However, important gaps remain in our understanding of the toxicity, environmental fate, and long-term impacts of many synthetic chemicals (Zimmerman et al., 2020). These uncertainties complicate decision-making, particularly during the early stages of chemical design

when toxicological information is needed to prevent the generation of hazardous substances (Maertens et al., 2021). In the absence of high-quality data, engineers may face significant uncertainties that result in unanticipated environmental persistence or health risks (Matlin et al., 2022).

Assessing progress toward hazardous chemical reduction presents additional challenges. Widely used green chemistry metrics such as atom economy and the E-factor are valuable tools for evaluating material efficiency, but they do not always adequately reflect the intrinsic toxicity and hazard-related aspects of waste (Sheldon, 2023). A major concern is that indicators often differ significantly between various assessment frameworks, which may lead to different outcomes for the same chemical or material (Caldeira et al., 2024). This limitation highlights the need for more comprehensive approaches that combine mass-based metrics with indicators related to toxicity and safety (Ruiz-Mercado et al., 2016).

Life Cycle Assessment (LCA) offers a broader perspective by evaluating environmental impacts across the entire value chain. Nevertheless, LCA is often data-intensive and subject to methodological uncertainties, particularly in the early stage of development where data availability is limited (Baldha & Kolli, 2023). These difficulties become even more pronounced in circular systems, where the huge diversity of additives and imperfect recoverability of materials require continuous tracking and dynamic data integration (Zuin & Kümmerer, 2022; Chen et al., 2020).

Another important challenge is the integration of multiple assessment tools into a coherent decision-making framework. Engineers must balance economic performance, environmental impacts, and hazard reduction objectives, which do not always align. Developing non-toxic chemical systems therefore requires multi-criteria evaluation approaches capable of addressing these trade-offs while minimizing the risk of regrettable substitutions (Tickner et al., 2018). Emerging digital tools, including Artificial Intelligence and Machine Learning, offer promising pathways to bridge these data gaps by predicting toxicological properties early in the design phase (Yadav et al., 2026).

4.4 System-Level and Regulatory Barriers

In addition to technical and economic constraints, system-level and regulatory factors significantly influence the adoption of green engineering strategies. Many regulatory systems have historically focused on risk management by controlling exposure to hazardous substances rather than eliminating hazards at their source (Brar et al., 2014). As a result, compliance with established exposure limits may receive greater emphasis than the implementation of inherently safer alternatives (Tickner et al., 2018). Recent initiatives like the European Green Deal aim to align regulatory frameworks with non-toxic chemistry; however, supporting Safe and Sustainable by Design (SSbD) approaches requires a more robust "science–policy interface" (SPI) to coordinate the evaluation and management of chemicals throughout their life cycle (Fuller et al., 2022; Caldeira et al., 2024).

The global reduction of hazardous chemicals is further complicated by jurisdictional differences and a fragmented research landscape. Companies must comply with varying national safety criteria and classification systems, creating obstacles for the adoption of green technologies across global supply chains (Tickner et al., 2018; Matlin et al., 2022). The absence of international harmonization increases regulatory uncertainty, which can be mitigated by moving toward property-based regulation. Unlike traditional list-based approaches, this framework addresses the underlying properties that cause concern (e.g., persistence, bioavailability), providing critical guidance to molecular designers (Anastas & Zimmerman, 2019).

Another significant challenge is the need for stronger coordination among industry, academia, and policy-makers to overcome the inertia of established infrastructures. Transitioning to a non-toxic chemical industry requires priority governance directions (PGD) that integrate cross-departmental collaboration with supportive business models (Chen et al., 2020). This includes the development of industry roadmaps and social mechanisms that drive behavioral changes across the sociotechnical system (Chung et al., 2023). Furthermore, integrating these principles into urban infrastructures, such as smart cities, through standardized indicators like ISO 37122 can help propel large-scale industrial transformation by linking urban metabolism with green chemistry principles (Oliveira et al., 2024). Without these integrated enabling conditions and the rethinking of chemistry for a circular economy, the benefits of green chemistry may remain confined to isolated applications (Zuin & Kümmerer, 2022)

CONCLUSION

This chapter has highlighted the central role of green chemistry–driven engineering in reducing hazardous chemicals through preventive and design-oriented approaches. Rather than relying primarily on waste treatment and end-of-pipe controls, green engineering seeks to address hazards at their source by integrating environmental, safety, and performance considerations into the design of chemical products and processes. The examples discussed throughout the chapter demonstrate that strategies such as catalyst development, safer solvent selection, process intensification, and resource-efficient process design can contribute substantially to reducing the generation and release of hazardous substances.

A recurring theme throughout the chapter is the importance of evaluating environmental performance using appropriate assessment tools and quantitative metrics. Approaches such as Life Cycle Assessment (LCA) and green chemistry metrics provide valuable support for identifying trade-offs and ensuring that improvements in one part of a system do not create unintended impacts elsewhere. At the same time, advances in digitalization, including Artificial Intelligence, machine learning, and real-time monitoring technologies, are expanding the ability of engineers to design, optimize, and manage chemical processes more effectively. Together, these tools support a more integrated approach to hazardous chemical reduction across the life cycle of chemical systems.

The chapter has also emphasized that the implementation of green engineering strategies is influenced by technical, economic, and regulatory constraints. Challenges related to process redesign, industrial investment, data availability, and regulatory alignment continue to affect the pace of adoption in many sectors. Nevertheless, ongoing developments in circular economy frameworks, safer-by-design approaches, and sustainability-driven innovation are creating new opportunities for addressing these barriers.

Ultimately, the transition toward more sustainable chemical production depends on integrating hazard reduction into the design and operation of chemical systems rather than treating it as a downstream environmental management issue. Embedding hazard elimination principles within engineering practice can support the development of chemical processes that are not only more efficient and economically viable but also safer for human health and the environment.

SONUÇ

Bu bölüm, tehlikeli kimyasalların azaltılmasında yeşil kimya temelli mühendislik yaklaşımlarının merkezi rolünü ortaya koymuştur. Atık arıtımına ve proses sonu (end-of-pipe) kontrol yöntemlerine öncelikli olarak dayanmak yerine, yeşil mühendislik; kimyasal ürün ve süreçlerin tasarım aşamalarına çevresel, güvenlik ve performans kriterlerini entegre ederek tehlikeleri kaynağında önlemeyi amaçlamaktadır. Bölüm boyunca ele alınan örnekler, katalizör geliştirme, daha güvenli çözücü seçimi, proses yoğunlaştırma ve kaynak verimliliğini artıran proses tasarımı gibi stratejilerin, tehlikeli maddelerin oluşumunu ve çevreye salınımını önemli ölçüde azaltabileceğini göstermektedir.

Bölüm boyunca öne çıkan temel temalardan biri, çevresel performansın uygun değerlendirme araçları ve nicel göstergeler kullanılarak analiz edilmesinin önemidir. Yaşam Döngüsü Değerlendirmesi (LCA) ve yeşil kimya metrikleri gibi yaklaşımlar, sistem içerisindeki ödünleşimleri (trade-off) belirlemede ve bir alandaki iyileştirmenin başka bir alanda istenmeyen etkiler yaratmamasını sağlamada önemli katkılar sunmaktadır. Bununla birlikte, yapay zekâ, makine öğrenmesi ve gerçek zamanlı izleme teknolojilerini kapsayan dijitalleşme alanındaki gelişmeler, mühendislerin kimyasal süreçleri daha etkin bir şekilde tasarlama, optimize etme ve yönetme kapasitesini artırmaktadır. Bu araçlar birlikte değerlendirildiğinde, kimyasal sistemlerin tüm yaşam döngüsü boyunca tehlikeli kimyasalların azaltılmasına yönelik daha bütünleşik bir yaklaşımı desteklemektedir.

Bölüm ayrıca, yeşil mühendislik stratejilerinin uygulanmasının teknik, ekonomik ve düzenleyici kısıtlamalardan etkilendiğini vurgulamıştır. Proseslerin yeniden tasarlanması, endüstriyel yatırım gereksinimleri, veri erişilebilirliği ve düzenleyici uyum gibi konular, birçok sektörde bu yaklaşımların benimsenme hızını etkilemeye devam etmektedir. Bununla birlikte, döngüsel ekonomi çerçeveleri, güvenli-tasarım (safer-by-design) yaklaşımları ve sürdürülebilirlik odaklı yeniliklerdeki gelişmeler, bu engellerin aşılmasına yönelik yeni fırsatlar yaratmaktadır.

Sonuç olarak, daha sürdürülebilir kimyasal üretime geçiş, tehlike azaltımının çevresel yönetimin süreç sonrasındaki bir unsuru olarak ele alınmasından ziyade, kimyasal sistemlerin tasarım ve işletim süreçlerine doğrudan entegre edilmesine bağlıdır. Tehlike ortadan kaldırma ilkelerinin mühendislik uygulamalarına yerleştirilmesi; yalnızca daha verimli ve ekonomik açıdan uygulanabilir değil, aynı zamanda insan sağlığı ve çevre açısından daha güvenli kimyasal süreçlerin geliştirilmesini de destekleyebilir.

REFERENCES

1. Ali, M., Mahmood, T. & Khan, F. (2026). Review of artificial intelligence applications in sustainable chemical engineering. *Discov Sustain*. https://doi.org/10.1007/s43621-026-03539-5
2. Alwi, S.R.W., Klemeš, J.J. &Varbanov, P.S. (2016). Cleaner energy planning, management and technologies: Perspectives of supply-demand side and end-of-pipe management, *Journal of Cleaner Production,* 136B, 1-13, https://doi.org/10.1016/j.jclepro.2016.07.181.
3. Anastas, P. T., & Warner, J. C. (1998). *Green Chemistry: Theory and Practice*. Oxford University Press.
4. Anastas, P. T., & Zimmerman, J. B. (2019). The periodic table of the elements of green and sustainable chemistry. *Green Chemistry, 21(24),* 6545-6566. https://doi.org/10.1039/C9GC01293A.
5. Baldha, M., & Kolli, S. K. (2023). Advancing sustainable chemistry: Innovations in green synthesis and process design. *Journal of Survey in Fisheries Sciences, 10(3),* 1946–1949. https://doi.org/10.53555/sfs.v10i3.2661
6. Boix, M., Montastruc, L., Pibouleau, L., Azzaro-Pantel, C., Domenech, S.. (2012). Industrial water management by multiobjective optimization: from individual to collective solution through eco-industrial parks, Journal of Cleaner Production, 22, 1, https://doi.org/10.1016/j.jclepro.2011.09.011.
7. Brar, S. K., Pulicharla, R., & Verma, M. (2014). Green chemistry: Design of safer chemical and process protocols for healthy environment. *Hydrology Current Research, 5*, e114. https://doi.org/10.4172/2157-7587.1000e114.
8. Caldeira, C., Abbate, E., Moretti, C., Mancini, L., & Sala, S. (2024). Safe and sustainable chemicals and materials: a review of sustainability assessment frameworks. *Green Chem.,* 26, 7456. https://doi.org/10.1039/d3gc04598f.
9. Chen, T.-L., Kim, H., Pan, S.-Y., Tseng, P.-C., Lin, Y.-P., & Chiang, P.-C. (2020). Implementation of green chemistry principles in circular economy system towards sustainable development goals: Challenges and perspectives. *Science of the Total Environment, 716,* 136998. https://doi.org/10.1016/j.scitotenv.2020.136998.
10. Chung, C., Kim, J., Sovacool, B.K., Griffiths, S., Bazilian, M., Yang, M. (2023). Decarbonizing the chemical industry: A systematic review of sociotechnical systems, technological innovations, and policy options, *Energy Research & Social Science,* 6, 102955, https://doi.org/10.1016/j.erss.2023.102955.
11. Fuller, R., Landrigan, P. J., Balakrishnan, K., Bathan, G., Bose-O'Reilly, S., Brauer, M., Caravanos, J., Chiles, T., Cohen, A., Corra, L., Cropper, M., Ferraro, G., Hanna, J., Hanrahan, D., Hu, H., Hunter, D., Janata, G., Kupka, R., Lanphear, B., Lichtveld, M., … Yan, C. (2022). Pollution and health: a progress update. The Lancet. Planetary health, 6(6), e535–e547. https://doi.org/10.1016/S2542-5196(22)00090-0.
12. Ghernaout, D., Elboughdiri, N., & Lajimi, R. (2021). Green chemistry and process intensification: Milestones on a sustainable development. *International Journal of Chemistry and Materials Research, 9(1),* 1–18. https://doi.org/10.18488/journal.64.2021.91.1.18.
13. He, L., Chen, Y., Kang, Y., Tian, P. &Zhao, H. (2018). Optimal water resource management for sustainable development of the chemical industrial park under multi-uncertainty and multi-pollutant control. Environ Sci Pollut Res 25, 27245–27259 (2018). https://doi.org/10.1007/s11356-018-2758-8

14. Joshi, D. R., & Adhikari, N. (2019). Green chemistry: Beginning, recent progress, and future challenges. *World Journal of Pharmacy and Pharmaceutical Sciences, 8(7),* 280–293. https://doi.org/10.20959/wjpps20197-14208.

15. Karagölge, Z., & Gür, B. (2016). Sustainable chemistry: Green chemistry. *Iğdır University Journal of the Institute of Science and Technology, 6(2),* 89–96. http://doi.org/10.21597/jist.2016218851.

16. Maertens, A., Golden, E., & Hartung, T. (2021). Avoiding Regrettable Substitutions: Green Toxicology for Sustainable Chemistry. *ACS Sustainable Chemistry & Engineering, 9(23),* 7749–7758. https://doi.org/10.1021/acssuschemeng.0c09435.

17. Matlin, S. A., Cornell, S. E., Krief, A., Hopf, H., & Mehta, G. (2022). Chemistry must respond to the crisis of transgression of planetary boundaries. *Chemical Science, 13,* 11710–11720. https://doi.org/10.1039/D2SC03603G

18. Morton, S. A., Counce, R. M., & Collier, J. R. (2004). Incorporating green engineering principles into chemical process design. American Society for Engineering Education, ASEE Southeast Section Conference 2004

19. Mukundan, S., Xuan, J., Dann, S.E., Wagner, J.L. (2023). Highly active and magnetically recoverable heterogeneous catalyst for hydrothermal liquefaction of biomass into high quality bio-oil, *Bioresource Technology,* 369, 128479, https://doi.org/10.1016/j.biortech.2022.128479.

20. Naeem, A., Wali Khan, I., Farooq, M., Mahmood, T., Ud Din, I., Ali Ghazi, Z., & Saeed, T. (2021). Kinetic and optimization study of sustainable biodiesel production from waste cooking oil using novel heterogeneous solid base catalyst. *Bioresource technology,* 328, 124831. https://doi.org/10.1016/j.biortech.2021.124831.

21. Oliveira, J. R. P., Tusset, A. M., Andrade, D. I., Balthazar, J. M., Pagani, R. N., & Lenzi, G. G. (2024). Action plans study: Principles of green chemistry, sustainable development, and smart cities. *Sustainability, 16(18),* 8041. https://doi.org/10.3390/su16188041.

22. Perno, M., Hvam, L., & Haug, A. (2022). Implementation of digital twins in the process industry: A systematic literature review of enablers and barriers. *Comput. Ind., 134*, 103558. https://doi.org/10.1016/j.compind.2021.103558.

23. Ruiz-Mercado, G. J., Carvalho, A., & Cabezas, H. (2016). Using green chemistry and engineering principles to design, assess, and retrofit chemical processes for sustainability. *ACS Sustainable Chemistry & Engineering, 4(11),* 6208–6221. https://doi.org/10.1021/acssuschemeng.6b02200.

24. Sheldon, R. A. (2023). The E factor at 30: a passion for pollution prevention. *Green Chemistry, 25,* 1704-1728. https://doi.org/10.1039/d2gc04747k.

25. Slater, C.S., Savelski, M., Hounsell, G. Pilipauskas, D. & Urbanski, F. (2012). Green design alternatives for isopropanol recovery in the celecoxib process. *Clean Techn Environ Policy* **14**, 687–698 https://doi.org/10.1007/s10098-011-0433-6.

26. Tickner, J.A., Jacobs, M.M., Malloy, T.F., Buck, T., Stone, A., Blake, A.A., & Edwards, S. (2018). Advancing Alternatives Assessment for Safer Chemical Substitution: A Research and Practice Agenda. *Integrated Environmental Assessment and Management,* 15, 6, 855–866, https://doi.org/10.1002/ieam.4094.

27. Trost, B.M. (1995). Atom Economy—A Challenge for Organic Synthesis: Homogeneous Catalysis Leads the Way. *Angewandte Chemie*, 34, 259-281. https://doi.org/10.1002/anie.199502591.

28. Wang, J., & Wang, S. (2018). Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants *Chemical Engineering Journal, 334,* 1502-1517. https://doi.org/10.1016/j.cej.2017.11.059.

29. Wang, Y., Ma, X., Li, H., Liu, B., Li, H., Yin, S., & Sato, T. (2016). Recent Advances in Visible-Light Driven Photocatalysis. In Advanced Catalytic Materials - Photocatalysis and Other Current Trends. InTech. https://doi.org/10.5772/61864

30. Yadav, S., Chandra, H., Tiwari, K.S., Bharty, M.K., Chandravanshi, R., Chauhan, D.S. & Quraishi, M.A. (2026).. A review on the role of artificial intelligence and data science in green and sustainable chemistry: Current trends and futuristic pathways. *Discov Chem Eng* **6**, 1. https://doi.org/10.1007/s43938-025-00104-w.

31. Zhao, W., Shen, Q., Nan, T., Zhou, M., Xia, Y., Hu, G., Zheng, Q., Wu, Y., Bian, T., Wei, T., Zhang, C. (2023). Cobalt-based catalysts for heterogeneous peroxymonosulfate (PMS) activation in degradation of organic contaminants: Recent advances and perspectives, Journal of Alloys and Compounds, 958, 170370, https://doi.org/10.1016/j.jallcom.2023.170370.

32. Zimmerman, J. B., Anastas, P. T., Erythropel, H. C., & Leitner, W. (2020). Designing for a green chemistry future. *Science, 367),* 397–400. https://doi.org/10.1126/science.aay306.

33. Zimmermann AW, Wunderlich J, Müller L, Buchner GA, Marxen A, Michailos S, Armstrong K, Naims H, McCord S, Styring P, Sick V and Schomäcker R (2020) Techno-Economic Assessment Guidelines for CO2 Utilization. Front. Energy Res. 8:5. https://doi.org/10.3389/fenrg.2020.00005.

34. Zuin, V.G., & Kümmerer, K. (2022). Chemistry and materials science for a sustainable circular polymeric economy. *Nature Reviews. Materials, 7*, 76 - 78. https://doi.org/10.1038/s41578-022-00415-2.

SOLVENTS IN GREEN CHEMISTRY

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ABSTRACT

Solvents are organic or inorganic substances, typically in the liquid or gas phase, that function to dissolve matter. They are widely utilized across numerous fields, ranging from scientific research to industrial applications. Solvents play a major role in advancements within chemical sciences; however, following the detection of the increasing environmental pollution they cause, a core principle of Green Chemistry was specifically dedicated to this issue. Representing the 5th principle of green chemistry, the primary objective is to discover and employ harmless, economical, high-performing, biodegradable, and reusable solvents to prevent environmental pollution. This section examines solvents, their current state of advancement, next-generation solvents, and their evaluation from a green chemistry perspective. While analytically demonstrating the effective performance of solvents, it highlights the significance of green solvents in sustainable analytical chemistry. Indeed, the adoption, increased production, and utilization of green solvents are of critical importance for future generations.

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1. INTRODUCTION

Chemistry, currently experiencing its golden age, qualitatively and quantitatively elucidates the structure and all properties of matter. Most answers to the demands of an increasing population and human needs following the Industrial Revolution, which was initiated by scientific advancements, have emerged from the science of chemistry. Factories and manufacturing plants have proliferated, and synthetic products synthesized in laboratories have rapidly begun to replace natural products. Chemistry has addressed all requirements necessary for a modern and prosperous standard of living.

There is virtually no field untouched by chemistry, ranging from materials of diverse compositions to plastics, synthetic-based pharmaceuticals to textiles, and long-shelf-life foods to paints.

In return for these rapid scientific and technological advancements over the past decades, it has been observed that air, soil, and water have become progressively polluted. This degradation has been attributed to waste products and the processing stages of the chemicals used. Despite the identification of these pollutants, the adverse effects of certain chemicals on human health and the environment are still not fully understood in all dimensions, even though they have been in use for decades. Environmental crises observed in industrial areas—such as animal mortality, the extinction of certain plant species, the presence of toxic substances in plant contents, the pollution of water and the atmosphere, depletion of the ozone layer, and the impacts of greenhouse gases—demonstrate the negative impacts of chemistry. Concurrently, they indicate that the methods for remediation also lie within the domain of chemistry.

Scientific pursuits addressing these challenges have led to the birth of a new discipline in chemistry. Termed "Green Chemistry," this field prioritizes human health and the environment, aiming to develop green and sustainable technologies as alternatives to existing methods and materials. The concept of green chemistry was established by Anastas and Warner as an approach to applied cchemistry that is defined on twelve guiding principles. Its primary objective is to reduce or eliminate hazardous substances during the design, synthesis, manufacturing, ad use ofchemical products, thereby promoting safer and more sustainable chemical processes (Figure 1) (Anastas & Warner, 1998).

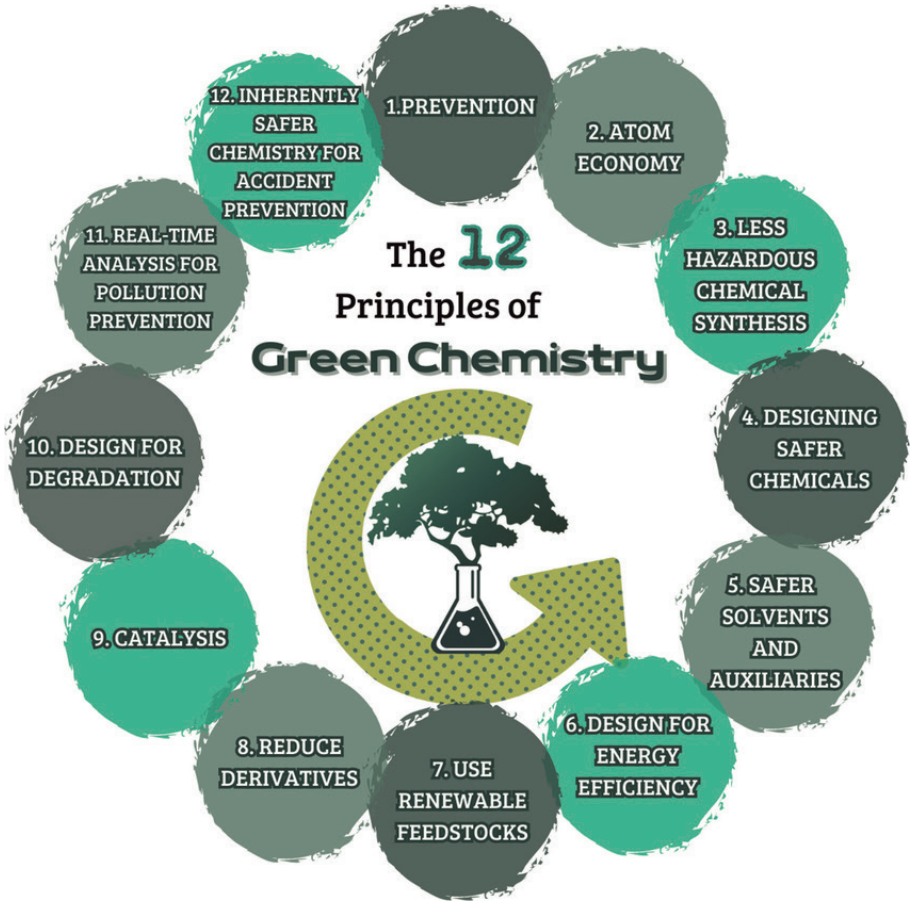

Figure 1. *Representation of the 12 principles of green chemistry proposed by P. Anastas and J. Warner. (Oliveira & Lenzi, 2023)*

Owing to its 12 critical principles, Green Chemistry is a continuously evolving branch of science. It aims to mitigate or eliminate the negative environmental impacts generated by the chemical sector by developing new chemicals and methodologies that are inherently non-toxic to living organisms and the environment. This requires meticulous attention due to laboratory waste originating from various stages of analytical methodologies, inherent risks in certain sample types, and the escalating energy consumption, emissions, and volumes of reagents and solvents resulting from modern instrumentation. (de la Guardia & Garrigues S, 2011).

The primary focus of this section is the 5th principle of green chemistry, which dictates the discovery and use of safer solvents. Consequently, this section presents current scientific research outcomes aimed at minimizing the use of auxiliary substances (such as solvents or separation agents) during chemical processes and ensuring they are harmless when their use is unavoidable.

2. SOLVENTS IN GREEN CHEMISTRY

2.1. An Overview of Solvents

When we mention a solvent, what simply comes to mind first are solids, liquids, or gases used to dissolve a substance and separate it into its components. In terms of quantity, the solute is the minor component, whereas the solvent is the major component. The solvent and solute generally form a homogeneous mixture. For a dissolution process to be considered successful, the primary characteristics evaluated are that the solution is homogeneous and clear.

Solvents, the indispensable components of chemical laboratories, are widely utilized in numerous sectors such as industry, healthcare, and food. In industry, solvents are employed for purposes such as dissolution, thinning, digestion, dilution, cleaning, and the formulation of new chemical substances and components. Furthermore, in research laboratories, they are used in areas such as biocatalysis, recovery of rare earth elements, extraction, purification, and the synthesis of biopolymers. The most general classifications of solvents are illustrated below (Figure 2).

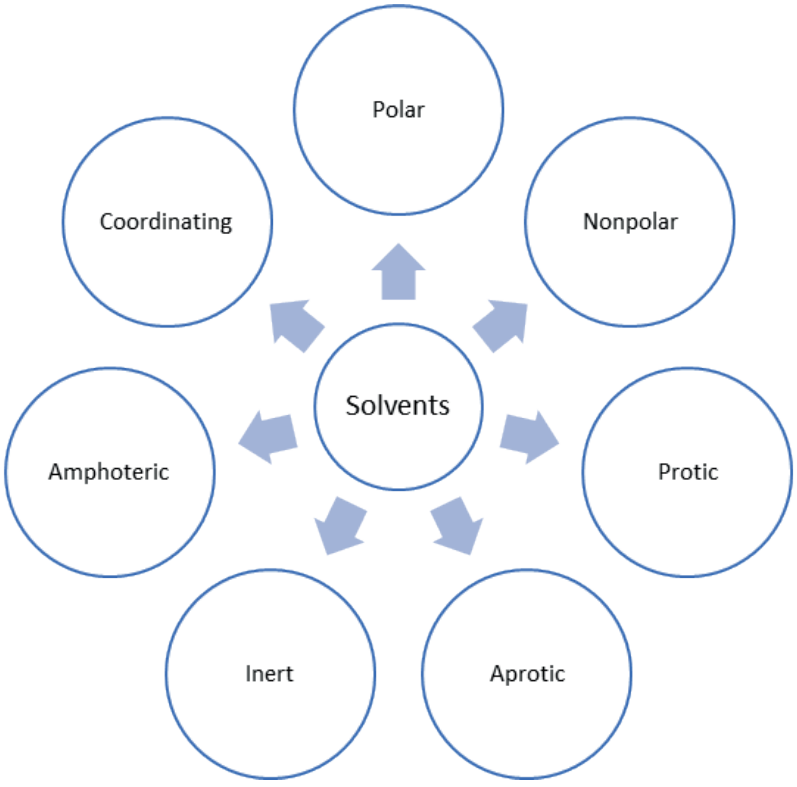

Figure 2. *Different Types of Solvents. (Sharma, 2023)*

2.2. Green and Non-Green (Conventional) Solvents

From the perspective of green chemistry, solvents are fundamentally classified into toxic, low-toxicity, and non-toxic categories. The most fundamental and non-toxic green chemistry solvent is water. Although water possesses a vast dissolving capacity, it cannot dissolve all substances. Due to its polar structure, it efficiently dissolves polar compounds. Moreover, when water bodies become polluted due to various factors, it can exert detrimental effects on the environment.

GreenSOL, a detailed solvent selection guide for analytical chemistry, evaluates solvents in accordance with green chemistry principles across their production, laboratory use, and waste management phases. Solvents are assigned impact category scores ranging from 1 (least appropriate) to 10 (highly appropriate). Additionally, the data in the table facilitates the selection of greener alternatives by enabling direct comparisons of solvents within the same chemical group or with similar properties. These data are also highly influential in waste management decisions. Solvent selections made based on these metrics lead to a reduced environmental footprint, ensure recycling and reuse, and safely achieve waste minimization (Table 1).

Green solvents aim to minimize the hazardous environmental impact of solvent consumption in chemical manufacturing (Menges, 2017). If green solvents—such as water, supercritical fluids, liquid polymers, and ionic liquids (ILs)—are utilized effectively, environmental degradation can be mitigated. Furthermore, low toxicity, favorable phase behavior, and optimal chemical, thermodynamic, biological degradability, and non-flammable characteristics are key features of novel green solvents or bio-solvents (Greer et al., 2020). Figure 3 illustrates different types of green solvents along with relevant examples.

For solvents to be classified as green chemistry solvents, they must possess characteristics such as non-toxicity, reusability, economic viability, accessibility, biodegradability, and non-hazardous waste profiles. Consequently, such solvents are limited in number.

Table 1. *Individual category scores of solvents along with composite scores for the Waste phase sub-categories Waste ENV and Waste Treatment (Stampolaki et al., 2026)*

GreenSOL		PRODUCTION		USE		WASTE						
Solvent	CAS Number	Prod CED	Prod ENV	Physical Hazards	Health Hazards	Aquatic Impact	Air Impact	Waste ENV	Biotreat.	Recycling	Incineration	Waste Treat.
Acetone	67-64-1	6	9	7	5	10	4	6	6	2	2	3
Acetonitrile	75-05-8	3	8	7	3	10	4	6	9	2	3	4
Benzene	71-43-2	7	9	4	1	6	5	5	9	4	6	6
Benzyl alcohol	100-51-6	3	7	10	6	10	8	9	10	6	4	6
Butan-1-ol	71-36-3	6	9	9	4	10	8	9	10	7	6	7
Butan-2-ol	78-92-2	3	8	9	4	10	8	9	10	6	4	6
N-Butyl acetate	123-86-4	4	8	7	5	7	8	7	10	7	6	7
N-Butylpyrrolidinone	3470-98-2	1	6	9	6	8	8	8	6	5	1	3
Carbon disulphide	75-15-0	7	8	2	1	5	4	4	5	4	4	4
Carbon tetrachloride	56-23-5	7	8	5	1	4	1	2	2	7	6	5
Chlorobenzene	108-90-7	4	7	8	3	3	8	4	6	9	6	7
Chloroform	67-66-3	7	1	9	1	9	4	6	2	7	5	4
Cumene	98-82-8	5	9	9	2	2	9	4	10	8	7	8
Cyclohexane	110-82-7	5	9	3	4	2	8	4	8	3	6	6
1,2-Dichlorobenzene	95-50-1	4	6	9	5	1	4	2	6	8	4	6
Dichloromethane	75-09-2	7	7	9	3	9	3	5	1	7	6	4
Diethanolamine	111-42-2	4	8	9	6	8	8	8	10	5	2	4
Diethyl ether	60-29-7	2	8	1	2	5	4	4	1	1	4	2
Diisopropyl ether	108-20-3	7	9	4	4	10	6	8	6	3	6	5
Dimethyl sulfoxide	67-68-5	7	5	9	10	10	8	9	10	5	2	5
N,N-Dimethylacetamide	127-19-5	4	8	10	3	10	8	9	10	6	3	6
N,N-Dimethylformamide	68-12-2	5	9	9	2	10	8	9	10	5	3	6
1,4-Dioxane	123-91-1	1	8	3	2	10	8	9	3	4	3	3
Ethane-1,2-diol	107-21-1	7	9	10	8	10	9	9	10	4	1	4
Ethanol	64-17-5	9	9	7	9	7	9	8	9	2	3	4
Ethyl acetate	141-78-6	5	8	7	4	9	8	8	8	2	3	4
Ethyl tertiary butyl ether	637-92-3	7	9	4	3	10	6	8	6	2	4	4
Heptane	142-82-5	9	10	3	5	1	7	3	10	5	6	7
Hexane	110-54-3	10	10	3	1	4	6	5	7	3	6	5
Isobutyl acetate	110-19-0	5	8	7	7	7	7	7	10	6	6	7
Isopropyl acetate	108-21-4	5	8	7	4	10	7	8	9	3	4	5
Methanol	67-56-1	9	10	7	3	10	5	7	8	2	3	3
Methyl acetate	79-20-9	7	9	7	4	9	3	6	5	1	1	2
4-Methylpentan-2-one	108-10-1	4	8	7	3	9	6	7	10	6	3	6
2-Methylpentane	107-83-5	8	9	3	4	2	6	4	6	3	6	5
N-Methylpyrrolidone	872-50-4	1	6	9	3	10	8	9	10	4	2	4
Octan-1-ol	111-87-5	1	9	9	6	2	8	4	10	8	6	8
Pentane	109-66-0	7	9	7	5	3	2	2	3	6	10	6
Pentan-1-ol	71-41-0	4	8	9	6	10	8	9	10	7	5	7
Propan-1-ol	71-23-8	5	8	7	5	10	7	8	10	4	3	5
Propan-2-ol	67-63-0	8	9	7	5	10	10	10	10	2	4	4
Propane-1,2-diol	57-55-6	4	7	10	10	10	8	9	10	5	2	4
Propyl acetate	109-60-4	2	7	7	5	8	8	8	10	7	6	7
Pyridine	110-86-1	1	4	7	4	8	8	8	8	5	4	5
Tetrachloroethylene	127-18-4	7	6	10	4	2	6	4	3	10	5	6
Tetrahydrofuran	109-99-9	1	7	7	3	10	5	7	2	2	4	3
Toluene	108-88-3	7	9	4	2	5	7	6	10	6	7	8
Triethanolamine	102-71-6	4	8	9	10	10	8	9	10	5	2	4
Water	7732-18-5	10	10	10	10	10	10	10	10	4	3	5

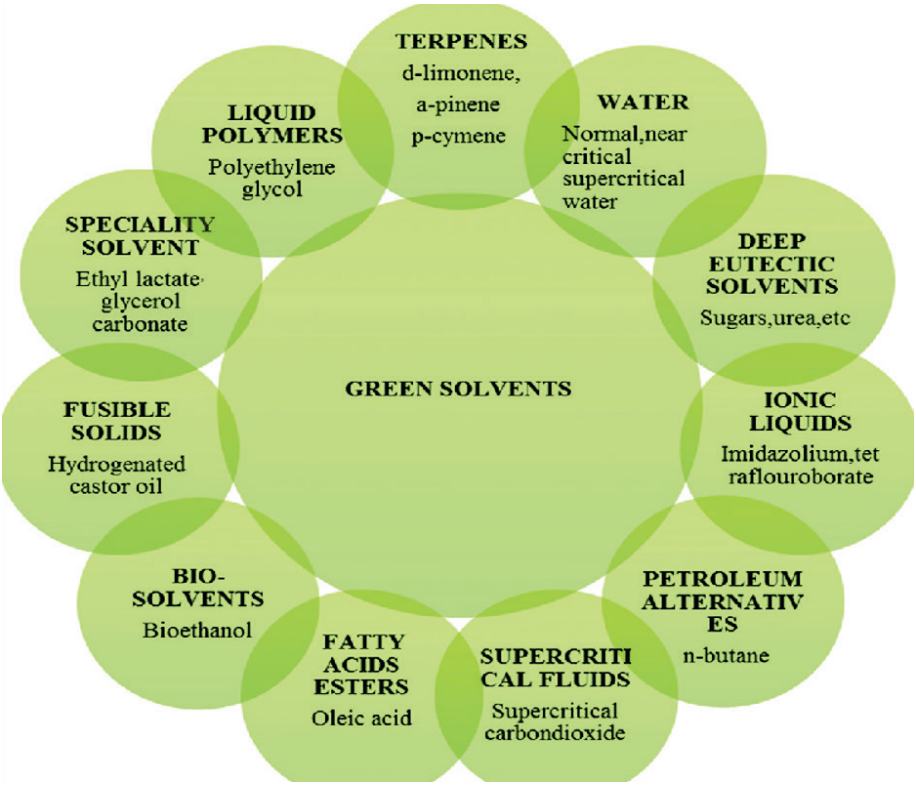

Figure 3. *Different types of green solvents (Dwivedi et al., 2021)*

2.3. Next-Generation Green Chemistry Solvents

Human activities represent the primary factor underlying the progressive pollution of nature and the serious threats posed to the survival of all living organisms in certain regions. Rapidly and accurately detecting pollution from industrial or other sources, and taking effective measures to prevent them, constitute the cornerstones of green chemistry, as stated above. When these pollutants increase, air, water, and soil suffer contamination, leading to severe consequences for humans, such as cancer, neurological disorders, allergies, cardiovascular diseases, and dermatological conditions. Therefore, pollution is a critical issue that must be addressed with gravity.

The determination of pollutants, particularly at low concentrations, is highly challenging. Analytical techniques such as spectrophotometric, electrochemical, and chromatographic methods have advanced significantly, particularly over the last decades, to detect trace amounts of elements like lead, zinc, arsenic, mercury, and nickel, as well as hazardous organic chemicals, making substantial progress in overcoming determination barriers. By employing preconcentration techniques, the concentrations of analytes are increased, matrix interference effects are eliminated through specific methods, and sensitivity is enhanced.

In recent years, exceptional success has been achieved, particularly in analytical chemistry, organic chemistry, and biochemistry, as an alternative to the solvents routinely used in preconcentration processes. Although the studied specimens vary across pharmaceutical and cosmetic samples, biological matrices, petroleum and petrochemical products, environmental samples, forensic evidence, and food and agricultural products, an increasing number of studies have been conducted with these techniques and solvents, generally yielding highly promising results.

We shall now present information regarding ILs and deep eutectic solvents (DESs), which are designated as "next-generation green solvents".

Ionic Liquids (ILs)

A major breakthrough in the field of solvents within green chemistry began in 1914 with Paul Walden's discovery of ethylammonium nitrate ($[EtNH_3][NO_3]$) (Passos et al., 2014). Today, ILs are defined as organic salts with melting temperatures below 100 °C, typically composed of an organic or inorganic anion and a bulky organic cation. That is, they are liquid below 100 °C. The large size and high charge dispersion of the ions prevent the formation of a regular crystal structure; hence, the structure is asymmetric. Consequently, ILs exist in the liquid phase at lower temperatures compared to characteristic inorganic salts.

Due to their ionic character, the majority of aprotic ILs exhibit exceptional dissolving capacity for various compounds, high ionic conductivity, negligible volatility and flammability, high thermal stability, and many other positive attributes (Dupont et al.,J, 2002; Freire et al 2012). In particular, their extremely low volatility significantly restricts their release into the atmosphere.

Ionic liquids are also referred to as "designer solvents". This is because their anionic and cationic properties can be easily modified, and millions of different anion-cation alternatives with diverse physicochemical properties are already available through this pathway. Thus, their toxicological profiles, biodegradability, selectivity in extraction/separation processes, and polarities can be tailored.

Owing to these characteristics, they are highly advantageous solvents (Passos et al., 2014; Ranke et al., 2007; Hallett et al., 2011). They are frequently utilized primarily in extraction and separation processes, chemical syntheses, analytical studies, and biocatalysis (Plechkova & Seddon 2008; Zhao 2006).

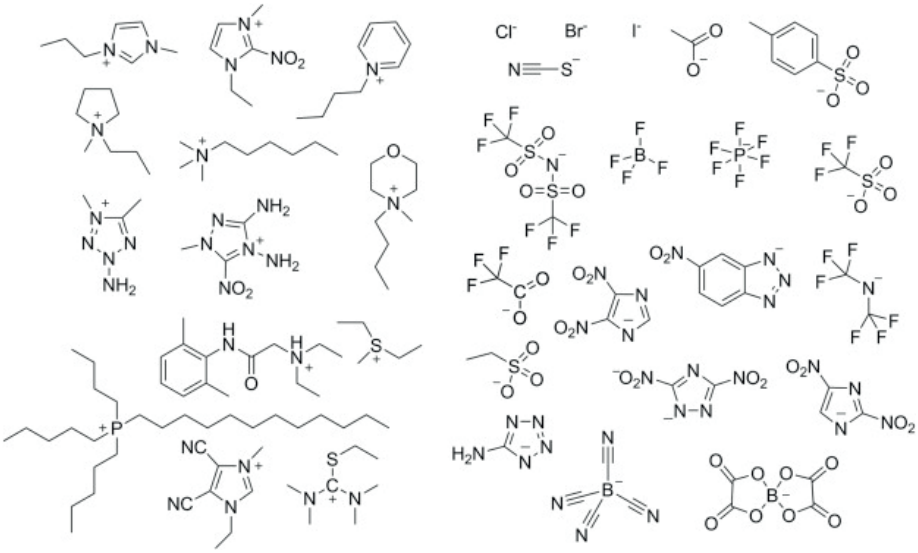

Figure 4. *Examples of IL-constituent ions (cations on the left and anions on the right) (Aspnohpm, 2021)*

With the ongoing development of ILs, IL-based materials such as magnetic ionic liquids (MILs) and polymeric ILs (PILs) have also become available today. Numerous studies have been conducted to enhance the efficiency of reaction steps by utilizing ILs in chemical and biological research (Figure 4). The most extensively studied ionic liquids consist of tetraalkyammonium, pyrrolidinium, imidazolium, phosphonium, and pyridinium-based cations combined with anions such as acetate ($[CH_3CO_2]^-$), bis(trifluoromethylsulfonyl) imide ($[NTf_2]^-$), bromide (Br^-), chloride (Cl^-), tetrafluoroborate ($[BF_4]^-$), and hexafluorophosphate ($[PF_6]^-$) (Freire et al.,2010).

In addition to their advantages, ILs also possess certain disadvantages. The viscosity of most ILs is high, which complicates processing and potentially diminishes extraction efficiency. Therefore, lower viscosities are generally required for optimum performance in extraction processes (Soni et al., 2025). Furthermore, it has been observed that some ILs are synthesized at a high cost, and some exhibit toxic properties. Consequently, the utilization of such ILs is restricted in certain industrial sectors.

Deep Eutectic Solvents (DES)

DESs were introduced in 2007 by Abbott and co-workers (Abbott et al., 2001). The fact that ionic liquids (ILs) are somewhat costly and that some exhibit toxic effects that are unfavorable from a green chemistry standpoint led to the emergence of a new generation of solvents called "Deep Eutectic Solvents (DES)". DESs are obtained by mixing two safe components (which are biodegradable, inexpensive, and renewable) to form a hydrogen-bonded eutectic mixture.

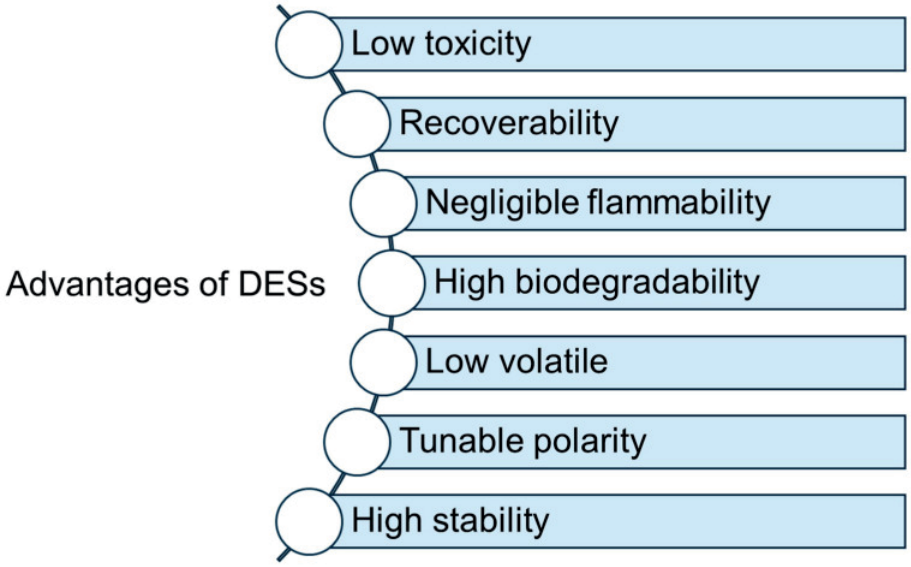

Figure 5. *Advantages of DESs. (Stanisz et al., 2024)*

Choline chloride (ChCl) is one of the most frequently utilized components in the formation of DESs. Choline chloride is a quaternary ammonium salt. It can be readily synthesized from fossil reserves through a process characterized by a very high atom economy, or it can be derived from biomass. It is biodegradable, highly cost-effective, and non-toxic. The physicochemical properties of DESs—such as refractive index, conductivity, density, surface tension, viscosity, and chemical inertness—are remarkably close to those of widely used ionic liquids (Figure 5). Characterized generally by a very large freezing point depression and remaining in the liquid phase at temperatures below 150 °C, most DESs are liquid between 25 °C and 70 °C (Zhang et al., 2012).

To date, various hydrogen bond donors have been investigated, and deep eutectic solvents have been formulated using amides, carboxylic acids, and alcohols (Figure 6). These liquids are straightforward to prepare and are relatively unreactive with water; many are biodegradable and feature relatively low production costs (Smith et al., 2014).

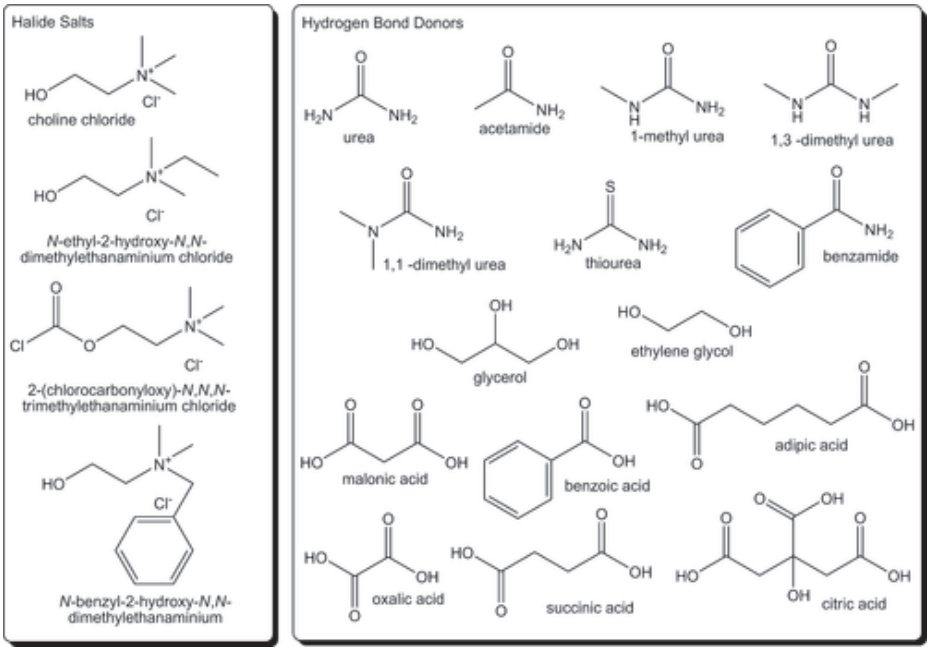

Figure 6. *Structures of some halide salts and hydrogen bond donors used in the formation of deep eutectic solvents. (Smith et al., 2014)*

It is reported that DESs are generally less chemically inert than ILs (Smith et al., 2014). Furthermore, like ILs, DESs possess "tailorable" properties. DESs offer distinct advantages over ILs, as they are generally cheaper, easier to prepare without requiring chemical reactions, and are composed of components derived from natural sources such as sugars, choline derivatives, amino acids, and organic acids. DESs also find widespread application in fields such as analytical chemistry, organic synthesis, biotechnology, and catalysis (Espino et al., 2016; Liu et al 2018; Paiva et al 2014; Vanda et al., 2018).

CONCLUSION

Understanding and implementing the principles of green chemistry across all production-related sectors is a vital imperative. Solvents represent one of the most fundamental substances utilized in research geared toward vital needs. In particular, the growing human population and the production required to meet its needs have brought about an increase in environmental pollution. Mitigating or preventing these impacts will secure our future environmental sustainability. To this end, the 5th principle among the 12 core principles of green chemistry targets the utilization of safe, inexpensive, biodegradable, and non-toxic solvents.

Primarily water, followed by glycerol, DESs, and ILs, are recognized as the primary green solvents. Their performance and successful manufacturing outcomes demonstrate that these are the most commercially utilized green solvents. Heavy metals, pesticides, toxic biological wastes, contaminated water bodies, and illicit drugs rank at the top of environmental pollution categories. The severe and chronic diseases, as well as fatalities, induced by these substances are now established facts. Therefore, the accurate, reliable, real-time, and high-sensitivity analytical determination of these substances is of paramount importance. It is required that the solvents utilized for these determinations do not generate environmental pollution, and that they possess characteristics such as biodegradability, low cost, and reusability. That is, they must be both economical and ecological.

However, factors such as cost, fluctuations in raw material sustainability, and engineering challenges arising in production design represent major obstacles commonly encountered. For this purpose, the most crucial feature of ILs and DESs that have emerged in recent years in green solvent research is their "designer solvent" capability, which is valuable for tailoring the affinities and polarities of these extraction solvents according to the target compound. ILs and DESs are also utilized in the dissolution stage of solid samples. Most ionic liquids (ILs) are selected based on their affinity for the target compounds. Nonetheless, many of these ILs possess non-negligible toxicity and low biodegradability; for green analytical chemistry purposes, there is a fundamental need to seek more sustainable ILs derived primarily from natural sources.

Although still in its infancy, DESs are also preferred hydrogen bond acceptor (HBA) types combined with hydrogen bond donors (HBDs) such as oxalic acid, n-butyric acid, p-chlorophenol, cholinium chloride, and itaconic acid as green chemistry-targeted solvents. Recent research on DESs reveals a growing interest within the scientific community toward establishing sustainable processes using more environmentally friendly solvents. Nevertheless, the fact that the use of DESs in monitoring contaminant compounds remains largely unexplored presents a great opportunity to expand knowledge in this field and discover the dual role of DESs as both extraction solvents and dissolving agents. Research on ILs and DESs as alternative solvents to widely used hazardous organic solvents makes a significant contribution to the 5th Principle of Green Chemistry.

In conclusion, although rapid progress is being made in the field of solvents from a green chemistry perspective, the fact that the toxicological profiles of next-generation solvents cannot be fully known indicates that more scientific studies need to be conducted in this field.

SONUÇ

Yeşil kimya ilkelerinin üretimle ilişkili tüm sektörlerde anlaşılması ve uygulanması günümüzde hayati bir gereklilik hâline gelmiştir. Çözücüler, temel ihtiyaçlara yönelik araştırma ve üretim süreçlerinde kullanılan en önemli maddelerden biridir. Özellikle artan dünya nüfusu ve bu nüfusun gereksinimlerini karşılamak amacıyla gerçekleştirilen üretim faaliyetleri, çevresel kirliliğin artmasına neden olmuştur. Bu etkilerin azaltılması veya önlenmesi, gelecekte çevresel sürdürülebilirliğin güvence altına alınmasına katkı sağlayacaktır. Bu doğrultuda, yeşil kimyanın 12 temel ilkesinden beşincisi; güvenli, düşük maliyetli, biyobozunur ve toksik olmayan çözücülerin kullanımını hedeflemektedir.

Başta su olmak üzere gliserol, derin ötektik çözücüler (DES'ler) ve iyonik sıvılar (IL'ler), günümüzde en önemli yeşil çözücüler olarak kabul edilmektedir. Performansları ve başarılı üretim uygulamaları, bu çözücülerin ticari açıdan en yaygın kullanılan yeşil çözücüler arasında yer aldığını göstermektedir. Ağır metaller, pestisitler, toksik biyolojik atıklar, kirlenmiş su kaynakları ve yasa dışı uyuşturucu maddeler çevre kirliliğinin başlıca nedenleri arasında bulunmaktadır. Bu maddelerin yol açtığı akut ve kronik hastalıklar ile ölümler artık bilimsel olarak kanıtlanmış gerçeklerdir. Bu nedenle söz konusu kirleticilerin doğru, güvenilir, gerçek zamanlı ve yüksek hassasiyetle analitik olarak belirlenmesi büyük önem taşımaktadır. Bu analizlerde kullanılan çözücülerin çevre kirliliğine neden olmaması, biyobozunur, düşük maliyetli ve yeniden kullanılabilir özelliklere sahip olması gerekmektedir. Başka bir ifadeyle, çözücüler hem ekonomik hem de ekolojik açıdan sürdürülebilir olmalıdır.

Bununla birlikte, maliyet, hammaddelerin sürdürülebilirliğindeki dalgalanmalar ve üretim tasarımında karşılaşılan mühendislik zorlukları gibi faktörler, bu alanda sıklıkla karşılaşılan önemli engeller arasında yer almaktadır. Son yıllarda yeşil çözücü araştırmalarında öne çıkan iyonik sıvılar (IL'ler) ve derin ötektik çözücülerin (DES'ler) en önemli avantajı, "tasarlanabilir çözücü (designer solvent)" özelliklerine sahip olmalarıdır. Bu özellik sayesinde, çözücülerin polariteleri ve hedef bileşiklere olan ilgileri istenilen uygulamaya göre ayarlanabilmektedir. IL'ler ve DES'ler aynı zamanda katı numunelerin çözündürülmesi aşamasında da kullanılmaktadır. Çoğu iyonik sıvı, hedef bileşiklere olan yüksek afinitelerine göre seçilmektedir. Ancak bu iyonik sıvıların bir kısmı dikkate değer düzeyde toksisiteye sahip olup düşük biyobozunurluk göstermektedir. Bu nedenle yeşil analitik kimya açısından, özellikle doğal kaynaklardan elde edilen daha sürdürülebilir iyonik sıvıların geliştirilmesine ihtiyaç duyulmaktadır.

Henüz gelişiminin erken aşamalarında olmasına rağmen, DES'ler de yeşil kimya odaklı çözücüler olarak tercih edilmektedir. Oksalik asit, n-bütirik asit, p-klorofenol, kolinyum klorür ve itakonik asit gibi hidrojen bağı vericileri (HBD) ile uygun hidrojen bağı alıcılarının (HBA) kombinasyonlarından oluşan DES sistemleri, çevre dostu çözücü alternatifleri sunmaktadır. DES'ler üzerine yapılan güncel çalışmalar, bilim dünyasında daha çevre dostu çözücüler kullanılarak sürdürülebilir süreçlerin geliştirilmesine yönelik ilginin giderek arttığını göstermektedir. Bununla birlikte,

DES'lerin kirletici bileşiklerin izlenmesi ve analizinde kullanımının hâlen büyük ölçüde araştırılmamış olması, bu alanda bilgi birikiminin artırılması ve DES'lerin hem ekstraksiyon çözücüsü hem de çözündürme ajanı olarak üstlenebileceği çift yönlü rolün ortaya çıkarılması açısından önemli fırsatlar sunmaktadır. Yaygın olarak kullanılan tehlikeli organik çözücülere alternatif olarak IL'ler ve DES'ler üzerine yürütülen araştırmalar, Yeşil Kimyanın 5. İlkesinin uygulanmasına önemli katkılar sağlamaktadır.

Sonuç olarak, yeşil kimya perspektifinden çözücü teknolojileri alanında hızlı ilerlemeler kaydedilmesine rağmen, yeni nesil çözücülerin toksikolojik profillerinin henüz tam olarak ortaya konulamamış olması, bu alanda daha kapsamlı bilimsel araştırmalara ihtiyaç duyulduğunu göstermektedir. Gelecekte gerçekleştirilecek çalışmaların, hem çevresel sürdürülebilirliği hem de insan sağlığını ön planda tutan daha güvenli, daha etkili ve daha sürdürülebilir çözücü sistemlerinin geliştirilmesine katkı sağlaması beklenmektedir.

REFERENCES

1. Abbott AP, Capper G, Davies DL, Munro H L, Rasheed R K, Tambyrajah V . (2001). Preparation of novel, moisture-stable, Lewisacidic ionic liquids containing quaternary ammonium salts with functional side chains. *Chem. Commun*., Oct.37(19). https://doi.org/10.1039/b106357j
2. ASPNOHPM: "Analytical Sample Preparation with Nano- and Other High-Performance Materials" (2021). *Book, Elsevier,* ISBN: 978-0-12-822139-6. https://doi.org/10.1016/C2019-0-03226-8
3. Anastas PT, Warner JC. Green Chemistry, Theory and Practice. (1998). *First Edition, Oxford University Press: Oxford, UK.* p 148. https://doi.org/10.1016/j.eiar.2004.06.006
4. de la Guardia M, Garrigues S. (2011). An ethical commitment and an economic opportunity. *In: de la Guardia M, Garrigues S (eds) Challenges in green analytical chemistry. Royal Society of Chemistry,* 1–12. https://doi.org/10.1039/9781849732963-00001
5. Dwivedi S., Fatima U., Gupta A., Khan T. (2021). Lawrence A., Green Solvents for Sustainable Chemistry: A Futuristic Approach, *Indian Journal of Advances in Chemical Science,* 9(4): 329-335. https://doi.org/10.22607/IJACS.2021.904014
6. Dupont J, De Souza RF, Suarez PAZ. (2002). Ionic liquid (molten salt) phase organometallic catalysis. *Chem Rev.,* 102 (10), 3667–3692. https://doi.org/10.1021/cr010338r
7. Espino M, de los Ángeles Fernández M, Gomez FJV, Silva MF. (2016). Natural designer solvents for greening analytical chemistry. *TrAC—Trends Anal Chem*., 76:126–136. https://doi.org/10.1016/j.trac.2015.11.006
8. Freire MG, Cláudio AFM, Araújo JMM, Coutinho J.A. P., Marrucho I.M., Lopes J.N.C., Rebelo L.P.N. (2012). Aqueous biphasic systems: a boost brought about by using ionic liquids. *Chem Soc Rev.,* 41:4966–4995. https://doi.org/10.1039/c2cs35151j
9. Freire MG, Neves CMSS, Marrucho IM, Coutinho J.A.P, Fernandes A.M. (2010). Hydrolysis of tetrafluoroborate and hexafluorophosphate counter ions in imidazolium-based ionic liquids. *J Phys Chem A*., 114:3744–3749. https://doi.org/10.1021/jp903292n
10. Greer A. J., Jacquemin J., Hardacre C., (2020). Industrial Applications of Ionic Liquids, *Multidisciplinary Digital Publishing Institute,* p1-2. https://doi.org/10.3390/molecules25215207
11. Hallett JP, Welton T. (2011). Room-temperature ionic liquids: Solvents for synthesis and catalysis. *Chem Rev*., 111:3508–3576. https://doi.org/10.1021/cr1003248
12. Liu Y, Friesen JB, McAlpine JB, Lankin D.C, Chen S.N, Pauli G.F. (2018). Natural deep eutectic solvents: properties, applications, and perspectives. *J Nat Prod.,* 81:679–690. https://doi.org/10.1021/acs.jnatprod.7b00945
13. Menges, N. (2017). The role of green solvents and catalysts at the future of drug design and of synthesis. *In: Green Chemistry, Ch. 5. Boston: USA*, p74-89. https://doi.org/10.5772/intechopen.71018
14. Oliveira J. R.P. and Lenzi G. G. October. (2023). Advances in the Use of Green and Sustainable Synthesis to Obtain Nanomaterials, *Green Chemistry for Environmental Sustainability - Prevention-Assurance-Sustainability (P-A-S) Approach.* https://doi.org/10.5772/intechopen.1002866

15. Paiva A, Craveiro R, Aroso I, Martins M, Reis R.L, Duarte A.R.C. (2014). Natural deep eutectic solvents—solvents for the 21st century. *ACS Sustain Chem Eng.,* 2:1063–1071. https://doi.org/10.1021/sc500096j

16. Passos H, Freire MG, Coutinho J.A.P. (2014). Ionic liquids solutions as extractive solvents of value-added compounds from biomass. *Green Chem.,* 16:4786–4815. https://doi.org/10.1039/c4gc00236a

17. Plechkova NV, Seddon KR (2008) Applications of ionic liquids in the chemical industry. *Chem Soc Rev.* 37:123–150. https://doi.org/10.1039/b006677j

18. Ranke J, Stolte S, Störmann R, Arning J, Jastroff B. (2007). Design of sustainable chemical products-the example of ionic liquids. *Chem Rev.* 107:2183–2206. https://doi.org/10.1021/cr050942s

19. Sharma K. Dec. 17 (2023). https://scienceinfo.com/different-types-of-solvents-properties-uses/

20. Smith EL, Abbott AP, Ryder KS. (2014). Deep eutectic solvents (DESs) and their applications. *Chem Rev* .,114:11060–11082. https://doi.org/10.1021/cr300162p

21. Stanisz M, Stanisz B.J., Cielecka-Piontek J. (2024). A Comprehensive Review on Deep Eutectic Solvents: Their Current Status and Potential for Extracting Active Compounds from Adaptogenic Plants, *Molecules,* 29, 4767. https://doi.org/10.3390/molecules29194767

22. Soni N., Yadav M., Malarvannan M, Sharma D., Paul D. (2025). Current developments and trends in hybrid extraction techniques for green analytical applications in natural products, *J. Chromatogr. B,* 1256, Article 124543. https://doi.org/10.1016/j.jchromb.2025.124543

23. Stampolaki E., Mondello A., Alladio E., Oliveri P., Mazzoleni A., Pena-Pereira F., Psillakis E. (2026). GreenSOL: Green solvent guide for analytical chemistry based on production-to-end-of-life assessment, *Trends in Analytical Chemistry*, 194 118531. https://doi.org/10.1016/j.trac.2025.118531

24. Vanda H, Dai Y, Wilson EG, Verpoorte R, Choi Y.H. (2018). Green solvents from ionic liquids and deep eutectic solvents to natural deep eutectic solvents. *Comptes Rendus Chim*. 21:628–638. https://doi.org/10.1016/j.crci.2018.04.002

25. Zhao H. (2006). Innovative applications of ionic liquids as "green" engineering liquids. *Chem. Eng. Commun*., 193:1660–1677. https://doi.org/10.1080/00986440600586537

26. Zhang Q, De Vigier O.K., Royer S, Je´rome F. (2012). Deep eutectic solvents: syntheses, properties and applications, *Chem. Soc. Rev.,* 41, 7108–7146. https://doi.org/10.1039/c2cs35178

CATALYSIS AS A CORE PRINCIPLE OF GREEN CHEMISTRY: DESIGN, APPLICATIONS, AND SUSTAINABILITY

NESRİN BUĞDAY*
SEDAT YAŞAR**

ABSTRACT

Catalysis is a central principle of green chemistry because it can improve selectivity, reduce waste, lower energy demand, and support renewable feedstocks and circular production models. However, a catalytic reaction should not be considered green solely because a catalyst is used. Its sustainability depends on the whole process, including feedstock origin, solvent choice, energy input, catalyst stability, metal toxicity and scarcity, separation requirements, safety, scalability, and life-cycle impacts. This chapter evaluates major catalytic approaches, including homogeneous, heterogeneous, organo-, bio-, nano-, single-atom, MOF-based, photo-, and electrocatalysis, as complementary strategies. It also emphasizes the combined use of sustainability metrics such as atom economy, E factor, PMI, life-cycle assessment, and techno-economic analysis. The chapter focuses on applications in sustainable synthesis, cross-coupling, mechanochemistry, biomass valorization, CO_2 conversion, water splitting, and environmental remediation, while discussing key challenges such as catalyst deactivation, recovery, reproducibility, solvent use, mass transfer, and scalability.

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1. INTRODUCTION

Green chemistry emerged as a fundamental concept for developing chemical processes that minimize waste, reduce risks, and optimize energy and resource use. Catalysis is essential in this context as it improves reaction selectivity, reduces energy requirements, minimizes the necessity for stoichiometric reagents, and facilitates more sustainable synthetic pathways. However, the mere use of a catalyst does not inherently render a process ecologically friendly. A technically green catalytic process must be evaluated based on the natural source of the feedstock, the solvent employed, the stability and recoverability of the catalyst, its toxicity, energy requirements, waste production, scalability, and its environmental impact throughout its entire life cycle (Figure 1). This chapter examines catalysis as a crucial, system-dependent approach for attaining chemically efficient and ecologically sustainable reactions.



Figure 1. *Process-Level Framework for Green Catalysis*

1.1. Green Chemistry: Concept and Scope

The historical importance of green chemistry lies in its redefinition of chemical efficiency. Earlier process improvements often focused on yield, throughput, and cost; the green chemistry framework added prevention of hazard and waste as primary design objectives. In this sense, green chemistry is not merely an environmental management policy but a scientific method for designing chemical transformations, products, and manufacturing systems that avoid avoidable harm at source. The foundational literature emphasizes that the most effective form of pollution control is molecular and process design before a hazardous material is generated (Anastas & Eghbali, 2010; Clark, 1999; Poliakoff et al., 2002; Kurul et al., 2025). Within this design philosophy, catalysis became a structural rather than peripheral concept. The ninth principle of green chemistry explicitly prioritizes catalytic reagents over stoichiometric reagents, yet the logic extends across several other principles: prevention, atom economy, safer synthesis, energy efficiency, reduced derivatization, renewable feedstocks, and inherently safer processes (Figure 2). A catalytic process therefore needs to be evaluated as a system in which reaction chemistry, separation, solvent use, energy source, catalyst production, and end-of-life management are connected (Anastas et al., 2001; Anastas & Eghbali, 2010).

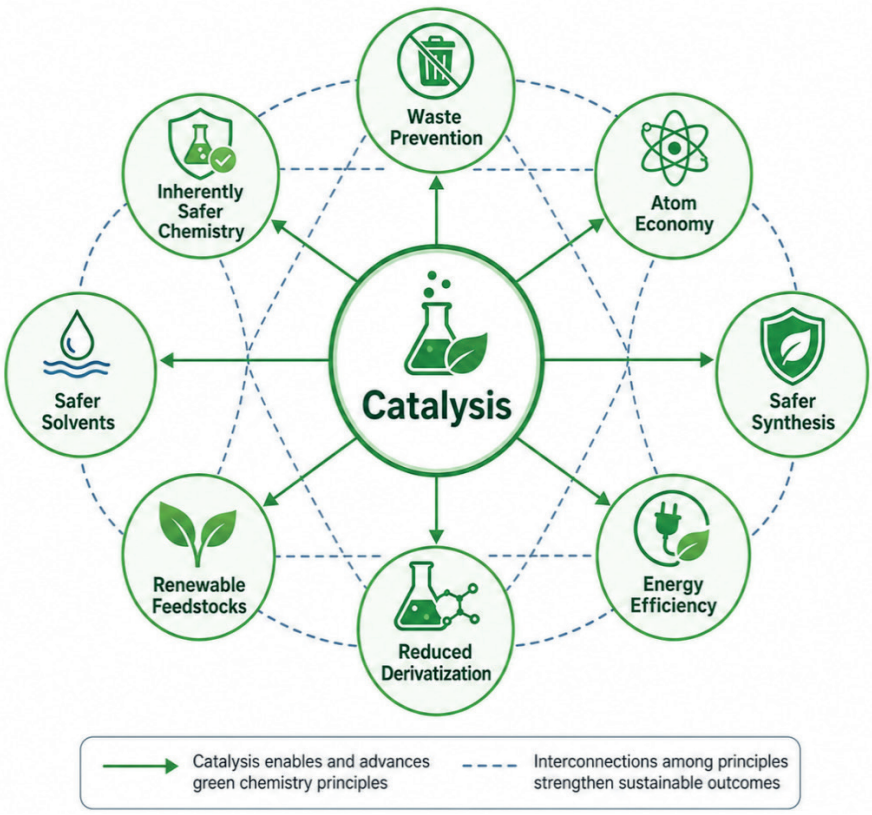

Figure 2. *Green chemistry principles and catalysis relationship*

A common complication in conversations about green catalysis is to combine the term 'catalytic' with 'sustainable.' This chapter refrains from that oversimplification. Catalysts can diminish waste and energy consumption; nevertheless, they may also introduce essential metals, toxic ligands, persistent supports, dilute processes, stringent purification requirements, or unstable intermediates. The primary inquiry is not the presence of a catalyst, but rather if the catalytic design enhances the sustainability profile in comparison to viable alternatives (García-Serna et al., 2022; Habib et al., 2023). The scope of green chemistry is therefore broader than the substitution of one solvent or reagent for another. It includes the choice of renewable or abundant feedstocks, the design of safer reagents and products, the reduction of derivatization steps, the minimization of auxiliary materials, energy-efficient processing, real-time control, inherently safer chemistry, and catalytic rather than stoichiometric transformations. Catalysis occupies a privileged position in this framework because it can improve selectivity, reduce activation barriers, allow milder conditions, lower material intensity, and support step-economical synthesis. However, the presence of a catalyst does not automatically guarantee sustainability; the whole system must be evaluated (Anastas & Eghbali, 2010; Horváth & Anastas, 2007; Li & Trost, 2008). Historically, catalysis has enabled large-scale chemical production, including ammonia synthesis, petrochemical transformations, polymerization, fine-chemical synthesis, and environmental abatement. Metrics and systems thinking give green chemistry a new meaning. A catalytic route that provides a high yield but requires a toxic solvent, rare metal, large excess of additives, energy-intensive purification, or poor catalyst recyclability may perform worse than expected. Conversely, a well-designed catalytic process can deliver high selectivity and operational simplicity while minimizing waste, emissions, and energy consumption (Thomas & Raja, 2005; Anastas et al., 2001; Sheldon, 2017).

1.2. Catalysis as a Central Strategy in Sustainable Chemical Processes

Catalysis is crucial to sustainable process design, as it enhances multiple facets of efficiency concurrently. Catalysts can diminish energy requirements, lessen byproduct formation, and facilitate otherwise difficult bond formations by decreasing activation barriers, accelerating reaction rates, strengthening selectivity, and allowing transformations under milder conditions. In industrial applications, significant sustainability improvements frequently occur when catalytic techniques streamline synthetic pathways, remove isolation or purification stages, and substitute salt-producing stoichiometric reagents with recoverable catalysts or cleaner redox agents like hydrogen, oxygen, or electrochemical equivalents (Anastas et al., 2001; García-Serna et al., 2022). The strategic significance of catalysis is particularly apparent in fine-chemical and pharmaceutical synthesis, where elevated process mass intensity frequently arises from multistep pathways, protecting-group alterations, surplus reagents, and solvent-heavy workup and purification procedures. Catalytic asymmetric synthesis, biocatalysis, cross-coupling, direct C–H functionalization, and telescoped one-pot methods might alleviate these challenges when developed with considerations for catalyst recovery, impurity management, solvent selection,

and regulatory compliance. Nonetheless, these processes should not be regarded as intrinsically sustainable; their environmental viability is contingent upon aspects such as catalyst loading, metal availability and toxicity, ligand utilization, substrate prefunctionalization, waste production, and scalability (Jimenez-Gonzalez et al., 2011; Becker et al., 2022; Roschangar et al., 2015).

Catalytic methods may substitute stoichiometric activation agents, mineral acids, strong bases, oxidants, and reducing agents that produce salts or toxic by-products. Solid acids, supported metals, organocatalysts, immobilized enzymes, and single-site catalysts exemplify how catalytic design can minimize neutralization waste, enhance selectivity, and facilitate catalyst separation. These benefits are particularly significant in industrial process development, where the environmental effect of a synthetic pathway is frequently influenced not only by the goal transformation but also by solvent utilization, workup, isolation, and disposal of ancillary products. Catalysis must concurrently be combined with reaction engineering. A catalyst that demonstrates efficacy in a screening vial may underperform at scale due to heat generation, mass-transfer constraints, fouling, catalytic degradation, susceptibility to oxygen or moisture, inadequate mixing, or variations in impurity profiles. Sustainable catalysis necessitates collaboration among catalyst discovery, mechanistic comprehension, process analytical technologies, safety engineering, and life-cycle evaluation. A pragmatic evaluation of catalysis must also recognize its constraints. Catalysts may become deactivated due to poisoning, sintering, fouling, leaching, alterations in the oxidation state, structural collapse, or irreversible binding of substrates and products. Homogeneous catalysts can pose challenges in separation and recycling, whereas heterogeneous catalysts may experience diffusional constraints and variability in active sites. Enzymes have remarkable selectivity; yet, their substrate range, stability, and compatibility with industrial conditions may necessitate protein modification or immobilization. These limitations do not undermine the significance of catalysis in green chemistry; instead, they illustrate the necessity of integrating catalyst design, process development, and sustainability assessment (Clark, 2002; Cole-Hamilton, 2003; Sheldon, 2017).

1.3. Relationship Between Catalysis, Atom Economy, Energy Efficiency, and Waste Minimization

Atom economy is a useful initial metric in sustainable reaction design because it evaluates the extent to which atoms from the starting materials are incorporated into the desired product rather than being lost as by-products. Introduced by Trost, this concept shifts attention from yield alone to the intrinsic efficiency of a chemical transformation (Figure 3). Catalysis can support atom-economical synthesis by enabling additions, hydrogenations, rearrangements, oxidations, couplings, and direct C–H functionalizations that reduce or avoid stoichiometric leaving groups and auxiliary reagents. However, atom economy should be regarded as a first filter rather than a complete measure of greenness, since it does not account for solvent use, catalyst preparation, excess reagents, purification requirements, energy demand,

or waste generated during workup. Therefore, it must be interpreted together with experimental yield, selectivity, mass balance, impurity profile, and process practicality (Trost, 1991; Li & Trost, 2008). Mass-based metrics such as the E factor and process mass intensity provide a more realistic assessment of material efficiency by considering actual inputs and waste streams. Sheldon's E factor quantifies the mass of waste generated per unit mass of product and has highlighted the particularly high waste burdens associated with fine-chemical and pharmaceutical manufacturing. PMI, which includes all materials used in a process, is especially valuable in pharmaceutical route development because it captures the cumulative impact of reagents, solvents, catalysts, workup operations, and purification steps.

A catalytic reaction with high yield and favorable atom economy may still exhibit poor PMI if it requires dilute conditions, chromatographic purification, repeated aqueous washes, or large volumes of hazardous solvent. Conversely, a slightly lower-yielding catalytic process may be more sustainable if it shortens the synthetic sequence, avoids intermediate isolations, enables solvent or catalyst recovery, and delivers a product stream that is easier to purify (Sheldon, 2017; Sheldon, 2018; Jimenez-Gonzalez et al., 2011). Energy efficiency represents another essential dimension of catalytic sustainability. Catalysts lower activation barriers and may allow reactions to proceed at lower temperature, lower pressure, shorter residence time, or safer operating conditions. Nevertheless, the energy performance of a process cannot be judged solely from the catalytic step, because downstream separations, solvent recovery, heating, cooling, compression, and drying may dominate the energy balance. Photocatalysis and electrocatalysis are attractive because they can couple chemical synthesis to solar energy or renewable electricity, but their sustainability depends on process-level parameters such as photon utilization, current density, overpotential, electrode or photocatalyst lifetime, electrolyte management, reactor efficiency, and product recovery. A credible claim of energy efficiency must therefore include both the catalytic transformation and the associated reactor and separation train (Hisatomi et al., 2014; Roger et al., 2017; Seh et al., 2017; Artz et al., 2018).

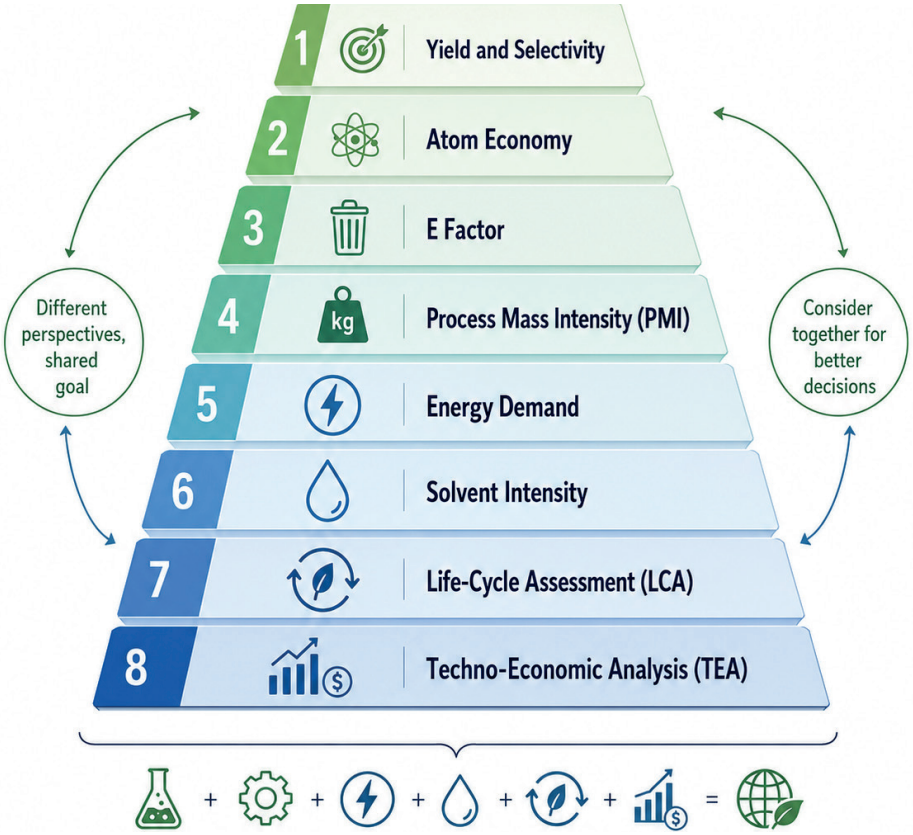

Figure 3. *Sustainability Metrics for Catalytic Processes*

Taken together, atom economy, E factor, PMI, and energy efficiency should be used as complementary rather than isolated metrics. Catalysis contributes most effectively to green chemistry when it improves selectivity, reduces stoichiometric reagent use, minimizes solvent and purification demands, shortens synthetic routes, and enables efficient recovery or recycling of catalysts and solvents. A rigorous sustainability assessment must, therefore, move beyond theoretical reaction metrics and evaluate the complete process from raw material input to the isolated product (Constable et al., 2002; Sheldon, 2018; Jiménez-González et al., 2012).

2. FUNDAMENTAL PRINCIPLES OF CATALYSIS IN GREEN CHEMISTRY

2.1. Definition and Basic Concepts of Catalysis

The mechanistic definition of catalysis has direct implications for sustainability. A catalyst accelerates a chemical reaction by providing an alternative pathway with a lower activation barrier and is regenerated at the end of the catalytic cycle (Figure 4). However, it does not alter the thermodynamic equilibrium; it only accelerates

the approach to equilibrium. Therefore, sustainable process design must consider not only catalytic activity but also equilibrium limitations, product inhibition, reversibility, and separation strategy. In reversible reactions, product removal, coupling with a downstream transformation, or appropriate reactor design may be as important as the intrinsic performance of the catalyst. Green catalysis thus requires the integration of kinetic, thermodynamic, and separation principles (Thomas & Raja, 2005; García-Serna et al., 2022). Catalytic cycles typically involve substrate binding, activation, chemical transformation, product release, and catalyst regeneration. Although these cycles are often represented in simplified schemes, real catalytic systems may include resting states, off-cycle species, induction periods, catalyst activation steps, and deactivation pathways. Each elementary step can influence both efficiency and sustainability. Strong substrate binding may facilitate activation but hinder product release, while highly reactive intermediates may increase reaction rates at the expense of selectivity. Similarly, robust ligands, supports, or enzyme environments can stabilize active species but may also increase catalyst synthesis complexity or affect recyclability (Thomas & Raja, 2005; Zaera, 2013).

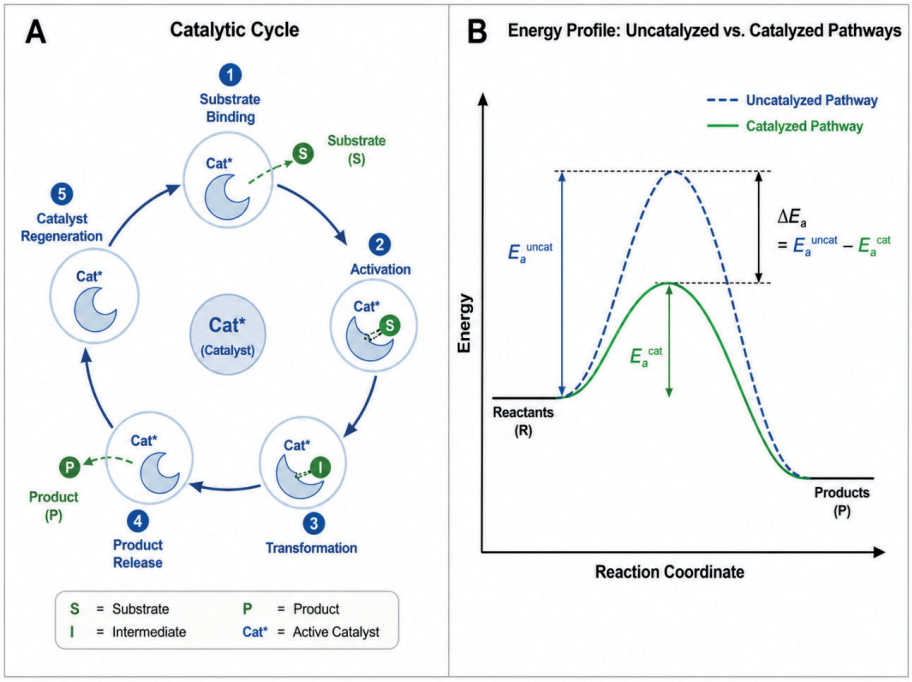

Figure 4. *Catalytic Cycle (A) and Activation Energy Profile (B)*

The nature of the active species differs substantially among catalytic systems. In homogeneous catalysis, ligand dissociation, coordination dynamics, oxidation-state changes, and solvent effects can determine activity and selectivity. In heterogeneous catalysis, the active site may be a defect, an interfacial ensemble, an isolated atom, a nanoparticle edge, or a dynamically reconstructed surface. In enzymatic catalysis,

the active site operates within a conformational and solvent-controlled environment that governs substrate orientation, transition-state stabilization, and product release. These distinctions are important because sustainability claims depend on understanding where and how catalysis actually occurs (Cole-Hamilton, 2003; Corma et al., 2010; Bell et al., 2021). Mechanistic evidence is therefore an essential component of green chemistry rather than a purely academic concern. Without identifying whether the active species is stable, soluble, heterogeneous, leached, aggregated, or transformed during the reaction, claims of low catalyst loading, recyclability, and long-term performance remain uncertain. Operando spectroscopy, kinetic analysis, poisoning experiments, isotope labeling, hot filtration, leaching tests, and post-reaction characterization can help distinguish genuine catalytic behavior from apparent activity caused by decomposition products, soluble leached species, or transient active forms (Phan et al., 2006; Molnár, 2011; Zaera, 2013).

A further distinction must be made between intrinsic and apparent catalytic activity. Apparent rates can be influenced by mass transfer, heat transfer, catalyst dispersion, particle size, solvent, pH, impurities, substrate concentration, and reactor geometry. For this reason, green catalysis assessments should report reaction conditions transparently and compare catalysts under process-relevant constraints rather than relying solely on initial rates or idealized screening data. This is particularly important in nanocatalysis, single-atom catalysis, photocatalysis, and electrocatalysis, where active-site density, accessibility, stability, and turnover frequency can be difficult to define accurately (Zaera, 2013; Somorjai & Park, 2008; Wang et al., 2018).

Collectively, sustainable catalysis requires optimization of the entire catalytic system rather than maximization of initial activity alone. Mechanistic understanding, catalyst stability, active-site accessibility, separation performance, and process integration must be evaluated together to avoid misleading sustainability claims and to design catalytic processes that are both chemically efficient and practically viable (García-Serna et al., 2022; Habib et al., 2023).

2.2. Homogeneous, Heterogeneous, and Biocatalytic Processes

Homogeneous, heterogeneous, and biological catalysts should not be ranked according to a single universal hierarchy of greenness. Each catalytic platform addresses specific sustainability challenges while introducing its limitations (Figure 5). Therefore, the appropriate choice of catalyst depends on the target transformation, product requirements, separation strategy, catalyst lifetime, impurity control, and general process design (Anastas et al., 2001; Li & Trost, 2008). Homogeneous catalysis operates when the catalyst and reactants are present in the same phase. This platform often provides well-defined active sites, high selectivity, tunable ligand environments, and mechanistic clarity. Transition-metal complexes have had a major impact on hydrogenation, hydroformylation, cross-coupling, metathesis, and C–H functionalization. From a sustainability perspective, homogeneous catalysts can be highly advantageous when they operate at low loading, provide excellent chemo-, regio-, or stereoselectivity, and reduce the number of synthetic steps. However,

catalyst separation, recycling, ligand residues, and metal contamination can be significant challenges, particularly in pharmaceutical synthesis where residual metal limits and impurity profiles are tightly regulated (Cole-Hamilton, 2003; Walsh et al., 2007). Heterogeneous catalysis uses catalysts in a different phase from the reactants, most commonly solid catalysts in liquid- or gas-phase processes. Solid acids, metal oxides, zeolites, supported nanoparticles, carbon materials, and porous frameworks can replace corrosive mineral acids, soluble metal salts, or stoichiometric reagents. Their main sustainability advantages arise from ease of separation, reusability, compatibility with fixed-bed reactors, and suitability for continuous processing. Nevertheless, heterogeneous catalysts are not inherently greener than homogeneous systems. Leaching, deactivation, pore blockage, support instability, diffusional limitations, mass-transfer effects, and active-site heterogeneity can reduce performance and complicate mechanistic interpretation. Therefore, leaching tests, hot filtration experiments, kinetic analysis, and post-reaction characterization must support recyclability and stability claims (Clark, 2002; Climent et al., 2011).

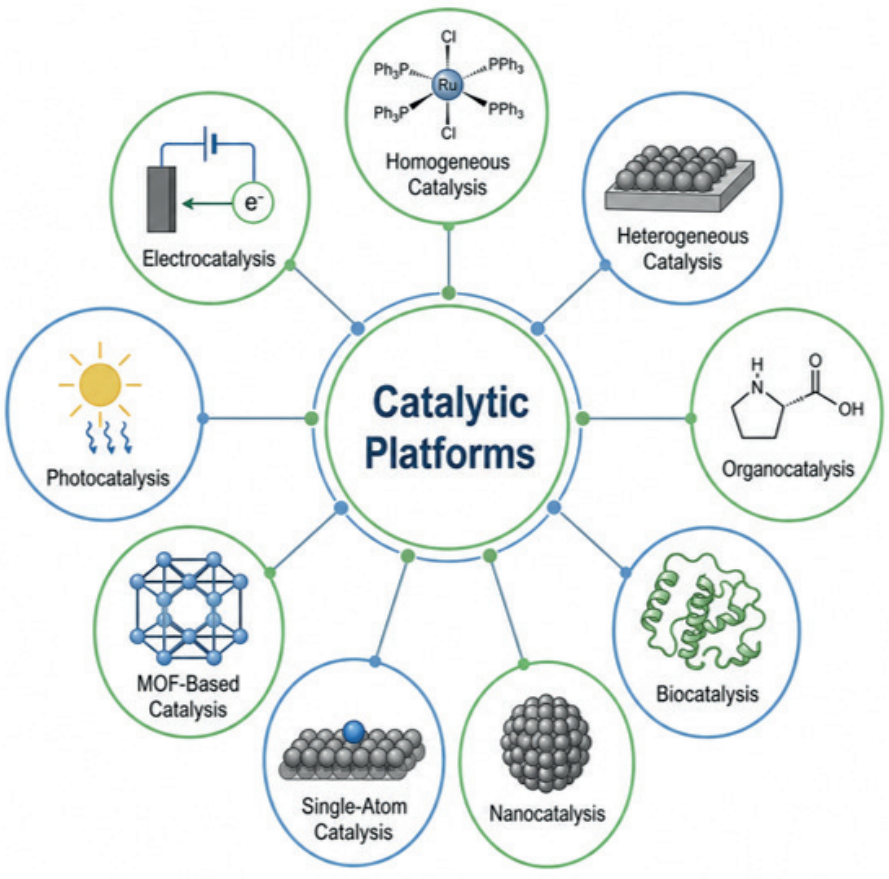

Figure 5. *Comparison of Major Catalytic Platforms*

Biocatalysis employs enzymes or whole cells to perform chemical transformations. Enzymes often function under mild conditions and can provide exceptional chemo-, regio-, and stereoselectivity. They are especially valuable in the synthesis of chiral building blocks, pharmaceutical intermediates, and highly functionalized molecules, where they may eliminate the need for protecting groups, resolution steps, or harsh reagents. Advances in directed evolution, enzyme engineering, immobilization, cofactor regeneration, and biocatalytic retrosynthesis have expanded substrate scope and improved process robustness. However, the sustainability of biocatalysis depends on enzyme production, stability, substrate concentration, solvent compatibility, cofactor demand, aqueous waste management, and downstream product recovery (Bell et al., 2021; Sheldon & Woodley, 2018; Wu et al., 2021). Hybrid catalytic strategies can combine advantages from different platforms. Homogeneous complexes may be immobilized on polymers, silica, carbon, metal–organic frameworks, or other porous supports to improve recovery and reuse. Enzymes can be immobilized on solid carriers to enhance operational stability and facilitate continuous processing. Nanoparticles can be stabilized in hydrophilic, amphiphilic, or structured media, while single-atom catalysts can be anchored on engineered supports to improve metal utilization and site definition. However, immobilization or support design should not be assumed to improve sustainability automatically. The added material, synthesis steps, mass-transfer effects, and possible loss of activity must be justified by clear gains in catalyst lifetime, selectivity, recovery, or process simplification (Astruc et al., 2005; Bakar et al., 2024; Wang & Astruc, 2019). The selection of a catalytic platform should therefore be route-specific rather than ideology-driven. A homogeneous asymmetric hydrogenation may be the most sustainable option if it avoids classical resolution, proceeds at low catalyst loading, and allows effective metal removal. A heterogeneous acid catalyst may be preferable for a fixed-bed esterification or dehydration process. An enzyme may be superior when it produces the desired stereoisomer directly under mild conditions and eliminates protection–deprotection steps. Green catalysis is thus best understood as a problem-oriented design strategy in which the catalyst class is chosen according to the complete process context rather than according to a universal preference for homogeneous, heterogeneous, or biological systems (García-Serna et al., 2022; Gallou et al., 2023).

2.3. Catalytic Activity, Selectivity, Stability, and Reusability

Catalytic activity must be evaluated together with selectivity and durability, rather than as an isolated performance parameter. Activity describes how rapidly a catalyst converts a substrate under defined conditions, but high initial conversion does not necessarily indicate a sustainable process. A very active catalyst may promote nonselective decomposition, generate difficult-to-remove impurities, deactivate rapidly, leach into the product stream, or rely on scarce and problematic materials. In process development, selectivity often has a stronger influence on environmental performance than reaction rate because every side product represents material loss and increases the burden of separation, purification, and waste treatment. High selectivity is therefore one of the most direct ways in which catalysis contributes to waste prevention and process efficiency (Sheldon, 2018; Thomas & Raja, 2005).

Catalyst stability determines whether activity and selectivity can be maintained during repeated use or extended operation. Stability has chemical, thermal, mechanical, and operational dimensions, all of which must be assessed under realistic reaction, separation, and storage conditions. A catalyst that is stable in a fresh substrate solution may deactivate in the presence of products, water, oxygen, sulfur compounds, chloride, nitrogen bases, polymers, acids, bases, or trace metal impurities. Heterogeneous catalysts may lose surface area through sintering, suffer pore blockage by heavy products, undergo coking, leach active components, or experience restructuring of the support. Homogeneous catalysts may form inactive dimers, nanoparticles, oxidized or reduced species, or ligand-degradation products. Enzymes may denature, aggregate, lose cofactors, or become incompatible with organic solvents, high substrate concentrations, or process additives unless engineered or immobilized (Astruc et al., 2005; Phan et al., 2006; Bell et al., 2021).

Reusability should therefore be interpreted quantitatively rather than rhetorically. Recycle experiments should report not only conversion but also selectivity, isolated yield, mass balance, catalyst recovery, active-site retention, leaching levels, turnover number, and structural changes after use. Reporting conversion alone can mask catalyst loss, product contamination, gradual deactivation, or transformation of the original catalyst into a different active species. This issue is particularly important for supported metals, magnetically recoverable nanocatalysts, metal–organic frameworks, single-atom catalysts, and immobilized homogeneous complexes, where apparent recyclability may conceal partial dissolution, active-site migration, aggregation, or changes in the true catalytic species (Phan et al., 2006; Polshettiwar et al., 2011).

A rigorous green chemistry assessment should connect recyclability to material flow and process performance. The number of reuse cycles is meaningful only when accompanied by evidence that the catalyst remains structurally and chemically intact, that active material is not being transferred into the product or waste streams, and that selectivity and mass balance are preserved. Sustainable catalysis therefore requires the combined evaluation of activity, selectivity, stability, reusability, characterization data, and mass-based process metrics. This integrated approach prevents misleading claims and ensures that catalytic performance translates into genuine reductions in waste, purification demand, and resource consumption (Sheldon, 2018; Jiménez-González et al., 2012).

2.4. Turnover Number, Turnover Frequency, and Catalyst Efficiency

Turnover number (TON) and turnover frequency (TOF) are useful metrics for evaluating catalytic performance, but they must be interpreted with caution. TON expresses the number of substrate molecules converted per active catalytic site before deactivation, whereas TOF represents the number of turnovers per active site per unit time under defined reaction conditions. These parameters allow comparison between catalysts only when the active-site concentration, reaction conditions, conversion range, and basis of calculation are clearly reported (Thomas & Raja, 2005; Zaera, 2013).

The reliability of TON and TOF depends strongly on how the active site is defined. For well-characterized molecular catalysts, the number of active sites can often be estimated from the catalyst concentration. However, this estimation is more challenging for nanoparticles, supported metals, single-atom catalysts, heterogeneous surfaces, and enzymes, where active sites may be unevenly distributed, partially inaccessible, or dynamically transformed during reaction. A TOF calculated from total metal loading may underestimate the intrinsic activity of exposed active sites, whereas a TOF based on uncertain or selectively chosen site counts may exaggerate catalytic performance. Therefore, reports should explicitly state whether TON and TOF are calculated based on total catalyst amount, total metal content, surface atoms, accessible active sites, enzyme active sites, or another defined basis (Yang et al., 2013; Wang et al., 2018; Mitchell & Pérez-Ramírez, 2021).

From a green chemistry perspective, TON and TOF should not be evaluated independently from catalyst lifetime, selectivity, recovery, and material efficiency. A catalyst with very high TOF but short operational lifetime may require frequent replacement, increasing cost, waste generation, and process interruptions. In contrast, a catalyst with moderate TOF but long-term stability in a continuous or fixed-bed reactor may provide superior sustainability. Similarly, the use of precious metals may be acceptable when catalyst loading is extremely low, TON is very high, recovery is efficient, and metal losses are minimal. Conversely, an earth-abundant metal catalyst may still be environmentally problematic if it requires high loading, toxic ligands, large reagent excesses, poor selectivity, or difficult purification (Sheldon, 2018; Mitchell & Pérez-Ramírez, 2021). Catalyst productivity should therefore be assessed as a process-level parameter rather than as a single kinetic value. In addition to TON and TOF, a practical evaluation should include reaction rate, selectivity, catalyst loading, cumulative lifetime, ease of separation, catalyst or metal residues, impurity profile, replacement frequency, cleaning requirements, cost, toxicity, and resource availability. In industrial settings, space-time yield, reactor productivity, downstream purification demand, and catalyst stability under realistic operating conditions can be as important as laboratory-scale TOF values (Roschangar et al., 2015; Becker et al., 2022).

Ultimately, TON and TOF are valuable descriptors of catalytic efficiency, but they do not by themselves define sustainability. A rigorous green chemistry assessment must connect these metrics to material flow, catalyst durability, recovery efficiency, product quality, and process energy demand. Clear reporting of calculation methods and active-site assumptions is essential to avoid misleading comparisons and to ensure that high catalytic activity translates into genuine environmental and practical advantages (Constable et al., 2002; Sheldon, 2018).

2.5. Catalysis and The Twelve Principles of Green Chemistry

The ninth principle of green chemistry, which states that catalytic reagents are preferable to stoichiometric reagents, provides the most direct conceptual link between catalysis and sustainability. However, catalytic design is not limited to this

single principle; it can influence nearly all twelve principles of green chemistry when integrated into a process-level strategy. Catalysis contributes to waste prevention by replacing stoichiometric acids, bases, oxidants, reductants, or metal-mediated reagents with recoverable catalytic systems. It can improve atom economy by enabling transformations in which a greater fraction of the reactant atoms is incorporated into the desired product. It can also support safer synthesis when hazardous or corrosive reagents are replaced by controlled catalytic processes using cleaner donors, acceptors, or redox inputs such as hydrogen, oxygen, water, or electricity (Anastas et al., 2001; Anastas & Eghbali, 2010).

Catalysis is also closely connected to energy efficiency, reduced derivatization, renewable feedstocks, and process control. Catalytic reactions may proceed under lower temperature or pressure, in continuous flow or intensified reactors, or with renewable electricity in electrochemical systems. In complex molecule synthesis, catalytic asymmetric reactions, enzymatic transformations, organocatalysis, transition-metal catalysis, and direct C–H functionalization can reduce the need for protection–deprotection sequences, stoichiometric activation, and resolution steps. These advantages are particularly important because derivatization and purification often dominate waste generation in pharmaceutical and fine-chemical synthesis. Similarly, catalytic upgrading of biomass-derived feedstocks can improve carbon efficiency when it selectively converts renewable substrates without excessive pretreatment, overoxidation, degradation, or solvent burden (Li & Trost, 2008; Anastas & Eghbali, 2010).

The twelve principles should therefore be understood as an interconnected design framework rather than as an isolated checklist. Improvements in one principle may create trade-offs in another. A solvent-free catalytic process may reduce solvent use but introduce heat transfer, mixing, or scale-up challenges. A water-based reaction may avoid organic solvents but generate dilute wastewater that is difficult to treat. A renewable feedstock may appear attractive but require energy-intensive pretreatment or purification. Catalysis can help manage these trade-offs by improving selectivity, reducing auxiliary materials, simplifying separations, and enabling milder conditions, but quantitative metrics are needed to determine whether the balance is favorable (Anastas & Eghbali, 2010; Horváth & Anastas, 2007; Kurul et al., 2025). For this reason, catalytic greenness must be demonstrated rather than assumed. A credible sustainability claim requires evidence based on yield, selectivity, catalyst loading, catalyst lifetime, catalyst recovery, solvent choice, auxiliary materials, workup requirements, impurity profile, safety, scalability, E factor, process mass intensity, and, when appropriate, life-cycle assessment. Catalysis should therefore be treated as a core principle of green chemistry, but not as an automatic guarantee of sustainability. Its real value depends on whether the catalytic method improves the complete process, from raw material input to isolated product and waste management (Jiménez-González et al., 2012; Kralisch et al., 2015; Sheldon, 2018).

3. DESIGN CRITERIA FOR GREEN CATALYSTS

3.1. Use of Earth-Abundant and Low-Toxicity Elements

The transition toward earth-abundant catalysts reflects both environmental and supply-chain considerations. Precious metals such as palladium, platinum, rhodium, iridium, and ruthenium can provide exceptional activity, selectivity, and functional-group tolerance, but their high cost, limited geological availability, and the environmental impacts associated with mining and refining raise important sustainability concerns. In this context, catalysts based on iron, nickel, copper, cobalt, manganese, and metal-free systems offer attractive alternatives when they can deliver comparable performance, durability, and process compatibility (Roger et al., 2017; Yang et al., 2013; Mitchell & Pérez-Ramírez, 2021; Thomas & Raja, 2005). However, replacing a precious metal with a more abundant element does not automatically make a catalytic process greener. Nickel salts, cobalt compounds, complex ligands, dopants, or specialized supports may introduce toxicity, regulatory, or end-of-life challenges. In addition, catalyst preparation can involve hazardous reagents, air- or moisture-sensitive procedures, chromatographic purification, high-temperature calcination, or solvents with significant environmental burdens. Therefore, elemental abundance must be evaluated together with catalyst loading, turnover number, selectivity, lifetime, recovery efficiency, toxicity, route-shortening impact, and the material and energy demands of catalyst synthesis (Kaur et al., 2024; García-Serna et al., 2022).

A complete assessment should consider the full catalyst life cycle, including raw material extraction, refining, ligand and support synthesis, activation, catalytic use, regeneration, and disposal. A catalyst containing a precious metal may still be sustainable if it operates at very low loading, achieves high turnover numbers, remains in a closed recovery loop, and enables a substantial reduction in waste, energy use, or synthetic steps (Figure 6). Conversely, an apparently benign or earth-abundant catalyst may be less sustainable if it requires large quantities, performs with poor selectivity, generates difficult impurities, or depends on energy-intensive preparation (Kralisch et al., 2015; Mitchell & Pérez-Ramírez, 2021).

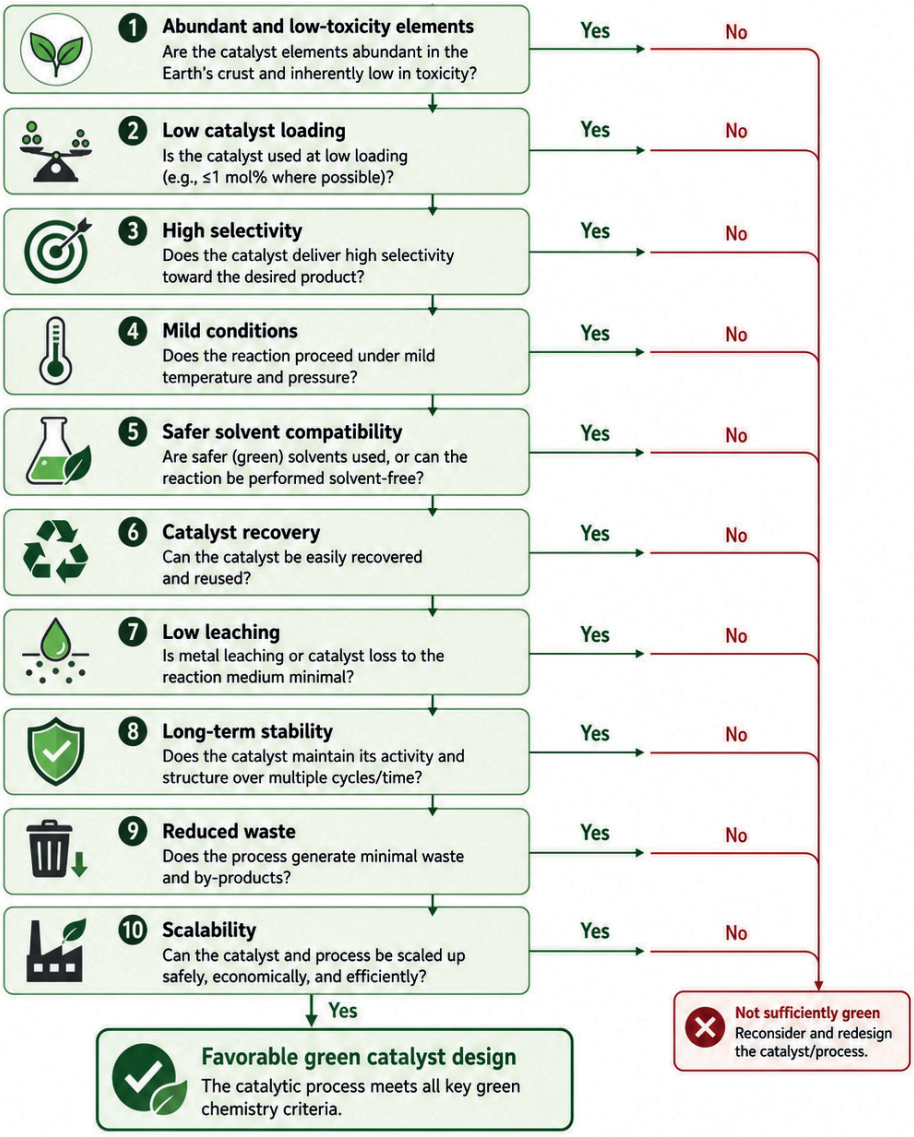

Figure 6. *Design Criteria for Green Catalysts*

Single-atom and low-nuclearity catalysts provide an important strategy for responsible metal use by maximizing the fraction of metal atoms available for catalysis. By isolating active atoms or small metal ensembles on suitable supports, these systems can improve metal utilization and reduce the total amount of critical material required. Their sustainability advantage is strongest when the isolated sites remain stable under working conditions, resist aggregation and leaching, and can be prepared at scale without excessive waste or energy demand. For this reason, rigorous structural verification before and after catalysis is essential, particularly because nominally isolated atoms may migrate, cluster, dissolve, or transform into different

active species during reaction (Yang et al., 2013; Wang et al., 2018; Zhang et al., 2018). The design goal is therefore not the complete elimination of precious metals, but the alignment of catalytic performance with responsible material use. Sustainable catalyst selection should balance abundance, toxicity, activity, selectivity, durability, recoverability, preparation burden, and general process benefit. Earth-abundant, precious-metal, metal-free, single-atom, and hybrid catalysts should all be judged by whether they reduce the total environmental and resource burden of the complete chemical process (Mitchell & Pérez-Ramírez, 2021; Wang et al., 2018).

3.2. Catalyst Recoverability and Recyclability

Recoverability is a decisive criterion in sustainable catalysis, particularly when the catalyst contains expensive, toxic, scarce, or regulated components. In fine-chemical and pharmaceutical manufacturing, even ppm-level metal residues can influence purification strategy, product quality, and regulatory compliance. Therefore, catalyst design must consider not only activity and selectivity but also how the catalyst is separated from the process stream. Practical recovery strategies include retention in a fixed-bed reactor, removal by filtration, magnetic separation, membrane capture, phase separation, or immobilization in a recyclable liquid or solid phase (Figure 7) (Cole-Hamilton, 2003; Phan et al., 2006; Becker et al., 2022).

Recyclability must be interpreted carefully because repeated laboratory use does not necessarily demonstrate true catalyst stability. A system may appear reusable even when soluble active species are continuously leached, redeposited, or transformed during the reaction. This issue is especially relevant in palladium-catalyzed cross-coupling, supported metal catalysis, nanoparticle systems, and immobilized homogeneous catalysts, where the active species may be homogeneous, heterogeneous, or dynamically exchanged between phases. For this reason, credible recyclability claims should be supported by leaching analysis, hot-filtration experiments, catalyst mass recovery, product impurity data, and structural characterization before and after use (Phan et al., 2006; Astruc et al., 2005; Molnár, 2011).

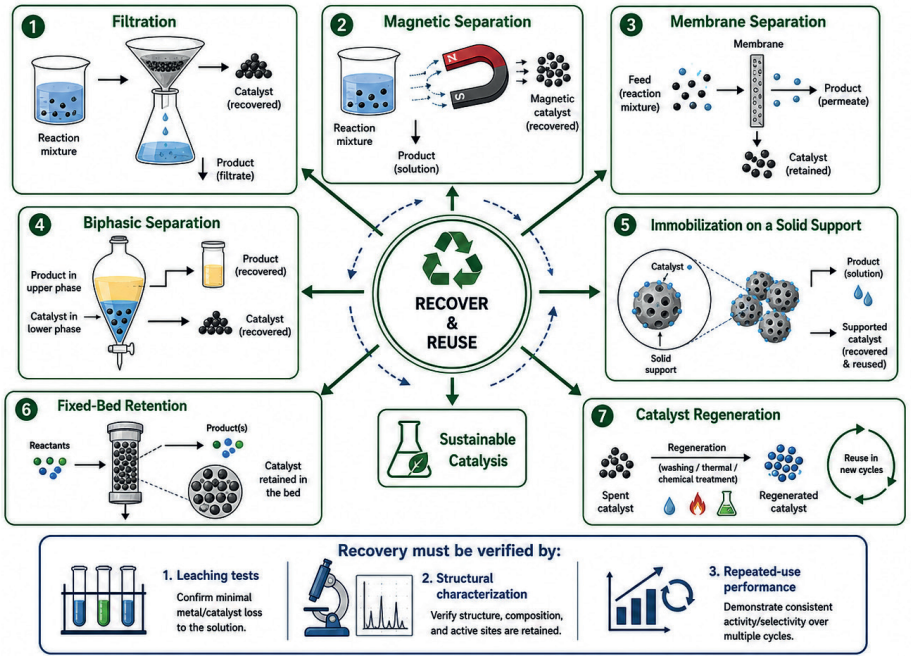

Figure 7. *Catalyst Recovery and Recyclability Strategies*

The evaluation of catalyst recovery should also account for changes in material structure and active-site accessibility. Porous catalysts may undergo pore blockage, framework degradation, or support restructuring after repeated exposure to water, acids, bases, oxidants, reductants, or coordinating substrates. Magnetic nanoparticles and supported metals may suffer from aggregation, surface oxidation, or partial dissolution. Immobilized enzymes may lose activity because of denaturation, support incompatibility, mass-transfer limitations, cofactor loss, or changes in the local microenvironment. Thus, recovery is meaningful only when activity, selectivity, mass balance, and catalyst integrity are maintained over repeated operation (Polshettiwar et al., 2011; Wang & Astruc, 2019; Bakar et al., 2024). In continuous processing, catalyst lifetime is often a more informative sustainability indicator than the number of batch recycle experiments. Time-on-stream, space-time yield, pressure drop, attrition resistance, regeneration efficiency, shutdown/startup stability, and long-term selectivity provide more realistic measures of process viability. A catalyst that works for hundreds of hours with stable conversion, selectivity, and impurity control may be more sustainable than a laboratory catalyst that is recycled several times but has a mass balance that becomes worse or leaching that becomes worse (Roschangar et al., 2015; Becker et al., 2022).

In general, recoverability and recyclability should be considered process-level properties instead of just claims of reuse. A rigorous green chemistry assessment must connect catalyst recovery to material flow, product purity, waste generation, operational stability, and regulatory requirements. Only when the catalyst can be efficiently retained, regenerated, or removed without creating additional purification

burdens can recyclability translate into genuine sustainability benefits (Sheldon, 2018; Jiménez-González et al., 2012).

3.3. Catalyst Selectivity and Reduction of By-Product Formation

Catalyst selectivity is one of the most direct links between catalyst design and waste prevention. Poor selectivity lowers isolated yield, consumes feedstock, generates structurally similar impurities, and increases the demand for solvent-, energy-, and time-intensive purification. This issue is especially critical in the synthesis of high-value products, where even minor impurities may require repeated crystallization, chromatography, reprocessing, or additional quality-control steps. In this sense, selectivity functions as an indirect mass-efficiency metric because every undesired product represents both material loss and an added downstream burden (Sheldon, 2017; Li & Trost, 2008).

Catalysts improve selectivity by controlling transition-state geometry, substrate orientation, electronic activation, and the local reaction environment. In homogeneous catalysis, ligand structure can tune steric and electronic effects around the metal center. In heterogeneous catalysis, zeolite pores, MOF cavities, support effects, and nanoparticle surface ensembles can influence substrate access to active sites, product diffusion, and desorption behavior (Thomas & Raja, 2005; Walsh et al., 2007; Corma et al., 2010). In biocatalysis, enzyme active sites provide highly organized microenvironments that control substrate positioning and transition-state stabilization. These effects can produce chemo-, regio-, diastereo-, enantio-, or site-selectivity, depending on the transformation and catalytic platform (Bell et al., 2021; Sheldon & Woodley, 2018). From a green chemistry perspective, the most valuable form of selectivity is route-level selectivity. This refers not only to the selective formation of a product in a single reaction but also to the ability to construct the desired molecular architecture without protecting groups, stoichiometric chiral auxiliaries, resolution steps, or unnecessary functional-group interconversions. Enzymes and organocatalysts can provide high stereoselectivity under mild conditions, while transition-metal catalysts can enable selective hydrogenation, cross-coupling, oxidation, reduction, and C–H functionalization. These advantages are most meaningful when they reduce the total number of operations, minimize purification demand, and avoid introducing new catalyst-related impurities (Enders et al., 2007; Han et al., 2021; Bell et al., 2021). Selectivity also underpins the step economy through tandem, cascade, and one-pot catalytic processes. In these strategies, reactive intermediates are generated and consumed within the same reaction environment, reducing the need for isolation, solvent exchange, and intermediate purification. Multifunctional heterogeneous catalysts containing acid, base, redox, or metal sites can be particularly useful when the different active sites are properly balanced and spatially organized. However, multifunctionality must be carefully controlled, because incompatible active sites, mismatched reaction rates, unstable intermediates, or excessive site density can lead to complex by-product networks (Climent et al., 2011; Huang et al., 2017; Enders et al., 2007).

Notably, high selectivity is not merely a desirable performance feature but a core sustainability requirement. A selective catalyst can improve yield, reduce waste, simplify purification, enhance product quality, and enable shorter synthetic routes. Sustainable catalyst design should therefore optimize selectivity together with activity, stability, recoverability, and process compatibility, ensuring that molecular control translates into measurable reductions in material use and environmental burden (Sheldon, 2017; Li & Trost, 2008).

3.4. Compatibility With Safer Solvents and Alternative Reaction Media

Solvent choice is a major determinant of sustainability because solvents often represent the largest mass input in pharmaceutical and fine-chemical processes. Green solvent selection guides evaluate solvents according to health and safety hazards, environmental persistence, volatility, flammability, recyclability, regulatory acceptance, and life-cycle impact. Therefore, a catalytic system should not be judged only by activity or yield; a catalyst that performs well only in chlorinated, highly toxic, or difficult-to-recover solvents may be less sustainable than a slightly less active system operating in a safer and recyclable medium (Clarke et al., 2018; Byrne et al., 2016; Prat et al., 2016; Jessop et al., 2012).

A green catalytic process should, where chemically and operationally feasible, operate in preferred solvents, water, bio-derived solvents, recyclable media, solvent-free conditions, or intensified reaction environments. However, no solvent or medium is inherently sustainable in all contexts. Water is inexpensive, nonflammable, and generally benign, but it can introduce problems related to substrate solubility, hydrolysis, wastewater generation, surfactant use, and product isolation. Bio-derived solvents may reduce fossil-resource dependence, yet their production route, toxicity, boiling point, and recovery efficiency must be considered. Supercritical fluids can offer tunable solvent properties and simplified separation in selected cases, but they may require specialized equipment and pressure control. Ionic liquids and deep eutectic solvents have attracted interest because of their low volatility and tunable properties, although cost, persistence, viscosity, toxicity, purification, and end-of-life management can limit their sustainability (Jessop, 2011; Li, 2005; Li & Chen, 2006; Welton, 1999).

Micellar, solvent-free, and mechanochemical systems further illustrate the need for process-level assessment. Micellar catalysis can enable hydrophobic organic reactions in water, sometimes under mild conditions, by using surfactant assemblies to create localized reaction environments. Nevertheless, the surfactant, aqueous waste stream, product extraction, and downstream purification must be included in the sustainability analysis. Solvent-free and mechanochemical approaches can substantially reduce solvent mass, but they require attention to mixing efficiency, heat transfer, milling energy, equipment wear, reproducibility, and scale-up (Lipshutz & Abela, 2008; James et al., 2012; Fantozzi et al., 2023; Tanaka & Toda, 2000).

Catalyst–solvent compatibility should therefore be designed deliberately rather than discovered empirically at the end of development. Hydrophilic ligands, amphiphilic supports, immobilized catalysts, surfactant-stabilized micelles, enzyme-compat-

ible co-solvents, and recyclable reaction phases can expand the range of greener media available for catalytic transformations. The final solvent choice should be guided not by solvent identity alone, but by the mass intensity of the process at each stage, safety, solvent recovery, catalyst stability, reaction selectivity, separation efficiency, and general environmental performance (Byrne et al., 2016; Prat et al., 2016; Clarke et al., 2018).

3.5. Mild Conditions, Process Intensification, and Operational Simplicity

Mild reaction conditions are an important objective in sustainable catalysis because they can reduce energy demand, improve process safety, and enhance functional-group tolerance. A catalyst that operates at lower temperature and pressure may also decrease equipment requirements and reduce risks associated with thermal runaway, high-pressure operation, or unstable intermediates. However, mild conditions alone do not make a process green. If a reaction is sluggish, highly dilute, dependent on large excesses of additives, or difficult to purify, its overall sustainability may still be poor. The relevant criterion is whether the catalyst provides acceptable productivity, selectivity, impurity control, and product quality under conditions that are practical for scale-up (Anastas & Eghbali, 2010; Thomas & Raja, 2005).

Process intensification links catalytic performance directly to reactor and process design. Fixed-bed heterogeneous catalysts, continuous-flow homogeneous systems combined with membrane or phase separation, immobilized enzymes, electrochemical flow cells, photoreactors, telescoped sequences, and one-pot catalytic processes can reduce solvent use, residence time, reactor inventory, and the need for intermediate isolation. These strategies are particularly valuable for hazardous intermediates, gas–liquid reactions, photochemical transformations, and exothermic oxidations, where improved heat and mass transfer can enhance both safety and efficiency. In such cases, sustainability arises not only from the catalyst itself but also from the integration of catalysis with an appropriate reactor configuration (Climent et al., 2011; Roger et al., 2017; James et al., 2012). Operational simplicity is also a key sustainability criterion. Complex procedures increase labor demand, material consumption, safety risks, and barriers to reproducibility. It may be difficult to justify catalysts that need glovebox handling, highly purified substrates, exotic or unstable ligands, long activation protocols, specialized additives, or chromatographic purification unless they offer significant route-level benefits. Conversely, a robust green catalyst should be readily available or scalable in preparation, reproducible in performance, tolerant of realistic impurities, compatible with practical workup, and suitable for catalyst recovery or removal (García-Serna et al., 2022; Becker et al., 2022).

Practical green catalysis must therefore bridge molecular performance and manufacturing reality. Low catalyst loading, mild operating conditions, high selectivity, simple workup, minimal auxiliary materials, stable performance, and compatibility with intensified processing should be considered together. A catalytic method is most sustainable when it not only performs efficiently in the laboratory but also reduces operational complexity, improves safety, simplifies purification, and remains viable under realistic process conditions (García-Serna et al., 2022; Roschangar et al., 2015).

4. CATALYTIC PLATFORMS AND REACTION MEDIA

4.1. Homogeneous Catalysis and Separation Strategies

Homogeneous catalysis has enabled many of the most selective transformations in modern synthetic chemistry, particularly in fine-chemical, pharmaceutical, and materials synthesis. Its main strength arises from the ability to tune the active site through ligand design. Steric environment, electronic properties, bite angle, chirality, and secondary coordination-sphere effects can be systematically modified to control activity and selectivity. These features have made homogeneous catalysts especially valuable in asymmetric hydrogenation, hydroformylation, cross-coupling, metathesis, oxidation, and C–H functionalization. From a green chemistry perspective, this high degree of molecular control can reduce side-product formation, improve functional-group tolerance, enable shorter synthetic routes, and minimize the need for protecting groups or resolution steps (Cole-Hamilton, 2003; Walsh et al., 2007; Deshmukh et al., 2025).

The principal sustainability challenge in homogeneous catalysis is catalyst separation and product purification. Because the catalyst and reactants are present in the same phase, recovery of the catalyst and removal of metal or ligand residues from the product stream can be difficult. This issue is particularly important in pharmaceutical synthesis, where residual metals and catalyst-derived impurities may affect regulatory compliance and require additional purification. Homogeneous catalysis can be highly sustainable when catalyst loading is low, turnover numbers are high, and selectivity is excellent. Catalyst residues can be easily removed by crystallization, scavenger extraction, membrane separation, or phase-based recovery (Cole-Hamilton, 2003; Becker et al., 2022). Several strategies have been developed to improve the recoverability of homogeneous catalysts. Immobilization on polymers, silica, carbon, or porous supports can simplify separation, but it may also reduce activity, change selectivity, or introduce mass-transfer limitations. Biphasic systems can retain the catalyst in a polar or aqueous phase while allowing product separation into another phase, although interphase mass transfer and solvent compatibility must be considered. Membrane-assisted separation can reduce catalyst carryover, provided that the membrane is stable under reaction conditions and compatible with the solvent, substrate, and catalyst. Fluorous, ionic-liquid, and thermomorphic systems may also enable catalyst recovery in selected cases, but the environmental profile, cost, persistence, and recyclability of the auxiliary phase must be included in the assessment (Cole-Hamilton, 2003; Welton, 1999).

The sustainability of homogeneous catalysis therefore depends on the complete process rather than on catalytic performance alone. A highly selective homogeneous catalyst may be the greenest option if it avoids stoichiometric reagents, eliminates resolution steps, operates at low loading, and provides a product stream that can be purified without excessive solvent or energy use. Conversely, it may be less sustainable if it requires expensive or toxic ligands, large excesses of base or additives, chlorinated solvents, chromatographic purification, or difficult metal removal. The

proper comparison should be against the best alternative route available, not an idealized version of catalysis (Walsh et al., 2007; Torborg & Beller, 2009).

Homogeneous catalysis should be evaluated as a balance between molecular precision and process practicality. Its green chemistry value is greatest when ligand-controlled selectivity, high turnover, low catalyst loading, efficient separation, impurity control, and route simplification are achieved together. Separation concepts such as immobilization, biphasic operation, membrane recovery, or recyclable phases should not be assumed to be inherently sustainable; they must demonstrate a net reduction in material use, waste generation, purification burden, and general process impact (Cole-Hamilton, 2003; Deshmukh et al., 2025).

4.2. Heterogeneous Catalysis, Solid Acids, and Catalytic One-Pot Synthesis

Heterogeneous catalysis is central to green chemistry because it combines catalytic performance with practical advantages such as physical separability, reusability, and compatibility with continuous processing. Solid catalysts can be employed in packed-bed, trickle-bed, slurry, or continuous-flow reactors, making them attractive for large-scale and intensified chemical production. These features can reduce catalyst loss, simplify product separation, lower solvent and workup requirements, and improve operational safety (Clark, 2002; Climent et al., 2011).

Solid acid catalysis illustrates both the promise and complexity of heterogeneous green catalysis. Zeolites, sulfated oxides, heteropoly acids, sulfonated carbons, acidic resins, metal oxides, and supported catalysts can replace corrosive mineral acids in esterification, alkylation, acetalization, dehydration, and biomass upgrading. Such replacement can reduce neutralization waste, salt formation, and equipment corrosion. However, long-term sustainability depends on more than acidity alone. Acid strength and density, pore architecture, hydrophobicity, water tolerance, coke formation, regeneration efficiency, and structural stability all determine whether the catalyst remains effective under realistic process conditions (Clark, 2002; Corma et al., 2007; Climent et al., 2014).

These considerations are particularly important in biomass conversion, where water, oxygenated substrates, acids, and humins can deactivate or restructure conventional solid catalysts. Hydrothermal stability, resistance to leaching, tolerance toward polar molecules, and control of coke formation become decisive design criteria. A catalyst that performs well with model substrates under dry conditions may not remain active or selective in complex biomass-derived feed streams (Corma et al., 2007; Climent et al., 2014). Heterogeneous catalysts are also valuable in one-pot, tandem, and cascade processes because multiple transformations can be combined without isolating intermediates. This strategy can reduce solvent use, shorten synthetic sequences, and decrease purification waste. Multifunctional catalysts containing acid, base, metal, and redox sites can enable sequential or cooperative reactions within a single reactor. However, the advantages of one-pot synthesis are realized only when the active sites are compatible and properly organized. Site strength, spatial separation, pore structure, hydrophobic–hydrophilic

balance, diffusion pathways, and intermediate stability must be carefully controlled to avoid catalyst poisoning, cross-deactivation, or uncontrolled by-product formation (Climent et al., 2011; Huang et al., 2017).

Heterogeneous catalysis offers major opportunities for sustainable process design, especially through catalyst recovery, continuous operation, solid acid replacement of mineral acids, and integration of sequential transformations. Nevertheless, heterogeneous systems should not be considered automatically green. Their sustainability must be demonstrated through long-term activity, selectivity, resistance to leaching and deactivation, regenerability, structural stability, and reduced process-level waste (Clark, 2002; Climent et al., 2011).

4.3. Nanocatalysis and Magnetically Recoverable Catalysts

Nanocatalysis exploits the strong dependence of catalytic behavior on surface atoms, particle size, morphology, support interactions, and interfacial structure. Metal nanoparticles, small clusters, carbon-based nanomaterials, graphene-related supports, and metal oxides can provide high surface area, tunable electronic properties, enhanced dispersion, and size- or shape-dependent selectivity. Because nanoscale catalysts may display features of both homogeneous and heterogeneous systems, their active species can sometimes involve surface sites, small clusters, leached metal species, or dynamically interconverting forms. This dual behavior makes nanocatalysis scientifically powerful but also requires careful mechanistic and stability assessment (Astruc et al., 2005; Narayanan & El-Sayed, 2005; Serp et al., 2003; Somorjai & Park, 2008; Zaera, 2013).

From a green chemistry perspective, nanocatalysts are most valuable when they reduce metal loading, improve selectivity, enable milder reaction conditions, or simplify catalyst recovery. Their high surface-to-volume ratio can increase metal utilization, while support effects and interfacial interactions can tune activity and product distribution. Magnetically recoverable nanocatalysts are a prominent example, as external magnetic separation can reduce the need for filtration, centrifugation, or complex catalyst-removal steps in selected liquid-phase reactions. However, magnetic recovery alone does not guarantee sustainability (Polshettiwar & Varma, 2010; Polshettiwar et al., 2011; Buğday et al., 2021a; Buğday et al., 2022a; Buğday et al., 2023).

A rigorous assessment of nanocatalysts must include the full material and preparation burden. The synthesis of the magnetic core, protective coating, stabilizer, support, active metal, ligand, or surface functional group may involve hazardous reagents, energy-intensive steps, organic solvents, or difficult purification. Therefore, any claimed benefit from easy recovery or lower catalyst loading should be weighed against the environmental cost of nanomaterial preparation, regeneration, and disposal (Kalidindi & Jagirdar, 2012; Gómez-López et al., 2020). Nanomaterial release is an additional concern in sustainable catalysis. A recyclable nanocatalyst should not simply shift the environmental burden from soluble chemical waste to nanoparticle contamination. Aggregation, dissolution, leaching, surface oxidation,

support degradation, and transformation of the active phase should be quantified during and after catalysis. Characterization before and after use, leaching tests, mass balance, particle-size analysis, and product impurity measurements are therefore essential for credible recyclability claims (Polshettiwar et al., 2011; Zaera, 2013; Sajini & Joseph, 2025).

Nanocatalysis offers important opportunities for greener chemical processes when high performance is combined with demonstrated containment, recoverability, regeneration, and low material burden. The most sustainable nanocatalyst systems are those that not only improve activity or selectivity but also maintain structural integrity, minimize metal or nanoparticle release, and reduce the environmental impact of the complete catalytic process (Polshettiwar & Varma, 2010; Kalidindi & Jagirdar, 2012).

4.4. Single-Atom and Low-Nuclearity Catalysts

Single-atom catalysts represent an important strategy for maximizing metal atom utilization and designing well-defined active sites on solid supports. By dispersing isolated metal atoms on oxides, carbons, nitrides, metal–organic frameworks, or defect-rich materials, these systems can reduce the amount of metal required while providing tunable coordination environments. This feature is particularly attractive when precious metals are involved, since each metal atom can, in principle, contribute to catalytic turnover. Single-atom catalysts have therefore attracted considerable interest in oxidation, hydrogenation, CO oxidation, electrocatalysis, and selected fine-chemical transformations (Yang et al., 2013; Wang et al., 2018). The sustainability promise of single-atom catalysis depends strongly on stability and accurate active-site verification. Isolated atoms should not be viewed as static surface decorations; under reaction conditions, they may migrate, aggregate, change oxidation state, bind strongly to reaction intermediates, or restructure together with the support. A material characterized as a single-atom catalyst before reaction may therefore operate through clusters, nanoparticles, leached species, or dynamically transformed sites during catalysis. For this reason, ex situ characterization alone is insufficient to support strong claims of stability, recyclability, or green performance (Wang et al., 2018; Zhang et al., 2018; Mitchell & Pérez-Ramírez, 2021).

Rigorous evaluation requires structural and chemical evidence before, during, and after catalysis. In situ and operando characterization, leaching tests, kinetic analysis, recycling experiments, and post-reaction microscopy or spectroscopy are essential to determine whether isolated atoms remain intact and whether they are truly responsible for catalytic activity. These requirements are especially important when sustainability claims are based on low metal loading, high atom efficiency, or reduced use of critical metals (Yang et al., 2013; Mitchell & Pérez-Ramírez, 2021).

Low-nuclearity catalysts and single-atom alloys further broaden the design space beyond strictly isolated atoms. In some reactions, a pair or small ensemble of atoms may be necessary for bond activation, hydrogen transfer, oxygen activation, or cooperative substrate binding. In other cases, isolated sites may be preferred because

they suppress overreaction, improve selectivity, or prevent undesired side pathways. Thus, the green design objective should not be to maximize atomic isolation in every case but to identify the minimum nuclearity that provides the required activity, selectivity, stability, and process compatibility (Mitchell & Pérez-Ramírez, 2021; Wang et al., 2018). As a whole, single-atom catalysis offers a powerful route toward responsible metal use, particularly for reactions that require scarce or expensive metals. Its true sustainability value, however, depends on whether isolated active sites can be prepared efficiently, maintained under realistic operating conditions, regenerated or recovered effectively, and shown to reduce the total environmental burden of the catalytic process (Wang et al., 2018; Zhang et al., 2018).

4.5. Metal—Organic Frameworks and Porous Catalytic Materials

Metal–organic frameworks (MOFs) are among the most versatile porous material platforms in contemporary catalyst design because they combine crystallinity, high surface area, modular metal nodes, functional organic linkers, and tunable pore environments. Unlike many conventional heterogeneous catalysts, MOFs can be engineered with a high degree of structural precision. Their metal nodes or clusters may function as Lewis acidic, redox-active, or coordinatively unsaturated catalytic centers, while organic linkers can be modified to introduce Brønsted acidity, basicity, chirality, photoactivity, or organocatalytic functionality. MOFs can also serve as hosts for metal nanoparticles, supports for molecular catalysts, matrices for enzyme immobilization, photocatalytic platforms, or sacrificial precursors for porous carbon-based catalysts (Lee et al., 2009; Corma et al., 2010; Liu et al., 2014).

The green chemistry value of MOFs should not be reduced merely to their high porosity. Their more significant contribution lies in the possibility of designing controlled catalytic microenvironments. MOF pores can preorganize substrates, regulate access to active sites, stabilize reactive intermediates, and influence product selectivity through confinement effects. These properties are especially important when selectivity depends not only on the intrinsic activity of the catalytic site but also on substrate orientation, molecular diffusion, local polarity, pore size, and the spatial arrangement of multiple active sites. In this respect, MOFs can be viewed as heterogeneous materials that partially mimic enzyme-like catalytic environments, although their selectivity, adaptability, and operational stability are generally more limited than those of natural enzymes (Pascanu et al., 2019; Wang & Astruc, 2019).

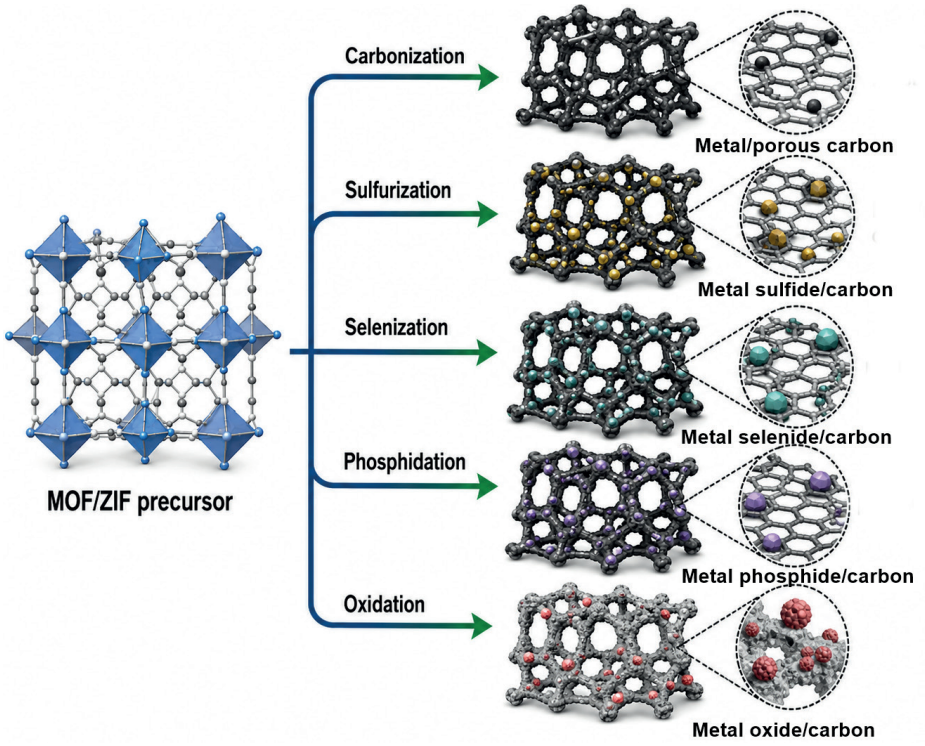

Figure 8. *MOF and MOF-Derived Porous Catalysts*

Multifunctional MOFs are particularly attractive for cascade and cooperative catalysis. A single framework may combine Lewis acidic nodes, Brønsted acidic linkers, basic nitrogen-containing groups, redox-active centers, photoactive units, or encapsulated metal nanoparticles. This structural integration can enable tandem transformations in which different catalytic functions operate within the same porous architecture. For example, acid–base cooperative sites may promote condensation and cyclization reactions, metal nanoparticles confined within MOF pores may catalyze hydrogenation or oxidation while the framework controls substrate access, and photoactive MOFs may couple light absorption with charge transfer and surface catalysis. Thus, MOFs are not merely passive supports; they can actively influence reaction pathways, intermediate stabilization, and catalytic selectivity (Huang et al., 2017; Dhakshinamoorthy et al., 2018).

MOF-derived porous catalytic materials constitute a closely related but distinct class. Through thermal treatment, carbonization, sulfurization, selenization, phosphidation, or oxidation, MOFs and zeolitic imidazolate frameworks (ZIFs) can be converted into porous carbons, nitrogen-doped carbons, metal/metal oxide–carbon composites, metal sulfide–carbon composites, metal selenide–carbon hybrids, or multimetallic nanoparticle–carbon systems (Figure 8). In this approach, the parent MOF or ZIF acts as both a sacrificial structural template and a chemical precursor. The organic linker contributes to carbon formation, nitrogen-containing ligands

generate heteroatom-doped carbon environments, and metal nodes or introduced metal ions form dispersed active phases. These architectures are relevant to green catalysis because they can combine high active-site dispersion, electronic conductivity, hierarchical porosity, and catalyst recoverability (Konnerth et al., 2020; Goetjen et al., 2020). The sustainability of MOF-derived nanocatalysts depends not only on catalytic activity but also on recovery, structural stability, and reduced material loss during reuse. Conventional nanoparticle catalysts often provide high surface activity, but their separation may require filtration, centrifugation, or additional immobilization strategies. Magnetic MOF-derived catalysts can simplify catalyst recovery and reduce operational waste in selected liquid-phase reactions. However, magnetic separation alone does not establish green performance. Recyclability, leaching behavior, conversion, selectivity, product purity, and post-reaction structural integrity must be demonstrated through rigorous characterization and mass-balance analysis (Wang & Astruc, 2019; Bakar et al., 2024). Despite their promise, MOFs and MOF-derived porous catalysts should not be described as inherently green. MOF synthesis may require large solvent volumes, metal salts, modulators, solvothermal heating, repeated washing, and activation steps. Some frameworks lose crystallinity or porosity in water, acids, bases, high-ionic-strength electrolytes, or coordinating solvents. MOF-derived catalysts may require high-temperature pyrolysis, sulfurization, or selenization, increasing energy demand and complicating life-cycle assessment. Therefore, their sustainability depends on synthesis method, solvent use, metal and linker availability, durability, catalyst lifetime, recyclability, leaching behavior, scalability, and end-of-life management (Pascanu et al., 2019; Yu et al., 2025). A balanced assessment should compare MOFs and MOF-derived catalysts with simple materials such as zeolites, metal oxides, carbons, supported metals, solid acids, and conventional heterogeneous catalysts. MOFs are most convincing when their structural complexity provides a clear advantage, such as higher selectivity, multifunctionality, improved recovery, enhanced stability, mild operating conditions, or unique confinement effects that cannot be achieved by simpler systems. Similarly, MOF-derived carbons are most valuable when the parent framework provides a real structural or chemical benefit, including uniform metal distribution, controlled heteroatom doping, hierarchical porosity, or improved active-site accessibility (Clark, 2002; Corma et al., 2010; Lee et al., 2009).

Consequently, MOFs and MOF-derived porous materials should be treated as powerful but conditional tools in green catalysis. They offer rational structural design, tunable microenvironments, high dispersion of active phases, and opportunities to integrate adsorption, activation, electron transfer, and catalyst recovery within a single material platform (Dhakshinamoorthy et al., 2018; Wang & Astruc, 2019; Yu et al., 2025).

4.6. Organocatalysis and Asymmetric Sustainable Synthesis

Organocatalysis employs small organic molecules to activate substrates through covalent or noncovalent pathways, including enamine, iminium, hydrogen-bonding,

phase-transfer, N-heterocyclic carbene, and Brønsted acid/base catalysis. The field has had a major impact on asymmetric synthesis, particularly following landmark proline-catalyzed aldol and iminium-catalyzed Diels–Alder reactions. Because organocatalysts can be structurally tunable, metal-free, and highly selective, they are widely used in medicinal chemistry, natural product synthesis, and the construction of complex chiral molecules (List, 2007; MacMillan, 2008; Dalko & Moisan, 2004). From a green chemistry perspective, the main advantages of organocatalysis are metal avoidance, stereochemical control, and potential operational simplicity. By eliminating transition-metal residues, organocatalytic methods can reduce concerns related to metal contamination, especially in pharmaceutical synthesis. Their value is particularly strong when a catalytic amount of an organic molecule replaces stoichiometric chiral auxiliaries, resolution steps, or metal-based transformations. In cascade, domino, and one-pot reactions, organocatalysis can rapidly generate molecular complexity, improve step economy, reduce intermediate isolation, and lower solvent use when the reaction and workup are well designed (Ahrendt et al., 2000; List et al., 2000; Han et al., 2021). However, organocatalysis should not be considered inherently green. Some organocatalytic reactions require relatively high catalyst loadings, long reaction times, dilute conditions, chlorinated solvents, or extensive chromatographic purification. In addition, certain organocatalysts require multistep synthesis, specialized functional groups, or limited recyclability, which can reduce their general sustainability benefits. Therefore, the environmental performance of an organocatalytic process must be evaluated through catalyst loading, catalyst synthesis, solvent choice, reaction concentration, selectivity, product purification, and process mass intensity (Antenucci et al., 2021; Walsh et al., 2007).

Recent developments directly address these limitations by focusing on recyclable organocatalysts, immobilized catalytic systems, aqueous organocatalysis, solvent-free methods, and mechanochemical asymmetric organocatalysis. These approaches aim to retain the selectivity and metal-free advantages of organocatalysis while reducing solvent demand, improving recovery, and simplifying workup. Thus, organocatalysis is most valuable for green chemistry when its molecular selectivity translates into route simplification, lower waste generation, safer purification, and practical process performance (Chauhan & Chimni, 2012; Antenucci et al., 2021; Han et al., 2021).

4.7. Biocatalysis, Enzyme Engineering, and Immobilization

Biocatalysis is a major pillar of sustainable synthesis because enzymes combine high selectivity with mild operating conditions. Hydrolases, transaminases, ketoreductases, alcohol dehydrogenases, monooxygenases, lyases, ene-reductases, and engineered metalloenzymes can perform transformations that are difficult to achieve selectively using conventional chemical methods. Their high chemo-, regio-, and stereoselectivity makes them especially valuable in the synthesis of pharmaceutical intermediates, fine chemicals, chiral building blocks, and highly functionalized molecules (Bell et al., 2021; Sheldon & Woodley, 2018). Modern biocatalysis is no longer limited to natural substrates or native enzyme functions. Directed evolution,

computational enzyme design, metagenomics, high-throughput screening, and biocatalytic retrosynthesis have greatly expanded the range of accessible reactions. It is now possible to design enzymes that change the range of substrates they can work with, make them more stereoselective, make them more stable in heat and solvents, boost their expression levels, and work in conditions that are relevant to industry. These developments have transformed biocatalysis from a niche synthetic tool into a practical platform for sustainable process development (Wu et al., 2021; Buller et al., 2023). Biocatalysis is valuable for green chemistry because it can replace long chemical sequences, avoid protecting groups, use fewer harsh reagents, make fewer side products, and work at lower temperatures and pressures. When optimized, an enzymatic route can lower waste generation, simplify purification, and improve process safety. However, the sustainability of biocatalysis should not be assumed solely based on enzymes. A complete assessment must include enzyme production, catalyst loading, substrate concentration, solvent compatibility, cofactor demand, cofactor regeneration, product isolation, and aqueous waste treatment (Sheldon & Woodley, 2018; Gallou et al., 2023).

Immobilization is an important strategy for improving enzyme recovery, stability, and process integration. Enzymes can be immobilized on porous supports, polymers, membranes, nanoparticles, or cross-linked aggregates to enhance reusability and enable continuous operation. Immobilized biocatalysts can also simplify product separation and facilitate coupling with cofactor recycling systems. Nevertheless, immobilization may reduce activity by introducing diffusional limitations, unfavorable enzyme orientation, mass-transfer resistance, or support-related material burdens. Therefore, the benefit of immobilization must be demonstrated through retained activity, operational stability, reusability, and reduced process mass intensity (Lozano & García-Verdugo, 2023; Bakar et al., 2024).

Consequently, biocatalysis is one of the most powerful tools in green chemistry when enzymatic selectivity is translated into route simplification, lower waste generation, safer reaction conditions, and efficient downstream processing. Its sustainability depends on integrating enzyme engineering, immobilization, cofactor management, solvent selection, and process design into a complete and scalable catalytic system (Bell et al., 2021; Gallou et al., 2023; Wu et al., 2021).

4.8. Photocatalysis and Electrocatalysis

Photocatalysis and electrocatalysis are central to the development of chemical transformations driven by light and electricity, particularly in the context of renewable energy integration (Figure 9). Semiconductor photocatalysts generate electron–hole pairs under illumination, while electrocatalysts mediate charge-transfer processes at electrode surfaces. These approaches connect green chemistry with solar fuels, water splitting, CO_2 reduction, hydrogen production, nitrogen reduction, oxygen electrocatalysis, energy storage, and organic electrosynthesis. The discovery of photoelectrochemical water splitting on TiO_2 provided an important foundation for solar-driven catalysis, and subsequent advances in semiconductor photocatalysts,

particulate water-splitting systems, and artificial photosynthesis have expanded the field toward sustainable fuel and chemical production (Hisatomi et al., 2014; Roger et al., 2017; Seh et al., 2017).

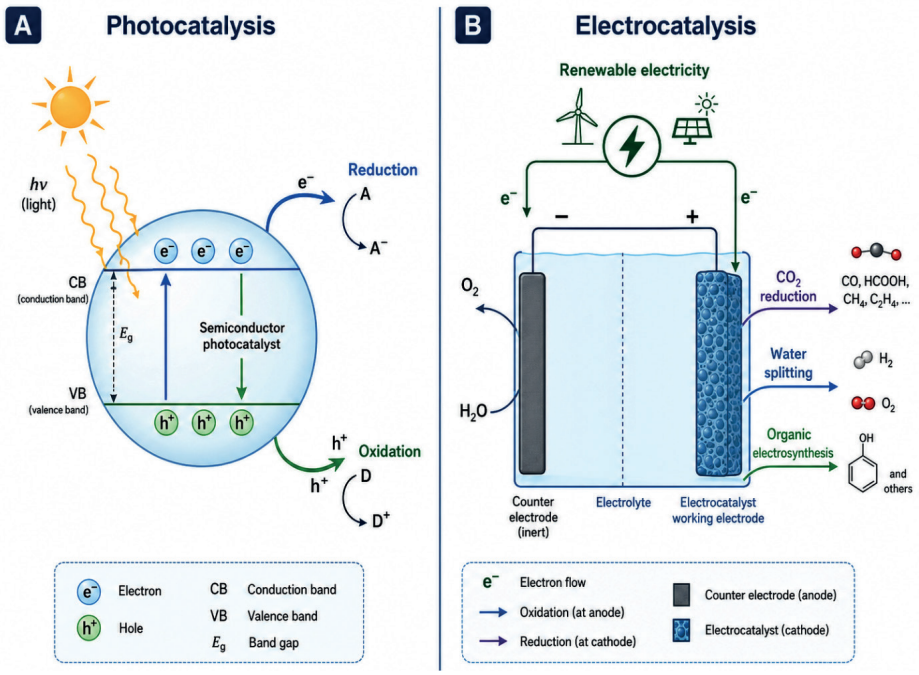

Figure 9. *Photocatalysis (A) and Electrocatalysis (B) in Green Chemistry*

The sustainability promise of photocatalysis depends on the efficient use of photons and the long-term stability of the catalytic system under realistic illumination and reaction conditions. A photocatalyst that performs well under high-intensity laboratory lamps, with sacrificial donors, rare elements, or unstable materials, may not translate into a genuinely sustainable process. Therefore, photocatalytic systems should be evaluated using parameters such as quantum yield, solar-to-chemical efficiency, catalyst durability, light absorption, charge separation efficiency, material abundance, reaction medium, and product separation. In this context, high activity alone is insufficient unless it is accompanied by efficient photon utilization, stable operation, and practical recovery or isolation of the desired product (Hisatomi et al., 2014; Chong et al., 2010).

Electrocatalysis offers a complementary strategy by replacing stoichiometric redox reagents with electrons supplied at an electrode. This can reduce chemical waste and enable precise control of redox potential, making electrocatalysis attractive for hydrogen evolution, oxygen evolution, oxygen reduction, CO_2 reduction, nitrogen reduction, and organic electrosynthesis. However, the sustainability of an electrocatalytic process depends not only on the catalyst but also on the electricity source, cell voltage, overpotential, faradaic efficiency, current density, electrolyte

composition, membrane stability, electrode lifetime, reactor design, and downstream separation. For reactions such as CO_2 reduction and water splitting, the catalyst is only one component of a larger electrochemical system (Roger et al., 2017; Seh et al., 2017). A credible green chemistry assessment of photo- and electrocatalysis must therefore be conducted at the system level. In CO_2 reduction, for example, selectivity, carbon efficiency, current density, energy input, electrolyte management, and separation of product mixtures remain major challenges. In water splitting, long-term stability, gas crossover, membrane durability, catalyst abundance, and device efficiency are decisive. Similarly, in organic electrosynthesis, solvent choice, supporting electrolyte, electrode material, product isolation, and scalability must be considered alongside conversion and yield (Artz et al., 2018; Nitopi et al., 2019).

Accordingly, photocatalysis and electrocatalysis provide powerful routes for linking chemical synthesis to renewable energy. Their green chemistry value is greatest when they reduce stoichiometric reagent use, operate with abundant and durable materials, achieve high selectivity and energy efficiency, and function in integrated reactor systems suitable for scale-up. The design target should therefore be a stable, efficient, and separable catalytic process or device, rather than a short-term demonstration of high activity under idealized laboratory conditions (Kondratenko et al., 2013; Artz et al., 2018).

5. APPLICATIONS OF CATALYSIS IN GREEN CHEMISTRY

5.1. Sustainable C-C and C-Heteroatom Bond Formation

Carbon–carbon and carbon–heteroatom bond formation is central to the synthesis of pharmaceuticals, agrochemicals, functional materials, and fine chemicals. Cross-coupling reactions, including Suzuki–Miyaura, Heck, Negishi, and related transformations, have transformed synthetic planning by enabling the union of complex molecular fragments under relatively mild conditions. From a green chemistry perspective, their value lies in reducing step count, improving selectivity, increasing functional-group tolerance, and avoiding less efficient stoichiometric bond-forming strategies. However, cross-coupling reactions should not be considered inherently green, since conventional protocols may involve precious metals, halogenated solvents, excess base, palladium residues, and inorganic salt waste (Miyaura & Suzuki, 1995; Jana et al., 2011; Han, 2013). The sustainability challenge is therefore to retain the strategic power of cross-coupling while reducing its material and environmental burdens. Greener approaches include lowering catalyst loading, improving catalyst recovery, replacing palladium with nickel, copper, iron, or other more abundant metals where feasible, using less hazardous bases, avoiding chlorinated solvents, and conducting reactions under milder or aqueous conditions. Aqueous and micellar cross-coupling systems show how to combine catalyst design and reaction medium. Micellar catalysis can enable hydrophobic substrates to react in water, sometimes at room temperature, thereby reducing organic solvent consumption in favorable cases. Nevertheless, surfactant synthesis, surfactant loading, recyclability, foaming,

wastewater treatment, and downstream product isolation must be included before such systems can be described as genuinely sustainable (Molnár, 2011; Lipshutz et al., 2012; Torborg & Beller, 2009; Lipshutz & Abela, 2008).

Direct C–H functionalization provides another important strategy for improving step economy because it can avoid prefunctionalized substrates and reduce the number of synthetic operations. This approach is particularly attractive when it enables late-stage diversification, direct installation of functional groups, or selective modification of complex molecules. However, C–H functionalization also presents sustainability challenges. Many methods require directing groups, transition-metal catalysts, stoichiometric oxidants, additives, or carefully controlled conditions to achieve useful chemo-, regio-, or site-selectivity. If the installation and removal of directing groups, oxidant waste, catalyst residues, or purification demands outweigh the reduction in steps, the apparent advantage may diminish (Deshmukh et al., 2025; Liu et al., 2019; Khan et al., 2021; Buğday et al., 2021b; Buğday et al., 2022b).

A greener bond-forming strategy must therefore be evaluated at the route level rather than at the level of a single transformation. Cross-coupling, aqueous catalysis, micellar systems, and C–H functionalization are most valuable when they demonstrably reduce the total number of steps, isolations, solvent use, auxiliary reagents, metal residues, and waste streams. The key design principle is not to label a bond-forming method as green by default, but to show that it improves yield, selectivity, process mass intensity, safety, scalability, and general environmental performance compared with the best available alternative route. (Li & Trost, 2008; Roschangar et al., 2015).

5.2. Mechanochemistry and Solvent-Minimized Synthesis

Mechanochemistry is an important approach in sustainable synthesis because it directly addresses one of the largest contributors to process mass intensity: solvent use. Ball milling, twin-screw extrusion, and related mechanical techniques can promote chemical transformations with little or no bulk solvent, making them attractive for organic synthesis, coordination chemistry, cocrystal formation, polymer modification, MOF synthesis, and catalytic reactions. In catalytic systems, mechanical energy can enhance contact between solid reactants and catalysts, generate fresh reactive surfaces, alter mixing and diffusion behavior, and sometimes enable reaction pathways that differ from those observed in solution. (James et al., 2012; Friščić et al., 2020; Chauhan & Chimni, 2012). The green chemistry value of mechanochemistry arises primarily from its potential to reduce solvent consumption, simplify workup, and intensify reaction conditions. Catalytic mechanochemistry has been explored in organocatalysis, metal-catalyzed cross-coupling, solid acid catalysis, and porous material synthesis, demonstrating that mechanical activation can be compatible with a wide range of catalytic platforms. In some cases, milling conditions can improve reaction rates, enable solvent-free transformations, or provide unusual selectivity by changing the local reaction environment. (Wang, 2013; Friščić et al., 2020; Tanaka & Toda, 2000). However, the sustainability advantage of mechanochemistry should be quantified rather than assumed. Although eliminating

bulk solvent can substantially reduce PMI and E factor, a complete assessment must also include grinding auxiliaries, milling media, jar and ball materials, energy input, temperature control, reaction time, cleaning requirements, reproducibility, and product isolation. Recent discussions of green metrics in mechanochemistry emphasize that solvent reduction is only one component of sustainability; a mechanochemical process is preferable only when its full material, energy, safety, and operational profile compares favorably with solution-based alternatives. (Fantozzi et al., 2023; James et al., 2012). Scale-up is a central issue in evaluating mechanochemical catalysis. Laboratory ball milling is valuable for discovery and optimization, but translation to larger-scale production often requires continuous technologies such as twin-screw extrusion. Continuous mechanochemistry can reduce solvent use, improve productivity, and provide better process control, but it also requires careful management of residence time, heat generation, torque, feed consistency, catalyst distribution, product discharge, and equipment wear. These factors determine whether the benefits observed at a small scale can be retained in a practical manufacturing setting. (Fantozzi et al., 2023; Sajini & Joseph, 2025).

Importantly, mechanochemistry offers a powerful route toward solvent-minimized and intensified catalytic synthesis, but it should not be described as inherently green. Its sustainability depends on whether solvent reduction is accompanied by favorable energy use, robust scale-up, efficient mixing, simple workup, catalyst stability, reproducibility, and lower process burden. Meeting these criteria allows catalytic mechanochemistry to significantly contribute to greener synthesis and process intensification. (Fantozzi et al., 2023; Friščić et al., 2020).

5.3. Biomass Valorization and Renewable Feedstocks

Biomass valorization is one of the most important tests of green catalysis because it combines renewable feedstock utilization with highly complex reaction chemistry. Lignocellulosic biomass is composed mainly of cellulose, hemicellulose, and lignin, each of which differs in structure, oxygen content, reactivity, and depolymerization behavior. Therefore, catalysts used in biomass conversion must transform water-rich, heterogeneous, and highly functionalized feedstocks into defined products without excessive degradation, repolymerization, or formation of low-value mixtures. (Huber et al., 2006; Corma et al., 2007; Alonso et al., 2010). Carbohydrate conversion illustrates both the opportunity and the difficulty of catalytic biomass upgrading. Cellulose- and hemicellulose-derived sugars can be converted into important platform chemicals such as 5-hydroxymethylfurfural, levulinic acid, sorbitol, glycols, and organic acids. These transformations may involve dehydration, hydrogenation, hydrogenolysis, oxidation, aldol condenzation, or hydrodeoxygenation, depending on the target product. However, each pathway requires careful control of acidity, redox properties, water tolerance, solvent effects, and side reactions such as humin, char, gas, or tar formation. The sustainability of a carbohydrate-based route therefore depends not only on conversion but also on product selectivity, catalyst lifetime, solvent system, separation of dilute products, and the origin of hydrogen or electricity used in the process. (Chheda et al., 2007; Van Putten et al., 2013; Climent

et al., 2014). Lignin valorization presents an even greater challenge because lignin is structurally heterogeneous, chemically recalcitrant, and prone to condenzation or repolymerization during processing. Catalytic depolymerization, reductive stabilization, selective oxidation, hydrodeoxygenation, and biological or catalytic funneling strategies aim to convert lignin into aromatic monomers, phenolic compounds, and other higher-value chemicals. A credible green route must demonstrate controlled product formation rather than merely converting a renewable feedstock into complex mixtures that require severe downstream upgrading or generate large waste streams. (Zakzeski et al., 2010; Gallezot, 2012).

Sustainable biomass conversion also requires process-level evaluation. Feedstock sourcing, land use, pretreatment severity, solvent choice, water management, catalyst stability, resistance to poisoning, tolerance toward oxygenated substrates, hydrogen source, product recovery, and integration into biorefineries all influence the final environmental profile. Because biomass-derived streams are often dilute, reactive, and impurity-rich, downstream separation and catalyst durability may dominate the sustainability of the route. (Corma et al., 2007; Gallezot, 2012; Kralisch et al., 2015). Metal-free catalysts have recently attracted attention in biomass valorization because they can reduce dependence on critical metals and limit metal leaching. Carbon materials, heteroatom-doped carbons, organocatalysts, and non-metal semiconductors can enable thermal, photocatalytic, and electrocatalytic biomass transformations. However, metal absence alone is not sufficient to establish greenness. These catalysts must be compared with conventional metal-based systems in terms of yield, selectivity, catalyst loading, operational lifetime, recovery, energy demand, and life-cycle impact. (Chauhan & Srivastava, 2025; Sánchez-Velandia et al., 2025).

Ultimately, biomass valorization demonstrates that renewable feedstocks do not automatically lead to sustainable chemistry. Green catalysis in this area requires selective conversion of complex biomass components into valuable products while minimizing degradation, solvent burden, energy input, catalyst loss, and downstream separation challenges. The most convincing biomass routes are those that combine renewable carbon use with high selectivity, robust catalysts, efficient separations, and integration into a broader biorefinery framework. (Corma et al., 2007; Alonso et al., 2010).

5.4. CO_2 Utilization, and Catalytic Conversion

CO_2 utilization is a major theme in sustainable catalysis because CO_2 is abundant, nonflammable, inexpensive, and available as a C_1 feedstock. However, its thermodynamic stability and kinetic inertness make catalytic conversion challenging. Effective CO_2 transformation generally requires energy input, reducing equivalents, or coupling with thermodynamically favorable reactions. Major catalytic routes include hydrogenation to methanol, methane, carbon monoxide, or hydrocarbons; electrochemical reduction to CO, formate, alcohols, ethylene, and other C_2 products; photocatalytic reduction; cycloaddition with epoxides to form cyclic carbonates; and incorporation into polymers or fine chemicals. (Aresta & Dibenedetto, 2007; Sakakura et al., 2007).

The central sustainability condition for CO_2 conversion is that the required energy and reducing equivalents must be low-carbon. If hydrogen is produced from fossil-based reforming without carbon management, or if electricity is supplied from carbon-intensive sources, CO_2 utilization may shift emissions upstream rather than reduce them. Therefore, the environmental value of CO_2-derived products depends strongly on system boundaries, including the electricity mix, hydrogen source, origin and purity of CO_2, product displacement, separation requirements, catalyst lifetime, and end-of-life carbon fate. Integrated catalysis and life-cycle assessment are essential for determining whether a given CO_2 conversion pathway provides a genuine reduction in environmental impact. (Artz et al., 2018; Kondratenko et al., 2013).

Catalyst design for CO_2 conversion focuses on activating CO_2, controlling intermediate binding, directing hydrogenation or electron-transfer steps, and improving product selectivity. In electrochemical CO_2 reduction, copper-based catalysts remain especially important because of their ability to form multi-carbon products, but competing hydrogen evolution, carbonate formation, limited carbon efficiency, electrolyte management, current density, catalyst stability, and separation of dilute product mixtures remain major challenges. For formate, CO, alcohol, and hydrocarbon production, the catalyst must balance activity with selectivity and long-term operational stability. (Kondratenko et al., 2013; Nitopi et al., 2019). In thermal CO_2 and COx hydrogenation, catalyst performance depends on the activation of CO_2 or CO, hydrogen dissociation, intermediate stabilization, and control of pathways leading to methanol, methane, CO, or higher hydrocarbons. Water, which is often formed as a by-product, can influence active-site structure, oxidation state, support properties, and reaction selectivity. It should therefore be treated as a design variable rather than merely as an undesired by-product. Water management, heat management, catalyst durability, and product separation are all critical to process viability. (Wang et al., 2024; Artz et al., 2018; Sakakura et al., 2007).

Overall, CO_2 conversion should not be considered inherently sustainable simply because it uses a greenhouse gas as a feedstock. Its green chemistry value depends on low-carbon energy input, high selectivity, efficient carbon utilization, durable catalysts, manageable separations, and meaningful displacement of fossil-derived products. Catalytic CO_2 utilization is most convincing when it is integrated with renewable electricity or low-carbon hydrogen, supported by life-cycle assessment, and designed as a complete process rather than as an isolated catalytic transformation. (Artz et al., 2018; Aresta & Dibenedetto, 2007).

5.5. Environmental Catalysis and Pollutant Abatement

Environmental catalysis applies catalytic principles to the removal, transformation, or detoxification of pollutants in air and water. Major applications include volatile organic compound oxidation, selective catalytic reduction of NOx, three-way catalysis for automotive emissions, photocatalytic degradation of organic contaminants, catalytic ozonation, catalytic wet-air oxidation, and treatment of industrial wastewater. These technologies are important because they can reduce hazardous

emissions and environmental exposure; however, their sustainability depends on more than pollutant conversion alone. Reaction products, energy demand, catalyst durability, possible leaching, and the formation of harmful intermediates or secondary waste must also be evaluated. (Chong et al., 2010; Li et al., 2011). Photocatalytic water treatment illustrates both the promise and the limitations of environmental catalysis. TiO_2 and visible-light-active semiconductors have been widely investigated for the degradation of dyes, pharmaceuticals, pesticides, and other organic contaminants. The practical challenge is not simply to degrade a model pollutant under laboratory illumination but to mineralize or selectively detoxify realistic contaminant mixtures in complex water matrices. Natural organic matter, inorganic ions, turbidity, pH, and competing radical scavengers can strongly influence performance. Therefore, visible-light activity, light penetration, mass transfer, catalyst immobilization, radical pathways, by-product identification, mineralization efficiency, catalyst loss, and regeneration must be considered together. (Chong et al., 2010; Hisatomi et al., 2014). Catalytic wet-air oxidation, catalytic ozonation, and related advanced oxidation processes require catalysts that activate oxygen, ozone, or peroxide efficiently while remaining stable in aqueous and often harsh chemical environments. Oxygen activation and transfer, radical generation, surface adsorption, and resistance to poisoning are key mechanistic factors. At the same time, catalysts must resist leaching, fouling, deactivation, and structural degradation during prolonged operation. These requirements are especially important for wastewater streams that have salts, acids, bases, suspended solids, or more than one organic contaminant. (Li et al., 2011; Chong et al., 2010).

In summary, environmental catalysis should be assessed according to its ability to reduce total environmental burden rather than merely to remove a target pollutant from one phase. A credible green process must demonstrate effective pollutant conversion or mineralization, low formation of toxic by-products, stable catalyst performance, limited catalyst release, manageable energy input, and feasible regeneration or disposal. The central design principle is that a catalytic treatment technology should solve an environmental problem without creating a new pollutant burden elsewhere in the process. (Bakar et al., 2024; Chong et al., 2010).

5.6. Pharmaceutical and Fine-Chemical Manufacturing

Pharmaceutical and fine-chemical manufacturing provide a stringent test of green catalysis because target molecules are often structurally complex, purity requirements are high, and synthetic routes commonly involve multiple steps, extensive solvent use, and demanding purification protocols. In these sectors, the environmental burden is frequently dominated not by the desired chemical transformation itself, but by workup, solvent consumption, isolation, and removal of impurities. Metrics such as process mass intensity and E factor are therefore especially important for evaluating whether a catalytic route provides a genuine sustainability advantage. (Jimenez-Gonzalez et al., 2011; Becker et al., 2022; Roschangar et al., 2015). Catalysis can reduce this burden by improving selectivity, enabling asymmetric

synthesis, avoiding protecting-group strategies, reducing resolution steps, supporting late-stage functionalization, and shortening synthetic sequences through telescoped or one-pot processes. The greatest benefits arise when a catalytic method improves the complete route rather than only the yield of an isolated step. A highly selective catalytic transformation can lower impurity formation, simplify crystallization or extraction, reduce chromatographic purification, and improve general material efficiency. (Torborg & Beller, 2009; Han et al., 2021; Li & Trost, 2008).

Biocatalysis has become particularly important in pharmaceutical and fine-chemical synthesis because enzymes can produce chiral alcohols, amines, acids, and other intermediates with high stereoselectivity under mild conditions. Directed evolution and enzyme engineering can transform a low-activity natural enzyme into a robust manufacturing catalyst with improved substrate scope, thermal stability, solvent tolerance, high substrate loading, and controlled impurity profile. When a biocatalytic step replaces classical resolution, stoichiometric chiral auxiliaries, or a multistep chemical sequence, the reduction in PMI and waste generation can be substantial. (Sheldon & Woodley, 2018; Gallou et al., 2023; Wu et al., 2021). Transition-metal catalysis also remains essential, especially in cross-coupling, hydrogenation, oxidation, and C–H functionalization. Its sustainability depends on catalyst loading, turnover number, ligand choice, solvent system, impurity profile, and efficient control of residual metals. In pharmaceutical processes, even low levels of metal or ligand-derived impurities can influence purification strategy and regulatory acceptability. Therefore, metal removal, catalyst recovery, and product purity must be considered from the beginning of route development. (Miyaura & Suzuki, 1995; Han, 2013; Deshmukh et al., 2025; Fırat et al., 2024; Khan et al., 2022; Khan et al., 2023; Yagmurlu et al., 2024). The selection of a catalytic strategy should be route-specific rather than trend-driven. Palladium, nickel, copper, iron, organocatalytic, biocatalytic, and direct functionalization approaches should be compared according to their process-level performance, including yield, selectivity, catalyst availability, safety, solvent burden, impurity control, scalability, regulatory compliance, and downstream purification. The best option is not necessarily the newest or most fashionable catalyst class, but the one that provides the lowest material, energy, safety, and purification burden for the target route. (Becker et al., 2022; Roschangar et al., 2015).

Industrial adoption also requires robustness and reproducibility. Metal catalysts must meet residue limits, enzymes must be produced consistently, immobilized systems must maintain stable performance, and solvent choices must satisfy health, safety, environmental, and regulatory constraints. Concepts such as the Green Aspiration Level and process-focused mass metrics emphasize that greener chemistry is not merely an academic feature of a reaction but a measurable improvement in manufacturing performance. In this context, green catalysis in pharmaceutical and fine-chemical production is best defined by its ability to deliver high-quality products through shorter, safer, cleaner, and more scalable processes. (Roschangar et al., 2015; Becker et al., 2022).

6. METRICS FOR SUSTAINABILITY, LIFE-CYCLE ASSESSMENT, AND SCALE-UP

6.1. Atom Economy, E Factor, PMI, and Related Metrics

Metrics make green chemistry operational by translating qualitative sustainability goals into measurable parameters. Atom economy is a predictive and reaction-centered metric because it evaluates the theoretical incorporation of reactant atoms into the desired product. In contrast, E factor and process mass intensity are empirical and process-centered metrics that account for actual material inputs and waste generation. Additional indicators such as reaction mass efficiency, carbon efficiency, effective mass yield, solvent intensity, and energy intensity provide further detail depending on the purpose of the assessment. (Constable et al., 2002; Sheldon, 2018). No single metric can fully define the greenness of a catalytic process. Yield measures product formation but does not capture waste from solvents, reagents, workup, or purification. Atom economy highlights intrinsic reaction design but ignores practical operating conditions. The E factor measures the mass of waste generated per mass of product, while PMI measures the total mass of all input materials per mass of product and is particularly useful in process chemistry because it includes solvents, reagents, catalysts, and auxiliary materials. Therefore, the most appropriate metric depends on the decision being made, such as route selection, solvent replacement, catalyst screening, scale-up, or life-cycle comparison. (Sheldon, 2018; Jiménez-González et al., 2012; Tobiszewski et al., 2015). Catalysis can improve green metrics in several ways. It may reduce the need for stoichiometric reagents, increase selectivity, avoid protecting-group steps, enable one-pot or telescoped sequences, lower solvent consumption, permit catalyst or solvent recovery, and allow reactions to proceed under milder conditions. These benefits can translate into lower PMI, reduced E factor, improved reaction mass efficiency, and lower energy intensity. However, catalytic processes can also worsen sustainability metrics if they require high dilution, large excesses of additives, elaborate ligand synthesis, difficult product separation, chromatographic purification, or frequent catalyst replacement. (Trost, 1991; Sheldon, 2017; Jimenez-Gonzalez et al., 2011). For this reason, metric analysis should include the complete experimental operation required to obtain the product at the desired purity. A useful approach is to calculate metrics at several levels. At the reaction level, yield, atom economy, selectivity, catalyst loading, and solvent amount should be considered. At the step level, workup, quenching, extraction, washing, drying, and purification should be included. At the route level, all synthetic steps from starting material to final product should be assessed. At the process level, solvent recovery, energy demand, waste treatment, catalyst life cycle, and cleaning operations should also be incorporated. (Jimenez-Gonzalez et al., 2011; Becker et al., 2022).

Collectively, green chemistry metrics should be used as complementary tools rather than isolated indicators. Catalysis provides genuine sustainability benefits only when improvements in activity or selectivity lead to measurable reductions in material input, waste formation, solvent use, energy demand, and purification

burden. A rigorous assessment should therefore compare catalytic and noncatalytic alternatives under equivalent product-purity and process-relevance criteria. (Constable et al., 2002; Tamargo et al., 2024; Tobiszewski et al., 2015).

6.2. System Boundaries and Life-Cycle Assessment

Life-cycle assessment is essential when evaluating catalytic processes that change the feedstock, energy source, solvent system, catalyst material, or end-of-life pathway. Laboratory metrics such as yield, atom economy, E factor, and process mass intensity describe important aspects of reaction and process efficiency, but they do not fully capture upstream and downstream impacts. A route that appears green within the reactor may become less favorable when raw material sourcing, hydrogen production, electricity generation, solvent manufacture, catalyst synthesis, emissions, waste treatment, product use, and disposal are included. LCA therefore complements laboratory-scale metrics by extending the assessment from reaction performance to system-level environmental impact. (Kralisch et al., 2015; Artz et al., 2018). The definition of system boundaries strongly influences the outcome of an LCA. This is particularly important for CO_2 utilization, biomass conversion, and electrochemical catalysis. In CO_2 hydrogenation, for example, the carbon footprint depends heavily on whether the hydrogen is produced from renewable electricity, low-carbon routes, or fossil reforming without carbon management. In biomass conversion, the apparent advantage of renewable carbon can be reduced by land use, fertilizer input, feedstock transport, pretreatment severity, dilute product streams, and energy-intensive separations. In electrocatalytic processes, the electricity mix, cell voltage, membrane material, electrolyte composition, electrode lifetime, and product separation can dominate the final environmental profile. (Kralisch et al., 2015; Jiménez-González et al., 2012). Catalyst materials should also be included within the life-cycle boundary. Metal extraction, refining, support synthesis, ligand production, calcination, activation, regeneration, catalyst replacement, and disposal can all contribute to environmental burden. This consideration is especially relevant for nanocatalysts, MOFs, single-atom catalysts, and other structurally complex materials. Although these systems may use small amounts of active metal or provide high catalytic performance, their synthesis may require multiple steps, large solvent volumes, high-temperature treatment, specialized precursors, or difficult purification. Their sustainability advantage must therefore be demonstrated through comparison with simpler catalytic alternatives under equivalent process conditions. (Mitchell & Pérez-Ramírez, 2021; Kralisch et al., 2015).

Overall, LCA should not replace reaction-level and process-level metrics but should be used alongside them. Mass-based metrics reveal material efficiency, while LCA identifies environmental burdens that occur outside the immediate reaction operation. A credible sustainability claim for catalysis should therefore integrate yield, selectivity, PMI, E factor, solvent and energy use, catalyst lifetime, recovery, and full life-cycle impacts. This combined approach helps determine whether a catalytic process genuinely reduces environmental burden or merely shifts it to another part of the value chain. (Artz et al., 2018; Sheldon, 2018).

6.3. Hazard, Safety, and Regulatory Dimensions

Hazard reduction is a core component of green catalysis because sustainability cannot be defined by yield or conversion alone. A catalytic route that relies on explosive oxidants, highly toxic ligands, persistent solvents, pyrophoric materials, or hazardous intermediates may not represent a genuine improvement, even if it provides high activity or selectivity. Solvent selection guides, reagent hazard assessments, and green analytical metrics are therefore valuable tools because they translate health, safety, environmental, and regulatory information into practical process decisions. (Anastas & Eghbali, 2010; Prat et al., 2016). Catalysts can contribute to inherently safer design by enabling reactions at lower temperature and pressure, replacing hazardous stoichiometric reagents with safer alternatives, improving selectivity, and reducing the quantity of hazardous intermediates present during operation. Continuous-flow catalysis can further improve safety by minimizing reactor hold-up, enhancing heat and mass transfer, improving control over exothermic reactions, and allowing incompatible steps to be separated or telescoped safely. Heterogeneous fixed-bed systems can also simplify catalyst containment and reduce operator exposure when they are robust and well controlled. (Anastas et al., 2001; Li & Trost, 2008). However, catalytic processes can introduce new safety risks that must be evaluated experimentally. Rapid exotherms, gas evolution, pressure buildup, catalyst ignition, pyrophoric solids, catalyst runaway, unexpected induction periods, or sudden deactivation can create operational hazards. Oxidations, hydrogenations, gas–liquid reactions, photochemical processes, and electrochemical systems require particular attention to heat release, mass transfer, flammability limits, pressure control, and emergency shutdown behavior. Therefore, a catalytic route should be considered safer only when its risk profile has been assessed under realistic process conditions. (Prat et al., 2016; Clarke et al., 2018). Regulatory constraints are especially important in pharmaceutical and fine-chemical synthesis. Metal residues, genotoxic impurities, ligand-derived by-products, residual solvents, enzyme-derived impurities, leachables from supports or membranes, and extractables from process equipment may require dedicated control strategies. These factors can increase purification burden, analytical complexity, solvent use, and process cost. Thus, a greener catalytic route must be compatible not only with laboratory conversion and selectivity, but also with product quality, impurity control, worker safety, environmental protection, and regulatory expectations. (Becker et al., 2022; Roschangar et al., 2015).

From a sustainability perspective, hazard reduction should be integrated into catalyst and process design from the beginning. The most sustainable catalytic processes are those that combine high selectivity and efficiency with safer reagents, preferred solvents, controlled reaction conditions, low hazardous inventory, manageable impurity profiles, and robust scale-up behavior. Green catalysis should therefore be understood as both a chemical and a safety-driven design strategy. (Anastas & Eghbali, 2010; Roschangar et al., 2015).

6.4. Scale-Up and Industrial Implementation

Scale-up changes the meaning of catalytic performance because factors that are minor in small-scale screening can become decisive in process operation. Heat transfer, mass transfer, mixing, residence time distribution, impurity tolerance, catalyst handling, filtration, drying, cleaning, and product isolation all influence whether a catalytic method can be implemented successfully. A catalyst that performs well in a small vial may become impractical at reactor scale if it forms fines, clogs filters, requires intense agitation, deactivates in the presence of trace impurities, or generates an impurity profile that complicates downstream purification. (García-Serna et al., 2022; Roschangar et al., 2015). Different catalytic platforms present distinct scale-up challenges. Heterogeneous catalysts must be evaluated for attrition, pressure drop, pore diffusion, fouling, coking, regeneration efficiency, and long-term time-on-stream performance. Homogeneous catalysts require robust strategies for catalyst separation, recycling, ligand control, and removal of metal residues from the product stream. Enzymes must be produced reproducibly and remain stable at industrially relevant substrate concentrations, solvent compositions, and operating times. Photocatalytic systems require effective photon management, light penetration, reactor geometry, and catalyst stability under illumination. Electrocatalytic processes depend on scalable electrode design, membrane performance, electrolyte stability, current density, cell voltage, and product separation. Mechanochemical reactions similarly require reactor designs that go beyond laboratory milling jars, with control of residence time, torque, heat generation, feed consistency, and product discharge. (Cole-Hamilton, 2003; Climent et al., 2011; Bell et al., 2021).

Industrial implementation also depends on economics, supply chain reliability, regulatory acceptability, and compatibility with existing plant equipment. A greener catalyst must be available at reasonable cost, reproducible across batches, safe to handle, and suitable for the required unit operations. The final process decision often involves balancing environmental benefit, catalyst robustness, impurity control, worker safety, capital investment, operating cost, regulatory risk, and product value. (Becker et al., 2022; Roschangar et al., 2015; Thomas & Raja, 2005).

Therefore, sustainable catalysis requires close integration of catalyst discovery with reaction engineering, process safety, analytical chemistry, manufacturing constraints, and sustainability assessment. A catalyst should not be evaluated only by novelty, activity, or selectivity in idealized laboratory conditions. Its green chemistry value is strongest when it reduces the number of unit operations, simplifies isolation, lowers solvent and energy demand, improves impurity control, and remains reliable under realistic feed composition and process conditions. (García-Serna et al., 2022; Jiménez-González et al., 2012).

7. CHALLENGES AND FUTURE PERSPECTIVES

7.1. Avoiding Greenwashing in Catalysis

Greenwashing in catalysis occurs when a catalytic method is described as sustainable on the basis of a single favorable feature while unfavorable process factors are ignored. The use of water as a solvent, a recyclable catalyst, a bio-derived feedstock, a metal-free system, visible light, or low catalyst loading can each contribute to greener chemistry, but none is sufficient by itself to establish sustainability (Figure 10). For example, an aqueous reaction may generate problematic wastewater, a recyclable catalyst may leach active metal, a rare-metal catalyst may be used at low loading but lost after each cycle, and a solvent-free reaction may require high mechanical energy or present scale-up difficulties (Sheldon, 2018; García-Serna et al., 2022). A transparent green catalysis claim must clearly define its basis of comparison. The catalytic process should be evaluated against a relevant comparator, such as a stoichiometric route, an older catalytic method, an industrial benchmark, or the best available alternative route. Without this reference point, claims of improvement cannot be meaningfully assessed. The system boundary should also be stated explicitly, including reaction scale, product purity, solvent and catalyst recovery, workup and purification materials, energy input, catalyst preparation, waste treatment, and end-of-life considerations (Kralisch et al., 2015; Artz et al., 2018).

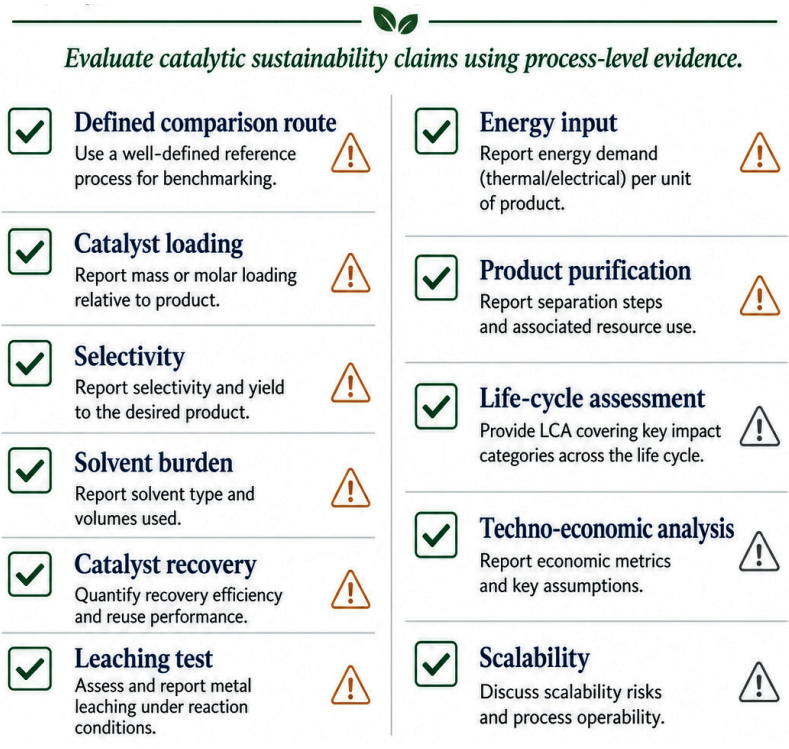

Figure 10. *Greenwashing Checklist for Catalytic Sustainability Claims*

Avoiding greenwashing does not require that a catalytic method be perfectly sustainable in every respect. Many valuable catalytic systems improve one or more dimensions of a process while leaving other issues unresolved. The scientific responsibility is to identify both the demonstrated advantages and the remaining trade-offs. A credible sustainability discussion should therefore report not only conversion and yield but also selectivity, solvent use, auxiliary materials, catalyst loading, catalyst lifetime, recovery efficiency, toxicity, leaching behavior, product impurity profile, and waste generation. (Habib et al., 2023; Kaur et al., 2024). Routine and transparent reporting of green metrics is essential for improving the reliability of sustainability claims. For catalytic reactions, publications should include catalyst loading, turnover number and turnover frequency where applicable, leaching data, recycling protocols, solvent mass, workup materials, product isolation methods, and comparisons with established routes. Specialized areas such as mechanochemistry, photocatalysis, electrocatalysis, and nanocatalysis also require field-specific metrics, including energy input, photon efficiency, faradaic efficiency, current density, catalyst stability, nanomaterial release, and scale-up behavior. (Sheldon, 2018; Tamargo et al., 2024).

Finally, green catalysis should be presented as evidence-based process improvement rather than as a label attached to an attractive reaction feature. A rigorous claim must show that the catalytic method reduces environmental burden under defined boundaries and relative to a meaningful comparator. Honest accounting of both benefits and limitations is the most effective way to distinguish genuine sustainable catalysis from greenwashing. (Yenare et al., 2025; García-Serna et al., 2022).

7.2. Critical Elements, Catalyst Lifetime, and Circularity

Critical-element dependence remains one of the major challenges in sustainable catalysis. Precious metals and rare elements can provide exceptional activity, selectivity, and stability in hydrogenation, cross-coupling, electrocatalysis, photocatalysis, and other demanding transformations. However, their limited availability, high cost, supply-chain vulnerability, and environmental impacts associated with mining and refining require careful management. Reducing dependence on critical elements requires the development of earth-abundant alternatives, metal-free catalysts, improved metal utilization, efficient catalyst recycling, recovery from spent catalysts, and design strategies based on circularity. (Mitchell & Pérez-Ramírez, 2021; Roger et al., 2017; Wang et al., 2018). The use of precious metals may still be justified in closed-loop, high-value, or highly efficient processes when catalyst loading is very low, turnover numbers are high, losses are minimal, and the catalyst provides a clear route-level advantage. In contrast, critical elements become problematic when they are dispersed into products, lost in waste streams, difficult to recover, or used at large scale in energy-related technologies. Earth-abundant catalysts, metal-free systems, single-atom catalysts, and low-nuclearity supported catalysts are promising alternatives, but they must meet the same requirements for activity, selectivity, lifetime, safety, and process compatibility. (Mitchell & Pérez-Ramírez, 2021; Roschangar et al., 2015). Catalyst lifetime is the bridge between

laboratory activity and circular material use. A catalyst that deactivates rapidly or must be replaced frequently increases material consumption, waste generation, operating cost, and process downtime. Longer lifetimes can be achieved through support design, active-site stabilization, poison-resistant formulations, controlled operating windows, regeneration protocols, and improved resistance to leaching, sintering, fouling, or ligand degradation. In some cases, a more complex catalyst may be justified if its extended operational lifetime significantly reduces total material demand and improves process reliability. (Habib et al., 2023; Polshettiwar et al., 2011). Circular catalyst design also requires end-of-life planning. Metals should be recoverable from spent catalysts, supports should be reusable, regenerable, recyclable, or environmentally benign, and catalyst manufacturing should avoid unnecessary solvent use, hazardous ligands, persistent supports, and waste-intensive preparation methods. Recovery and regeneration should therefore be treated as design specifications from the beginning rather than as afterthoughts at the end of process development. (Kralisch et al., 2015; Mitchell & Pérez-Ramírez, 2021; Lozano & García-Verdugo, 2023).

Genarally, sustainable catalysis is both a reaction-design and materials-design challenge. The goal is not simply to eliminate all precious or rare elements but to use catalytic materials responsibly across their full life cycle. A circular approach to catalysis should integrate element abundance, catalyst productivity, durability, recoverability, regeneration, safe decommissioning, and compatibility with continuous operation. Only when these factors are considered together can catalytic performance translate into reduced resource pressure and genuine sustainability. (Yenare et al., 2025; Habib et al., 2023).

7.3. Integration of Renewable Electricity, CO_2, and Biomass

The integration of renewable electricity, CO_2, water, nitrogen, and biomass into coherent chemical production systems will shape the future of green catalysis. Electrocatalytic and photocatalytic processes can convert renewable energy into chemical bonds, while CO_2 and biomass-derived feedstocks can diversify carbon sources beyond fossil resources. These opportunities connect catalysis with solar fuels, power-to-X chemistry, biorefineries, sustainable nitrogen fixation, hydrogen production, and low-carbon chemical manufacturing. The central challenge is to combine these inputs in ways that are thermodynamically feasible, kinetically efficient, economically viable, and environmentally beneficial. (Kondratenko et al., 2013; Artz et al., 2018; Roger et al., 2017). Biorefineries represent one important direction for future catalytic development. Biomass-derived platform molecules can be upgraded into fuels, monomers, solvents, and chemical intermediates when catalysts are able to tolerate water, oxygenated substrates, variable feed composition, and naturally occurring impurities. Selective dehydration, hydrogenation, oxidation, hydrogenolysis, and C–C bond-forming reactions can increase the value of biomass streams, but the overall sustainability depends on feedstock sourcing, pretreatment severity, catalyst stability, product selectivity, and separation of dilute

products. (Huber et al., 2006; Corma et al., 2007; Climent et al., 2014). A second major direction is Power-to-X chemistry, in which renewable electricity is used to produce hydrogen, syngas, methanol, ammonia, hydrocarbons, or other energy carriers and chemical feedstocks. Electrocatalysis and photocatalysis are especially important in this context because they can replace stoichiometric redox reagents with electrons or photons. However, the sustainability of these processes depends on the electricity source, catalyst durability, current density, overpotential, faradaic efficiency, reactor design, product separation, and infrastructure requirements. (Roger et al., 2017; Seh et al., 2017; Nitopi et al., 2019).

Hybrid catalytic systems may become increasingly important. Biomass-derived intermediates can be upgraded electrochemically, CO_2 can be converted through hydrogenation, electroreduction, or coupling with epoxides, and enzymes can be combined with chemocatalysts in cascade or one-pot sequences. Such integrations can improve step economy and resource efficiency when reaction rates, catalyst compatibility, intermediate stability, and separation strategies are well controlled. Nevertheless, combining individually attractive components does not automatically create a sustainable system. (Artz et al., 2018; Bell et al., 2021; Wang et al., 2024). These future directions also introduce important trade-offs. CO_2 conversion requires low-carbon energy and efficient product recovery. Biomass processing requires sustainable land use, controlled pretreatment, and selective upgrading. Electrochemical processes require durable electrodes, membranes, electrolytes, and scalable reactor architectures. Nitrogen and water activation require catalysts that operate efficiently under practical conditions without relying on scarce materials or excessive energy input. Catalysis is therefore necessary but not sufficient; system-level design determines whether these integrations deliver genuine environmental benefits. (Artz et al., 2018; Corma et al., 2007; Nitopi et al., 2019).

In general, the next step in green catalysis will be to move from separate catalytic reactions to chemical systems that are low-carbon, circular, and work together. The most convincing progress will come from combining high selectivity, long-lasting catalysts, renewable energy sources, responsible use of feedstock, efficient separations, and life-cycle assessment. Future green catalysis should therefore be evaluated not only by catalytic activity but also by its ability to reduce total material, energy, and environmental burdens across the complete value chain. (Yenare et al., 2025; Artz et al., 2018).

7.4. From Catalyst Discovery to Process Design

Catalyst discovery must increasingly be integrated with process design in the earliest stages of development. Although activity screening under idealized laboratory conditions can identify promising catalytic systems, process success depends on a broader set of criteria, including selectivity, stability, recoverability, safety, productivity, impurity control, and scalability. A catalyst that produces high conversion in a screening experiment may not be suitable for implementation if it requires dilute conditions, problematic solvents, difficult separation, poor impurity tolerance, or

extensive downstream purification. (García-Serna et al., 2022; Jiménez-González et al., 2012). The future of green catalysis therefore requires a shift from optimizing isolated catalyst performance to designing complete catalytic processes. Academic studies often focus on new ideas and activities, but processes that are useful in industry need to achieve a balance between cost, strength, safety, regulatory acceptability, environmental impact, and consistent product quality. Bridging this gap requires early consideration of solvent choice, substrate concentration, catalyst loading, catalyst separation, feedstock variability, impurity profile, heat and mass transfer, and scale-up behavior. (Becker et al., 2022; Roschangar et al., 2015). A mature green catalysis workflow should combine mechanistic understanding, high-throughput experimentation, operando characterization, reaction engineering, process analytical technology, digital process monitoring, sustainability metrics, life-cycle assessment, and techno-economic analysis. These tools can help identify not only the most active catalyst but also the catalytic system that provides the best performance for a defined product, route, and manufacturing context. (Kralisch et al., 2015; Sheldon, 2018; García-Serna et al., 2022).

Ultimately, the aim of green catalysis is not simply to discover new catalysts but to design catalytic processes that are selective, durable, safe, recoverable, scalable, and demonstrably lower in environmental burden. This process-oriented approach ensures that improvements observed at the molecular or laboratory scale translate into genuine sustainability benefits in practical chemical production. (Yenare et al., 2025; Habib et al., 2023).

CONCLUSION

Catalysis is a fundamental principle of green chemistry, as it provides a molecular basis for waste prevention, selectivity, energy efficiency, safer reagent use, renewable feedstock conversion, and process intensification. However, catalysis should not be considered an automatic indicator of sustainability. The true environmental value of catalysis depends on the **entire context of the process**, including feedstock source, solvent and auxiliary material utility, catalyst composition, active site stability, energy input, separation strategy, product purity, waste treatment, scalability, and life-cycle outcomes.

The primary catalytic platforms should be understood as **complementary rather than hierarchical**:

- **Homogeneous catalysis** offers high tunability and selectivity;
- **Heterogeneous catalysis** enables recovery and continuous operation;
- **Organocatalysis** can avoid transition metal residues and support asymmetric synthesis;
- **Biocatalysis** provides exceptional selectivity under mild conditions;
- **Nanocatalysis and single-atom catalysis** increase active site exposure and metal utilization;
- **MOFs (Metal-Organic Frameworks)** create tunable porous microenvironments;
- **Photocatalysis and electrocatalysis** couple chemical synthesis with light and renewable electricity.

Each platform can solve specific sustainability challenges while introducing new constraints. Therefore, the greenest catalytic choice is route-specific and must be determined by process performance rather than the catalyst class alone.

Metrics and Assessment

Reliable assessment of sustainable catalysis requires **quantitative and comparative metrics**. Atom economy, E-factor, process mass intensity, solvent intensity, energy demand, hazard assessment, life cycle assessment (LCA), and techno-economic analysis (TEA) define different dimensions of performance. Since improvements in one category can increase burdens in another, a single metric is never sufficient. Therefore, a **unified assessment** is imperative to determine when catalysis truly reduces material consumption, waste generation, energy demand, toxicity, and purification burdens, and when further process optimization is required.

Future Outlook

Future progress in green catalysis will depend on **integrating catalyst design with process design** from the earliest stages of development. The most valuable catalysts will not just be the most active ones, but those that are selective, durable,

recoverable, scalable, safe, and compatible with low-impact solvents, renewable energy, and practical separation strategies.

Mechanistic understanding, operando characterization, high-throughput experimentation, reaction engineering, digital process monitoring, life-cycle thinking, and techno-economic analysis will all be fundamental to this development.

Under this integrated framework, catalysis ceases to be merely a "green label"; it transforms into a **disciplined strategy** for designing chemical technologies that are efficient at the molecular level, robust at the process level, and demonstrably lower in environmental and resource burdens across the entire value chain.

SONUÇ

Kataliz, atık önleme, seçicilik, enerji verimliliği, daha güvenli reaktif kullanımı, yenilenebilir ham madde dönüşümü ve proses yoğunlaştırma için moleküler bir temel sağladığından **yeşil kimyanın temel bir ilkesidir**. Ancak kataliz, sürdürülebilirliğin otomatik bir göstergesi olarak değerlendirilmemelidir. Katalizin gerçek çevresel değeri; ham madde kaynağı, çözücü ve yardımcı malzeme kullanımı, katalizör bileşimi, aktif bölge kararlılığı, enerji girdisi, ayırma stratejisi, ürün saflığı, atık arıtımı, ölçeklenebilirlik ve yaşam döngüsü sonuçları dahil olmak üzere **prosesin tüm bağlamına** bağlıdır.

Başlıca katalitik platformlar, hiyerarşik olmaktan ziyade birbirini tamamlayıcı olarak anlaşılmalıdır:

- **Homojen kataliz** yüksek ayarlanabilirlik ve seçicilik sunar;
- **Heterojen kataliz** geri kazanımı ve sürekli çalışmayı mümkün kılar;
- **Organokataliz** geçiş metali kalıntılarından kaçınabilir ve asimetrik sentezi destekleyebilir;
- **Biyokataliz** ılıman koşullar altında olağanüstü seçicilik sağlar;
- **Nanokataliz ve tek atom katalizi** aktif bölge maruziyetini ve metal kullanımını artırır;
- **MOF'lar (Metal-Organik Kafes Yapılar)** ayarlanabilir gözenekli mikro çevreler oluşturur;
- **Fotokataliz ve elektrokataliz** ise kimyasal sentezi ışık ve yenilenebilir elektrikle ilişkilendirir.

Her platform, yeni kısıtlamalar getirirken belirli sürdürülebilirlik sorunlarını çözebilir. Dolayısıyla, en yeşil katalitik seçim **rotaya özgüdür** ve yalnızca katalizör sınıfından ziyade proses performansına göre belirlenmelidir.

Sürdürülebilir katalizin güvenilir bir şekilde değerlendirilmesi, **nicel ve karşılaştırmalı metrikler** gerektirir. Atom ekonomisi, E-faktörü, proses kütle yoğunluğu, çözücü yoğunluğu, enerji talebi, tehlike değerlendirmesi, yaşam döngüsü analizi (LCA) ve tekno-ekonomik analiz (TEA) performansın farklı boyutlarını tanımlar. Tek bir kategorideki iyileştirmeler bir diğerindeki yükleri artırabileceğinden, tek bir metrik asla yeterli değildir. Bu nedenle, katalizin malzeme kullanımını, atık oluşumunu, enerji talebini, toksisiteyi ve saflaştırma yüklerini ne zaman gerçekten azalttığını ve ne zaman daha fazla proses optimizasyonu gerektiğini belirlemek için **birleşik bir değerlendirme** yapılması zorunludur.

Yeşil katalizde gelecekteki ilerleme, geliştirmenin en erken aşamalarından itibaren **katalizör tasarımı ile proses tasarımının entegre edilmesine** bağlı olacaktır. En değerli katalizörler sadece en aktif olanlar değil; seçici, dayanıklı, geri kazanılabilir, ölçeklenebilir, güvenli ve düşük etkili çözücülerle, yenilenebilir enerjiyle ve pratik ayırma stratejileriyle uyumlu olanlar olacaktır. Mekanistik anlayış, operando karakterizasyonu, yüksek verimli deneyler, reaksiyon mühendisliği, dijital proses izleme,

yaşam döngüsü düşüncesi ve tekno-ekonomik analizin tümü bu gelişim için temel öneme sahip olacaktır.

Bu entegre çerçeve altında kataliz, sadece bir "yeşillik etiketi" olmaktan çıkar; moleküler düzeyde verimli, proses düzeyinde sağlam ve tüm değer zinciri boyunca çevresel ve kaynak yükü kanıtlanabilir şekilde daha düşük olan kimyasal teknolojiler tasarlamak için disiplinli bir stratejiye dönüşür.

REFERENCES

1. Ahrendt, K. A., Borths, C. J., & MacMillan, D. W. (2000). New strategies for organic catalysis: the first highly enantioselective organocatalytic Diels– Alder reaction. *Journal of the American Chemical Society*, *122*(17), 4243-4244. https://doi.org/10.1021/ja000092s
2. Alonso, D. M., Bond, J. Q., & Dumesic, J. A. (2010). Catalytic conversion of biomass to biofuels. *Green chemistry*, *12*(9), 1493-1513. https://doi.org/10.1039/C004654J
3. Anastas, P. T., Kirchhoff, M. M., & Williamson, T. C. (2001). Catalysis as a foundational pillar of green chemistry. *Applied Catalysis A: General*, *221*(1-2), 3-13. https://doi.org/10.1016/S0926-860X(01)00793-1
4. Anastas, P., & Eghbali, N. (2010). Green chemistry: principles and practice. *Chemical Society Reviews*, *39*(1), 301-312. https://doi.org/10.1039/B918763B
5. Antenucci, A., Dughera, S., & Renzi, P. (2021). Green chemistry meets asymmetric organocatalysis: a critical overview on catalysts synthesis. *ChemSusChem*, *14*(14), 2785-2853. https://doi.org/10.1002/cssc.202100573
6. Aresta, M., & Dibenedetto, A. (2007). Utilisation of CO_2 as a chemical feedstock: opportunities and challenges. *Dalton Transactions*, (28), 2975-2992. https://doi.org/10.1039/B700658F
7. Artz, J., Müller, T. E., Thenert, K., Kleinekorte, J., Meys, R., Sternberg, A., ... & Leitner, W. (2018). Sustainable conversion of carbon dioxide: an integrated review of catalysis and life cycle assessment. *Chemical Reviews*, *118*(2), 434-504. https://doi.org/10.1021/acs.chemrev.7b00435
8. Astruc, D., Lu, F., & Aranzaes, J. R. (2005). Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis. *Angewandte Chemie International Edition*, *44*(48), 7852-7872. https://doi.org/10.1002/anie.200500766
9. Bakar, B., Buğday, N., Birhanlı, E., Boran, F., Ulu, A., Yaşar, S., ... & Ateş, B. (2024). Facile construction of a robust and recyclable laccase/metal–organic framework-808 with boosted stability for biodegradation of Reactive Blue 171 and Reactive Blue 198 from aqueous media. *Molecular Catalysis*, *562*, 114203. https://doi.org/10.1016/j.mcat.2024.114203
10. Becker, J., Manske, C., & Randl, S. (2022). Green chemistry and sustainability metrics in the pharmaceutical manufacturing sector. *Current Opinion in Green and Sustainable Chemistry*, *33*, 100562. https://doi.org/10.1016/j.cogsc.2021.100562
11. Bell, E. L., Finnigan, W., France, S. P., Green, A. P., Hayes, M. A., Hepworth, L. J., ... & Flitsch, S. L. (2021). Biocatalysis. *Nature Reviews Methods Primers*, *1*(1), 46. https://doi.org/10.1038/s43586-021-00044-z
12. Buğday, N., Altın, S., & Yaşar, S. (2021a). Palladium nanoparticle supported on nitrogen-doped porous carbon: Investigation of structural properties and catalytic activity on Suzuki–Miyaura reactions. *Applied Organometallic Chemistry*, *35*(11), e6403. https://doi.org/10.1002/aoc.6403
13. Buğday, N., Altin, S., & Yaşar, S. (2022a). Porous carbon-supported CoPd nanoparticles: High-performance reduction reaction of nitrophenol. *Applied Organometallic Chemistry*, *36*(8), e6797. https://doi.org/10.1002/aoc.6797
14. Buğday, N., Khan, S., Yaşar, S., & Özdemir, İ. (2021b). CH Bond activation of 2-isobutylthiazole at C5 position catalysed by Pd-N-heterocyclic carbene complexes. *Journal of Organometallic Chemistry*, *937*, 121730. https://doi.org/10.1016/j.jorganchem.2021.121730
15. Buğday, N., Khan, S., Yaşar, S., Bulut, F., Boulebd, H., Karabıyık, H., ... & Özdemir, İ. (2022b). Pd-NHC complex catalyzed CH bond activation reactions of caffeine and 2-isobuthylthiazole. *Molecular Catalysis*, *530*, 112590. https://doi.org/10.1016/j.mcat.2022.112590

16. Buğday, N., Yaşar, S., Altin, S., Duygulu, O., & Önal, Y. (2023). Magnetic Cu/Co nanoparticles supported on nitrogen-doped porous carbon derived from Cu/Co@ aZIF: investigation of catalytic activity and structural properties. *Applied Organometallic Chemistry*, *37*(3), e7017. https://doi.org/10.1002/aoc.7017

17. Buller, R., Lutz, S., Kazlauskas, R. J., Snajdrova, R., Moore, J. C., & Bornscheuer, U. T. (2023). From nature to industry: Harnessing enzymes for biocatalysis. *Science*, *382*(6673), eadh8615. https://doi.org/10.1126/science.adh8615

18. Byrne, F. P., Jin, S., Paggiola, G., Petchey, T. H., Clark, J. H., Farmer, T. J., ... & Sherwood, J. (2016). Tools and techniques for solvent selection: green solvent selection guides. *Sustainable Chemical Processes*, *4*(1), 7. https://doi.org/10.1186/s40508-016-0051-z

19. Chauhan, A., & Srivastava, R. (2025). Biomass valorization with metal-free catalysts: innovations in thermocatalytic, photocatalytic, and electrocatalytic approaches. *Chemical Society Reviews*, *54*(15), 7114-7173. https://doi.org/10.1039/D5CS00304K

20. Chauhan, P., & Chimni, S. S. (2012). Mechanochemistry assisted asymmetric organocatalysis: A sustainable approach. *Beilstein Journal of Organic Chemistry*, *8*(1), 2132-2141. https://doi.org/10.3762/bjoc.8.240

21. Chheda, J. N., Huber, G. W., & Dumesic, J. A. (2007). Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angewandte Chemie International Edition*, *46*(38), 7164-7183. https://doi.org/10.1002/anie.200604274

22. Chong, M. N., Jin, B., Chow, C. W., & Saint, C. (2010). Recent developments in photocatalytic water treatment technology: a review. *Water Research*, *44*(10), 2997-3027. https://doi.org/10.1016/j.watres.2010.02.039

23. Clark, J. H. (1999). Green chemistry: challenges and opportunities. *Green Chemistry*, *1*(1), 1-8. https://doi.org/10.1039/A807961G

24. Clark, J. H. (2002). Solid acids for green chemistry. *Accounts of Chemical Research*, *35*(9), 791-797. https://doi.org/10.1021/ar010072a

25. Clarke, C. J., Tu, W. C., Levers, O., Brohl, A., & Hallett, J. P. (2018). Green and sustainable solvents in chemical processes. *Chemical Reviews*, *118*(2), 747-800. https://doi.org/10.1021/acs.chemrev.7b00571

26. Climent, M. J., Corma, A., & Iborra, S. (2011). Heterogeneous catalysts for the one-pot synthesis of chemicals and fine chemicals. *Chemical Reviews*, *111*(2), 1072-1133. https://doi.org/10.1021/cr1002084

27. Climent, M. J., Corma, A., & Iborra, S. (2014). Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. *Green Chemistry*, *16*(2), 516-547. https://doi.org/10.1039/C3GC41492B

28. Cole-Hamilton, D. J. (2003). Homogeneous catalysis--new approaches to catalyst separation, recovery, and recycling. *Science*, *299*(5613), 1702-1706. https://doi.org/10.1126/science.1081881

29. Constable, D. J., Curzons, A. D., & Cunningham, V. L. (2002). Metrics to 'green' chemistry—which are the best?. *Green Chemistry*, *4*(6), 521-527. https://doi.org/10.1039/B206169B

30. Corma, A., Garcia, H. I., & Llabrés i Xamena, F. X. (2010). Engineering metal organic frameworks for heterogeneous catalysis. *Chemical Reviews*, *110*(8), 4606-4655. https://doi.org/10.1021/cr9003924

31. Corma, A., Iborra, S., & Velty, A. (2007). Chemical routes for the transformation of biomass into chemicals. *Chemical Reviews*, *107*(6), 2411-2502. https://doi.org/10.1021/cr050989d

32. Dalko, P. I., & Moisan, L. (2004). In the golden age of organocatalysis. *Angewandte Chemie International Edition*, *43*(39), 5138-5175. https://doi.org/10.1002/anie.200400650

33. Deshmukh, D. S., Singh, S., Badgujar, K. C., Humne, V. T., Korpe, G. V., & Bhanage, B. M. (2025). Green innovations in C–H bond functionalisation: exploring homogeneous recyclable catalytic systems. *Green Chemistry*, *27*(20), 5667-5708. https://doi.org/10.1039/D5GC00278H

34. Dhakshinamoorthy, A., Li, Z., & Garcia, H. (2018). Catalysis and photocatalysis by metal organic frameworks. *Chemical Society Reviews*, *47*(22), 8134-8172. https://doi.org/10.1039/C8CS00256H

35. Enders, D., Grondal, C., & Hüttl, M. R. (2007). Asymmetric organocatalytic domino reactions. *Angewandte Chemie International Edition*, *46*(10), 1570-1581. https://doi.org/10.1002/anie.200603129

36. Fantozzi, N., Volle, J. N., Porcheddu, A., Virieux, D., García, F., & Colacino, E. (2023). Green metrics in mechanochemistry. *Chemical Society Reviews*, *52*(19), 6680-6714. https://doi.org/10.1039/D2CS00997H

37. Fırat, T., Buğday, N., Yaşar, Ş., Boulebd, H., Mansour, L., Koko, W. S., ... & Yaşar, S. (2024). Bridged NHC-Pd (II) complexes: synthesis, DFT calculations, molecular docking, and investigation of catalytic and biological activities. *Journal of Organometallic Chemistry*, *1011*, 123129. https://doi.org/10.1016/j.jorganchem.2024.123129

38. Friščić, T., Mottillo, C., & Titi, H. M. (2020). Mechanochemistry for synthesis. *Angewandte Chemie*, *132*(3), 1030-1041. https://doi.org/10.1002/ange.201906755

39. Gallezot, P. (2012). Conversion of biomass to selected chemical products. *Chemical Society Reviews*, *41*(4), 1538-1558. https://doi.org/10.1039/C1CS15147A

40. Gallou, F., Gröger, H., & Lipshutz, B. H. (2023). Status check: biocatalysis; its use with and without chemocatalysis. How does the fine chemicals industry view this area?. *Green Chemistry*, *25*(16), 6092-6107. https://doi.org/10.1039/D3GC01931D

41. García-Serna, J., Pinero-Hernanz, R., & Durán-Martín, D. (2022). Inspirational perspectives and principles on the use of catalysts to create sustainability. *Catalysis Today*, *387*, 237-243. https://doi.org/10.1016/j.cattod.2021.11.021

42. Goetjen, T. A., Liu, J., Wu, Y., Sui, J., Zhang, X., Hupp, J. T., & Farha, O. K. (2020). Metal–organic framework (MOF) materials as polymerization catalysts: a review and recent advances. *Chemical Communications*, *56*(72), 10409-10418. https://doi.org/10.1039/D0CC03790G

43. Gómez-López, P., Puente-Santiago, A., Castro-Beltrán, A., do Nascimento, L. A. S., Balu, A. M., Luque, R., & Alvarado-Beltrán, C. G. (2020). Nanomaterials and catalysis for green chemistry. *Current Opinion in Green and Sustainable Chemistry*, *24*, 48-55. https://doi.org/10.1016/j.cogsc.2020.03.001

44. Habib, U., Ahmad, F., Awais, M., Naz, N., Aslam, M., Urooj, M., ... & Shabbir, M. J. (2023). Sustainable catalysis: navigating challenges and embracing opportunities for a greener future. *J. Chem. Environ*, *2*(2), 14-53. https://doi.org/10.56946/jce.v2i2.205

45. Han, B., He, X. H., Liu, Y. Q., He, G., Peng, C., & Li, J. L. (2021). Asymmetric organocatalysis: an enabling technology for medicinal chemistry. *Chemical Society Reviews*, *50*(3), 1522-1586. https://doi.org/10.1039/D0CS00196A

46. Han, F. S. (2013). Transition-metal-catalyzed Suzuki–Miyaura cross-coupling reactions: a remarkable advance from palladium to nickel catalysts. *Chemical Society Reviews*, *42*(12), 5270-5298. https://doi.org/10.1039/C3CS35521G

47. Hisatomi, T., Kubota, J., & Domen, K. (2014). Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chemical Society Reviews*, *43*(22), 7520-7535. https://doi.org/10.1039/C3CS60378D

48. Horváth, I. T., & Anastas, P. T. (2007). Innovations and green chemistry. *Chemical Reviews*, *107*(6), 2169-2173. https://doi.org/10.1021/cr078380v

49. Huang, Y. B., Liang, J., Wang, X. S., & Cao, R. (2017). Multifunctional metal–organic framework catalysts: synergistic catalysis and tandem reactions. *Chemical Society Reviews*, *46*(1), 126-157. https://doi.org/10.1039/C6CS00250A

50. Huber, G. W., Iborra, S., & Corma, A. (2006). Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical Reviews*, *106*(9), 4044-4098. https://doi.org/10.1021/cr068360d

51. James, S. L., Adams, C. J., Bolm, C., Braga, D., Collier, P., Friščić, T., ... & Waddell, D. C. (2012). Mechanochemistry: opportunities for new and cleaner synthesis. *Chemical Society Reviews*, *41*(1), 413-447. https://doi.org/10.1039/C1CS15171A

52. Jana, R., Pathak, T. P., & Sigman, M. S. (2011). Advances in transition metal (Pd, Ni, Fe)-catalyzed cross-coupling reactions using alkyl-organometallics as reaction partners. *Chemical Reviews*, *111*(3), 1417-1492. https://doi.org/10.1021/cr100327p

53. Jessop, P. G. (2011). Searching for green solvents. *Green Chemistry*, *13*(6), 1391-1398. https://doi.org/10.1039/C0GC00797H

54. Jessop, P. G., Jessop, D. A., Fu, D., & Phan, L. (2012). Solvatochromic parameters for solvents of interest in green chemistry. *Green Chemistry*, *14*(5), 1245-1259. https://doi.org/10.1039/C2GC16670D

55. Jiménez-González, C., Constable, D. J., & Ponder, C. S. (2012). Evaluating the "Greenness" of chemical processes and products in the pharmaceutical industry—a green metrics primer. *Chemical Society Reviews*, *41*(4), 1485-1498. https://doi.org/10.1039/C1CS15215G

56. Jimenez-Gonzalez, C., Ponder, C. S., Broxterman, Q. B., & Manley, J. B. (2011). Using the right green yardstick: why process mass intensity is used in the pharmaceutical industry to drive more sustainable processes. *Organic Process Research & Development*, *15*(4), 912-917. https://doi.org/10.1021/op200097d

57. Kalidindi, S. B., & Jagirdar, B. R. (2012). Nanocatalysis and prospects of green chemistry. *ChemSusChem*, *5*(1), 65-75. https://doi.org/10.1002/cssc.201100377

58. Kaur, A., Goyal, A., Kumari, S., Garg, M., Sharma, S., Akram, M., ... & Kumar Sahu, S. (2024). Green chemistry and catalysis: An emerging sustainable approach in synthetic chemistry. In *BIO Web of Conferences* (Vol. 86, p. 01027). EDP Sciences. https://doi.org/10.1051/bioconf/20248601027

59. Khan, S., Buğday, N., Rehman, A. U., Haq, I. U., Yaşar, S., & Özdemir, İ. (2022). Synthesis, molecular docking, and biological evaluation of 5-alkyl (aryl)-2-isobutylthiazole derivatives: As α-amylase, α-glucosidase, and protein kinase inhibitors. *Applied Organometallic Chemistry*, *36*(5), e6641. https://doi.org/10.1002/aoc.6641

60. Khan, S., Buğday, N., Yaşar, S., Ullah, N., & Özdemir, İ. (2021). Pd-N-heterocyclic carbene complex catalysed C–H bond activation of 2-isobutylthiazole at the C5 position with aryl bromides. *New Journal of Chemistry*, *45*(14), 6281-6292. https://doi.org/10.1039/D1NJ00514F

61. Khan, S., Buğday, N., Yaşar, Ş., Haq, I. U., & Yaşar, S. (2023). Synthesis, biological evaluation and molecular docking studies of 8-(hetero) aryl caffeine derivatives. *Journal of Organometallic Chemistry*, *997*, 122794. https://doi.org/10.1016/j.jorganchem.2023.122794

62. Kondratenko, E. V., Mul, G., Baltrusaitis, J., Larrazábal, G. O., & Pérez-Ramírez, J. (2013). Status and perspectives of CO_2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. *Energy & Environmental Science*, *6*(11), 3112-3135. https://doi.org/10.1039/C3EE41272E

63. Konnerth, H., Matsagar, B. M., Chen, S. S., Prechtl, M. H., Shieh, F. K., & Wu, K. C. W. (2020). Metal-organic framework (MOF)-derived catalysts for fine chemical production. *Coordination Chemistry Reviews*, *416*, 213319. https://doi.org/10.1016/j.ccr.2020.213319

64. Kralisch, D., Ott, D., & Gericke, D. (2015). Rules and benefits of life cycle assessment in green chemical process and synthesis design: a tutorial review. *Green Chemistry*, *17*(1), 123-145. https://doi.org/10.1039/C4GC01153H

65. Kurul, F., Doruk, B., & Topkaya, S. N. (2025). Principles of green chemistry: building a sustainable future. *Discover Chemistry*, *2*(1), 68. https://doi.org/10.1007/s44371-025-00152-9

66. Lee, J., Farha, O. K., Roberts, J., Scheidt, K. A., Nguyen, S. T., & Hupp, J. T. (2009). Metal–organic framework materials as catalysts. *Chemical Society Reviews*, *38*(5), 1450-1459. https://doi.org/10.1039/B807080F

67. Li, C. J. (2005). Organic reactions in aqueous media with a focus on carbon– carbon bond formations: a decade update. *Chemical Reviews*, *105*(8), 3095-3166. https://doi.org/10.1021/cr030009u

68. Li, C. J., & Chen, L. (2006). Organic chemistry in water. *Chemical Society Reviews*, *35*(1), 68-82. https://doi.org/10.1039/B507207G

69. Li, C. J., & Trost, B. M. (2008). Green chemistry for chemical synthesis. *Proceedings of the National Academy of Sciences*, *105*(36), 13197-13202. https://doi.org/10.1073/pnas.0804348105

70. Li, J., Chang, H., Ma, L., Hao, J., & Yang, R. T. (2011). Low-temperature selective catalytic reduction of NO_x with NH_3 over metal oxide and zeolite catalysts—A review. *Catalysis today*, *175*(1), 147-156. https://doi.org/10.1016/j.cattod.2011.03.034

71. Lipshutz, B. H., & Abela, A. R. (2008). Micellar catalysis of Suzuki– Miyaura cross-couplings with heteroaromatics in water. *Organic Letters*, *10*(23), 5329-5332. https://doi.org/10.1021/ol801712e

72. Lipshutz, B. H., Taft, B. R., Abela, A. R., Ghorai, S., Krasovskiy, A., & Duplais, C. (2012). Catalysis in the service of green chemistry: Nobel prize-winning palladium-catalysed cross-couplings, run in water at room temperature. *Platinum Metals Review*, *56*(2), 62-74. https://doi.org/10.1595/147106712X629761

73. List, B. (2007). Introduction: organocatalysis. *Chemical Reviews*, *107*(12), 5413-5415. https://doi.org/10.1021/cr078412e

74. List, B., Lerner, R. A., & Barbas, C. F. (2000). Proline-catalyzed direct asymmetric aldol reactions. *Journal of the American Chemical Society*, *122*(10), 2395-2396. https://doi.org/10.1021/ja994280y

75. Liu, J., Chen, L., Cui, H., Zhang, J., Zhang, L., & Su, C. Y. (2014). Applications of metal–organic frameworks in heterogeneous supramolecular catalysis. *Chemical Society Reviews*, *43*(16), 6011-6061. https://doi.org/10.1039/C4CS00094C

76. Liu, M., Wu, J., & Hou, H. (2019). Metal–Organic Framework (MOF)-based materials as heterogeneous catalysts for C– H bond activation. *Chemistry–A European Journal*, *25*(12), 2935-2948. https://doi.org/10.1002/chem.201804149

77. Lozano, P., & García-Verdugo, E. (2023). From green to circular chemistry paved by biocatalysis. *Green Chemistry*, *25*(18), 7041-7057. https://doi.org/10.1039/D3GC01878D

78. MacMillan, D. W. (2008). The advent and development of organocatalysis. *Nature*, *455*(7211), 304-308. https://doi.org/10.1038/nature07367

79. Mitchell, S., & Pérez-Ramírez, J. (2021). Atomically precise control in the design of low-nuclearity supported metal catalysts. *Nature Reviews Materials*, *6*(11), 969-985. https://doi.org/10.1038/s41578-021-00360-6

80. Miyaura, N., & Suzuki, A. (1995). Palladium-catalyzed cross-coupling reactions of organoboron compounds. *Chemical Reviews*, *95*(7), 2457-2483. https://doi.org/10.1021/cr00039a007

81. Molnár, Á. (2011). Efficient, selective, and recyclable palladium catalysts in carbon–carbon coupling reactions. *Chemical Reviews*, *111*(3), 2251-2320. https://doi.org/10.1021/cr100355b

82. Narayanan, R., & El-Sayed, M. A. (2005). Catalysis with transition metal nanoparticles in colloidal solution: nanoparticle shape dependence and stability. *The Journal of Physical Chemistry B*, *109*(26), 12663-12676. https://doi.org/10.1021/jp051066p

83. Nitopi, S., Bertheussen, E., Scott, S. B., Liu, X., Engstfeld, A. K., Horch, S., ... & Chorkendorff, I. (2019). Progress and perspectives of electrochemical CO_2 reduction on copper in aqueous electrolyte. *Chemical Reviews*, *119*(12), 7610-7672. https://doi.org/10.1021/acs.chemrev.8b00705

84. Pascanu, V., González Miera, G., Inge, A. K., & Martín-Matute, B. (2019). Metal–organic frameworks as catalysts for organic synthesis: a critical perspective. *Journal of the American Chemical Society*, *141*(18), 7223-7234. https://doi.org/10.1021/jacs.9b00733

85. Phan, N. T., Van Der Sluys, M., & Jones, C. W. (2006). On the nature of the active species in palladium catalyzed Mizoroki–Heck and Suzuki–Miyaura couplings–homogeneous or heterogeneous catalysis, a critical review. *Advanced Synthesis & Catalysis*, *348*(6), 609-679. https://doi.org/10.1002/adsc.200505473

86. Poliakoff, M., Fitzpatrick, J. M., Farren, T. R., & Anastas, P. T. (2002). Green chemistry: science and politics of change. *Science*, *297*(5582), 807-810. https://doi.org/10.1126/science.297.5582.807

87. Polshettiwar, V., & Varma, R. S. (2010). Green chemistry by nano-catalysis. *Green Chemistry*, *12*(5), 743-754. https://doi.org/10.1039/B921171C

88. Polshettiwar, V., Luque, R., Fihri, A., Zhu, H., Bouhrara, M., & Basset, J. M. (2011). Magnetically recoverable nanocatalysts. *Chemical Reviews*, *111*(5), 3036-3075. https://doi.org/10.1021/cr100230z

89. Prat, D., Wells, A., Hayler, J., Sneddon, H., McElroy, C. R., Abou-Shehada, S., & Dunn, P. J. (2016). CHEM21 selection guide of classical-and less classical-solvents. *Green Chemistry*, *18*(1), 288-296. https://doi.org/10.1039/C5GC01008J

90. Roger, I., Shipman, M. A., & Symes, M. D. (2017). Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nature Reviews Chemistry*, *1*(1), 0003. https://doi.org/10.1038/s41570-016-0003

91. Roschangar, F., Sheldon, R. A., & Senanayake, C. H. (2015). Overcoming barriers to green chemistry in the pharmaceutical industry–the Green Aspiration Level™ concept. *Green Chemistry*, *17*(2), 752-768. https://doi.org/10.1039/C4GC01563K

92. Sajini, T., & Joseph, J. (2025). Microwave-assisted synthesis of nanomaterials: a green chemistry perspective and sustainability assessment. *RSC Sustainability*, *3*(11), 4911-4935. https://doi.org/10.1039/D5SU00584A

93. Sakakura, T., Choi, J. C., & Yasuda, H. (2007). Transformation of carbon dioxide. *Chemical Reviews*, *107*(6), 2365-2387. https://doi.org/10.1021/cr068357u

94. Sánchez-Velandia, J. E., Gallego-Villada, L. A., Mäki-Arvela, P., Sidorenko, A., & Yu. Murzin, D. (2025). Upgrading biomass to high-added value chemicals: synthesis of monoterpenes-based compounds using catalytic green chemical pathways. *Catalysis Reviews*, *67*(2), 371-496. https://doi.org/10.1080/01614940.2024.2329553

95. Seh, Z. W., Kibsgaard, J., Dickens, C. F., Chorkendorff, I. B., Nørskov, J. K., & Jaramillo, T. F. (2017). Combining theory and experiment in electrocatalysis: Insights into materials design. *Science*, *355*(6321), eaad4998. https://doi.org/10.1126/science.aad4998

96. Serp, P., Corrias, M., & Kalck, P. (2003). Carbon nanotubes and nanofibers in catalysis. *Applied Catalysis A: General*, *253*(2), 337-358. https://doi.org/10.1016/S0926-860X(03)00549-0

97. Sheldon, R. A. (2017). The E factor 25 years on: the rise of green chemistry and sustainability. *Green Chemistry*, *19*(1), 18-43. https://doi.org/10.1039/C6GC02157C

98. Sheldon, R. A. (2018). Metrics of green chemistry and sustainability: past, present, and future. *ACS Sustainable Chemistry & Engineering*, *6*(1), 32-48. https://doi.org/10.1021/acssuschemeng.7b03505

99. Sheldon, R. A., & Woodley, J. M. (2018). Role of biocatalysis in sustainable chemistry. *Chemical Reviews*, *118*(2), 801-838. https://doi.org/10.1021/acs.chemrev.7b00203

100. Somorjai, G. A., & Park, J. Y. (2008). Colloid science of metal nanoparticle catalysts in 2D and 3D structures. Challenges of nucleation, growth, composition, particle shape, size control and their influence on activity and selectivity. *Topics in Catalysis*, *49*(3), 126-135. https://doi.org/10.1007/s11244-008-9077-0

101. Tamargo, R. J. I., Cosiñero, H. S. O., Potato, D. N. C., & Dumrigue, A. H. P. (2024). Metrics of green chemistry and sustainability. *Sustainable Green Catalytic Processes*, 225-258. https://doi.org/10.1002/9781394212767.ch10

102. Tanaka, K., & Toda, F. J. C. R. (2000). Solvent-free organic synthesis. *Chemical Reviews*, *100*(3), 1025-1074. https://doi.org/10.1021/cr940089p

103. Tobiszewski, M., Marć, M., Gałuszka, A., & Namieśnik, J. (2015). Green chemistry metrics with special reference to green analytical chemistry. *Molecules*, *20*(6), 10928-10946. https://doi.org/10.3390/molecules200610928

104. Thomas, J.M., & Raja, R. (2005). Designing catalysts for clean technology, green chemistry, and sustainable development. *Annu. Rev. Mater. Res.*, *35*(1), 315-350. https://doi.org/10.1146/annurev.matsci.35.102003.140852

105. Torborg, C., & Beller, M. (2009). Recent applications of palladium-catalyzed coupling reactions in the pharmaceutical, agrochemical, and fine chemical industries. *Advanced Synthesis & Catalysis*, *351*(18), 3027-3043. https://doi.org/10.1002/adsc.200900587

106. Trost, B. M. (1991). The atom economy—a search for synthetic efficiency. *Science*, *254*(5037), 1471-1477. https://doi.org/10.1126/science.1962206

107. Van Putten, R. J., Van Der Waal, J. C., De Jong, E. D., Rasrendra, C. B., Heeres, H. J., & de Vries, J. G. (2013). Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. *Chemical Reviews*, *113*(3), 1499-1597. https://doi.org/10.1021/cr300182k

108. Walsh, P. J., Li, H., & de Parrodi, C. A. (2007). A green chemistry approach to asymmetric catalysis: solvent-free and highly concentrated reactions. *Chemical Reviews*, *107*(6), 2503-2545. https://doi.org/10.1021/cr0509556

109. Wang, A., Li, J., & Zhang, T. (2018). Heterogeneous single-atom catalysis. *Nature Reviews Chemistry*, *2*(6), 65-81. https://doi.org/10.1038/s41570-018-0010-1

110. Wang, G. W. (2013). Mechanochemical organic synthesis. *Chemical Society Reviews*, *42*(18), 7668-7700. https://doi.org/10.1039/C3CS35526H

111. Wang, M., Zhang, G., Wang, H., Wang, Z., Zhou, Y., Nie, X., ... & Guo, X. (2024). Understanding and Tuning the Effects of H_2O on Catalytic CO and CO_2 Hydrogenation. *Chemical Reviews*, *124*(21), 12006-12085. https://doi.org/10.1021/acs.chemrev.4c00282

112. Wang, Q., & Astruc, D. (2019). State of the art and prospects in metal–organic framework (MOF)-based and MOF-derived nanocatalysis. *Chemical Reviews*, *120*(2), 1438-1511. https://doi.org/10.1021/acs.chemrev.9b00223

113. Welton, T. (1999). Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chemical Reviews*, *99*(8), 2071-2084. https://doi.org/10.1021/cr980032t

114. Wu, S., Snajdrova, R., Moore, J. C., Baldenius, K., & Bornscheuer, U. T. (2021). Biocatalysis: enzymatic synthesis for industrial applications. *Angewandte Chemie International Edition*, *60*(1), 88-119. https://doi.org/10.1002/anie.202006648

115. Yagmurlu, A., Buğday, N., Yaşar, Ş., Boulebd, H., Mansour, L., Koko, W. S., ... & Yaşar, S. (2024). Synthesis, DFT calculations, and investigation of catalytic and biological activities of back-bond functionalized re-NHC-Cu complexes. *Applied Organometallic Chemistry*, *38*(7), e7545. https://doi.org/10.1002/aoc.7545

116. Yang, X. F., Wang, A., Qiao, B., Li, J. U. N., Liu, J., & Zhang, T. (2013). Single-atom catalysts: a new frontier in heterogeneous catalysis. *Accounts of Chemical Research*, *46*(8), 1740-1748. https://doi.org/10.1021/ar300361m

117. Yenare, P. P., Patare, R. D., Sonawane, B. P., & Sanap, K. K. (2025). Green chemistry innovation: a systematic review on sustainable catalysis and its strategic future directions. *Catalysis Science & Technology*. **15**, 7295-7323. https://doi.org/10.1039/D5CY00559K

118. Yu, W., Lu, Z., Jiang, H., Li, A., & Chen, L. (2025). Metal-organic framework composites for green catalysis: Coordination chemistry approaches to sustainable energy and environmental solutions. *Coordination Chemistry Reviews*, *542*, 216864. https://doi.org/10.1016/j.ccr.2025.216864

119. Zaera, F. (2013). Nanostructured materials for applications in heterogeneous catalysis. *Chemical Society Reviews*, *42*(7), 2746-2762. https://doi.org/10.1039/C2CS35261C

120. Zakzeski, J., Bruijnincx, P. C., Jongerius, A. L., & Weckhuysen, B. M. (2010). The catalytic valorization of lignin for the production of renewable chemicals. *Chemical Reviews*, *110*(6), 3552-3599. https://doi.org/10.1021/cr900354u

121. Zhang, L., Ren, Y., Liu, W., Wang, A., & Zhang, T. (2018). Single-atom catalyst: a rising star for green synthesis of fine chemicals. *National Science Review*, *5*(5), 653-672. https://doi.org/10.1093/nsr/nwy077

CATALYTIC VALORIZATION OF LIGNOCELLULOSIC BIOMASS AS RENEWABLE FEEDSTOCKS WITHIN GREEN CHEMISTRY PRINCIPLES

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ABSTRACT

The increasing demand for sustainable chemical production has intensified interest in renewable feedstocks as alternatives to fossil-based resources. Lignocellulosic biomass, due to its abundance, renewability, and carbon-neutral nature, represents a key platform for green and sustainable chemical processes. Within the framework of Green Chemistry Principle No. 7—the use of renewable feedstocks—this chapter focuses on the catalytic valorization of lignocellulosic biomass for the production of value-added chemicals. Emphasis is placed on the development and application of environmentally benign catalysts that enable efficient, selective, and low-impact conversion pathways. The chapter critically discusses biomass composition, pretreatment strategies, catalyst design, and green catalytic processes aligned with sustainability metrics. By bridging fundamental catalysis with green chemistry principles, this contribution highlights lignocellulosic biomass as a practical and scalable renewable feedstock for future sustainable chemical technologies.

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1. INTRODUCTION

Biomass is not a recently discovered form of alternative energy. In fact, it has been used since the beginning of human civilisation. It was first used for heating, cooking, and so on. For centuries, biomass resources such as wood and plants, along with oils and products derived from them, such as turpentine, were used. However, the proven efficiency and practicality of coal and crude oil for everyday use led to a decline in the use of biomass and an increase in the use of fossil fuels. Fossil fuels became the preferred fuel in most countries, topping the list of energy consumers until the 1970s (Smith, 2019). The consequences of the 1973 Arab-Israeli conflict had a long-lasting impact on the global economy and politics. OPEC, led by Saudi Arabia, imposed an oil embargo and reduced oil production by 5% each month. This caused the price of refined petroleum products to rise, with the price of gasoline increasing by an average of 57% between 1972 and 1975. The domino effect of the oil embargo forced chemical industries worldwide to seek alternative sources of surface carbon for production (Bueno Moron et al., 2025). Besides economic factors, biomass is considered a viable alternative to fossil fuels for fuel and chemical production due to the depletion of fossil fuel reserves and the environmental pollution they cause, including global warming (Chowdhury et al., 2025).

Biomass is produced through the process of photosynthesis, using sunlight, water, and carbon dioxide. As an abundant and ubiquitous resource, biomass is the only renewable source of organic carbon. Using biomass as a raw material is essential for transitioning to a circular bioeconomy (Anakwenze et al., 2026). Green chemistry aims to increase sustainability and reduce environmental impacts by using renewable materials in chemical processes. Given as an example of a renewable resource, biomass has the potential to be used for various applications, including the production of biofuels, bioenergy, biomolecules, biomaterials, and biological products (Isikgor & Becer, 2015).

This section will discuss the importance of lignocellulosic biomass (LCB) as a sustainable carbon source and renewable raw material in the context of the 7th Principle of Green Chemistry. It will also provide information on its structure, pretreatments, catalytic processes, products obtained from LCB, and its potential future applications.

2. GREEN CHEMISTRY PRINCIPLE NO. 7: USE OF RENEWABLE FEEDSTOCKS DEFINITION AND SIGNIFICANCE

Today, chemical products derived from fossil fuels have become an integral part of life. Organic chemicals such as methanol, ethylene, and propylene are the building blocks of the chemical industry. The demand for more sustainable chemicals has led to many research projects investigating the processing of renewable raw materials to produce these building block chemicals and final products (Lopez et al., 2023). The industrial application of the seventh principle of green chemistry is particularly important in terms of the Earth's carbon balance. Increased carbon

emissions cause an increase in the average global temperature. Carbon traps the heat emitted by the Earth while allowing sunlight to penetrate (Choudhury et al., 2023). Fossil fuel sources, such as oil, natural gas, and coal, contain carbon that has been present on Earth for millions of years. Extracting and processing this carbon adds 'new' carbon to our atmosphere, thereby altering the global carbon balance. In contrast, renewable carbon sources ensure a net carbon balance by circulating carbon that is already present in the atmosphere and biosphere. It is essential that these building block chemicals are gradually replaced by biomass from fossil fuel sources (Clark et al., 2015).

The use of renewable raw materials, as set out in the 7th principle of green chemistry, facilitates the transition from a linear to a circular economy model. The linear economy (LE) is based on the 'take-produce-use-dispose' model, also known as 'cradle-to-grave'. In this model, the economic priority is the single use of raw materials. The circular economy, on the other hand, optimises material consumption in line with sustainability principles. In this model, the useful life of materials is extended through reuse, recycling, and recovery, using a cradle-to-cradle approach (Harris et al., 2025; Neves & Marques, 2022). The circular economy model makes it possible to achieve carbon balance. Life Cycle Assessment (LCA) can be used to evaluate processes according to the circular economy model. LCA is an analytical tool that quantifies the environmental impacts of a product or service throughout its entire life cycle – from raw material extraction and production to use and disposal (Curran, 2013).

3. LIGNOCELLULOSIC BIOMASS: STRUCTURE AND COMPOSITION CELLULOSE, HEMICELLULOSE, AND LIGNIN AVAILABILITY AND RESOURCE POTENTIAL

LCB is the primary structural component of plant cell walls and one of the most abundant sources of renewable organic carbon in nature. Plants convert carbon dioxide absorbed from the atmosphere through photosynthesis into organic compounds, which they store in their cell walls, thereby forming continuously renewable LCB. This biological process makes LCB a key component of the biological carbon cycle while also positioning it as a strategic carbon source for sustainable bio-based production (Makaveckas et al., 2025; Wang et al., 2023).

The key characteristic that distinguishes LCB from other biological materials is its hierarchical biocomposite structure composed of cellulose, hemicellulose, and lignin. Rather than being randomly distributed within the cell wall, these biopolymers assemble in a specific structural organization, thereby determining the biomass's mechanical strength, chemical stability, and resistance to biological degradation. Therefore, the structural properties of LCB are shaped not only by the chemical structures of its components but also by their organization within the cell wall and their interactions with one another (Carpita & McCann, 2020; Wang et al., 2021).

The plant cell wall consists of two main layers: the primary and secondary cell walls, depending on the stage of development. While the primary cell wall is a thin

and flexible structure found in cells that continue to grow, the secondary cell wall, which forms in later stages of development, exhibits a thicker and more durable structure. The characteristic properties of LCB stem largely from the secondary cell wall. The primary components of this layer are structural polysaccharides such as cellulose and hemicellulose, along with the phenolic biopolymer lignin. While cellulose microfibrils form the mechanical skeleton of the cell wall, hemicellulose creates a binding polysaccharide matrix between these microfibrils. Lignin, in turn, embeds itself within this polysaccharide network, imparting stiffness, hydrophobic properties, and resistance to biological degradation to the cell wall. Therefore, understanding the structure and properties of the LCB requires a separate evaluation of the structural characteristics of cellulose, hemicellulose, and lignin—the components of the cell wall—as well as their respective functions within the cell wall (de Souza et al., 2023; Guerriero et al., 2016; Isikgor & Becer, 2015).

3.1. Cellulose

Cellulose is the primary structural polysaccharide that forms the supporting skeleton of the plant cell wall. It is found in high concentrations, particularly in the secondary cell wall, and accounts for approximately 35–50% of the dry weight of the cell wall, depending on the plant species. Its linear molecular structure makes cellulose the primary biopolymer that forms the supporting framework of the plant cell wall (Marinho, 2025; Sulis et al., 2025).

Chemically, cellulose is a linear homopolysaccharide composed of glucose units linked by β-(1→4) glycosidic bonds. The hydroxyl groups present along the chain facilitate the formation of intramolecular and intermolecular hydrogen bonds, allowing cellulose chains to assemble in an orderly manner. This ordered organization results in the formation of elementary fibrils, which in turn combine to form microfibrils; these microfibrils constitute the fundamental scaffold that provides the mechanical strength of the plant cell wall (Marinho, 2025). Cellulose has a semicrystalline structure composed of crystalline and amorphous regions. While cellulose chains in crystalline regions are highly ordered and tightly packed, chain organization in amorphous regions is more disordered. The distribution of crystalline and amorphous regions within the cell wall is one of the key factors determining the characteristic structural and physical properties of cellulose (Carpita & McCann, 2020; Wang et al., 2024).

3.2. Hemicellulose

Hemicellulose is the second most abundant group of structural polysaccharides in the plant cell wall, after cellulose. Depending on the plant species and the composition of the cell wall, it accounts for approximately 20–35% of the cell wall's dry weight. Hemicellulose, found in both primary and secondary cell walls, is one of the main components of the matrix phase surrounding cellulose microfibrils (Fertonani et al., 2025; He et al., 2024).

In terms of its chemical structure, hemicellulose is a group of polysaccharides comprising branched heteropolysaccharides formed by the combination of various monosaccharides in varying proportions. In this respect, it differs from cellulose, which has a specific repeating unit. Its structure primarily consists of xylose, mannose, glucose, galactose, arabinose, and uronic acid derivatives. Depending on the plant species, xylans, mannans, glucomannans, and xyloglucans constitute the main components of hemicellulose (Gautam et al., 2025). Unlike cellulose, hemicellulose has shorter polymer chains and a lower degree of polymerization. In the plant cell wall, hemicellulose interacts with cellulose microfibrils, contributing to the organization of the cell wall matrix. This structural arrangement helps maintain the integrity of the cell wall and contributes to the formation of its mechanical properties. The monosaccharide composition and degree of branching of hemicellulose vary depending on the plant species and the developmental stage of the cell wall. Differences in monosaccharide composition and degree of branching play a significant role in determining the organization of hemicellulose within the cell wall matrix and its interactions with other cell wall components (Carpita & McCann, 2020; Gautam et al., 2025).

3.3. Lignin

Lignin is the primary aromatic biopolymer that confers mechanical strength and hydrophobic properties to the cell wall. Found in high concentrations particularly in the secondary cell wall, lignin accounts for approximately 15–30% of the cell wall's dry weight, depending on the plant species. In addition to maintaining the structural integrity of the cell wall, it plays a significant role in the functioning of the vascular tissues (Vásquez-Garay et al., 2021). The basic building blocks of lignin consist of three different monolignols: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These monolignols link together in various ways to form a three-dimensional, amorphous polymer network characteristic of lignin. As a result of polymerization, p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) structural units are formed, respectively. These structural units are the fundamental components that make up the chemical structure of lignin (Karunarathna & Smith, 2020). In the plant cell wall, lignin is located between the cellulose microfibrils and the hemicellulose matrix, contributing to the mechanical properties and structural integrity of the cell wall. Thanks to its aromatic polymer structure, it imparts hydrophobic properties to the cell wall and plays a particularly important role in the formation of the functional properties of the secondary cell wall. Depending on the plant species, variations in the monolignol composition affect the chemical structure and structural organization of lignin, leading to diversity among different plant species (Emonet & Hay, 2022).

3.4. Availability and Resource Potential

Each year there are billions of metric tons of plant biomass created as a result of agricultural production, forestry and bio-based industries. What was considered low value waste before becomes a valuable renewable carbon resource for biofuels, biochemicals and other bio-based products. Besides high productivity, LCB has

another advantage – it can be produced continuously and from different biological sources (Mujtaba et al., 2023).

The main sources of LCB are agricultural residues, forestry biomass, energy crops, industrial lignocellulosic byproducts, and the lignocellulosic fraction of municipal solid waste. The main sources of agricultural residues are straws, stalks, cobs and husks from harvesting of such plants as wheat, corn and rice. Forestry biomass includes woody materials like wood, bark, branches, pruning waste and wood chips. The sources of energy crops are species used for obtaining high yields of biomass. Industrial byproducts refer to lignocellulosic materials from pulp and paper, and wood industries mainly from sugarcane bagasse. The fraction of municipal solid waste that can be degraded to bioenergy and other products (paper, cardboard and yard waste) is the major source of lignocellulosic feedstock (Broda et al., 2022; Ge et al., 2011; Zabed et al., 2019). Such diverse sources of LCB are the basis for its high production potential. Approximately 181.5 billion metric tons of LCB are produced annually in the world, and only 8.2 billion metric tons of it is used. This proves that there is plenty of unused LCB potential. The effective use of it would lead to more efficient use of regional resources, renewable carbon sources and production of high value bio-based products (Trezza et al., 2025).

The reason for wide geographic distribution of LCB is the common practice of agricultural production, forestry and bio-based industries in many parts of the world. Among the leading countries in this matter are China, USA, Brazil and India (Zhao et al., 2022). Therefore, in contrast to fossil resources which are confined to certain deposits, LCB is continuously produced in almost any region where the production of plant-based materials is carried out. This makes it possible to source raw materials locally and create supply chains in the region. Also, the possibility to use biological residues created during the production process as raw materials creates a condition for developing the concept of circular bioeconomy. The fact that a significant part of LCB consists of such residual biomass reduces the dependence on the first generation biomass resources and direct competition with food production. Having such properties, LCB appears to be not only an abundant raw material but also a strategically important resource for creating sustainable and renewable carbon-based production systems (Albashabsheh & Stamm, 2021; Trezza et al., 2025).

3.5. Challenges in Biomass Utilization

The major issue that affects the production of bio-based products from LCB is biomass recalcitrance, meaning that the structure of biomass prevents its utilization. This resistance to breakdown results from the influence of physical and chemical properties of the cell wall. One of the most influential factors causing recalcitrance is a physical barrier created by lignin. Lignin creates a hydrophobic structure around the polysaccharides in the cell wall, thus preventing the penetration of chemicals and hydrolytic enzymes into the inner parts of the cell wall (Deng et al., 2023; Wang et al., 2021). Another factor that affects the structure of biomass is LCC (lignin-carbohydrate complexes), which are formed between lignin and carbohy-

drates. LCC increases the structural resistance of the cell wall by creating different covalent bonds between lignin and hemicellulose, as well as to some extent between lignin and cellulose, hence complicating the process of separation of lignin from polysaccharides. This not only makes it harder to remove lignin during pretreatment but also limits the access to cellulose (Abolore et al., 2024; Ren et al., 2024). The crystallinity of cellulose also contributes to recalcitrance significantly. Due to the presence of hydrogen bonds between cellulose chains in the crystalline parts, the cellulose is tightly arranged. Such arrangement hinders the access of enzymes and chemicals to the cellulose chains, thus decreasing the hydrolysis and sugar conversion (Mujtaba et al., 2023). The lack of porosity of the cell wall is another factor that limits the process of biomass breakdown due to the difficulty of reagent diffusion into the cell wall. The insufficient pore volume makes it hard for cellulase enzymes (especially large ones) to reach the inner part of the cell wall (Deng et al., 2023). Furthermore, LCB's low specific surface area is another problem because it decreases the amount of reactive surface, making it difficult for chemicals to react with the biomass (Mujtaba et al., 2023).

4. PRETREATMENT STRATEGIES FOR LIGNOCELLULOSIC BIOMASS GREEN PRETREATMENT APPROACHES

When producing biofuels from LCB, it is necessary to use a pretreatment approach to separate the resistant and complex structures that hold cellulose, hemicellulose, and lignin together, and prevent their breakdown. Pretreating biomass is a crucial step in increasing carbohydrate yield. Lignin, a component of LCB, creates a barrier that hinders the action of enzymes, necessitating its separation through an effective pretreatment method (Saravanan et al., 2022). Pretreatment plays a significant role in preparing the biomass for enzymatic hydrolysis and depolymerisation by separating its main components (Barakat et al., 2014). Pretreatment is initiated to achieve one or more of the following: dissolution of hemicellulose and/or lignin, modification of lignin structure, reduction of particle size and increase of surface area, and reduction of the crystalline structure of cellulose (Rajendran et al., 2018). Pretreatment techniques for LCB generally employ physical, chemical, and biological methods. These methods can be employed individually or in combination, for example, in physical-chemical or chemical-biological processes (Meenakshisundaram et al., 2022).

4.1. Physical Methods

The main purpose of physical methods is to increase the surface area of lignocellulosic biomass by reducing its particle size through processes such as grinding and extrusion. The methods also aim to reduce the degree of polymerisation and crystallinity through microwave and ultrasonic treatments. Physical methods have the advantage of being environmentally friendly; however, their main disadvantage is their high energy consumption (Baruah et al., 2018).

Extrusion

During extrusion pretreatment, biomass is processed in an extruder while being mixed at various shear and temperature settings, depending on the screw design. Physical pretreatment using an extruder can be employed either independently or in combination with chemical or biological pretreatment (Karimipour-Fard et al., 2024). A study investigating key extrusion factors and sugar yield improvement found that optimum glucose, xylose, and combined sugar recoveries were 48.79%, 24.98% and 40.07%, respectively, at a moisture content of 27.50% and screw speed of 80 rpm. The surface area of the pretreated samples was reported to have increased significantly compared to the control samples (from 73.20 m^2/g to 438.50 m^2/g) (Zhang et al., 2012). Another study investigated the alkali effect during the extrusion process by pumping a NaOH solution into the extruder at a ratio of 6 g NaOH/100 g dry wheat straw. This resulted in increased cellulose content (46.90% in the straw extruder and 37.80% in untreated straw) and decreased lignin content (15.40% in the straw extruder and 19.80% in untreated straw). As a result of these changes in pretreatment, the enzymatic digestibility of wheat straw increased 13-fold for glucan and 11-fold for xylan hydrolysis compared to the untreated material (Coimbra et al., 2016).

Ultrasound

Ultrasound is produced using piezoelectric transducers. These materials vibrate in response to an alternating current, creating pressure waves. These pressure waves have regions of compression (high pressure) and regions of dilution (low pressure), which lead to the separation of liquid molecules and the formation of bubbles. When these bubbles reach a critical size, they collapse inwards, releasing a large amount of energy and creating conditions of high pressure (1000 atm) and high temperature (5000 K), known as 'hot spots' (Bussemaker & Zhang, 2013; Nalawade & Gogate, 2024). In their study, García et al. applied ultrasound treatment to different solvents (water, acetic acid, and sodium hydroxide) to evaluate its effect on various fractionation processes. For the water and acetic acid processes, they observed that a higher delignification rate was achieved with ultrasound, with lignin removal increasing from 17.30% to 45.60%. The use of ultrasound in fractionation processes has been found to have an effect on the physicochemical properties of the resulting products (García et al., 2011).

Grinding

Grinding is the most effective method of reducing biomass size; it produces particles smaller than 1 mm. This significantly increases the surface area and reactivity of the material. Various types of grinders can be used for this process, including disc mills, wet disc mills, hammer mills, drum ball mills, planetary ball mills, vibrating ball mills, roller mills, rod mills, and jet mills (Di Domenico et al., 2025). Zhang et al. pre-processed cotton and corn stalks in a ball mill. The resulting compositions were 43.64% cellulose, 10.85% hemicellulose, and 19.90% lignin for cotton stalks, and 34.72% cellulose, 18.53% hemicellulose, and 20.12% lignin for corn stalks.

They concluded that there was no statistically significant difference between the pretreated and untreated materials for both raw materials alone. In continuation of the study, alkali was added to the medium. The results showed that the lignin removal rate increased gradually with higher alkali concentrations and that, compared to conventional NaOH pretreatment, pretreatment with alkali-assisted ball milling yielded comparable lignin removal rates and higher hemicellulose removal rates without requiring additional solvent or heating (Zhang et al., 2025).

Microwave Irradiation

Microwave irradiation is a physical method used to pretreat lignocellulosic biomass in an electromagnetic field. The earliest studies to apply microwave irradiation are those of Ooshima et al. (1984) (Ooshima et al., 1984) and Azuma et al. (1984) (Azuma et al., 1984). Microwaves (MW) are a form of electromagnetic energy located between infrared and radio frequencies in the electromagnetic spectrum, with wavelengths between 1 cm and 1 m (Kostas et al., 2017). The cellulose in the lignocellulosic biomass structure is polar when exposed to an electric field. When this energy vibrates, the molecules heat up strongly, creating hot spots. The resulting high heat and vibration lead to the degradation of the lignocellulosic biomass structure (Aguilar-Reynosa et al., 2017). Advantages of using microwave irradiation as a pretreatment include ease of use, low energy requirements, rapid heating, minimal inhibitor formation, and cellulose structure degradation (Kumar & Sharma, 2017).

4.2. Chemical Pretreatment

Alkaline Pretreatment

Alkaline pretreatment is a chemical pretreatment method based on treating lignocellulosic biomass with an alkaline solution. Alkaline pretreatment methods are generally performed at ambient temperature and pressure. Alkaline pretreatment involves a saponification reaction that helps break the ester bonds between hemicellulose and lignin and cellulose. As a result of the reaction, hemicellulose and lignin dissolve in the alkaline solution. The swelling of lignocellulose helps to increase the surface area by reducing the overall crystallinity and degree of polymerization of the biomass structure. Various alkaline reagents commonly used for alkaline pretreatment are sodium, potassium, calcium, and ammonium hydroxides (Baruah et al., 2018; Kumar & Sharma, 2017; Roy et al., 2020). A study using NaOH as an alkali investigated the determination of pretreatment time, solid/liquid ratio, and NaOH concentration that would increase enzymatic saccharification and ethanol fermentation of hazelnut shells. Maximum glucose recovery (48.33 g/100 g cellulose) was achieved with 6% NaOH for 72 hours at a solid/liquid ratio of 1/10. Under these conditions, it was determined that 41.18% of lignin was removed (Hosgün et al., 2017).

Acidic Pretreatment

Acid pretreatment of lignocellulosic biomass is a chemical process that breaks down the structure by severing glycosidic bonds using either organic or inorganic

acids. Although it can be performed with either concentrated or dilute acid, the use of the former leads to the formation of inhibitory compounds such as furfural, 5-hydroxymethylfurfural, phenolic acids, and aldehydes. Concentrated acid is also toxic and corrosive, requiring corrosion-resistant equipment (Maurya et al., 2015). The effects of reaction temperature (75-175 °C), reaction time (0-7.2 hours), solution-feed ratio (4–20 mL/g), and phosphoric acid concentration (0–6.67% by weight) variables on xylose yield by applying phosphoric acid pretreatment to pine sawdust were investigated by Cao et al. They reported that maximum xylose production (90.95%) was obtained at a reaction temperature of 106.7 °C, reaction time of 4.57 hours, phosphoric acid concentration of 4.49%, and solution feed rate of 12.51 mL/g (Cao et al., 2018).

Organic Solvents

Pure lignin, cellulose, and hemicellulose can be obtained using organic solvents or water-organic solvent mixtures in the presence of an inorganic acid catalyst. Methanol, ethanol, acetone, glycerin, ethylene glycol, triethylene glycol, and tetrahydrofurfuryl alcohol are chemicals that can be used as organic solvents (Baksi et al., 2023). During pretreatment with organic solvents, the lignocellulosic biomass separates into its major macromolecular structures due to the breaking of the internal bonds of lignin and hemicellulose. Two main separations occur in this process. First, the biomass is treated with an organic solvent, which breaks down much of the lignin and hemicellulose into small particles with a low molecular weight that dissolve in the solvent as a liquid. Secondly, the lignin-rich liquids are diluted, dried, and precipitated to obtain xylose and high-purity lignin (Zhang et al., 2016). The advantages of pretreatment with organic solvents include easy solvent recovery and the ability to isolate both lignin as a solid material and carbohydrates as a syrup. However, organic solvents are expensive, and some are toxic. The volatility of organic solvents can also lead to risky situations (Zhao et al., 2009). In a study in which acetone was used as an organic solvent and sulfuric acid as a catalyst, mustard (Brassica juncea) biomass was pretreated. The effects of acetone concentration, acid catalyst concentration, and treatment time were investigated. Following pretreatment, the cellulose content increased from 36.50% to 58.20% (w/w). The maximum glucose yield obtained was 13.67 g per 100 g of biomass under the following conditions: 80% (w/w) acetone, 0.4% (w/w) acid catalyst, and a pretreatment time of 90 minutes (Singh et al., 2021).

Deep Eutectic Solvents

Chemical pretreatment methods often involve the use of acidic, alkaline, or organic solvents. These liquids are generally toxic, difficult to recycle or reuse, and expensive. In recent years, the use of deep eutectic solvents, which eliminate these disadvantages, has become quite common. Deep eutectic solvents are mostly obtained by mixing a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD) that can complex with the halide ion of the quaternary ammonium salt. Deep eutectic solvents can donate and accept protons, and this property enhances

their solubility by making it possible to form hydrogen bonds with other compounds. Particularly acidic deep eutectic solvents, namely lactic, malic, and oxalic-based ones, are quite effective for lignin removal (Satlewal et al., 2018). In a study investigating the pretreatment of sunflower stalks using a choline chloride (HBA) and formic acid (HBD) based DES to facilitate lignin removal and produce cellulose-rich substrates for enzymatic hydrolysis, the effects of key treatment parameters, including ChCl/FA molar ratio (1:1, 1:2, 2:1), pretreatment time (4 hours, 6 hours, 8 hours), and temperature (90 °C, 110 °C, 130 °C), on glucose recovery were examined. It was determined that DES pretreatment, at a 1:2 ChCl/FA ratio, 110 °C temperature, and 6 hours, approximately doubled the enzymatic hydrolysis yield of sunflower stalks compared to crude biomass, removing 87.6% of the lignin (Özuyar & Hoşgün, 2025).

4.3. Physicochemical Pretreatment

Steam Explosion

Steam explosion is a process that has been known since the 19th century and has been used in the production of wood chipboard. Today, it is the most widely used physicochemical pretreatment method in the hydrothermal processing of woody biomass. Two fractions are obtained from steam explosion: a solid fraction rich in insoluble cellulose and lignin, and a liquid fraction rich in soluble sugars. Temperature, holding time, chip size, and moisture content are the most important parameters affecting steam explosion (Alvira et al., 2016; Rabemanolontsoa & Saka, 2016). Steam explosion pretreatment of rapeseed stalks was carried out at temperatures between 185 and 215 °C and processing times 2.5 - 7.5 minutes. The initial composition of the biomass was found to be 31.6% ± 0.3 cellulose, 17.4% ± 0.1 hemicellulose, and 17.8% ± 0.5 lignin. The solid matter recovery efficiency, calculated based on the initial biomass weight, was 74% at the lowest temperature. The composition of this sample was found to be 40.7% ± 0.55 cellulose, 18.5% ± 0.23 hemicellulose, and 29.5% ± 0.33 lignin (López-Linares et al., 2015).

Ammonia Fiber Expansion

Ammonia fiber expansion (AFEX), essentially a combination of steam explosion and alkaline treatment methods, is similar to steam explosion in that it uses liquid ammonia instead of steam. Due to the basic nature of ammonia, intermolecular ester bonds between hemicellulose and lignin are broken, as in alkaline pretreatment. During pretreatment, lignocellulosic biomass is subjected to high temperature (90–100 °C) and high-pressure (1–5.2 MPa) conditions. Hemicellulose and lignin are partially removed, reducing cellulose crystallinity (Chen et al., 2017; Liao et al., 2020). Using the ammonia fiber expansion method, empty fruit clusters of date palm trees were pretreated under conditions of 1:1 ammonia/biomass loading, 135 °C temperature, and 45 min holding time. The total fermentable sugar yield (glucose and xylose) increased from 0.15 g g^{-1} for empty fruit clusters of untreated raw date palm trees to 0.53 g g^{-1} for empty fruit clusters of date palm trees pre-treated with AFEX after 72 hours of enzymatic hydrolysis. A more than threefold increase in

sugar yield was observed from the hydrolysis of empty fruit clusters of date palm trees pre-treated with AFEX (Abdul et al., 2016).

Liquid Hot Water

Liquid hot water is one of the hydrothermal pretreatment methods that requires rapid pressure reduction and no catalyst or chemical addition. Similar to the steam blasting method, it uses water in liquid form at high temperatures (usually between 170 and 230 °C) and high pressure (>5 MPa) instead of steam. This process causes hemicellulose hydrolysis and lignin removal, making the cellulose in biomass more accessible whilst preventing the formation of fermentation inhibitors, which occur at higher temperatures. Using water as a pretreatment solvent results in a low-cost solvent, which is advantageous for large-scale applications (Agbor et al., 2011; Maurya et al., 2015). A study optimising the temperature and retention time for the liquid hot water pretreatment of wheat straw for ethanol production showed that the optimal conditions were 188 °C for 40 minutes. This resulted in a recovery yield of 43.6% of the hemicellulose-derived sugar content in the raw material, as well as an enzymatic hydrolysis yield of 79.8% of the theoretical value. However, when the response variables were analysed separately, 71.2% hemicellulose sugar recovery was achieved at 184 °C for 24 minutes. Conditions at 214 °C for 2.7 minutes resulted in a maximum enzymatic hydrolysis yield of 90.6% of the theoretical value. Therefore, the authors concluded that a two-stage pretreatment would be the most suitable process configuration to ensure maximum recovery of fermentable (Pérez et al., 2008).

4.4. Biological Pretreatment

This is a method that mostly uses fungal and bacterial species or enzymes in the processing of lignocellulosic biomass. Biological pretreatment essentially takes advantage of the natural ability of some microorganisms to break down lignin in lignocellulosic biomass or cell wall components (carbohydrates, lipids, and proteins) in microalgae. In a typical microbial pretreatment process, cells are allowed to grow on the biomass either by immersion culture or solid-state cultivation techniques, then they multiply and carry out their metabolism (Zabed et al., 2019). Some bacteria (e.g., Clostridium sp., Cellulomonas sp., Bacillus sp., Thermomonospora sp., Streptomyces sp., etc.) and various fungi (e.g., Phanerochaete chrysosporium, Trichoderma reesei, Trichoderma viride, Aspergillus niger, etc.) are commonly used in the biological pretreatment process (Rezania et al., 2020). When biological pretreatment is performed using fungi, the process is simple because the fungi can grow directly on the biomass, eliminating the need for any steps for enzyme extraction or recovery. Three common fungal species are used in fungal pretreatment: white rot, brown rot, and soft rot (Prasongsuk et al., 2022). Biological pretreatments have many advantages, such as being cost-effective, easy to use, low energy consumption, and lacking chemical additives. However, they also have disadvantages, such as a low hydrolysis rate, the need for a large sterile area, and a long processing time (Capolupo & Faraco, 2016). The effectiveness of biological pretreatment depends

on various factors such as biomass composition, inoculum concentration, aeration rate, moisture content, incubation time, incubation temperature, pH, and the type of microorganism used (Ummalyma et al., 2019). In a study using white rot fungi such as Ganoderma lucidum, Phanerochaete chrysosporium, Pleurotus ostreatus, Pleurotus pulmonarius, and Trametes sp. in the biological pretreatment of Eucalyptus grandis sawdust, it was observed that biological pretreatment reduced the initial delay, increased the readily hydrolyzable fraction, and formed a second hydrolyzable fraction. The formation of the readily hydrolyzable cellulose fraction was ranked as follows: P. ostreatus (16.7% total cellulose) > P. pulmonarius (15.4%) > Trametes sp. (10.1%) P. chrysosporium (2.8%) ≈ crude (2.8%). For the second hydrolyzable fraction, the total amount of reducing sugars released after 48 hours of saccharification of the sawdust was determined to increase from 2.5 μmol/mL to 48.0 μmol/mL (Castoldi et al., 2014).

5. CATALYST DEVELOPMENT FOR BIOMASS VALORIZATION DESIGN CRITERIA FOR GREEN CATALYSTS: HETEROGENEOUS CATALYSTS

Advanced catalytic strategies, particularly heterogeneous catalysts, are essential for the effective transformation of the complex structure of biomass into valuable products and the advancement of sustainable biorefining processes. Research in this area could increase the efficiency and economic viability of products derived from renewable resources. Efficient catalyst design and application are vital for the development of sustainable biorefining technologies. Compared to homogeneous catalysts, heterogeneous catalysts used in biomass processing stand out due to their ease of recovery and separation from the reaction mixture, as well as their thermal and chemical stability and suitability for continuous reactor operation (Hosgün et al., 2020).

Heterogeneous catalysts designed for the conversion of lignocellulosic biomass must meet certain requirements. These include minimising mass transfer limitations, stability under aqueous and hydrothermal conditions, adjustable hydrophobicity to aid product/reactant adsorption, and resistance to impurities present in fermentation liquids. In order to fulfil these criteria, a catalyst must have a high surface area, be hydrophobic and hydrothermally stable over a wide pH range, and have optimisable pore size (Wilson & Lee, 2016).

Heterogeneous catalysts play a vital part in converting lignocellulosic biomass into platform chemicals and fuels, such as furfural, 5-hydroxymethylfurfural (5-HMF), levulinic acid and glycerin. Developing and applying these solid catalysts is crucial for achieving selective, efficient and environmentally friendly conversions under conditions that are relevant to industry. They are generally used in reactions such as dehydration, hydrogenation, etherification, oxidation, and dehydrogenation, which enable the conversion of lignocellulosic biomass into valuable chemicals and fuels. The literature generally describes these reactions as being catalysed by metal oxides, zeolites, and metal-organic frameworks (Lakhani & Srifa, 2026).

5.1. Metal Oxides

Oxides of the lanthanides, actinides, and transition metals found in the periodic table are used as catalysts. These metal oxides have a porous structure and can be synthesised using various methods, including sol-gel, hydrothermal, template-assisted, and solvothermal approaches. They provide an abundance of active sites for catalytic transformations, and their hierarchical pore structure, consisting of micro-, meso-, and macro-pores, facilitates the diffusion of reactants and products during catalytic reactions (Mondal et al., 2024). Depending on their surface structure and chemical composition, metal oxides exhibit Lewis and Brønsted acidity. Transition metal oxides, including TiO_2, ZrO_2, and SnO_2, exhibit Lewis acidity through the release of Ti^{4+}, Zr^{4+}, and Sn^{4+} cations, respectively, and their acid strengths can be adjusted through synthesis and calcination. Brønsted acidity in metal oxides is primarily related to the presence of surface hydroxyl groups (M–OH) (Balasubramanian et al., 2025). Using metal oxides in binary or ternary configurations can affect Lewis and Brønsted acidity. Treatment with mineral acids such as sulfuric and phosphoric acids can also enhance the activity of metal oxides. The advantages of metal oxides include a high surface area, tunable pore structure, thermal stability, and redox properties. Disadvantages include synthesis complexity, catalyst deactivation, cost, and limitations in mass transfer.

Rattanasak et al. synthesized sulfated tin oxide (SO_4^{2-}/SnO_2) and sulfated iron-tin oxide ($SO_4^{2-}/Fe\text{-}SnO_2$) to obtain levulinic acid from palm oil empty cluster fibers. The sulfated iron-tin oxide catalyst exhibited a higher sulfur content and a greater number of Brønsted acid sites compared to sulfated tin oxide, while iron doping was found to reduce the number of Lewis acid sites. The effects of reaction temperature (180–220 °C), reaction time (1–6 hours), and catalyst loading (0–4% w/w) on levulinic acid yield were investigated, and the optimum reaction temperature was determined to be 200 °C for both catalysts. High temperatures above 200 °C resulted in a decrease in levulinic acid yield due to increased humin formation and other degradation pathways. At 200 °C, the sulfated iron-tin oxide catalyst achieved a maximum levulinic acid yield of 31.2% by weight (w/w) from pre-treated palm oil cluster fiber, while sulfated tin oxide catalyst yielded a maximum yield of 24.1% by weight (w/w) from pre-treated oil palm cluster fiber under similar conditions (Rattanasak et al., 2025). The efficacy of Al_2O_3-TiO_2-ZrO_2 ternary mixed oxide catalysts, synthesized by the sol-gel method, in the conversion of glucose and fructose to 5-hydroxymethylfurfural (HMF) was evaluated in a two-phase THF/H_2O system at a pressure of 30 bar Ar and a temperature of 175 °C for a reaction time of 3 hours. The ternary mixed oxide catalysts showed high catalytic activity and achieved 99% glucose conversion. This was attributed to a direct dehydration pathway facilitated by the abundant Lewis acid site in the catalysts, bypassing the fructose isomerization step. All ternary mixed oxide catalysts achieved 99% fructose conversion (Cortez-Elizalde et al., 2022). A study was conducted to investigate the effect of heat treatment on niobium pentoxide (Nb_2O_5) catalysts used for the stepwise dehydration of glucose in water to produce 5-hydroxymethylfurfural (HMF). The

textural properties, acidity, and catalytic performance of the catalyst were evaluated in relation to variations in treatment temperature and atmosphere. The optimal reaction conditions for screening the catalysts were determined to be 180 ˚C for 2 hours, based on studies with commercial Nb_2O_5. The best-performing catalyst was mesoporous amorphous niobium oxide, prepared by thermally treating niobic acid in air at 300 ˚C. This catalyst achieved a remarkable yield of 66% glucose conversion and 37% HMF in 90 minutes. Catalysts processed at higher temperatures (550 ˚C) with low total acidity and a high LA/BA ratio have been reported to be more effective in catalyzing the initial isomerization step of glucose to fructose, but less efficient in the subsequent dehydration to HMF (Morawa Eblagon et al., 2020).

5.2. Zeolites

Zeolites are a family of crystalline aluminosilicates. They are made up of tetrahedral units of silicon (Si) and aluminium (Al) atoms surrounded by four oxygen (O) atoms. These units form SiO_4 and AlO_4, which are linked together by sharing oxygen corners. The silicon atoms in the structure have a charge of +4. When silicon is replaced by aluminium (3+), a net negative charge is released in the skeleton. To counterbalance this, the voids in the lattice structure accommodate various cations, such as H^+, Na^+, K^+, and Mg^{2+} (Tempelman et al., 2021). Zeolites' most important properties are their favourable Brønsted/Lewis acid ratio, double meso-/microporosity, and excellent mass transfer capability. These properties make zeolites good candidates for numerous applications, including catalysis, adsorption, and separation. Zeolite acidity depends on the Si/Al atomic ratio. The number of Al atoms is proportional to the number of Brønsted acid sites. Transition metal-containing zeolites are of particular interest due to their Lewis acidity. For instance, Ti or Sn species in the structure of hydrophobic zeolites, such as high-silica zeolites, present unique Lewis acid sites even in the presence of protic polar solvents, such as water. Lewis acidity in Sn-Beta zeolites proceeds via a hydride shift (1,2-shift) mechanism to isomerise glucose to fructose, explaining its exceptional selectivity (De et al., 2016). In zeolites, Brønsted acid sites (Si–OH–Al) protonate the hydroxyl groups of glucose or fructose to form oxocarbenium intermediates, which then undergo dehydration to produce HMF via successive water elimination (Lakhani & Srifa, 2026). Micropore restriction stabilises basic transition states and suppresses excessive reactions, such as humin formation.

In a study in which the most suitable catalyst for the production of 5-hydroxymethylfurfural (HMF) from glucose was determined to be H-β(30) zeolite with high total, Lewis, and Brønsted acidity, the highest HMF yield (84%) and selectivity (88%) were obtained under the following reaction conditions: a water-THF volume ratio of 2:4, a reaction temperature of 160 ˚C, and a reaction time of 2 hours in a two-phase reaction medium of water, NaCl, and THF (Xing et al., 2022). Kobkeatthawin et al. investigated the selective conversion of glucose to HMF and humins using ZSM-5 zeolite catalysts modified with iron and tungsten. Commercial proton-form ZSM-5 was pretreated with dilute nitric acid

and then impregnated with iron and tungsten to form Fe/De-HZSM5 and W/De-HZSM5 catalysts. The Fe-modified ZSM-5 catalysts exhibited high selectivity for HMF production, achieving a yield of 61.1% under optimised conditions. This was attributed to increased Lewis acidity, which facilitates the rate-limiting glucose-fructose isomerisation reaction. While increasing the temperature generally increased the conversion of glucose, an increase in the yield of HMF was observed up to approximately 170 ˚C for Fe-based catalysts and up to 190 ˚C for W-based catalysts (Kobkeatthawin et al., 2024). In research where zeolite Y was synthesised from coal fly ash (an industrial waste product) and subsequently used as a catalyst in the conversion of glucose to 5-hydroxymethylfurfural (HMF) under optimised conditions (140 ˚C for six hours at 15 bar pressure), the catalyst achieved 98% glucose conversion and 78% HMF selectivity. Characterisation studies revealed the presence of Lewis and Brønsted acidic regions, indicating higher total acidity than standard Zeolite Y (Andola et al., 2025).

5.3. Metal-Organic Frameworks (MOFs)

Metal Organic Frameworks stand out as rivals to conventional porous materials because of their high accessible internal surface areas, adjustable pore openings, and thermal and physical stability (Qian et al., 2020). MOFs consist of both organic and inorganic components. The organic components, known as bridging ligands or linkers, include conjugate bases of carboxylic acids, anions such as organophosphorus compounds and sulfonic acid salts, as well as heterocyclic compounds. The inorganic elements are metal ions or clusters, known as secondary structural units (SBUs). The final framework is controlled by the metal ion and the primary structural unit (PSU) (Yusuf et al., 2022). MOFs can be doped with various functional materials, such as metal nanoparticles (NPs), metal oxides, quantum dots, carbon materials, molecules, polyoxometalates, polymers, and enzymes, to create MOF composites with diverse functions. MOFs can be divided into various groups according to their component units. MOF composites are classified according to the functional materials added (Tong et al., 2019).

In a study in which amino (-NH_2) functionalisation was used as a catalyst for the conversion of fructose to 5-hydroxymethylfurfural (5-HMF) in the MIL-53(Al) metal-organic framework, an exceptional 5-HMF yield of 84.3% was obtained under optimised reaction conditions (170 ˚C for 6 hours) in a two-phase system consisting of tetrahydrofuran (THF) and a saturated sodium chloride (NaCl) solution. The researchers interpreted this as indicating that the amino groups stabilise the MOF structure during sulfonation, contribute to fructose adsorption and activation via hydrogen bonds, and concentrate the substrate near the active acid sites (Yu, Zhang, Zhang, et al., 2026). In another study, the same research group investigated the development and application of MIL-53(Al) for the conversion of cellulose to 5-HMF. Catalytic conversion of cellulose in a two-phase system of tetrahydrofuran (THF)/NaCl-H_2O was achieved under optimum conditions (190 ˚C for 8 hours), yielding 5-HMF at 63.8% alongside 6.3% levulinic acid and 23.9% formic acid (Yu, Zhang, Li, et al., 2026). A study investigating the catalytic conversion of

glucose to 5-hydroxymethylfurfural (5-HMF) focused particularly on the development and application of mixed metal-organic frameworks (MOFs), specifically Fe/MIL-101(Cr) and MIL-101(Cr, Fe), which were synthesised via post-synthesis modification and single-step methods. These mixed-metal MOFs demonstrated a synergistic effect, leading to enhanced catalytic activity in the conversion of glucose to 5-HMF compared to single-metal MOFs and sulfonic acid-functionalised MOFs. This improved performance was attributed to the combined presence of Lewis acid sites from Cr(III) and Fe(III) ions, as well as enhanced Brønsted acidity from bridging hydroxyl groups. Under optimised conditions (a DMSO/water system at 170 °C for two hours), a 5-HMF yield of 55.8% was obtained using Fe/MIL-101(Cr) (Lu et al., 2023).

6. GREEN CATALYTIC CONVERSION PATHWAYS CONVERSION OF POLYSACCHARIDES INTO PLATFORM CHEMICALS LIGNIN VALORIZATION THROUGH CATALYTIC ROUTES

The effective utilization of LCB as a sustainable carbon source depends on its processing using selective catalytic strategies tailored to the structural properties of its components. In this context, the modern biorefinery approach addresses the polysaccharide (cellulose and hemicellulose) and lignin fractions through separate yet integrated reaction networks. It aims to convert the carbon in biomass into bioenergy, biofuels, and high-value-added chemicals with the highest possible efficiency (Mika et al., 2018; Sethupathy et al., 2022; Xiong et al., 2021). In this regard, it contributes to reducing dependence on fossil fuels and strengthening the circular bioeconomy while ensuring the efficient use of renewable resources.

6.1. Catalytic Conversion of Polysaccharides into Platform Chemicals

The catalytic conversion of polysaccharides is based on the selective transformation of cellulose and hemicellulose structures, in the presence of acidic catalysts, into platform chemicals with lower molecular weights and rich in oxygen-containing functional groups. Rather than a single-step reaction, this process proceeds as a reaction network. The key steps of the reaction network are: i) activation and cleavage of the glycosidic bond, ii) ring opening and sugar isomerization, iii) dehydration reaction, iv) rehydration reaction, and v) retro-aldol cleavage. At the end of this reaction network, cellulose is converted to 5-hydroxymethylfurfural (5-HMF), while hemicellulose is converted to furfural (Dutta, 2024; Pattnaik et al., 2021; Xiong et al., 2021).

Activation and Cleavage of Glycosidic Bonds

The acid-catalyzed hydrolysis of polysaccharide fractions is based on the formation of an oxocarbenium intermediate following the protonation of β-1,4-glycosidic bonds, and the formation of free monosaccharides via nucleophilic attack of water molecules on this intermediate. In the reaction mechanism catalyzed by Brønsted acid active sites, homogeneous mineral acids (H_2SO_4, HCl, and H_3PO_4) and het-

erogeneous solid acid catalysts (zeolites, sulfonated carbons, and metal oxides) are commonly used (Swiatek et al., 2020). Due to its high degree of crystallinity and dense hydrogen bonding network, cellulose presents high energy barriers to bond breaking. This inherent resistance limits its conversion by making cellulose less reactive than hemicellulose under dilute acid conditions. This conversion yields glucose (Kim et al., 2026). Hemicellulose, on the other hand, with its amorphous structure and lower degree of crystallinity, breaks down easily, yielding monosaccharides such as xylose, arabinose, mannose, and galactose. The natural resistance created by these structural properties positions hemicellulose as the primary reactant and xylose as the first stable product in the initial step of the catalytic conversion mechanism of polysaccharides (Swiatek et al., 2020).

The acidity of the reaction medium is one of the key process parameters determining the balance between conversion rate and product selectivity. While an increase in acid concentration accelerates hydrolysis, it can also promote side reactions that lead to the formation of humic substances and other degradation products. Therefore, determining the optimal reaction conditions is of critical importance for maintaining the selectivity of the target product and limiting side reactions (du Pasquier et al., 2023; Lorenci Woiciechowski et al., 2020).

Isomerization and Structural Redirection

The aldose-type monosaccharides formed in the previous step are redirected to their ketose forms—which are more reactive structures—through isomerization reactions. Isomerization begins with the conversion of the cyclic monosaccharide structure, which is stable in an aqueous medium, to an open-chain form as a result of its interaction with acidic or basic active sites. The transition from a cyclic to an open-chain structure provides the structural flexibility necessary for the carbonyl group to shift along the carbon skeleton. Subsequently, the carbonyl group moves from the C-1 position to the C-2 position, converting the aldose structure into a ketose structure (Mika et al., 2018; Roman-Leshkov et al., 2010). Aldose/ketose isomerization proceeds via different reaction mechanisms depending on the type of catalyst used. The mechanisms involved in this transformation and their characteristic features are presented in Table 1. Isomerization, which requires high activation energy, is considered the rate-determining step of the integrated reaction network. At the end of this process, glucose is converted to fructose, and xylose is converted to xylulose (Moliner et al., 2010).

Basis catalysts exhibit low stability and low selectivity; in contrast, Lewis acid catalysts can carry out the aldose/ketose conversion in an aqueous medium with high selectivity. Within this group, heterogeneous Lewis acids stand out in modern biorefinery applications due to their ease of separation, reusability, and high thermal stability. Bifunctional catalysts, which contain both Lewis and Brønsted acidic active sites, catalyze the isomerization and dehydration steps sequentially, enabling the production of platform chemicals with high yield and selectivity (Mika et al., 2018).

Table 1. *Catalysts used in aldose/ketose isomerization and reaction mechanisms*

Type of Catalyst	Active site	Catalytic role	Catalyst	Reference
Homogeneous Lewis acids	Lewis	1,2-hydride shift	$CrCl_3$, $AlCl_3$, $FeCl_3$, $SnCl_4$	(Dutta et al., 2012; Li et al., 2018; Mika et al., 2018)
Homogeneous Lewis acids	Lewis	1,2-hydride shift	Sn-Beta, Ti-Beta, Zr-Beta	(Bermejo-Deval et al., 2014; Gounder & Davis, 2013; Jain & Kassaye, 2024)
Basic catalytic systems	Basic active sites	Enediol mechanism	Hydrotalcites, MgO-based systems	(Li et al., 2020; Van Putten et al., 2013)
Bifunctional catalysts	Lewis + Brønsted	Sequential isomerization–dehydration	Sn-Beta/H-Beta, Nb-based systems	(Gao et al., 2019; Tang et al., 2020)

Dehydration Reactions

In the dehydration mechanism catalyzed by Brønsted acidic active sites, the reaction network proceeds via sequential proton (H+) transfers. The protonation of hydroxyl groups is followed by water elimination, resulting in the formation of unstable, high-energy intermediate products with carbocation, enol, and enediol structures. Subsequent structural rearrangements lead to the formation of a stable furan ring. Through this transformation mechanism, the carbon flow from the polysaccharide fractions is preserved, directing fructose toward 5-HMF and xylose toward furfural (Pattnaik et al., 2021; Schutyser et al., 2018; Van Putten et al., 2013).

Rehydration Reactions

Brønsted acids (mineral acids, acidic resins, zeolites, metal oxides, etc.) under aqueous and acidic conditions force the 6-carbon 5-HMF structure to undergo rehydration, causing its ring structure to open. As a result of this reaction, the carbon skeleton breaks down, forming 5-carbon levulinic acid (LA) and 1-carbon formic acid (FA) in equimolar amounts. Simultaneously, sugars and furanic components are catalyzed toward condensation and polymerization reactions, forming dark-colored, insoluble, and carbon-rich humin structures. Humin formation, which proceeds in parallel under system conditions, reduces the selectivity toward LA (Alonso et al., 2010; Patil & Lund, 2011).

LA exhibits a more stable structure compared to 5-HMF and is considered the final step in the transformation mechanism. However, the modern biorefinery approach treats it not as a final product but as a secondary feedstock source that facilitates the formation of end products. The hydrogenation mechanism is the most important conversion step for LA. Hydrogenation, which occurs in the presence of catalysts such as Ru/C or Ru/Sn/C, yields γ-valerolactone (GVL). GVL, which falls into the category of high-performance green solvents, is used not only as a fuel additive but also as a polymer feedstock (Alonso et al., 2010; Gallezot, 2012).

The esterification of LA with ethyl alcohol results in ethyl levulinate (EL), which is used as a biofuel additive. Through hydrodeoxygenation reactions involving LA and GVL, liquid alkanes (hexane, pentane, etc.) are produced. The FA formed simultaneously acts as a hydrogen donor in subsequent conversion mechanisms, thereby supporting the formation of GVL. Thanks to this property, it minimizes the hydrogen supply requirement necessary for biorefinery applications. In addition, by exhibiting an autocatalytic effect, it also supports the conversion of fructose to 5-HMF (Alonso et al., 2010; Sheldon, 2014; Van Putten et al., 2013).

Retro-Aldol Degradation

Retro-aldol degradation (RAC) occurs following the hydrolysis step in the catalytic conversion of polysaccharide fractions and is defined as a secondary conversion network that proceeds in competition with dehydration reactions (Li et al., 2024). RAC redirects the carbon flow away from furans toward small, oxygen-containing valuable chemicals in the presence of metals with Lewis acid properties, such as tungsten (W), tin (Sn), and lanthanum (La). The C-C backbone of sugar molecules is broken down, resulting in the formation of smaller molecules such as glyceraldehyde, 1,3-dihydroxyacetone (DHA), glycolaldehyde, and erythrose. Lactic acid, propylene glycol, and ethylene glycol are obtained depending on the hydrogenation or isomerization of these molecules by active catalytic centers in the system (Dutta, 2024).

Current Catalytic Strategies

Current studies on the catalytic evaluation of the polysaccharide fraction focus on the development of bifunctional catalysts—which combine Brønsted acid sites and Lewis acid sites—capable of carrying out the hydrolysis, isomerization, and dehydration steps within the same reaction environment. In addition, studies have demonstrated that the use of biphasic solvent systems, ionic liquids, and deep eutectic solvents (DES)—particularly by limiting humin formation—increases product yield (Mika et al., 2018; Xiong et al., 2021). One-pot transformation strategies, meanwhile, enable the direct synthesis of platform chemicals without the need to isolate intermediates, thereby improving atom economy and process efficiency (Gallezot, 2012). Finally, nanocatalysis, single-atom catalysts (SACs), microwave-assisted reactions, and mechanocatalytic pretreatments offer lower energy consumption and high product selectivity (Dutta, 2024; Jain & Kassaye, 2024).

6.2. Catalytic Valorization of Lignin

Lignin valorization is the process that enables the conversion of the Earth's "only renewable source of aromatic carbon" into high-value-added aromatic chemicals, fuels, and functional materials. Oxidative depolymerization, reductive depolymerization, and "lignin-first" approaches constitute the primary catalytic conversion pathways. Thanks to this conversion network, lignin is no longer viewed merely as a low-energy fuel but is instead recognized as a raw material source that contributes to the development of a circular economy (Sun et al., 2018).

Catalytic Depolymerization Strategies

Catalytic depolymerization is based on the catalytic breakdown of the complex network structure that holds lignin's phenylpropanoid units together. Although various homogeneous acid catalysts, such as HCl, H_2SO_4, and HNO_3, are effective in depolymerization, they present significant disadvantages at the industrial scale. For this reason, heterogeneous catalysts (such as supported noble metals like Pd, Au, and Ru, as well as Ni, Co, and perovskite-type mixed oxides) are preferred due to their high selectivity and ease of recovery (Mankar et al., 2022; Ullah et al., 2022).

i. Oxidative Depolymerization

This is a conversion process based on the oxidative breakdown of C–O and, to a lesser extent, C–C bonds in the lignin structure in the presence of molecular oxygen (O_2) and hydrogen peroxide (H_2O_2). The process generally takes place in an aqueous alkaline medium under mild conditions. In this conversion mechanism, where the aromatic ring is largely preserved, vanillin, syringaldehyde, and various aromatic acids (vanillic acid, syringic acid) are formed. Under harsh reaction conditions and with the use of strong antioxidants, the aromatic ring opens to form dicarboxylic acids such as succinic acid or maleic acid. To enhance the selectivity and product yield of oxidative polymerization, perovskite-type heterogeneous catalysts such as Pd/γ-Al_2O_3, Au/CeO_2, and $LaMnO_3$, $LaCoO_3$ are preferred (Abdelaziz et al., 2022).

ii. Reductive Depolymerization

Reductive depolymerization is considered a conversion process that operates in the opposite direction to the oxidative polymerization occurring during lignin biosynthesis. Lignin is converted into phenolic compounds with lower molecular weights in the presence of hydrogen donors such as hydrogen, methanol, ethanol, or 2-propanol. This process encompasses hydrogenolysis, hydrogenation, and hydrodeoxygenation (HDO) reactions (Upton & Kasko, 2016). The hydrogenolysis mechanism selectively breaks ether bonds-primarily the β-O-4 bond—to decompose lignin into monomers or dimers. The resulting intermediates are highly reactive. Due to these properties, they tend to form stable C-C bonds with one another. Concurrently proceeding hydrogenation reactions, meanwhile, saturate the reactive intermediates, thereby maximizing monomer yield. The phenolic mixture formed at this stage has a high oxygen content. This means they exhibit low energy density and limited chemical stability. Hydrodeoxygenation (HDO) also ensures that excess oxygen is removed as water. As a result, products with lower oxygen content and higher energy density, such as arenes or cycloalkanes, are obtained (Mankar et al., 2022). To improve HDO efficiency, catalysts containing metals with strong oxidative properties-such as Ru, Re, Mo, W, Fe, and Co-are used (Wang et al., 2023).

iii. Lignin-First Approach

In traditional biorefinery processes, lignin can lose its structural integrity due to the operating conditions it is exposed to during the separation of cellulose and hemicellulose fractions. In contrast, the lignin-first approach targets lignin

in the early stages of the LCB conversion process, unlike traditional sugar-focused approaches. It aims to increase the theoretical yield of aromatic monomers by ensuring the preservation of structural elements—primarily the β-O-4 ether bonds—throughout the conversion mechanism. The reductive catalytic fractionation (RCF) process serves this purpose by simultaneously separating lignin from the LCB matrix, depolymerizing it, and stabilizing the resulting reactive intermediates (Guan et al., 2025). Thanks to this strategic approach, recondensation reactions are minimized, resulting in monophenols obtained at high yields and a cellulose/hemicellulose residue that is highly suitable for hydrolysis (Mankar et al., 2022).

Current Catalytic Strategies

Current strategies for the catalytic valorization of lignin involve achieving maximum atom economy. The concept of "full-utilization" introduced in the context of lignin valorization involves conversion of not only aromatic nucleus but also of side chains and methoxy groups into useful products (Upton & Kasko, 2016). The bonds within the side chains are activated through amine-assisted pre-functionalization to produce phenols and amine derivatives while methoxy groups are turned into acetic acid and tertiary amines selectively through methyl transfer (Zhang et al., 2023). Single-atom and bimetallic catalysts synthesized for this particular purpose play an important role in increasing atom economy because of high TON (metal utilization efficiency) and monophenol selectivity (Wang et al., 2025). Moreover, electro-catalytic and photo-catalytic approaches are referred to as the next-generation catalytic strategies for lignin valorization thanks to low energy consumption and high selectivity (Wang et al., 2023).

6.3. Selectivity and Process Efficiency

The conversion efficiency of the main fractions of LCB - polysaccharides and lignin – cannot be assessed by the high conversion rate alone. The economic and industrial efficiency of the conversion process depend on the degree of selectivity – that is, the fraction of biomass carbon targeted for production of certain products – as well as the efficiency of the process ensuring the maximum output and, hence, minimization of carbon loss. Due to structural differences between the two fractions, selectivity and efficiency can be measured according to different parameters for each. The key distinctions are presented in Table 2. (Mika et al., 2018; Sethupathy et al., 2022).

Table 2. *Comparison of selectivity and process efficiency in the catalytic conversion of polysaccharides and lignin*

Parameter	Catalytic Conversion of Polysaccharides	Catalytic Valorization of Lignin
Selectivity	Directing the carbon flow toward target platform chemicals such as 5-HMF and LA	Selective cleavage of β-O-4 ether bonds, preservation of the aromatic ring, and isolation of the aromatic monomer
Secondary reactions	Humin formation, excessive dehydration, and carbon fragmentation	Recondensation, overhydrogenation, and overoxidation of the aromatic ring
Key factors determining process efficiency	Optimization of catalyst acidity and selectivity, solvent system, temperature, and reaction conditions	Catalyst selectivity and stability, prevention of recondensation, and high yield of the aromatic monomer

7. SUSTAINABLE EVALUATION OF CATALYTIC BIOMASS CONVERSION TECHNIQUES

Sustainability evaluation of catalytic biomass techniques depends on various indicators for economic, environmental, and technical performance. Contribution of these parameters towards sustainability is determined using measurement approaches, such as TEA and LCA. These measurements are helpful in comparison of various biomass conversion techniques by taking into consideration the environmental issues, such as carbon efficiency, energy consumption, and greenhouse gas emission. Carbon Efficiency (CE) and Atom Economy (AE) are among important indicators for assessing the performance of catalytic biomass processes. Thus, currently developed catalytic techniques try to enhance the yield while reducing waste production (Mujtaba et al., 2023). The sustainability of catalytic biomass processes is also closely linked to green chemistry metrics. According to the PASE (Pot, Atom, and Step Economy) concept, multi-step conversions should be done in one pot, minimize the number of steps involved and enhance atom economy. Besides being cost-effective and time-saving, it helps to reduce CAPEX (Preethi et al., 2021). Quantitative estimation of the amount of waste produced, such as E-factors, together with catalyst reusability contribute to improving the environmental performance of these processes (Vilaplana et al., 2021).

8. TRANSITION TO INDUSTRIAL BIOREFINERIES: CHALLENGES, SOLUTIONS, AND FUTURE APPROACHES

During the scale-up process, the heterogeneous nature of biomass, the need for pretreatment, maintaining catalyst stability and selectivity, product separation and purification processes, and process control are among the primary engineering challenges limiting the industrial applicability and commercialization of biorefinery technologies (Narayanaperumal et al., 2026). First, the dispersed geographical loca-

tion, seasonality, and low density of biomass complicate logistics and increase costs for raw materials, and thus negatively affect the economic viability of the biorefinery processes. Second, due to its recalcitrance, biomass requires pre-treatment before the catalytic conversion, which is an energy-intensive process and one of the most costly stages in the biorefinery technology. Moreover, high CAPEX and OPEX costs create serious barriers to the implementation of biorefinery facilities. Biofuels and chemicals can compete with fossil fuel alternatives not only because of efficiency but also because of carbon pricing and effective economic incentives (Adnan, 2025).

To overcome technical and economic problems, the biorefinery technologies are heading towards the integration and flexibility of the production process. Thus, integrated biorefineries, which simultaneously produce biofuels and valuable chemicals, and modular/mobile biorefineries, which can be located closer to biomass sources, become the main technologies that facilitate technical and economic viability of the biorefineries. One more important tendency in the transformation of the biorefinery technologies is the digitalization. The artificial intelligence and machine learning methods accelerate the process of catalyst design and reaction optimization through data-driven approach and help to determine optimum process conditions faster. Moreover, high-throughput experimental platforms (HTE), process analytical technologies (PAT), continuous flow reactors and advanced process simulation allow monitoring the processes of catalytic conversion in real time and controlling them accurately (Parveen & Slater, 2025). Incorporating the life cycle assessment (LCA) and techno-economic analysis (TEA) in process design helps to evaluate not only energy consumption but also environmental impact and economic efficiency of the process (Preethi et al., 2021).

In conclusion, the industrial success of biorefineries requires an integrated and interdisciplinary approach that combines the fields of catalysis, process engineering, digital technologies, and sustainability assessments.

CONCLUSION

Lignocellulosic biomass is the only sustainable, renewable source of organic carbon that can reduce our dependence on fossil fuels and combat environmental pollution. In accordance with the 7th Principle of Green Chemistry, using biomass as a raw material enables the transition from a linear (take-produce-dispose) economic model to a circular (cradle-to-cradle) one, thereby helping to preserve the global carbon balance. Lignocellulosic biomass consists of three tightly bonded organic polymers. This structure poses the greatest challenge to the efficient extraction of fuels and chemicals. Physical, chemical, physicochemical, and biological pretreatment strategies are vital for breaking down this structure and increasing sugar yield. Studies show that methods such as extrusion, ultrasound, microwaves, and deep eutectic solvents effectively increase the surface area and remove lignin. In the conversion of biomass into platform chemicals (e.g., 5-HMF and levulinic acid), heterogeneous catalysts such as metal oxides, zeolites, and metal-organic frameworks (MOFs) play a critical role. These catalysts increase the applicability and economic efficiency of industrial-scale processes by providing high selectivity, thermal stability, and ease of recovery. Future research focusing on improving catalyst stability, reducing energy demand, and minimizing environmental impact will enable the large-scale industrial application of a sustainable biorefinery model based on renewable resources.

SONUÇ

Lignoselülozük biyokütle, fosil yakıtlara olan bağımlılığımızı azaltabilecek ve çevre kirliliğiyle mücadele edebilecek tek sürdürülebilir, yenilenebilir organik karbon kaynağıdır. Yeşil Kimya'nın 7. İlkesi uyarınca, biyokütlenin ham madde olarak kullanılması, doğrusal (al-üret-at) ekonomik modelden döngüsel (beşikten beşiğe) bir modele geçişi sağlayarak küresel karbon dengesinin korunmasına yardımcı olur. Lignoselüloz dökümlü biyokütle, birbirine sıkıca bağlı üç organik polimerden oluşur. Bu yapı, yakıtların ve kimyasalların verimli bir şekilde özütlenmesinin (ekstraksiyonunun) önündeki en büyük engeli teşkil etmektedir. Fiziksel, kimyasal, fizikokimyasal ve biyolojik ön işlem stratejileri, bu yapıyı parçalamak ve şeker verimini artırmak için hayati öneme sahiptir. Çalışmalar; ekstrüzyon, ultrason, mikrodalga ve derin ötektik çözücüler gibi yöntemlerin yüzey alanını artırmada ve lignini uzaklaştırmada etkili olduğunu göstermektedir. Biyokütlenin platform kimyasallarına (örneğin 5-HMF ve levulinik asit) dönüştürülmesinde; metal oksitler, zeolitler ve metal-organik kafes yapılar (MOF'lar) gibi heterojen katalizörler kritik bir rol oynamaktadır. Bu katalizörler; yüksek seçicilik, termal kararlılık ve kolay geri kazanım sağlayarak endüstriyel ölçekli süreçlerin uygulanabilirliğini ve ekonomik verimliliğini artırır. Katalizör kararlılığını artırmaya, enerji talebini azaltmaya ve çevresel etkiyi en aza indirmeye odaklanan gelecek çalışmalar, yenilenebilir kaynaklara dayalı sürdürülebilir bir biyorafineri modelinin büyük ölçekli endüstriyel uygulamalarına olanak tanıyacaktır.

REFERENCES

1. Abdelaziz, O. Y., Clemmensen, I., Meier, S., Costa, C. A. E., Rodrigues, A. E., Hulteberg, C. P., & Riisager, A. (2022). On the Oxidative Valorization of Lignin to High-Value Chemicals: A Critical Review of Opportunities and Challenges. ChemSusChem, 15(20), e202201232. https://doi.org/10.1002/cssc.202201232
2. Abdul, P. M., Jahim, J. M., Harun, S., Markom, M., Lutpi, N. A., Hassan, O., Balan, V., Dale, B. E., & Nor, M. T. M. (2016). Effects of changes in chemical and structural characteristic of ammonia fibre expansion (AFEX) pretreated oil palm empty fruit bunch fibre on enzymatic saccharification and fermentability for biohydrogen. Bioresource Technology, 211, 200–208. https://doi.org/10.1016/j.biortech.2016.02.135
3. Abolore, R. S., Jaiswal, S., & Jaiswal, A. K. (2024). Green and sustainable pretreatment methods for cellulose extraction from lignocellulosic biomass and its applications: A review. Carbohydrate Polymer Technologies and Applications, 7, 100396. https://doi.org/10.1016/j.carpta.2023.100396
4. Adnan, M. A. (2025). Economic and environmental analysis of biomass-based methanol production: A comparative study with fossil-based alternative. Biomass & Bioenergy, 194, 107634. https://doi.org/10.1016/j.biombioe.2025.107634
5. Agbor, V. B., Cicek, N., Sparling, R., Berlin, A., & Levin, D. B. (2011). Biomass pretreatment: Fundamentals toward application. Biotechnology Advances, 29(6), 675–685. https://doi.org/10.1016/j.biotechadv.2011.05.005
6. Aguilar-Reynosa, A., Romaní, A., Rodríguez-Jasso, R. M., Aguilar, C. N., Garrote, G., & Ruiz, H. A. (2017). Microwave heating processing as alternative of pretreatment in second-generation biorefinery: An overview. Energy Conversion and Management, 136, 50–65. https://doi.org/10.1016/j.enconman.2017.01.004
7. Albashabsheh, N. T., & Stamm, J. L. H. (2021). Optimization of lignocellulosic biomass-to-biofuel supply chains with densification: Literature review. Biomass & Bioenergy, 144. https://doi.org/10.1016/j.biombioe.2020.105888
8. Alonso, D. M., Bond, J. Q., & Dumesic, J. A. (2010). Catalytic conversion of biomass to biofuels. Green chemistry, 12(9), 1493–1513. https://doi.org/10.1039/c004654j
9. Alvira, P., Negro, M. J., Ballesteros, I., González, A., & Ballesteros, M. (2016). Steam Explosion for Wheat Straw Pretreatment for Sugars Production. Bioethanol, 2(1). https://doi.org/10.1515/bioeth-2016-0003
10. Anakwenze, V. N., Osilo, C. B., Isiaka, A. B., Chidubem-Nwachinemere, N., Osuala, O. J., Ezemba, C. C., Okoli, U. O., Ekwealor, C. C., Anaukwu, C. G., & Ekwealor, I. A. (2026). Lignocellulosic biomass as sustainable resource for bioproducts production: its properties, potential use, by-products, and economical importance. In Bioproducts From Lignocellulosic Biomass (pp. 1–76). Elsevier. https://doi.org/10.1016/b978-0-443-21604-6.00009-7
11. Andola, S. C., Singh, K., Bhati, K., Singh, G., & Malik, R. (2025). Valorization of Coal Fly Ash into Zeolite Y Catalyst for Enhanced Glucose to 5-Hydroxymethylfurfural Conversion. ACS Sustainable Resource Management, 2(12), 2416–2429. https://doi.org/10.1021/acssusresmgt.5c00362
12. Azuma, J., Tanaka, F., & Koshijima, T. (1984). Enhancement of enzymic susceptibility of lignocellulosic wastes by microwave irradiation. Hakko Kogaku Zasshi, 62(4), 377–384.

13. Baksi, S., Saha, D., Saha, S., Sarkar, U., Basu, D., & Kuniyal, J. C. (2023). Pretreatment of lignocellulosic biomass: review of various physico-chemical and biological methods influencing the extent of biomass depolymerization. International Journal of Environmental Science and Technology, 20(12), 13895–13922. https://doi.org/10.1007/s13762-023-04838-4

14. Balasubramanian, S., Shanmugam, R., Basha, A. C., Sriariyanun, M., Shanmugam, S. R., & Venkatachalam, P. (2025). An Overview of Solid Acid Catalysts in Lignocellulose Biorefineries. Catalysts, 15(5), 432. https://doi.org/10.3390/catal15050432

15. Barakat, A., Mayer-Laigle, C., Solhy, A., Arancon, R. A. D., de Vries, H., & Luque, R. (2014). Mechanical pretreatments of lignocellulosic biomass: towards facile and environmentally sound technologies for biofuels production. Rsc Advances, 4(89), 48109–48127. https://doi.org/10.1039/c4ra07568d

16. Baruah, J., Nath, B. K., Sharma, R., Kumar, S., Deka, R. C., Baruah, D. C., & Kalita, E. (2018). Recent Trends in the Pretreatment of Lignocellulosic Biomass for Value-Added Products. Frontiers in Energy Research, 6, 141. https://doi.org/10.3389/fenrg.2018.00141

17. Bermejo-Deval, R., Orazov, M., Gounder, R., Hwang, S. J., & Davis, M. E. (2014). Active Sites in Sn-Beta for Glucose Isomerization to Fructose and Epimerization to Mannose. Acs Catalysis, 4(7), 2288–2297. https://doi.org/10.1021/cs500466j

18. Broda, M., Yelle, D. J., & Serwańska, K. (2022). Bioethanol production from lignocellulosic biomass—challenges and solutions. Molecules, 27(24), 8717. https://doi.org/10.3390/molecules27248717

19. Bueno Moron, J., van Klink, G. P. M., & Gruter, G.-J. M. (2025). Lignocellulose saccharification: historical insights and recent industrial advancements towards 2nd generation sugars. RSC Sustainability, 3(3), 1170–1211. https://doi.org/10.1039/d4su00600c

20. Bussemaker, M. J., & Zhang, D. K. (2013). Effect of Ultrasound on Lignocellulosic Biomass as a Pretreatment for Biorefinery and Biofuel Applications. Industrial & Engineering Chemistry Research, 52(10), 3563–3580. https://doi.org/10.1021/ie3022785

21. Cao, L. C., Chen, H. H., Tsang, D. C. W., Luo, G., Hao, S. L., Zhang, S. C., & Chen, J. M. (2018). Optimizing xylose production from pinewood sawdust through dilute-phosphoric-acid hydrolysis by response surface methodology. Journal of Cleaner Production, 178, 572–579. https://doi.org/10.1016/j.jclepro.2018.01.039

22. Capolupo, L., & Faraco, V. (2016). Green methods of lignocellulose pretreatment for biorefinery development. Applied Microbiology and Biotechnology, 100(22), 9451–9467. https://doi.org/10.1007/s00253-016-7884-y

23. Carpita, N. C., & McCann, M. C. (2020). Redesigning plant cell walls for the biomass-based bioeconomy. J Biol Chem, 295(44), 15144–15157. https://doi.org/10.1074/jbc.REV120.014561

24. Castoldi, R., Bracht, A., de Morais, G. R., Baesso, M. L., Correa, R. C. G., Peralta, R. A., Moreira, R. D. P. M., Polizeli, M. D. T. D., de Souza, C. G. M., & Peralta, R. M. (2014). Biological pretreatment of sawdust with white-rot fungi: Study of degradation patterns and saccharification kinetics. Chemical Engineering Journal, 258, 240–246. https://doi.org/10.1016/j.cej.2014.07.090

25. Chen, H. Y., Liu, J. B., Chang, X., Chen, D. M., Xue, Y., Liu, P., Lin, H. L., & Han, S. (2017). A review on the pretreatment of lignocellulose for high-value chemicals. Fuel Processing Technology, 160, 196–206. https://doi.org/10.1016/j.fuproc.2016.12.007

26. Choudhury, T., Kayani, U. N., Gul, A., Haider, S. A., & Ahmad, S. (2023). Carbon emissions, environmental distortions, and impact on growth. Energy Economics, 126, 107040. https://doi.org/10.1016/j.eneco.2023.107040

27. Chowdhury, P., Mahi, N. A., Yeassin, R., Chowdhury, N. U. R., & Farrok, O. (2025). Biomass to biofuel: Impacts and mitigation of environmental, health, and socioeconomic challenges. Energy Conversion and Management-X, 25, 100889. https://doi.org/10.1016/j.ecmx.2025.100889

28. Clark, J. H., Farmer, T. J., Hunt, A. J., & Sherwood, J. (2015). Opportunities for Bio-Based Solvents Created as Petrochemical and Fuel Products Transition towards Renewable Resources. International Journal of Molecular Sciences, 16(8), 17101–17159. https://doi.org/10.3390/ijms160817101

29. Coimbra, M. C., Duque, A., Saéz, F., Manzanares, P., Garcia-Cruz, C. H., & Ballesteros, M. (2016). Sugar production from wheat straw biomass by alkaline extrusion and enzymatic hydrolysis. Renewable Energy, 86, 1060–1068. https://doi.org/10.1016/j.renene.2015.09.026

30. Cortez-Elizalde, J., Silahua-Pavón, A. A., Córdova-Pérez, G. E., Arévalo-Pérez, J. C., Guerra-Que, Z., Espinosa-González, C. G., Ortíz-Chi, F., Godavarthi, S., & Torres-Torres, J. G. (2022). Production of 5-Hydroxymethylfurfural from glucose using Al2O3-TiO2-ZrO2 ternary catalysts. Catalysis Today, 392-393, 116–130. https://doi.org/10.1016/j.cattod.2021.11.006

31. Curran, M. A. (2013). Life Cycle Assessment: a review of the methodology and its application to sustainability. Current Opinion in Chemical Engineering, 2(3), 273–277. https://doi.org/10.1016/j.coche.2013.02.002

32. De, S., Duttab, S., & Saha, B. (2016). Critical design of heterogeneous catalysts for biomass valorization: current thrust and emerging prospects. Catalysis Science & Technology, 6(20), 7364–7385. https://doi.org/10.1039/c6cy01370h

33. de Souza, W. R., Mitchell, R. A. C., & Cesarino, I. (2023). Editorial: The plant cell wall: advances and current perspectives. Front Plant Sci, 14, 1235749. https://doi.org/10.3389/fpls.2023.1235749

34. Deng, W. P., Feng, Y. C., Fu, J., Guo, H. W., Guo, Y., Han, B. X., Jiang, Z. C., Kong, L. Z., Li, C. Z., Liu, H. C., Nguyen, P. T. T., Ren, P. N., Wang, F., Wang, S., Wang, Y. Q., Wang, Y., Wong, S. S., Yan, K., Yan, N.,…Zhou, H. (2023). Catalytic conversion of lignocellulosic biomass into chemicals and fuels. Green Energy & Environment, 8(1), 10–114. https://doi.org/10.1016/j.gee.2022.07.003

35. Di Domenico, G., Cioccolo, E., Bianchini, L., Venanzi, R., Colantoni, A., Picchio, R., Cozzolino, L., & Di Stefano, V. (2025). A Systematic Review of Mechanical Pretreatment Techniques of Wood Biomass for Bioenergy. Energies, 18(13), 3294. https://doi.org/10.3390/en18133294

36. du Pasquier, J., Paës, G., & Perré, P. (2023). Principal factors affecting the yield of dilute acid pretreatment of lignocellulosic biomass: A critical review. Bioresource Technology, 369, 128439. https://doi.org/10.1016/j.biortech.2022.128439

37. Dutta, S. (2024). Catalytic Transformation of Carbohydrates into Renewable Organic Chemicals by Revering the Principles of Green Chemistry. ACS omega, 9(25), 26805–26825. https://doi.org/10.1021/acsomega.4c01960

38. Dutta, S., De, S., Saha, B., & Alam, M. I. (2012). Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels. Catalysis Science & Technology, 2(10), 2025–2036. https://doi.org/10.1039/c2cy20235b

39. Emonet, A., & Hay, A. (2022). Development and diversity of lignin patterns. Plant Physiol, 190(1), 31–43. https://doi.org/10.1093/plphys/kiac261

40. Fertonani, D. M. M., Pedrosa, B. S., Silva, W. G., Rubim, J. M. F., Rinaldi, J. C., Girotto, E. M., Guilherme, M. R., & Rinaldi, A. W. (2025). A Comprehensive Overview of Cellulose and Its Derivatives: Structural Features and Emerging Applications. Journal of Applied Polymer Science, 143(4). https://doi.org/10.1002/app.58090

41. Gallezot, P. (2012). Conversion of biomass to selected chemical products. Chem Soc Rev, 41(4), 1538–1558. https://doi.org/10.1039/c1cs15147a

42. Gao, D. M., Shen, Y. B., Zhao, B. H., Liu, Q., Nakanishi, K., Chen, J., Kanamori, K., Wu, H. P., He, Z. Y., Zeng, M. M., & Liu, H. C. (2019). Macroporous Niobium Phosphate-Supported Magnesia Catalysts for Isomerization of Glucose-to-Fructose. ACS Sustainable Chemistry & Engineering, 7(9), 8512–8521. https://doi.org/10.1021/acssuschemeng.9b00292

43. García, A., Alriols, M. G., Llano-Ponte, R., & Labidi, J. (2011). Ultrasound-assisted fractionation of the lignocellulosic material. Bioresource Technology, 102(10), 6326–6330. https://doi.org/10.1016/j.biortech.2011.02.045

44. Gautam, D., Rana, V., Sharma, S., Walia, Y. K., Kumar, K., Umar, A., Ibrahim, A. A., & Baskoutas, S. (2025). Hemicelluloses: A Review on Extraction and Modification for Various Applications. Chemistryselect, 10(24). https://doi.org/10.1002/slct.202406050

45. Ge, X., Burner, D. M., Xu, J., Phillips, G. C., & Sivakumar, G. (2011). Bioethanol production from dedicated energy crops and residues in Arkansas, USA. Biotechnol J, 6(1), 66–73. https://doi.org/10.1002/biot.201000240

46. Gounder, R., & Davis, M. E. (2013). Titanium-Beta Zeolites Catalyze the Stereospecific Isomerization of D-Glucose to L-Sorbose via Intramolecular C5-C1 Hydride Shift. Acs Catalysis, 3(7), 1469–1476. https://doi.org/10.1021/cs400273c

47. Guan, J. Y., Tse, H. Y., Wang, H. M., Zhao, W. C., Patria, R. D., Li, M. M. J., Cheng, S., Wang, T., & Leu, S. Y. (2025). Novel control of fractionation-depolymerization for rapid dissociation of lignin-associated xylan: toward complete lignocellulosic biomass valorization in lignin-first biorefinery. Green chemistry, 27(43), 13834–13848. https://doi.org/10.1039/d5gc02925b

48. Guerriero, G., Hausman, J. F., Strauss, J., Ertan, H., & Siddiqui, K. S. (2016). Lignocellulosic biomass: Biosynthesis, degradation, and industrial utilization. Engineering in life sciences, 16(1), 1–16. https://doi.org/10.1002/elsc.201400196

49. Harris, S., Romare, M., & Zhang, Y. Q. (2025). Comparative life cycle assessment of circular and linear product versions for a motorboat and smartphone☆. Sustainable Production and Consumption, 57, 213–225. https://doi.org/10.1016/j.spc.2025.03.023

50. He, Y., Liu, Y. Q., & Zhang, M. (2024). Hemicellulose and unlocking potential for sustainable applications in biomedical, packaging, and material sciences: A narrative review. International Journal of Biological Macromolecules, 280. https://doi.org/10.1016/j.ijbiomac.2024.135657

51. Hosgün, E. Z., Berikten, D., Kivanç, M., & Bozan, B. (2017). Ethanol production from hazelnut shells through enzymatic saccharification and fermentation by low-temperature alkali pretreatment. Fuel, 196, 280–287. https://doi.org/10.1016/j.fuel.2017.01.114

52. Hosgün, H. L., Türe, A. G., Hosgün, E. Z., & Bozan, B. (2020). Synthesis 5-hydroxymethylfurfural (5-HMF) from fructose over cetyl trimethylammonium bromide-directed mesoporous alumina catalyst: effect of cetyl trimethylammonium bromide amount and calcination temperature. Reaction Kinetics Mechanisms and Catalysis, 129(1), 337–347. https://doi.org/10.1007/s11144-019-01699-2

53. Isikgor, F. H., & Becer, C. R. (2015). Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. Polymer Chemistry, 6(25), 4497–4559. https://doi.org/10.1039/c5py00263j

54. Jain, S., & Kassaye, S. (2024). Efficient Production of Platform Chemicals from Lignocellulosic Biomass by Using Nanocatalysts: A Review. Reactions, 5(4), 842–859. https://doi.org/10.3390/reactions5040044

55. Karimipour-Fard, P., Chio, C., Brunone, A., Marway, H., Thompson, M., Abdehagh, N., Qin, W., & Yang, T. C. (2024). Lignocellulosic biomass pretreatment: Industrial oriented high-solid twin-screw extrusion method to improve biogas production from forestry biomass resources. Bioresource Technology, 393, 130000. https://doi.org/10.1016/j.biortech.2023.130000

56. Karunarathna, M. S., & Smith, R. C. (2020). Valorization of Lignin as a Sustainable Component of Structural Materials and Composites: Advances from 2011 to 2019. Sustainability, 12(2). https://doi.org/10.3390/su12020734

57. Kim, G., Nadeau, B., & Song, H. (2026). Acid-Catalyzed Pretreatment of Lignocellulosic Biomass: Feed-Stock-Dependent Reactivity, Kinetics, and Xylose-Selective Catalytic Performance. Catalysts, 16(5), 433. https://doi.org/10.3390/catal16050433

58. Kobkeatthawin, T., Thiensuwan, N., Chotirattanachote, A., Chaowamalee, S., & Ngamcharussrivichai, C. (2024). Selectivity control in catalytic glucose dehydration using iron and tungsten-modified ZSM-5 catalysts. Materials Today Sustainability, 28, 101005. https://doi.org/10.1016/j.mtsust.2024.101005

59. Kostas, E. T., Beneroso, D., & Robinson, J. P. (2017). The application of microwave heating in bioenergy: A review on the microwave pre-treatment and upgrading technologies for biomass. Renewable & Sustainable Energy Reviews, 77, 12–27. https://doi.org/10.1016/j.rser.2017.03.135

60. Kumar, A. K., & Sharma, S. (2017). Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. Bioresources and Bioprocessing, 4(1), 7. https://doi.org/10.1186/s40643-017-0137-9

61. Lakhani, P., & Srifa, A. (2026). Emerging Heterogeneous Catalysis for Valorization of Biomass-Derived Platform Molecules: The Systematic Review Toward Sustainable Biorefinery Applications. Advanced Energy and Sustainability Research, 7(2), e202500402. https://doi.org/10.1002/aesr.202500402

62. Li, G. B., Liu, W., Ye, C. L., Li, X. Y., & Si, C. L. (2018). Chemocatalytic Conversion of Cellulose into Key Platform Chemicals. International Journal of Polymer Science, 2018(1), 4723573. https://doi.org/10.1155/2018/4723573

63. Li, X. X., Zhang, L. L., Wang, S. S., & Wu, Y. L. (2020). Recent Advances in Aqueous-Phase Catalytic Conversions of Biomass Platform Chemicals Over Heterogeneous Catalysts. Frontiers in chemistry, 7, 948. https://doi.org/10.3389/fchem.2019.00948

64. Li, Y., Zhang, Y. C., Li, Z. Y., Zhang, H. Y., & Fu, P. (2024). Reaction pathways and selectivity in the chemo-catalytic conversion of cellulose and its derivatives to ethylene glycol: A review. Chinese Journal of Chemical Engineering, 66, 310–331. https://doi.org/10.1016/j.cjche.2023.09.013

65. Liao, Y. H., de Beeck, B. O., Thielemans, K., Ennaert, T., Snelders, J., Dusselier, M., Courtin, C. M., & Sels, B. F. (2020). The role of pretreatment in the catalytic valorization of cellulose. Molecular Catalysis, 487, 110883. https://doi.org/10.1016/j.mcat.2020.110883

66. López-Linares, J. C., Ballesteros, I., Tourán, J., Cara, C., Castro, E., Ballesteros, M., & Romero, I. (2015). Optimization of uncatalyzed steam explosion pretreatment of rapeseed straw for biofuel production. Bioresource Technology, 190, 97–105. https://doi.org/10.1016/j.biortech.2015.04.066

67. Lopez, G., Keiner, D., Fasihi, M., Koiranen, T., & Breyer, C. (2023). From fossil to green chemicals: sustainable pathways and new carbon feedstocks for the global chemical industry. Energy & Environmental Science, 16(7), 2879–2909. https://doi.org/10.1039/d3ee00478c

68. Lorenci Woiciechowski, A., Dalmas Neto, C. J., Porto de Souza Vandenberghe, L., de Carvalho Neto, D. P., Novak Sydney, A. C., Letti, L. A. J., Karp, S. G., Zevallos Torres, L. A., & Soccol, C. R. (2020). Lignocellulosic biomass: Acid and alkaline pretreatments and their effects on biomass recalcitrance – Conventional processing and recent advances. Bioresource Technology, 304, 122848. https://doi.org/10.1016/j.biortech.2020.122848

69. Lu, C., Zhou, Y., Li, L., Chen, H., & Yan, L. (2023). Conversion of glucose into 5-hydroxymethylfurfural catalyzed by Cr-and Fe-containing mixed-metal metal–organic frameworks. Fuel, 333, 126415. https://doi.org/10.1016/j.fuel.2022.126415

70. Makaveckas, T., Simoneliene, A., & Sipailaite-Ramoskiene, V. (2025). Lignin Valorization from Lignocellulosic Biomass: Extraction, Depolymerization, and Applications in the Circular Bioeconomy. Sustainability, 17(21), 9913. https://doi.org/10.3390/su17219913

71. Mankar, A. R., Modak, A., & Pant, K. K. (2022). Recent advances in the valorization of lignin: a key focus on pretreatment, characterization, and catalytic depolymerization strategies for future biorefineries. Advanced Sustainable Systems, 6(3), 2100299. https://doi.org/10.1002/adsu.202100299

72. Marinho, E. (2025). Cellulose: A comprehensive review of its properties and applications. Sustainable Chemistry for the Environment, 100283. https://doi.org/10.1016/j.scenv.2025.100283

73. Maurya, D. P., Singla, A., & Negi, S. (2015). An overview of key pretreatment processes for biological conversion of lignocellulosic biomass to bioethanol. 3 Biotech, 5(5), 597–609. https://doi.org/10.1007/s13205-015-0279-4

74. Meenakshisundaram, S., Fayeulle, A., Léonard, E., Ceballos, C., Liu, X., & Pauss, A. (2022). Combined Biological and Chemical/Physicochemical Pretreatment Methods of Lignocellulosic Biomass for Bioethanol and Biomethane Energy Production—A Review. Applied Microbiology, 2(4), 716–734. https://doi.org/10.3390/applmicrobiol2040055

75. Mika, L. T., Cséfalvay, E., & Németh, A. (2018). Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability. Chemical Reviews, 118(2), 505–613. https://doi.org/10.1021/acs.chemrev.7b00395

76. Moliner, M., Román-Leshkov, Y., & Davis, M. E. (2010). Tin-containing zeolites are highly active catalysts for the isomerization of glucose in water. Proceedings of the National Academy of Sciences of the United States of America, 107(14), 6164–6168. https://doi.org/10.1073/pnas.1002358107

77. Mondal, S., Ruidas, S., Chongdar, S., Saha, B., & Bhaumik, A. (2024). Sustainable Porous Heterogeneous Catalysts for the Conversion of Biomass into Renewable Energy Products. ACS Sustainable Resource Management, 1(8), 1672–1704. https://doi.org/10.1021/acssusresmgt.4c00190

78. Morawa Eblagon, K., Malaika, A., Ptaszynska, K., Pereira, M. F. R., & Figueiredo, J. L. (2020). Impact of Thermal Treatment of Nb2O5 on Its Performance in Glucose Dehydration to 5-Hydroxymethylfurfural in Water. Nanomaterials, 10(9), 1685. https://doi.org/10.3390/nano10091685

79. Mujtaba, M., Fraceto, L. F., Fazeli, M., Mukherjee, S., Savassa, S. M., de Medeiros, G. A., Pereira, A. D. S., Mancini, S. D., Lipponen, J., & Vilaplana, F. (2023). Lignocellulosic biomass from agricultural waste to the circular economy: a review with focus on biofuels, biocomposites and bioplastics. Journal of Cleaner Production, 402, 136815. https://doi.org/10.1016/j.jclepro.2023.136815

80. Nalawade, K., & Gogate, P. (2024). Ultrasound-Assisted Pretreatment of Sustainable Biomass. In V. Bisaria (Ed.), Handbook of Biorefinery Research and Technology: Biomass Logistics to Saccharification (pp. 403–428). Springer Netherlands. https://doi.org/10.1007/978-94-007-6308-1_68

81. Narayanaperumal, S., Suyambulingam, I., Divakaran, D., Senthamaraikannan, P., Selvan, A., Avudaiappan, S., & Ayrilmis, N. (2026). A Critical Review on Green Conversion Techniques of Biomass Waste to Value-Added Bioproducts: Advances, Challenges, and Future Technological Strategies. Global Change Biology Bioenergy, 18(5), e70118. https://doi.org/10.1111/gcbb.70118

82. Neves, S. A., & Marques, A. C. (2022). Drivers and barriers in the transition from a linear economy to a circular economy. Journal of Cleaner Production, 341, 130865. https://doi.org/10.1016/j.jclepro.2022.130865

83. Ooshima, H., Aso, K., Harano, Y., & Yamamoto, T. (1984). Microwave Treatment of Cellulosic Materials for Their Enzymatic-Hydrolysis. Biotechnology Letters, 6(5), 289–294. https://doi.org/Doi 10.1007/Bf00129056

84. Özuyar, D., & Hoşgün, E. Z. (2025). Acidic Deep Eutectic Solvent Pretreatment of Sunflower Stalks to Improve Enzymatic Hydrolysis and Lignin Recovery. Applied Biochemistry and Biotechnology, 198(2), 1004–1024. https://doi.org/10.1007/s12010-025-05538-0

85. Parveen, F., & Slater, A. G. (2025). Digitalisation of catalytic processes for sustainable production of biobased chemicals and exploration of wider chemical space. Catalysis Science & Technology, 15(6), 1689–1701. https://doi.org/10.1039/d4cy01525h

86. Patil, S. K. R., & Lund, C. R. F. (2011). Formation and Growth of Humins via Aldol Addition and Condensation during Acid-Catalyzed Conversion of 5-Hydroxymethylfurfural. Energy & Fuels, 25(10), 4745–4755. https://doi.org//10.1021/ef2010157

87. Pattnaik, F., Tripathi, S., Patra, B. R., Nanda, S., Kumar, V., Dalai, A. K., & Naik, S. (2021). Catalytic conversion of lignocellulosic polysaccharides to commodity biochemicals: a review. Environmental Chemistry Letters, 19(6), 4119–4136. https://doi.org/10.1007/s10311-021-01284-x

88. Pérez, J. A., Ballesteros, I., Ballesteros, M., Sáez, F., Negro, M. J., & Manzanares, P. (2008). Optimizing Liquid Hot Water pretreatment conditions to enhance sugar recovery from wheat straw for fuel-ethanol production. Fuel, 87(17-18), 3640–3647. https://doi.org/10.1016/j.fuel.2008.06.009

89. Prasongsuk, S., Bankeeree, W., Lotrakul, P., Abd-Aziz, S., & Punnapayak, H. (2022). Biological Pretreatment of Lignocellulosic Biomass. In S. Abd-Aziz, M. Gozan, M. F. Ibrahim, & L. Y. Phang (Eds.), Biorefinery of Oil Producing Plants for Value-Added Products (1 ed., pp. 161–177). Wiley. https://doi.org/10.1002/9783527830756.ch9

90. Preethi, Gunasekaran, M., Kumar, G., Karthikeyan, O. P., Varjani, S., & Banu, R. J. (2021). Lignocellulosic biomass as an optimistic feedstock for the production of biofuels as valuable energy source: Techno-economic analysis, Environmental Impact Analysis, Breakthrough and Perspectives. Environmental Technology & Innovation, 24, 102080. https://doi.org/10.1016/j.eti.2021.102080

91. Qian, Q. H., Asinger, P. A., Lee, M. J., Han, G., Rodriguez, K. M., Lin, S., Benedetti, F. M., Wu, A. X., Chi, W. S., & Smith, Z. P. (2020). MOF-Based Membranes for Gas Separations. Chemical Reviews, 120(16), 8161–8266. https://doi.org/10.1021/acs.chemrev.0c00119

92. Rabemanolontsoa, H., & Saka, S. (2016). Various pretreatments of lignocellulosics. Bioresource Technology, 199, 83–91. https://doi.org/10.1016/j.biortech.2015.08.029

93. Rajendran, K., Drielak, E., Varma, V. S., Muthusamy, S., & Kumar, G. (2018). Updates on the pretreatment of lignocellulosic feedstocks for bioenergy production-a review. Biomass Conversion and Biorefinery, 8(2), 471–483. https://doi.org/10.1007/s13399-017-0269-3

94. Rattanasak, U., Chisti, Y., Jitpinit, S., & Nuithitikul, K. (2025). Production of levulinic acid from oil palm empty fruit bunch fiber using novel tin oxide catalysts. Cleaner Engineering and Technology, 29, 101111. https://doi.org/10.1016/j.clet.2025.101111

95. Ren, W. T., Zhang, D. S., Zhou, Y., Wang, H., Xia, L. M., Tan, C. S., Guo, F., Zhang, X. X., Yang, R. L., & Yu, Y. (2024). Lignin's complex role in lignocellulosic biomass Recalcitrance: A case study on bamboo. Chemical Engineering Journal, 490, 151422. https://doi.org/10.1016/j.cej.2024.151422

96. Rezania, S., Oryani, B., Cho, J., Talaiekhozani, A., Sabbagh, F., Hashemi, B., Rupani, P. F., & Mohammadi, A. A. (2020). Different pretreatment technologies of lignocellulosic biomass for bioethanol production: An overview. Energy, 199, 117457. https://doi.org/10.1016/j.energy.2020.117457

97. Roman-Leshkov, Y., Moliner, M., Labinger, J. A., & Davis, M. E. (2010). Mechanism of glucose isomerization using a solid Lewis acid catalyst in water. Angew Chem Int Ed Engl, 49(47), 8954–8957. https://doi.org/10.1002/anie.201004689

98. Roy, R., Rahman, M. S., & Raynie, D. E. (2020). Recent advances of greener pretreatment technologies of lignocellulose. Current Research in Green and Sustainable Chemistry, 3, 100035. https://doi.org/10.1016/j.crgsc.2020.100035

99. Saravanan, A., Senthil Kumar, P., Jeevanantham, S., Karishma, S., & Vo, D.-V. N. (2022). Recent advances and sustainable development of biofuels production from lignocellulosic biomass. Bioresource Technology, 344, 126203. https://doi.org/10.1016/j.biortech.2021.126203

100. Satlewal, A., Agrawal, R., Bhagia, S., Sangoro, J., & Ragauskas, A. J. (2018). Natural deep eutectic solvents for lignocellulosic biomass pretreatment: Recent developments, challenges and novel opportunities. Biotechnology Advances, 36(8), 2032–2050. https://doi.org/10.1016/j.biotechadv.2018.08.009

101. Schutyser, W., Renders, T., Van den Bosch, S., Koelewijn, S. F., Beckham, G. T., & Sels, B. F. (2018). Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. Chemical society reviews, 47(3), 852–908. https://doi.org/10.1039/c7cs00566k

102. Sethupathy, S., Morales, G. M., Gao, L., Wang, H., Yang, B., Jiang, J., Sun, J., & Zhu, D. (2022). 10.1016/j.biortech.2022.126696. Bioresource Technology, 347, 126696. https://doi.org/10.1016/j.biortech.2022.126696

103. Sheldon, R. A. (2014). Green and sustainable manufacture of chemicals from biomass: state of the art. Green chemistry, 16(3), 950–963. https://doi.org/10.1039/c3gc41935e

104. Singh, S., Sinha, R., & Kundu, S. (2021). Role of organosolv pretreatment on enzymatic hydrolysis of mustard biomass for increased saccharification. Biomass Conversion and Biorefinery, 12(5), 1657–1668. https://doi.org/10.1007/s13399-020-01251-6

105. Smith, M. D. (2019). An Abbreviated Historical and Structural Introduction to Lignocellulose. In M. D. Smith (Ed.), Understanding Lignocellulose: Synergistic Computational and Analytic Methods (Vol. 1338, pp. 1–15). American Chemical Society. https://doi.org/10.1021/bk-2019-1338.ch001

106. Sulis, D. B., Lavoine, N., Sederoff, H., Jiang, X., Marques, B. M., Lan, K., Cofre-Vega, C., Barrangou, R., & Wang, J. P. (2025). Advances in lignocellulosic feedstocks for bioenergy and bioproducts. Nat Commun, 16(1), 1244. https://doi.org/10.1038/s41467-025-56472-y

107. Sun, Z. H., Bottari, G., Afanasenko, A., Stuart, M. C. A., Deuss, P. J., Fridrich, B., & Barta, K. (2018). Complete lignocellulose conversion with integrated catalyst recycling yielding valuable aromatics and fuels. Nature catalysis, 1(1), 82–92. https://doi.org/10.1038/s41929-017-0007-z

108. Swiatek, K., Gaag, S., Klier, A., Kruse, A., Sauer, J., & Steinbach, D. (2020). Acid Hydrolysis of Lignocellulosic Biomass: Sugars and Furfurals Formation. Catalysts, 10(4), 437. https://doi.org/10.3390/catal10040437

109. Tang, B., Li, S., Song, W. C., Yang, E. C., Zhao, X. J., Guan, N. J., & Li, L. D. (2020). Fabrication of Hierarchical Sn-Beta Zeolite as Efficient Catalyst for Conversion of Cellulosic Sugar to Methyl Lactate. ACS Sustainable Chemistry & Engineering, 8(9), 3796–3808. https://doi.org/10.1021/acssuschemeng.9b07061

110. Tempelman, C. H. L., Oozeerally, R., & Degirmenci, V. (2021). Heterogeneous Catalysts for the Conversion of Glucose into 5-Hydroxymethyl Furfural. Catalysts, 11(7), 861. https://doi.org/10.3390/catal11070861

111. Tong, P., Liang, J., Jiang, X., & Li, J. (2019). Research Progress on Metal-Organic Framework Composites in Chemical Sensors. Critical Reviews in Analytical Chemistry, 50(4), 376–392. https://doi.org/10.1080/10408347.2019.1642732

112. Trezza, A., Mahboob, L., Visibelli, A., Geminiani, M., & Santucci, A. (2025). Lignin Waste Valorization in the Bioeconomy Era: Toward Sustainable Innovation and Climate Resilience. Applied Sciences-Basel, 15(14), 8038. https://doi.org/10.3390/app15148038

113. Ullah, M., Liu, P., Xie, S., & Sun, S. (2022). Recent Advancements and Challenges in Lignin Valorization: Green Routes towards Sustainable Bioproducts. Molecules, 27(18), 6055. https://doi.org/10.3390/molecules27186055

114. Ummalyma, S. B., Supriya, R. D., Sindhu, R., Binod, P., Nair, R. B., Pandey, A., & Gnansounou, E. (2019). Biological pretreatment of lignocellulosic biomass—Current trends and future perspectives. In Second and Third Generation of Feedstocks (pp. 197–212). Elsevier. https://doi.org/10.1016/b978-0-12-815162-4.00007-0

115. Upton, B. M., & Kasko, A. M. (2016). Strategies for the Conversion of Lignin to High-Value Polymeric Materials: Review and Perspective. Chemical Reviews, 116(4), 2275–2306. https://doi.org/10.1021/acs.chemrev.5b00345

116. Van Putten, R.-J., Van Der Waal, J. C., De Jong, E., Rasrendra, C. B., Heeres, H. J., & de Vries, J. G. (2013). Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. Chemical reviews, 113(3), 1499–1597. https://doi.org/g/10.1021/cr300182k

117. Vásquez-Garay, F., Carrillo-Varela, I., Vidal, C., Reyes-Contreras, P., Faccini, M., & Mendonça, R. T. (2021). A Review on the Lignin Biopolymer and Its Integration in the Elaboration of Sustainable Materials. Sustainability, 13(5). https://doi.org/10.3390/su13052697

118. Vilaplana, F., Ventura, S. P., Sudarsanam, P., Abdoulmoumine, N., & Carrier, D. J. (2021). Effective assessment practices for using sustainability metrics: biomass processing. In (Vol. 9, pp. 14654–14656): ACS Publications.

119. Wang, C. W., Zhang, W. L., Qiu, X. Q., & Xu, C. B. (2024). Hydrothermal treatment of lignocellulosic biomass towards low-carbon development: Production of high-value-added bioproducts. EnergyChem, 6(6), 100133. https://doi.org/10.1016/j.enchem.2024.100133

120. Wang, F. Q., Ouyang, D. H., Zhou, Z. Y., Page, S. J., Liu, D. H., & Zhao, X. B. (2021). Lignocellulosic biomass as sustainable feedstock and materials for power generation and energy storage. Journal of Energy Chemistry, 57, 247–280. https://doi.org/10.1016/j.jechem.2020.08.060

121. Wang, S., Li, X., Ma, R., & Song, G. (2025). Catalytic Hydrogenolysis of Lignin into Serviceable Products. Acc Chem Res, 58(4), 529–542. https://doi.org/10.1021/acs.accounts.4c00644

122. Wang, S. Y., Cheng, A. H., Liu, F. H., Zhang, J. J., Xia, T., Zeng, X., Fan, W., & Zhang, Y. (2023). Catalytic conversion network for lignocellulosic biomass valorization: a panoramic view. Industrial Chemistry & Materials, 1(2), 188–206. https://doi.org/10.1039/d2im00054g

123. Wilson, K., & Lee, A. F. (2016). Catalyst design for biorefining. Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences, 374(2061), 20150081. https://doi.org/10.1098/rsta.2015.0081

124. Xing, X., Guan, Y., Zhang, L., Shi, X., Wu, H., Gao, H., & Xu, S. (2022). Efficient formation of 5-hydroxymethylfurfural from glucose through H-β zeolite catalyst in the recyclable water-tetrahydrofuran biphasic system. Catalysis Today, 404, 229–236. https://doi.org/10.1016/j.cattod.2022.01.009

125. Xiong, S. S., Guan, Y. S., Luo, C., Zhu, L. J., & Wang, S. R. (2021). Critical Review on the Preparation of Platform Compounds from Biomass or Saccharides via Hydrothermal Conversion over Carbon-Based Solid Acid Catalysts. Energy & Fuels, 35(18), 14462–14483. https://doi.org/10.1021/acs.energyfuels.1c02672

126. Yu, M., Zhang, X.-F., Li, M., Song, J., & Yao, J. (2026). Design of MIL-53(Al) with acidbase cooperative catalytic sites for the oriented conversion of cellulose. Journal of Environmental Chemical Engineering, 14(2), 121220. https://doi.org/10.1016/j.jece.2026.121220

127. Yu, M., Zhang, X. F., Zhang, D., Qiu, J., & Yao, J. (2026). A Stable Sulfonated Catalyst Derived From Amino-Functionalized MIL-53-NH2 for Efficient Fructose to 5-Hydroxymethylfurfural. ChemCatChem, 18(5), e70662. https://doi.org/10.1002/cctc.70662

128. Yusuf, V. F., Malek, N. I., & Kailasa, S. K. (2022). Review on Metal-Organic Framework Classification, Synthetic Approaches, and Influencing Factors: Applications in Energy, Drug Delivery, and Wastewater Treatment. ACS omega, 7(49), 44507–44531. https://doi.org/10.1021/acsomega.2c05310

129. Zabed, H. M., Akter, S., Yun, J. H., Zhang, G. Y., Awad, F. N., Qi, X. H., & Sahu, J. N. (2019). Recent advances in biological pretreatment of microalgae and lignocellulosic biomass for biofuel production. Renewable & Sustainable Energy Reviews, 105, 105–128. https://doi.org/10.1016/j.rser.2019.01.048

130. Zhang, B., Meng, Q., Liu, H., & Han, B. (2023). Catalytic Conversion of Lignin into Valuable Chemicals: Full Utilization of Aromatic Nuclei and Side Chains. Acc Chem Res, 56(24), 3558–3571. https://doi.org/10.1021/acs.accounts.3c00514

131. Zhang, H., Jia, X., Ding, K., Liang, X., He, Y., Guo, X., Zhou, L., Han, L., & Xiao, W. (2025). Optimizing lignocellulose conversion: A comparative study of alkali-assisted ball milling pretreatment of cotton stalk and corn stover. J Biotechnol, 408, 15–27. https://doi.org/10.1016/j.jbiotec.2025.08.018

132. Zhang, K., Pei, Z. J., & Wang, D. H. (2016). Organic solvent pretreatment of lignocellulosic biomass for biofuels and biochemicals: A review. Bioresource Technology, 199, 21–33. https://doi.org/10.1016/j.biortech.2015.08.102

133. Zhang, S. J., Xu, Y. X., & Hanna, M. A. (2012). Pretreatment of Corn Stover with Twin-Screw Extrusion Followed by Enzymatic Saccharification. Applied Biochemistry and Biotechnology, 166(2), 458–469. https://doi.org/10.1007/s12010-011-9441-6

134. Zhao, L., Sun, Z. F., Zhang, C. C., Nan, J., Ren, N. Q., Lee, D. J., & Chen, C. (2022). Advances in pretreatment of lignocellulosic biomass for bioenergy production: Challenges and perspectives. Bioresour Technol, 343, 126123. https://doi.org/10.1016/j.biortech.2021.126123

135. Zhao, X. B., Cheng, K. K., & Liu, D. H. (2009). Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. Applied Microbiology and Biotechnology, 82(5), 815–827. https://doi.org/10.1007/s00253-009-1883-1

GREEN IONIC LIQUIDS FOR BIOMASS PRETREATMENT: FROM FUNDAMENTALS TO TECHNOLOGICAL APPLICATIONS

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ABSTRACT

Lignocellulosic biomass is a strategic raw material for sustainable biofuel and biochemical production due to its high carbon content and renewable nature. However, its complex and recalcitrant structure, composed of cellulose, hemicellulose, and lignin, necessitates highly efficient pretreatment techniques. This chapter examines alternative, environmentally friendly pretreatment technologies in line with the principles of green chemistry and sustainability. Particular focus is placed on the design approaches of ionic liquids (ILs) as 'green' solvents, evaluating their effectiveness in fractionating lignocellulosic components to enhance enzymatic hydrolysis. Furthermore, the chapter critically addresses key sustainability challenges—including toxicity potential, recovery requirements, operational costs, and industrial scalability. Concluding that while IL-based pretreatments offer significant opportunities for sustainable biorefining, the transition to industrial application requires further holistic research, specifically integrating environmental impact assessments and comprehensive life cycle analysis (LCA).

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1. INTRODUCTION

The progressive depletion of fossil-based resources, coupled with escalating greenhouse gas emissions and the severe impacts of climate change, has catalyzed a global paradigm shift toward a sustainable bioeconomy. In this urgent transition, the design of innovative chemical processes that rely on renewable raw materials is paramount. Green chemistry serves as a foundational framework for this transformation, advocating for technologies that inherently minimize waste generation, maximize energy efficiency, and utilize safer chemical alternatives. Consequently, replacing traditional, hazardous industrial processes with sustainable and eco-friendly methodologies has evolved from a conceptual ideal into an absolute necessity for modern chemical engineering.

Within this context, this chapter explores the utilization of green ionic liquids (ILs) as a revolutionary solvent platform designed to overcome the natural resistance of lignocellulosic biomass. Often referred to as "designer solvents," ionic liquids offer tailored physicochemical properties capable of fractionating complex plant matrices under moderate conditions. The fundamental mechanism of ILs in fractionating the lignocellulosic biomass matrix to enhance enzymatic saccharification efficiency is illustrated in Figure 1.

To fully appreciate the disruptive potential of ionic liquids in this domain, it is essential to first understand the intricate structural complexity of lignocellulosic matrices and the inherent limitations of conventional processing methods. Accordingly, this chapter is systematically structured to guide the reader from fundamental biomass chemistry to advanced technological implementations. We begin by dissecting the chemical architecture of plant cell walls—specifically the tightly interwoven network of cellulose, hemicellulose, and lignin—and evaluating why traditional physical and chemical pretreatments often fail to meet modern sustainability metrics. Building upon these foundational concepts, the text transitions into a detailed classification of ionic liquid generations, critically exploring their unique dissolution mechanisms, green solvent advantages, and synergistic integrations with auxiliary techniques such as microwave and ultrasound processing. Finally, a comprehensive analysis of current economic bottlenecks, ecotoxicity profiles, and lifecycle assessments is presented, offering a holistic roadmap for the future of industrial-scale, IL-mediated biorefineries.

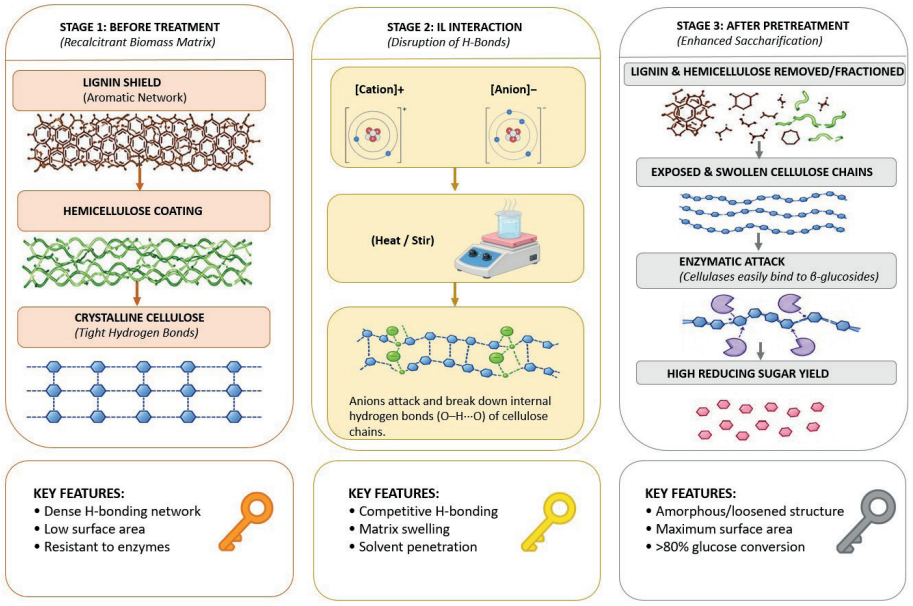

Figure 1. *Multi-stage mechanistic pathway of ionic liquid (IL)-mediated lignocellulosic biomass pretreatment and enhanced saccharification. Stage 1 (Before Treatment): Illustrates the pristine, highly recalcitrant biomass matrix where crystalline cellulose is tightly protected by an outer lignin shield and a dense hemicellulose coating. Stage 2 (IL Interaction): Demonstrates the competitive hydrogen-bonding attack where IL anions aggressively disrupt the internal macro-fibril networks (O–H··· O), prompting matrix swelling and enhanced solvent penetration under controlled heating and stirring. Stage 3 (After Pretreatment): Depicts the successfully fractionated biomass architecture showcasing exposed, amorphous cellulose chains that offer maximum surface area accessibility for cellulase enzymes, ultimately maximizing reducing sugar conversion efficiency (>80%)*

1.1. Lignocellulosic Biomass from a Green Chemistry and Sustainability Perspective: Definition, Importance, and Transformation Potential

As a result of industrialization, population growth, and the increasing use of fossil fuel-based production systems, the sustainable use of natural resources has become one of the most important research topics today. The risk of fossil resources being depleted over time, the increasing greenhouse gas emissions, and the environmental problems caused by climate change have made it necessary to develop and use alternative production systems based on renewable resources. In this context, lignocellulosic acid, a renewable resource, is one of the key areas of research. Lignocellulosic Biomass (LCB) is an important biological resource in facilitating the transition to a sustainable bioeconomy (Devi et al., 2022; Gohain & Borgohain, 2025).

LCB refers to renewable resources consisting of the basic structural components of plant cell walls, primarily cellulose, hemicellulose, and lignin. LCB sources include agricultural residues, forest waste, energy crops, food processing by-products, and various industrial biological wastes. Because LCB is the most abundant renewable biological resource on Earth, it is of great importance for sustainable production systems (Arevalo-Gallegos et al., 2017; Bohrpi et al., 2026).

Cellulose, a key component of LCB, is a linear polysaccharide composed of D-glucose subunits linked by β-(1→4) glycosidic bonds. Hemicellulose, on the other hand, is a more complex and branched heteropolysaccharide structure composed of different monosaccharide structures such as xylose, arabinose, mannose, galactose, and glucose. Lignin is an aromatic polymer composed of phenylpropanoid units, providing mechanical strength to the plant structure and making it resistant to biological degradation. The complex structure created by these three components is the main reason for the natural stability of LCB (Silva et al., 2024).

From a green chemistry perspective, one of the most important advantages of LCBs is that they are a raw material source that does not compete with the food chain. Raw material sources are classified as first, second, third, and fourth generation raw material sources (Lee et al., 2022). Unlike first-generation raw material sources such as corn, beet, sugarcane, or oilseeds, second-generation LCBs are mostly derived from waste generated as a result of agricultural and industrial activities. Thus, while making it possible to utilize waste, they also contribute to minimizing environmental burdens. Especially when considering the circular economy approach, the return of biological waste to the economy provides a great advantage in terms of sustainable resource management (Aiguobarueghian et al., 2024).

The applications of LCB extend beyond its status as a renewable raw material source. This type of biomass is also considered an alternative production method for many chemicals, materials, and industrial products derived from fossil fuels. Biorefineries have come to the forefront, especially recently. With the development of this concept, LCB is considered as a versatile raw material for energy production, as well as for the production of numerous bio-based products (Figure 2). This approach aims to utilize various fractions of biomass for different purposes, similar to how crude oil is converted into different products in petroleum refineries (Sheraz et al., 2025).

When evaluated from a sustainability perspective, LCBs can contribute to the development of carbon neutral or low-carbon production systems. Plants play an important role in the carbon cycle by absorbing carbon dioxide from the atmosphere during their growth stages and producing biomass. Therefore, LCB resources, when evaluated with appropriate and sustainable management strategies, can contribute to the creation of alternative production systems with lower net carbon emissions compared to fossil fuels (Sharma et al., 2024).

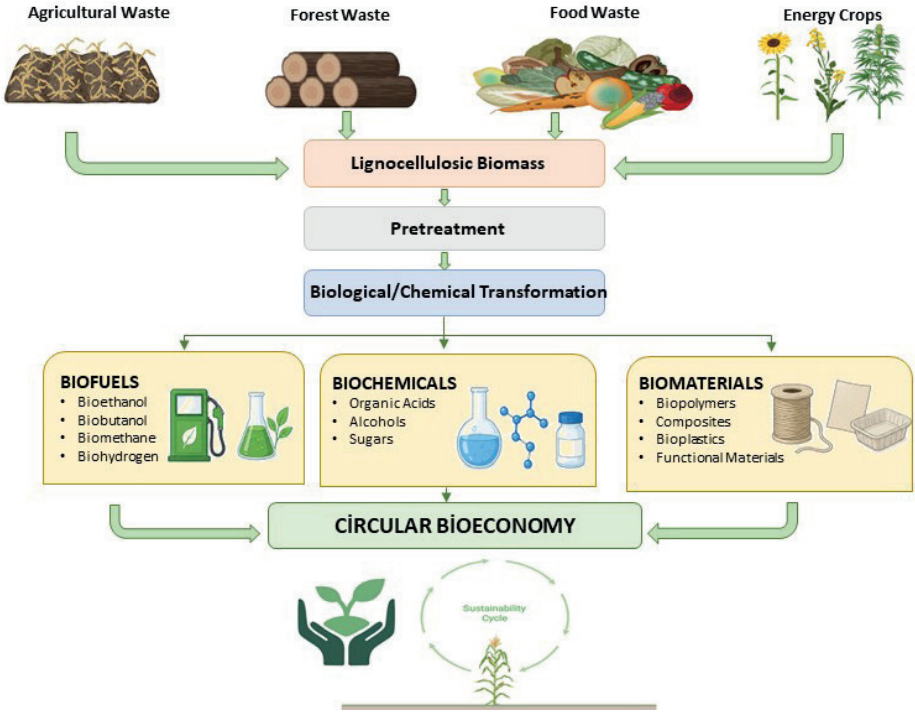

Figure 2. *Schematic workflow of lignocellulosic biomass (LCB) valorization within a circular bioeconomy framework. Diversified renewable feedstocks—including agricultural, forest, and food wastes alongside energy crops—undergo sequential pretreatment and biological/chemical transformation stages. This cascading biorefinery process yields three distinct value-added streams: biofuels (bioethanol, biobutanol, biomethane, biohydrogen), biochemicals (organic acids, alcohols, sugars), and biomaterials (biopolymers, composites, bioplastics, functional materials), ultimately driving a closed-loop sustainability cycle.*

LCB has a very broad transformation potential. Its cellulose and hemicellulose structures, being rich in carbohydrates, form suitable substrates for various biological and chemical transformation processes. Sugars derived from cellulose and hemicellulose can then be transformed into a wide variety of products for use in different biotechnological or chemical processes. Similarly, lignin can currently be used as a potential source in the production of aromatic compounds and various bio-based materials (Maitra et al., 2024). Therefore, it is important to know the chemical components of LCBs depending on the application to be investigated (Table 1).

Table 1. *Chemical composition of major lignocellulosic biomass resources*

Biomass Feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Wheat straw	35–40	30–35	15–15	(Tufail et al., 2021)
Rice straw	32.1	24	18	(Okolie et al., 2021)
Corn stover	40	22	18	(Okolie et al., 2021)
Corn cob	45	35	15	(Sun & Cheng, 2002)
Sugarcane bagasse	42.4	35.3	20.8	(Okolie et al., 2021)
Sugarcane leaves	50.8	30.9	16.7	(Palliprath et al., 2020)
Cotton seed hairs	80-95	5-20	0	(Sun & Cheng, 2002)
Sunflower shell	48.4	34.6	17	(Okolie et al., 2021)
Soybean straw	24.99	11.91	17.64	(Xu et al., 2007)
Barley straw	32.5	25.7	23	(Okolie et al., 2021)
Oat straw	37.6	23.3	12.9	(Okolie et al., 2021)
Hemp bast/stalk	57–77	9–14	5–9	(Stevulova et al., 2014)
Hemp hurds	45.66	24.57	21.67	(Stevulova et al., 2014)
Flax straw	28.7	26.8	22.5	(Okolie et al., 2021)
Miscanthus spp.	47.5	20.9	21.4	(Okolie et al., 2021)
Switchgrass	30-50	10-40	5-20	(Okolie et al., 2021)
Bamboo	46.76	12.18	25.27	(Tsegaye et al., 2020)
Poplar wood	43.8	14.8	29.1	(Okolie et al., 2021)
Hardwoods	40–55	24-40	18–25	(Sun & Cheng, 2002)
Softwoods	40–50	25–35	25–35	(Sun & Cheng, 2002)
Pine wood	38.8	23.6	20.4	(Okolie et al., 2021)
Banana pseudostem	56.4	24.7	12	(Diarsa & Gupte, 2021)
Orange peel	10	15	2	(Mohapatra et al., 2017)
Apple pomace	11.6	10	18.9	(Gowman et al., 2019)
Olive husk	24	23.6	48.4	(Okolie et al., 2021)

However, some important points should be considered when evaluating LCB in terms of sustainability. The fact that biomass is a renewable resource alone is not sufficient for environmental sustainability. Factors such as energy use, chemical use, and waste generation in the processes of collecting, transporting, processing, and converting biomass must also be taken into account. Thus, today, it is emphasized that in addition to biomass being a renewable resource, its conversion processes must also comply with green chemistry principles (Onwukamike et al., 2018).

In conclusion, LCB is considered a fundamental building block of a sustainable bioeconomy due to its high availability, renewable nature, ability to be obtained from waste sources, and suitability for a wide variety of transformation pathways, making it a viable option for future bio-based production systems. However, to fully realize this potential, it is necessary to develop sustainable transformation strategies that address environmental, economic, and technological dimensions together.

2. PRETREATMENT REQUIREMENTS AND KEY OBJECTIVES BASED ON GREEN CHEMISTRY FOR SUSTAINABLE BIOMASS CONVERSION

The effective utilization of LCBs in sustainable production systems requires overcoming various technical obstacles arising from the natural structure of biomass. Although LCBs are abundant and renewable resources worldwide, their resistance to biological and chemical degradation limits the efficiency of conversion processes. The most significant challenge in LCB conversion stems from the highly complex structure of the plant cell wall. In particular, lignin forms a hydrophobic barrier surrounding the cellulose and hemicellulose structures used as substrates. This limits the access of chemical reactants and biological catalysts to the substrate. This situation is discussed in the literature. This is defined as biomass recalcitrance and is considered one of the most significant obstacles in LCB conversion processes (Singhvi & Gokhale, 2019).

The crystallinity of biomass is another factor affecting conversion processes. Due to the dense hydrogen bonds between cellulose molecules, regions with high crystallinity are formed, and these regions are more resistant to chemical or biological degradation. Furthermore, the high degree of polymerization and low surface area of cellulose are other structural characteristics that limit conversion efficiency. Therefore, one of the main aims of an effective pretreatment process is to reduce the crystalline structure of cellulose and increase its accessible surface area (Cheng et al., 2011).

When the entire LCB structure is evaluated, one of the main objectives of pretreatment is to increase the efficiency of biomass by altering its physical and chemical structure, preparing it for subsequent conversion steps. In this context, many structural changes are among the objectives, such as lignin removal, partial dissolution of hemicellulose, disruption of crystalline cellulose structure, and increased porosity. As a result of pretreatment that can achieve these objectives, the accessibility of biomass increases, and the efficiency of conversion processes is significantly improved (Sun et al., 2022).

However, the purpose of the pretreatment to be carried out is not only to increase conversion efficiency. With the increasing value given to the concept of sustainability today, the environmental performance of pretreatment technologies has also become an important factor. Some traditional pretreatment methods have disadvantages such as high energy consumption, intensive chemical use, and secondary waste generation. This situation increases the overall environmental impact of conversion processes and is inconsistent with sustainability goals. Therefore, it is necessary to adopt approaches for developing environmentally friendly pretreatment strategies (Chen et al., 2024)

At this point, green chemistry principles are an important approach for the development and application of sustainable pretreatment technologies. According to the green chemistry approach, a conversion process is expected to have a struc-

ture that provides high product yield, as well as minimal energy requirements, low waste generation, the use of safe chemicals, and minimizing environmental impacts (Beach et al., 2009).

One of the fundamental characteristics that pretreatment technologies should possess within the framework of green chemistry principles is the use of hazardous chemical raw materials in the minimum possible amount. While strong acids and bases can yield positive results on most biomass, they have many limitations in terms of sustainability due to corrosion problems, equipment costs, and waste management requirements. Therefore, research continues into safer solvent systems and environmentally friendly reagents (Reza et al., 2021).

Some pretreatment methods require high temperatures and pressures, thus consuming significant amounts of energy. However, green chemistry principles suggest that energy requirements should be kept to a minimum and processes should be implemented under more moderate conditions. Therefore, research into alternative technologies operating at low temperatures continues, especially recently (Hessel et al., 2022). In short, for a pretreatment technology to be considered successful, it is not enough for it to simply demonstrate high performance at the laboratory scale. The environmental impact, economic feasibility, and industrial scalability of the method must also be considered and evaluated.

3. PRETREATMENT STRATEGIES APPLIED TO LIGNOCELLULOSIC BIOMASS: EVALUATION OF TRADITIONAL METHODS FROM A SUSTAINABILITY PERSPECTIVE

Various pretreatment technologies developed to minimize the structural resistance of LCBs constitute one of the most important steps in biomass conversion processes. Numerous physical, chemical, and physicochemical pretreatment methods have been developed and studied to date. While traditional pretreatment methods are still widely used today, they present various advantages and disadvantages in terms of sustainability criteria (Chopra et al., 2024).

Physical pretreatment methods for biomass Physical pretreatment methods encompass applications aimed at increasing surface area by reducing particle size. Grinding, crushing, and mechanical crushing are the most common techniques among physical pretreatment methods. Although physical pretreatment methods are considered environmentally advantageous due to the absence of chemical use, their high energy consumption is a significant disadvantage. Reaching fine particle sizes, in particular, can significantly increase energy requirements and negatively impact process economics. In most cases, physical pretreatment methods are insufficient on their own and are applied in combination with other pretreatment technologies (Sitotaw et al., 2023).

Physicochemical pretreatment methods is steam blasting. The steam blasting method involves subjecting biomass to high pressure followed by a sudden pressure

drop. Due to the resulting mechanical effects, significant changes occur in the biomass structure, with some hemicellulose dissolving and the lignocellulosic matrix structure loosening. In addition to steam blasting, methods such as AFEX, CO_2 blasting, and electrical catalysis are also preferred. These methods are considered more environmentally friendly than many traditional pretreatment methods because they limit the use of additional chemicals. However, high-temperature applications are considered a significant disadvantage, as they produce inhibitor compounds such as furfural and 5-hydroxymethylfurfural (Kumar & Sharma, 2017).

Among chemical pretreatment methods, acid pretreatments are one of the most effective methods that have long been used in LCB conversion. Pretreatments using sulfuric acid, in particular, facilitate the hydrolysis of hemicellulose and increase the availability of polysaccharides. Although acid pretreatments can provide high conversion efficiencies, they present significant challenges such as corrosion problems, the need for neutralization, and the generation of large amounts of chemical waste. In addition, furan derivatives and organic acids formed during pretreatment can have inhibitory effects in subsequent biological conversion steps (Cheah et al., 2020). Therefore, although acid- based pretreatments are technically successful, they have various limitations from a sustainability perspective.

Alkaline pretreatments are among the frequently preferred methods today due to their effectiveness in lignin removal. Pretreatments carried out using alkaline solvents such as sodium hydroxide, calcium hydroxide, and ammonia cause deformation in the lignin structure, increasing its accessibility to cellulose. A significant advantage is the lower inhibitor formation compared to acid pretreatments. However, the need for significant chemical use and subsequent washing steps for effective pretreatment can lead to substantial water consumption. Furthermore, the environmental impact of the process can increase if the chemicals used in the pretreatment are not recovered (Zhao et al., 2021).

Organosolv pretreatment also holds a valuable position among chemical methods. In this approach, the aim is to remove the lignin structure using ethanol, methanol, acetone, or various organic reagents. Organosolv processes provide an advantage for biorefinery applications by enabling the production of high-purity lignin. However, the process can become complex due to many reasons such as solvent costs, solvent recovery requirements, and safety risks (Wei Kit Chin et al., 2020). The use of volatile organic reagents in pretreatment is a particularly important issue to consider in terms of environmental sustainability.

Another important issue is the scalability of traditional pretreatment methods. Although many pretreatment methods yield positive results in laboratory conditions, they face numerous challenges on an industrial scale due to factors such as energy consumption and equipment costs. This situation plays a decisive role in the economic viability of biomass conversion technologies. Therefore, recent research has focused on developing alternative methods that generate lower environmental impact while maintaining high conversion efficiency.

4. ALTERNATIVE AND ENVIRONMENTALLY FRIENDLY PRETREATMENT TECHNOLOGIES DEVELOPED IN ACCORDANCE WITH GREEN CHEMISTRY PRINCIPLES

New generation pretreatment methods designed in accordance with green chemistry principles (Figure 3) aim to provide lower energy requirements, use of recoverable solvents, reduced waste generation, and safer process opportunities (Yaylaci, 2025).



Figure 3. *Overview of next-generation lignocellulosic biomass pretreatment technologies developed in accordance with green chemistry principles. The schematic highlights sustainable methodologies—ranging from advanced green solvents (Ionic Liquids and Deep Eutectic Solvents) and biological systems to physical/energetic interventions (Microwave, Ultrasound, Plasma, and Supercritical CO_2)—designed to minimize environmental footprints by lowering energy requirements, utilizing recyclable media, and reducing toxic waste generation.*

One of the methods that has recently attracted attention is ionic liquid. These are pretreatments performed using ionic liquids (ILs). Ionic liquids are solvent systems composed entirely of ions and generally have low vapor pressure. Ionic liquids can disrupt hydrogen bonds in the LCB structure and increase cellulose

accessibility. In particular, imidazolium -based ionic liquids have been shown in various studies to be effective in deactivating the lignin structure and increasing cellulose accessibility (Rahman et al., 2025).

Deep eutectic solvents (DES) also hold an important place among sustainable pretreatment technologies. DES systems are often produced by mixing hydrogen bond acceptors, such as choline chloride, with hydrogen bond donors, consisting of organic acids, alcohols, or amides, in specific ratios (Li et al., 2023). These solvents are easy to produce, relatively inexpensive, and have very limited environmental impact. Furthermore, many DES systems are biodegradable and have low toxicity. Recently, the success achieved in removing lignin from cell walls and breaking down biomass structures has increased the importance of this technology in terms of green chemistry principles.

Biological pretreatment methods are also among the environmentally friendly alternatives in line with green chemistry principles. In this method, partial degradation of the lignin structure is achieved using various microorganisms and enzyme systems, primarily white rot fungi (Baksi et al., 2023). Oxidative enzymes such as laccases, manganese peroxidases, and lignin peroxidases are particularly effective in the degradation of lignin. Biological pretreatment technologies are considered advantageous from an environmental perspective due to their low energy requirements and minimal chemical use. However, the long pretreatment times and the possibility of carbohydrate losses in some cases are among the factors that limit the industrial applicability of this method (Woźniak et al., 2025).

Microwave-assisted pretreatment methods are another technology that has been widely researched and applied recently. By utilizing microwave energy, rapid and homogeneous heat transfer can be achieved within biomass, thus significantly reducing processing times. Microwave methods can be applied alone or in combination with acids, alkalis, or various solvents. Studies show that microwave pretreatment, along with lignin removal, can also be used in enzymatic processes. This shows that it is a promising method in terms of increasing digestibility (Woźniak et al., 2025). In addition, the short pre-processing times can provide significant advantages in terms of energy efficiency.

Another technology, ultrasound- assisted pretreatment methods, is also important in sustainable biomass processing applications. Ultrasonic waves create a cavitation effect in the liquid medium, causing physical changes on the biomass surface and supporting the breakdown of cellular structures. This process can contribute to more effective penetration of solvents into the biomass and increase conversion efficiency. It has been reported that ultrasound pretreatment, especially when used in conjunction with low chemical consumption, can reduce environmental impacts (Sharma et al., 2022).

In recent years, plasma technology has been applied in the processing of LCBs. The cold plasma method can induce physical and chemical changes on the biomass surface without the need for high temperatures. After plasma applications, an increase in the surface roughness of the biomass, modification of functional groups,

and improvement in biomass accessibility occur. This method, which is still in the research phase, is considered one of the important alternatives in the future in terms of green chemistry principles due to its low chemical use and short processing times (Abolore et al., 2025).

Carbon dioxide- based technologies are also among the environmentally friendly, alternative pretreatment technologies. Applications using supercritical carbon dioxide, in particular, have the potential to minimize the use of organic solvents. Supercritical CO_2 is attracting interest in sustainable process applications due to its low toxicity, easy recovery, and relatively low environmental impact. However, the high pressure requirement still represents a significant limitation in terms of investment costs (Bertran-Llorens et al., 2024).

Current research focuses not only on developing a single pretreatment technology but also on creating hybrid systems that integrate different methods. For example, approaches such as microwave-DES combinations, ultrasound - assisted biological pretreatments, or ionic liquid-enzyme integrations aim to utilize the advantages of each method. It is thought that such hybrid systems can provide lower energy consumption and higher conversion efficiency (Woźniak et al., 2025).

From the perspective of green chemistry principles, an ideal pretreatment method is expected to provide high yield, use recoverable solvents, produce minimum waste, have low energy requirements, and limit the formation of toxic byproducts. Therefore, it is predicted that future pretreatment research will focus not only on biomass accessibility performance but also on environmental and economic sustainability indicators.

5. USE OF IONIC LIQUIDS IN SUSTAINABLE BIOMASS PRETREATMENT: DEFINITION, CLASSIFICATION AND GREEN SOLVENT APPROACHES

Ionic liquids (ILs) are defined as salts composed entirely of ions and generally existing in the liquid state below 100°C (Amsel et al., 2022). However, this definition is relatively arbitrary and is mainly used to distinguish ionic liquids from molten salts (Torriero & Bond, 2008). In the literature, terms such as 'low-temperature molten salts', 'ionic fluids', and 'liquid organic salts' are also used (Wilkes, 2002). More generally, they are classified as low-temperature and high-temperature ionic liquids based on the boiling point of water (Sharma et al., 2021).

Unlike conventional molten salts, ionic liquids exhibit superior physicochemical properties such as low melting points, negligible vapor pressure, high thermal stability, high ionic conductivity, non-flammability, and tunable solvent characteristics (Tomar & Jain, 2022). Formed by the interaction of an organic cation with an organic or inorganic anion (Figure 4, Figure 5), they can be designed with desired properties by modifying the ion structures (de Jesus & Maciel Filho, 2022).

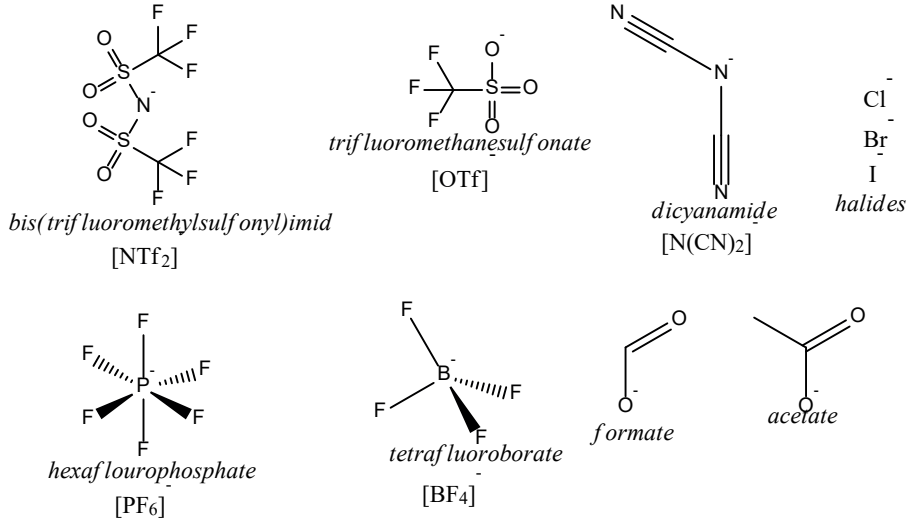

Figure 4. *Examples of frequently used organic and inorganic anions in ionic liquid (IL) preparation. The selection of the anion plays a critical role in determining the final physicochemical properties of the IL, particularly its viscosity, thermal stability, and its specific capacity to disrupt the hydrogen-bonding network of biomass.*

The history of ionic liquids dates back many years. Since the discovery of ethanolammonium nitrate, one of the earliest compounds considered an ionic liquid, numerous ionic liquids have been developed (Sun & Armstrong, 2010). They are generally classified into four generations (Figure 6).

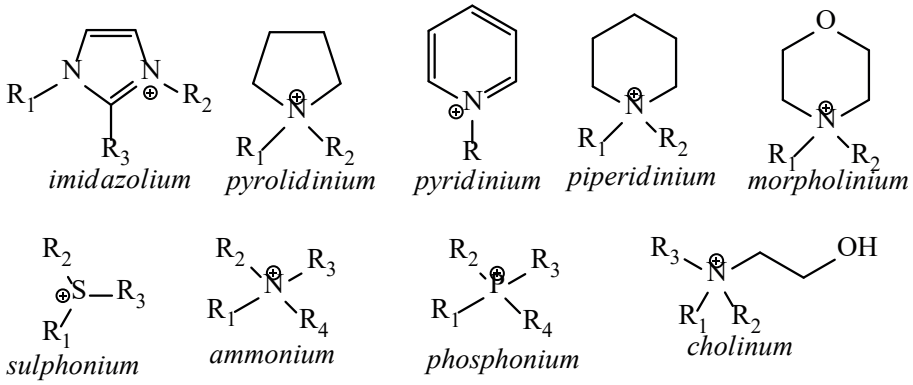

Figure 5. *Commonly utilized organic cations in the synthesis of ionic liquids. Modifying the core cation ring structure or altering the attached alkyl chain lengths allows for the precise tuning of the solvent's hydrophobicity, melting point, and overall efficacy during biomass dissolution processes.*

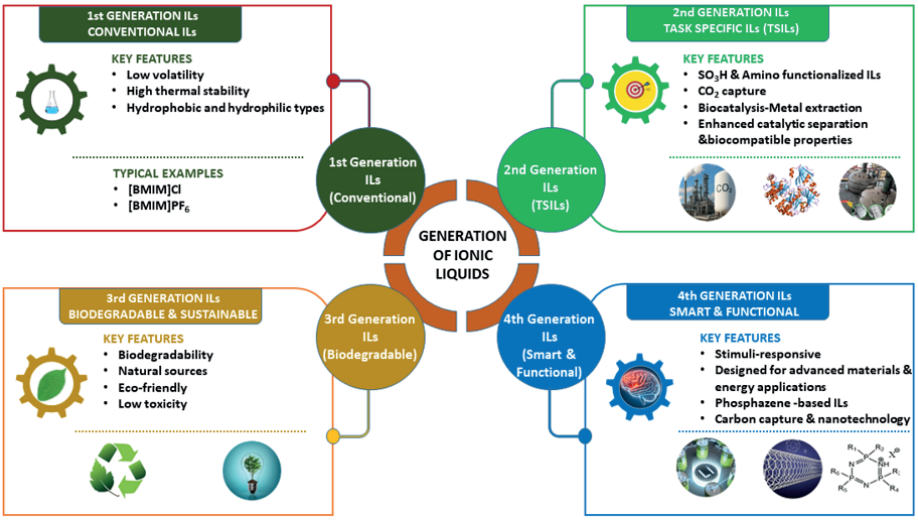

Figure 6. *Historical timeline and structural evolution of ionic liquids (ILs) classified across four technological generations (adapted with visual and conceptual modifications from Liu et al., 2016). The progression conceptualizes the structural paradigm shift from conventional, tuneable green solvents (1st Gen) and task-specific functionalized matrixes (2nd Gen) to completely bio-derived, highly biodegradable regimes (3rd Gen). The timeline culminates in next-generation, stimuli-responsive "smart" systems (4th Gen) designed for reversible chemical operations, showcasing how molecular engineering directly dictates macro-scale sustainability and process adaptability.*

First-generation ILs consist of compounds developed as alternatives to conventional organic solvents, characterized by properties such as low volatility and high thermal stability. Major examples of this group include 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]) (Dharaskar et al., 2013). However, low biodegradability, environmental toxicity, and high production costs have been among the main disadvantages of this generation. (Dias et al., 2017; Sheldon, 2016; Zhuang et al., 2022).

Second-generation ionic liquids are defined as task-specific ionic liquids (TSILs) and possess tunable physical and chemical properties. Although they exhibit greater biocompatibility and environmental friendliness, high synthesis costs and complex purification processes have also emerged as significant limitations of this generation (Hough et al., 2007; Yang et al., 2011).

Third-generation ionic liquids have provided significant advantages over previous generations in terms of low production cost, ease of synthesis, biodegradability, and sustainability (Dias et al., 2019; Moshikur et al., 2020). In the synthesis of these ionic liquids, naturally derived components such as choline, amino acids, and organic acids are generally used. Although they have found wide application in biopharmaceutical applications, biocatalysis, and green solvent systems, their relatively low thermal stability limits their use in industrial applications that require high temperatures (Wang et al., 2024).

Fourth-generation ionic liquids are referred to as "smart ionic liquids"(Alreshidi et al., 2025). These ionic liquids possess stimuli-responsive properties, enabling them to respond to external stimuli such as temperature, light, electric fields, and magnetic fields. Magnetic ionic liquids and photo-responsive ionic liquids, owing to their tunable structures, demonstrate significant potential for use particularly in catalysis and advanced functional material applications (Imahori et al., 2012; Sayyahi et al., 2015).

5.1. Green chemistry approach

Ionic liquids (ILs) are among the sustainable solvent systems developed in accordance with the principles of green chemistry due to their negligible vapor pressures, high thermal and chemical stability, tunable physicochemical properties, and recyclable structures. Compared to conventional organic solvents, their ability to significantly reduce volatile organic compound emissions and minimize solvent losses contributes to the reduction of environmental impacts. In addition, their ability to be recovered and reused after the process increases resource efficiency while also enabling the reduction of waste generation. In recent years, the use of ionic liquids in combination with microwave- and ultrasound-assisted technologies has provided significant advantages in terms of shortening processing times and reducing energy requirements. Furthermore, the development of choline-based ionic liquids exhibiting greater biocompatibility and biodegradability has increased interest in sustainable biorefinery applications and has encouraged the use of these solvents in environmentally friendly biomass processing processes (Neupane et al., 2017; Ocreto et al., 2022; Vieira et al., 2020)

5.2. Application of ionic liquids in biomass pretreatment

The use of ionic liquids in lignocellulosic biomass pretreatment attracted researchers' attention following the demonstration that cellulose could be dissolved in certain ionic liquids. Swatloski and co-workers carried out one of the first significant studies in this field by demonstrating that cellulose could be dissolved in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) (Swatloski et al., 2002). In subsequent studies, various imidazolium-based ionic liquids were shown to be effective in the fractionation of cellulose, hemicellulose, and lignin, which are the main components of lignocellulosic biomass, thereby laying the foundations of ionic liquid-based biomass fractionation technologies. These solvents contribute to the reduction of cellulose crystallinity, partial dissolution of lignin, and the formation of a structure that is more accessible for enzymatic hydrolysis by weakening the hydrogen bonds within the biomass structure. In particular, 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) is among the most widely used ionic liquids due to its ability to increase lignin solubility and improve the enzymatic digestibility of cellulose. As a result, high sugar conversion yields from different lignocellulosic feedstocks have been reported (Liang et al., 2017; Vieira et al., 2020). In recent years, amino acid-derived cholinium-based ionic liquids have attracted considerable attention because of their effectiveness in biomass pretreatment and their sustainability performance. In particular, systems such as cholinium lysinate ([Ch][Lys]) are

considered promising alternative solvents for biorefinery applications (Neupane et al., 2017). Table 2 presents various ionic liquids used for the dissolution of different biomass types, demonstrating that many ionic liquids have been reported to exhibit high efficiency in the dissolution of lignocellulosic biomass throughout the process.

Table 2. *Various ionic liquids used in the dissolution of different lignocellulosic biomasses*

Lignocellulosic biomass	Ionic liquid	Antisolvent	Temp. (°C)	Time	Findings	Reference
Sugarcane tops	[TMA]$MeSO_4$	Acetone	60	4 h	1.57-fold increase in sugar yield	(Sharma et al., 2023)
Pine sapwood	[Bmim][HSO_4] (20% H_2O)	Methanol	120	22 h	81.7% lignin extraction	(Buettner et al., 2022)
Rice straw	[EMIM]Ac	Water	90–130	2–6 h	Increased dissolution and fermentable sugar	(Liu et al., 2021)
Oil palm biomass	[Bmim][Cl]	Acetone/ Water (1:1)	110	8 h	54% lignin yield	(Roy & Chundawat, 2023)
Sugarcane bagasse	[MEA]OAc	DMSO	150	NR*	Increased delignification, dissolution, and ethanol production	(Nakasu et al., 2021)
Eucalyptus	[Bmim][OAc]	Water	120	30 min.	16.97% lignin extraction and good biomass	(Ziaei-Rad et al., 2021)
Red oak	[Emim][OAc]	Acetone/ Water (1:1)	110	35 h	Delignification and 34.9% lignin recovery	(Sun et al., 2009)
Oil palm frond (OPF)	[EMIM]Ac	Acetonitril	90–99	3 h	Decrease in crystallinity index	(Avid et al., 2022)
Maple wood flour	[Emim][OAc]	0.1 N NaOH	90	70 h	Over 80% lignin recovery	(Espinosa et al., 2017)
Microcrystalline cellulose	[C_3SO_3Hmim][H_2PO_4]	Water	160	30 min.	3.5% levulinic acid yield	(Frink et al., 2014)
Avicel	[EMIM]DEP	Water	40	24 h	70% cellulose-to-glucose conversion	(Kamiya et al., 2008)
Sugarcane bagasse	[EMIM]DEP	Acetone/ Water (1:1)	50	24 h	82.86% glucose yield after delignification	(Montoya-Rosales et al., 2020)
Beech, eucalyptus, cotton	[EMIM]Ac	Methanol	40	4 h	Significant decrease in cellulase activity	(Ebner et al., 2014)
Switch grass	[EMIM]Ac	Water	70	72 h	81.2% glucose and 87.4% xylose release	(Hou et al., 2013)

Lignocellulosic biomass	Ionic liquid	Antisolvent	Temp. (°C)	Time	Findings	Reference
Bagasse powder	[EMIM]Ac + ChoAc	Acetone/ Water (1:1) or Water	25–50	48 h	80% cellulose and 72% hemicellulose saccharification	(Fougere et al., 2016)
Eucalyptus grandis	[Amim][Cl]	Water or Methanol	120	5 h	96% biomass recovery and complete ionic liquid recovery	(Wang et al., 2021)
Hornbeam	[HMMorp] HSO_4	Acetonitril	150	3 h	91% lignin removal and 95% glucose yield	(Umagiliyage et al., 2015)
Sorghum bicolor	[Ch][GlcA], [Bet][GlcA]	Water	140	3 h	75% glucose yield and 47% xylose yield	(Kim et al., 2026)
Miscanthus giganteus, Pinus sylvestris, Salix viminalis	[Bmim] $[MeSO_4]$, [Bmim] $[HSO_4]$	Water	120	30 min.	90% glucose and 25% hemicellulose recovery	(Brandt et al., 2011)
Sugarcane bagasse	[C4mim]Cl, [C2mim]Cl, [C2mim]OAc	Water	130	24 h	60% lignin removal, 83% saccharification yield, and 100% ionic liquid recovery	(Karatzos et al., 2012)
Hybrid aspen and Norway spruce	$[C{=}C_2C_1im]$ $[MeCO_2]$, $[C_4C_1im]$ $[MeCO_2]$, $[C_4C_1im][Cl]$, and $[C_4C_1im]$ $[HSO_4]$	Water	120	1-3 h	High saccharification yield in acetate-based ionic liquids	(Gräsvik et al., 2014)
Sorghum	[Eth][OAc]	Water	120	3 h	Low cost, 30% GHG reduction	(Achinivu et al., 2022)
Corn stover	[Ch][Lev], [EA][Lev]	Water	140	3 h	High delignification with increased glucose yield	(Chen et al., 2022)
Sorghum	[EthA][OAc], [PropA][OAc], [MAEthA] [OAc], and [DMAEthA] [OAc]	Water	120	3 h	73.6% glucose yield and 51.4% xylose yield	(Achinivu et al., 2024)
Sorghum bicolor	Schiff-base(iminium) ILs	Water	120	3 h	87% glucose and 76% xylose release	(Choudhary et al., 2022)

*NR: Not Reported

6. ADVANTAGES OF IONIC LIQUIDS IN THE SCOPE OF GREEN CHEMISTRY AND THEIR UNIQUE EFFECTS ON LIGNOCELLULOSIC STRUCTURE

Lignocellulosic biomass has a complex and recalcitrant structure composed of cellulose, hemicellulose, and lignin (Figure 7). The strong hydrogen bonds and lignin–carbohydrate interactions within this structure make the deconstruction of biomass difficult. For the efficient utilization of biomass, it must be partially or completely dissolved. For this purpose, ionic liquids are being investigated as effective media for the dissolution of biomass with high efficiency under mild conditions.

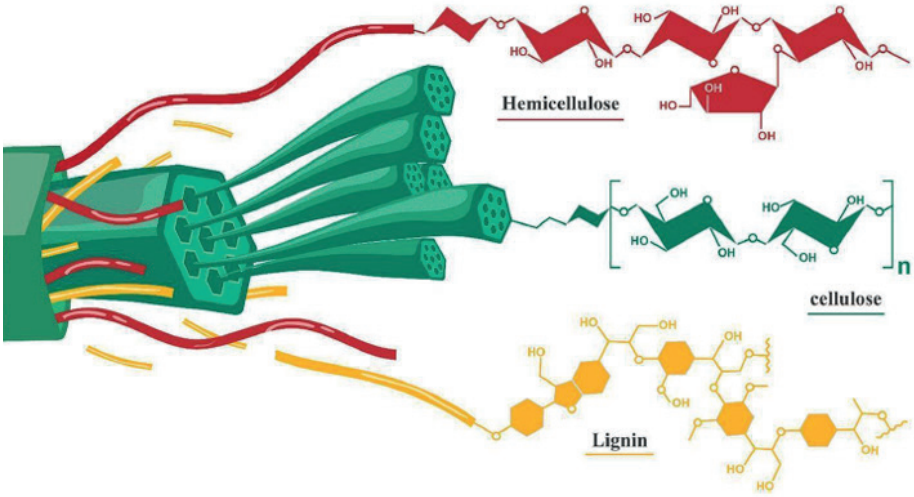

Figure 7. *Complex and recalcitrant structural organization of lignocellulosic biomass. The multi-scale diagram delineates the highly ordered crystalline cellulose microfibrils, the amorphous hemicellulose matrix coating, and the surrounding, protective cross-linked lignin network that together form the structural barrier in plant cell walls (reproduced with permission from Verdía Barbará et al., 2025). Understanding this dense architecture is crucial for designing selective green solvents capable of bypassing biomass recalcitrance.*

Cellulose constitutes approximately 35–50% of the dry weight of lignocellulosic biomass. Cellulose, which is linked by β-1,4-glycosidic bonds, is insoluble in water and many organic solvents. Zhu et al. reported that ionic liquids (ILs) are capable of dissolving cellulose through a dissolution mechanism based on the high hydrogen-bond basicity of their anions (Zhu et al., 2006). In addition, Payal and co-workers demonstrated that room-temperature ionic liquids are strong hydrogen-bond acceptors and moderate hydrogen-bond donors (Payal et al., 2015). Furthermore, a study conducted by Liu et al. showed that ionic liquids containing imidazolium-, pyridinium-, ammonium-, and phosphonium-based cations, together with anions such as chloride, acetate, formate, and dialkyl phosphate, possess the ability to dissolve cellulose(Liu et al., 2016). As can be seen from the literature, ionic liquids facilitate biomass processing primarily by disrupting the hydrogen bonds between cellulose chains, thereby reducing its crystalline structure and making the

biomass more accessible. This enhances the efficiency of enzymatic hydrolysis and facilitates the production processes of biofuels and biochemicals (Brandt et al., 2013; da Costa Lopes et al., 2013). Figure 8 illustrates the mechanism of cellulose dissolution in ionic liquids, demonstrating that the breaking of hydrogen bonds within the cellulose structure leads to the disruption of the polymeric structure by ionic liquid components.

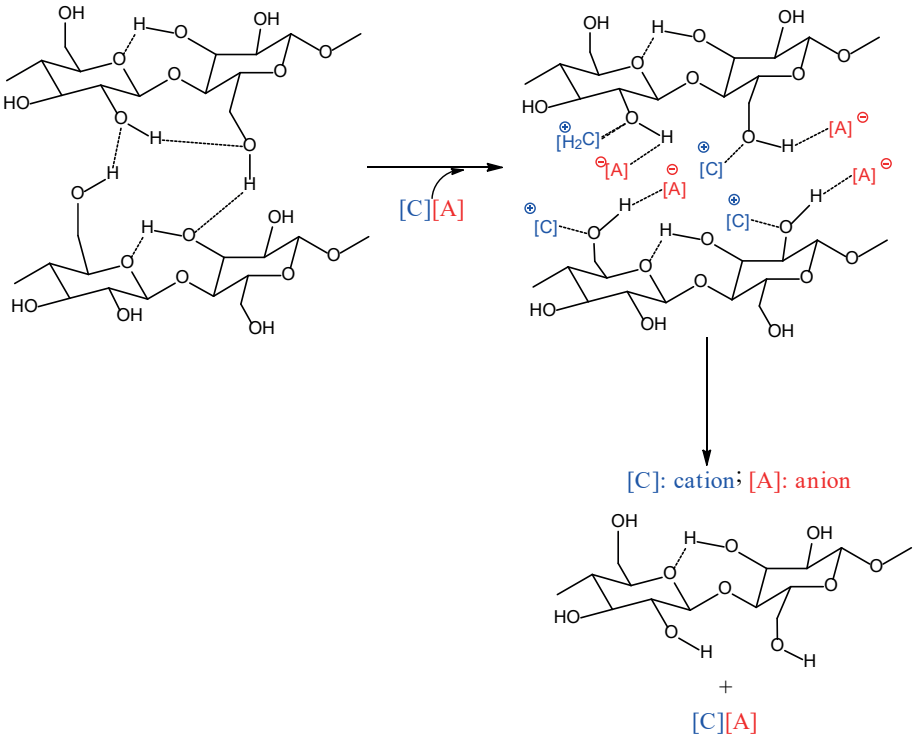

Figure 8. *Molecular-level mechanism of crystalline cellulose deconstruction mediated by advanced ionic liquid (IL) interactions (re-drawn and adapted with visual modifications from Yoo et al., 2017). The schematic chronicles how the high hydrogen-bond basicity of the IL anion effectively targets and cleaves the inter- and intra-molecular hydrogen-bonding networks that stabilize cellulose microfibrils (as seen anatomically in Figure 7). Concurrently, the IL cation interacts with the cellulose oxygen atoms to provide steric hindrance, preventing re-crystallization and facilitating full polymeric solubilization by disrupting the ordered chain alignment.*

Lignin is another important component of lignocellulosic biomass (Figure 9). Possessing a three-dimensional amorphous network structure, lignin contains C–O–C and C(O)–O–C type ether/ester linkages. These bonds contribute to the recalcitrant nature of lignin and, consequently, to its limited solubility in most solvents. The recovery of high-purity lignin from lignocellulosic biomass is a critical step. The lignin-dissolving capacity of ionic liquids is one of their major advantages. In particular, imidazolium-based ionic liquids containing acetate and chloride anions have been shown to dissolve lignin effectively and facilitate biomass fractionation. Pu and co-workers investigated the solubility of lignin in various aprotic ionic liquids.

In their study, ionic liquids containing [BMIM], [MMIM], and [HMIM] cations together with [CF_3SO_3], [$MeSO_4$], [Cl], [Br], and [PF_6] anions were evaluated, and the results showed that lignin solubility depends more strongly on the type of anion than on the type of cation used. Specifically, in ionic liquids based on the [BMIM] cation, lignin solubility followed the order [$MeSO_4$] > [Cl] ≈ [Br] ≫ [PF_6]. They also reported that ionic liquids containing bulky BF_4^- and PF_6^- anions exhibited lower lignin solubility (Abushammala & Mao, 2020; Pu et al., 2007; Qasim et al., 2021) (Table 3).

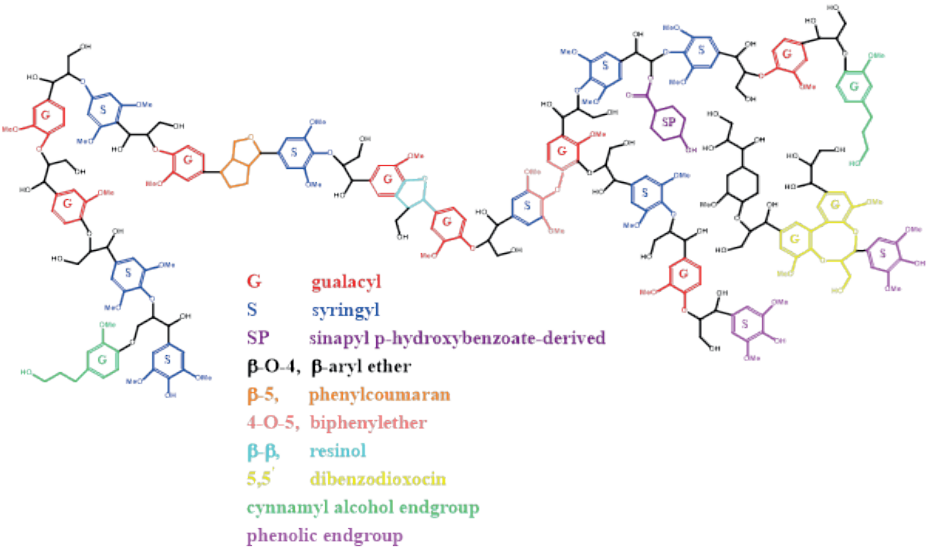

Figure 9. *Complex, three-dimensional amorphous macromolecular architecture of the native lignin network (re-drawn and adapted with visual modifications from Singh, 2019). The color-coded schematic details the heterogeneous distribution of guaiacyl (G), syringyl (S), and functionalized monomeric units interconnected through robust inter-monomer networks. The visualization contrasts predominant ether motifs, such as the abundant β-O-4 and 4-O-5 linkages, with condensed carbon-carbon (C–C) bonds (β-5, β-β, and 5,5' dibenzodioxocin rings), which collectively dictate the structural recalcitrance and chemical resistance of biomass during biorefinery fractionation.*

From a green chemistry perspective, the recoverability and reusability of ionic liquids provide a significant advantage. Through appropriate recycling systems, these solvents can be reused after the process, thereby reducing chemical waste generation and supporting the environmental sustainability of the processes. In addition, when used in combination with microwave- and ultrasound-assisted pretreatment methods, they reduce energy requirements and enhance the dissolution efficiency of biomass fractions. Their ability to effectively dissolve particularly the lignin fraction of biomass facilitates the breakdown of the lignocellulosic structure, thereby improving the performance of subsequent conversion processes. Therefore, current research focuses on the development of environmentally friendly ionic liquids that combine high dissolution efficiency with low toxicity, recyclability, and economic feasibility (Rodríguez, 2021; Salleh et al., 2025; Yoo et al., 2017).

Table 3. *Solubility of lignin in various ionic liquids*

Ionic liquids	Solvent Temp. (˚C)	Solubility	Reference
[BMIM][Cl]	75	13.9 g/L	(Pu et al., 2007)
[DMEA][OAc], [EMIM][OAc], [BzMIM][Cl]	90	10–30 %	(Fu et al., 2010)
[Py][CH_3COO], [HMIM][CH_3COO], [Pyrr][CH3COO]	90	>50 wt%	(Achinivu et al., 2014)
[Py][HCOO], [Py][CH_3COO], [Py][CH_3CH_2COO]	75	710 g/L	(Rashid et al., 2016)
[MMIM][$MeSO_4$], [BMIM][CF_3SO_3], [AMIM][Cl], [EMIM][OAc], [BMIM][Cl], [BMIM][PF_6], [BMIM][BF_4], [BzMIM][Cl]	90	0.1–>50 wt%	(Lee et al., 2009)
[EMIM][CF_3SO_3], [EMIM][CH_3CO_2], [P_{4444}][CF_3CO_2], [Py_{14}][CF_3CO_2]	60	40 wt%	(Akiba et al., 2017)
[CyanoMIM][Br], [PMIM][Br], [BMIM][Cl]	80–90	62.4–87.8 mg/g	(Lateef et al., 2009)
[$CH_3(OCH_2CH_2)_2$–EMI][CH_3COO], [$CH_3(OCH_2CH_2)_3$–EMI][CH_3COO]	110	>21 %	(Zhao et al., 2010)
[CNMIM][Br], [PrMIM][Br]	90	6–9.5 %	(Lateef et al., 2009)
Choline-based ionic liquids	90	1–22 %	(Liu et al., 2012)

7. LIMITATIONS, ENVIRONMENTAL IMPACTS AND POTENTIAL RISKS OF IONIC LIQUIDS IN TERMS OF SUSTAINABILITY

Although ionic liquids offer many advantages in lignocellulosic biomass studies and other application areas, there are also various technical, economic, and environmental challenges that limit their industrial-scale use. Therefore, the sustainability performance of ionic liquids should be evaluated not only in terms of their solvent properties but also in relation to factors such as life-cycle impacts and process integration.

One of the most important disadvantages of ionic liquids is their high production cost. The synthesis of many ionic liquids involves multi-step reactions, high purity requirements, and energy-intensive purification processes. This particularly limits economic feasibility in large-scale applications and makes it difficult for them to compete with conventional solvents. In addition, the economic viability of ionic liquids largely depends on efficient recovery and reuse strategies. Although their high thermal and chemical stability provides an advantage in terms of reuse, in some systems the recovery processes may require additional energy consumption and equipment, which increases process costs and complicates scale-up studies (Brandt et al., 2013; Qasim et al., 2021).

Although ionic liquids are often described as "green solvents" due to their low vapor pressures and reusability potential, it is not possible to evaluate all ionic liquids within this category from an environmental perspective. Studies have shown that some ionic liquids can exhibit toxic effects, particularly on microorganisms, algae, and aquatic organisms. These effects are largely associated with the cation structure, anion type, alkyl chain length, and the hydrophobic character of the compound. In particular, imidazolium-based ionic liquids with long alkyl chains have been reported to exhibit higher toxicity (Abushammala & Mao, 2020). Furthermore, some ionic liquids degrade slowly in natural environments and may pose a risk of environmental accumulation. Their persistence, especially when introduced into aquatic environments, raises significant concerns regarding ecotoxicological impacts. In cases where the solvent cannot be fully recovered after the process, waste management issues may also negatively affect the environmental performance of ionic liquids (Salleh et al., 2025; Yoo et al., 2017).

From a process performance perspective, the high viscosity of ionic liquids represents a significant operational disadvantage. High viscosity reduces mass transfer rates, makes mixing and pumping operations more difficult, and can lead to efficiency losses particularly in extraction, separation, and biomass pretreatment applications. In addition, high viscosity may increase energy consumption during processing, thereby partially reducing their sustainability advantages (da Costa Lopes et al., 2013; Figure 10).

Finally, although a large number of studies and patents have been developed on ionic liquids, the transfer of laboratory-scale successes to industrial applications is still considered a major challenge. The requirement to simultaneously meet performance, cost, recoverability, and environmental safety criteria limits the widespread adoption of commercial applications. Therefore, current research focuses on the development of ionic liquids that are low-cost, biodegradable, low-toxicity, and highly recoverable, aiming to provide more practical solutions for sustainable biorefineries and other industrial processes (Kaur et al., 2022; Ovejero-Pérez et al., 2024; Rodríguez, 2021).

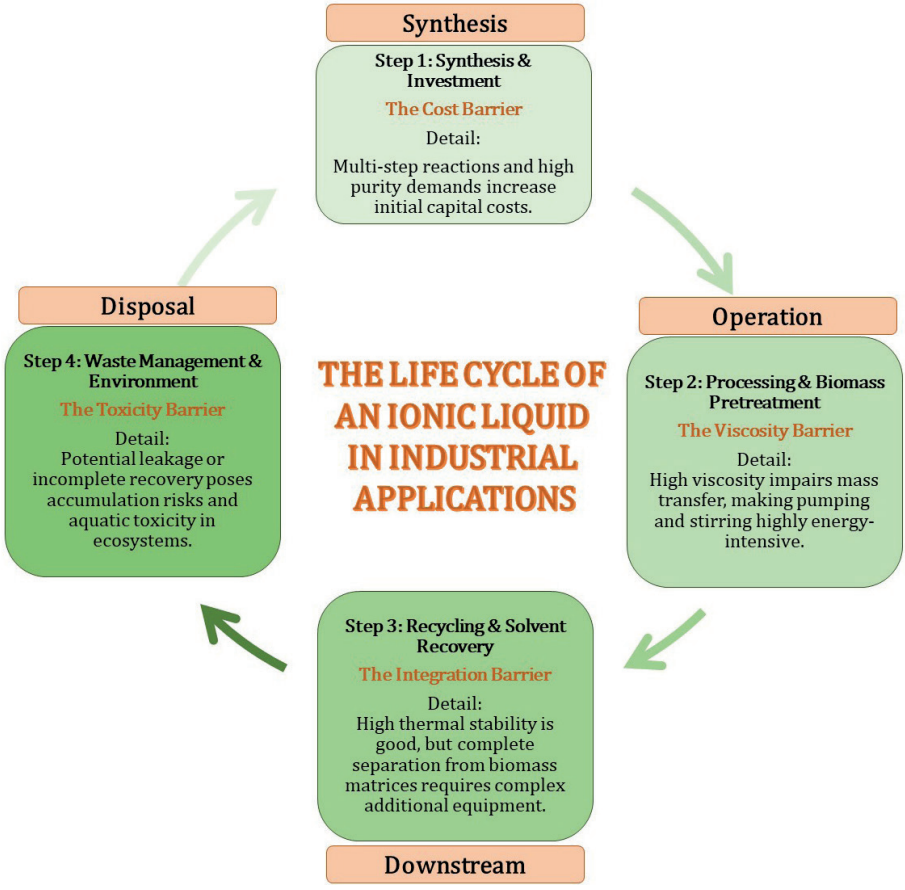

Figure 10. *Comprehensive map of the technical, economic, and environmental challenges limiting the industrial-scale application of ionic liquids in biomass processing. The framework categorizes the critical bottlenecks—such as high manufacturing costs, high operational viscosity, ecotoxicological risks in aquatic systems, and complex recycling requirements—that must be simultaneously resolved to bridge the gap between laboratory-scale successes and commercial biorefineries.*

8. GENERAL REVIEW AND FUTURE PERSPECTIVES: MULTIDISCIPLINARY RESEARCH AND APPLICATION AREAS IN LINE WITH GREEN CHEMISTRY PRINCIPLES

Ionic liquids have recently become one of the innovative solvent systems attracting significant attention in sustainable biorefinery technologies. Thanks to their high dissolution capacity, selective fractionation properties, and recyclable nature in the pretreatment of lignocellulosic biomass, they offer important advantages in the production of biofuels, biopolymers, and value-added chemicals. The development of ionic liquids in line with green chemistry principles is considered a strategic approach for reducing dependence on fossil-based chemicals and enabling the transition to a low-carbon economy (Brandt et al., 2013; Yoo et al., 2017).

A significant portion of future research is focused on the synthesis of bio-based and biodegradable ionic liquids. In particular, choline-based ionic liquids and deep eutectic solvents (DES) are considered promising alternatives due to their low toxicity and lower production costs. In addition, ionic liquids have potential applications in multidisciplinary fields such as nanotechnology, catalysis, membrane technologies, carbon capture systems, and pharmaceutical applications (Abushammala & Mao, 2020; Salleh et al., 2025).

From the perspective of industrial-scale applicability, the development of solvent recovery technologies is of critical importance. Energy-efficient recycling systems, process integration, and hybrid pretreatment technologies are expected to be at the center of future studies. In addition, AI-assisted molecular design and computational chemistry approaches are expected to enable the targeted synthesis of ionic liquids. In this way, it will become possible to develop low-cost and environmentally friendly solvents optimized for specific types of biomass (Qasim et al., 2021). The emerging trends, key technology focus areas, and expected sustainability outcomes for next-generation ionic liquid-mediated biorefineries are comprehensively summarized in Table 4.

The technological matrix outlined in Table 4 highlights a transition from trial-and-error laboratory experiments to highly predictable, targeted engineering platforms. To fully realize these sustainability outcomes, next-generation ionic liquids must expand into multidisciplinary applications beyond biomass pretreatment, such as catalysis, advanced membrane separations, and carbon capture systems. Their tunable frameworks allow for dual-function applications, including capturing carbon dioxide and upgrading bio-derived intermediates within integrated biorefineries. Furthermore, their emerging use in nanotechnology as surface modifiers and in pharmaceuticals as biocompatible drug delivery vehicles shifts the paradigm from single-purpose extraction to a multi-product circular infrastructure.

Table 4. *Emerging trends and future directions in ionic liquid-mediated biorefineries*

Research Focus Area	Key Technologies / Approaches	Expected Sustainability Outcomes
Next-Generation Solvents	Choline-based ILs, Deep Eutectic Solvents (DES)	Lower production costs, high biodegradability, minimal aquatic toxicity
Process Intensification	Hybrid systems (Microwave/ Ultrasound + ILs)	Reduced energy consumption, accelerated dissolution rates
Advanced Recovery	Energy-efficient recycling and closed-loop systems	Near-complete solvent reuse, minimized chemical waste generation
Digital Chemistry	AI-assisted molecular design, Computational chemistry	Targeted synthesis of task-specific ILs optimized for diverse biomass types

Simultaneously, the paradigm shift toward 'Digital Chemistry' represents the most disruptive catalyst for accelerating green solvent development. Traditional screening is inherently constrained by nearly infinite cation-anion pairings; how-

ever, integrating artificial intelligence (AI), machine learning, and computational chemistry enables the virtual screening of task-specific solvents optimized for diverse biomass matrices. These digital frameworks can predict thermodynamic behaviors, viscosity constraints, and ecotoxicological impacts prior to physical synthesis, drastically reducing development timelines and chemical waste. Ultimately, synchronizing these computational advancements with closed-loop engineering infrastructures will successfully bridge the gap between laboratory breakthroughs and commercially viable biorefineries.

CONCLUSION

The growing demand for sustainable biomass conversion processes has emphasised the necessity for eco-friendly pretreatment methods that simultaneously enhance process efficiency and environmental responsibility. While ionic liquids have shown a remarkable ability to overcome biomass resistance, their true significance extends beyond biomass fractionation. They show how solvent engineering can help move away from conventional chemical processing and towards more sustainable and circular biorefining systems.

The future success of ionic liquid-based technologies is not going to depend on their ability to increase sugar yield or lignin extraction efficiency, according to the latest evidence. Instead, the factors that determine their industrial significance are factors such as solvent recoverability, cost-effectiveness, environmental friendliness, and how well they can be integrated into the biorefining infrastructures that already exist. A holistic sustainability framework is therefore essential for evaluating ionic liquids.

Significant progress can be expected in the coming years, as recent advances in bio-based ionic liquids, hybrid pretreatment systems and computational solvent design indicate. A combination of life cycle assessment, technical-economic analysis and process intensification strategies in green solvent development is key to designing efficient and environmentally friendly pretreatment platforms.

In conclusion, while ionic liquids offer significant opportunities in sustainable biomass processing technologies, they are complex systems requiring simultaneous evaluation of economic, toxicological, and environmental aspects. With increased interdisciplinary research in the future, ionic liquids are expected to become safer, more economical, and more environmentally friendly. Ultimately, bridging the gap between molecular design and industrial scalability will position ionic liquids not merely as alternative solvents, but as foundational pillars of the next-generation, zero-waste circular bioeconomy.

SONUÇ

Sürdürülebilir biyokütle dönüşüm süreçlerine yönelik artan talep, süreç verimliliğini ve çevresel sorumluluğu eş zamanlı olarak artıran çevre dostu ön işlem yöntemlerinin gerekliliğini vurgulamıştır. İyonik sıvılar, biyokütle direncini aşmada olağanüstü bir yetenek göstermiş olsa da bunların gerçek önemi yalnızca biyokütle fraksiyonasyonu ile sınırlı değildir. İyonik sıvılar, çözücü mühendisliğinin geleneksel kimyasal işlemeden uzaklaşarak daha sürdürülebilir ve döngüsel biyorafineri sistemlerine doğru ilerlemeye nasıl yardımcı olabileceğini göstermektedir.

Gelişmiş kanıtlara göre, iyonik sıvı tabanlı teknolojilerin gelecekteki başarısı, yalnızca şeker verimini veya lignin ekstraksiyon verimliliğini artırma yeteneklerine bağlı olmayacaktır. Aksine, bunların endüstriyel önemini belirleyen unsurlar; çözücülerin ne kadar kolay geri kazanılabildiği, maliyet etkinliği, çevre dostu olmaları ve mevcut biyorafineri altyapılarına ne kadar iyi entegre edilebildikleri gibi faktörler olacaktır. Bu nedenle, iyonik sıvıları değerlendirmek için bütünsel bir sürdürülebilirlik çerçevesi esastır.

Biyo-bazlı iyonik sıvılar, hibrit ön işlem sistemleri ve hesaplamalı çözücü tasarımındaki son gelişmelerin de gösterdiği gibi, önümüzdeki yıllarda bu alanda önemli ilerlemeler beklenmektedir. Yeşil çözücü geliştirmede yaşam döngüsü değerlendirmesi (LCA), teknik-ekonomik analiz ve süreç yoğunlaştırma stratejilerinin bir kombinasyonu, verimli ve çevre dostu ön işlem platformları tasarlamanın anahtarıdır.

Sonuç olarak; iyonik sıvılar sürdürülebilir biyokütle işleme teknolojilerinde önemli fırsatlar sunarken, aynı zamanda ekonomik, toksikolojik ve çevresel yönlerin eş zamanlı olarak değerlendirilmesini gerektiren karmaşık sistemlerdir. Gelecekte artan disiplinlerarası araştırmalarla birlikte, iyonik sıvıların daha güvenli, daha ekonomik ve daha çevre dostu hale gelmesi beklenmektedir. Nihayetinde, moleküler tasarım ile endüstriyel ölçeklenebilirlik arasındaki köprüyü kurmak, iyonik sıvıları yalnızca alternatif çözücüler olarak değil, yeni nesil, sıfır atıklı döngüsel biyoekonominin temel taşları olarak konumlandıracaktır.

REFERENCES

1. Abolore, R. S., Jaiswal, S., & Jaiswal, A. K. (2025). A comprehensive review of the application of cold plasma technology in lignocellulosic biomass pretreatment. *Biofuels, bioproducts and biorefining*, *19*(2), 453-468. https://doi.org/10.1002/bbb.2706
2. Abushammala, H., & Mao, J. (2020). A review on the partial and complete dissolution and fractionation of wood and lignocelluloses using imidazolium ionic liquids. *Polymers*, *12*(1), 195. https://doi.org/10.3390/polym12010195
3. Achinivu, E. C., Blankenship, B. W., Baral, N. R., Choudhary, H., Kakumanu, R., Mohan, M., Baidoo, E. E., Scown, C. D., George, A., & Simmons, B. A. (2024). Biomass pretreatment with distillable ionic liquids for an effective recycling and recovery approach. *Chemical Engineering Journal*, *479*, 147824. https://doi.org/10.1016/j.cej.2023.147824
4. Achinivu, E. C., Cabrera, M., Umar, A., Yang, M., Baral, N. R., Scown, C. D., Simmons, B. A., & Gladden, J. M. (2022). In situ synthesis of protic ionic liquids for biomass pretreatment. *ACS Sustainable Chemistry & Engineering*, *10*(37), 12090-12098. https://doi.org/10.1021/acssuschemeng.2c01211
5. Achinivu, E. C., Howard, R. M., Li, G., Gracz, H., & Henderson, W. A. (2014). Lignin extraction from biomass with protic ionic liquids. *Green Chemistry*, *16*(3), 1114-1119. https://doi.org/10.1039/C3GC42306A
6. Aiguobarueghian, I., Adanma, U. M., Ogunbiyi, E. O., & Solomon, N. O. (2024). Waste management and circular economy: A review of sustainable practices and economic benefits. *World Journal of Advanced Research and Reviews*, *22*(2), 1708-1719. https://doi.org/10.30574/wjarr.2024.22.2.1517
7. Akiba, T., Tsurumaki, A., & Ohno, H. (2017). Induction of lignin solubility for a series of polar ionic liquids by the addition of a small amount of water. *Green Chemistry*, *19*(9), 2260-2265. https://doi.org/10.1039/C7GC00626H
8. Alreshidi, M. A., Yadav, K. K., Gunasekaran, S., Gacem, A., Sambandam, P., Subbiah, G., Bhutto, J. K., Palanivel, S., Fallatah, A. M., & El-Khair, M. A. A. (2025). A review on the evolution of ionic liquids: Sustainable synthesis, applications, and future prospects. *Materials Today Sustainability*, *31*, 101160. https://doi.org/10.1016/j.mtsust.2025.101160
9. Amsel, A.-K., Olsson, O., & Kümmerer, K. (2022). Inventory of biodegradation data of ionic liquids. *Chemosphere*, *299*, 134385. https://doi.org/10.1016/j.chemosphere.2022.134385
10. Arevalo-Gallegos, A., Ahmad, Z., Asgher, M., Parra-Saldivar, R., & Iqbal, H. M. (2017). Lignocellulose: a sustainable material to produce value-added products with a zero waste approach—a review. *International journal of biological macromolecules*, *99*, 308-318. https://doi.org/10.1016/j.ijbiomac.2017.02.097
11. Avid, A., Ochoa, J. L., Huang, Y., Liu, Y., Atanassov, P., & Zenyuk, I. V. (2022). Revealing the role of ionic liquids in promoting fuel cell catalysts reactivity and durability. *Nature Communications*, *13*(1), 6349. https://doi.org/10.1038/s41467-022-33895-5
12. Baksi, S., Saha, D., Saha, S., Sarkar, U., Basu, D., & Kuniyal, J. (2023). Pre-treatment of lignocellulosic biomass: review of various physico-chemical and biological methods influencing the extent of biomass depolymerization. *International Journal of Environmental Science and Technology*, *20*(12), 13895-13922. https://doi.org/10.1007/s13762-023-04838-4

13. Beach, E. S., Cui, Z., & Anastas, P. T. (2009). Green Chemistry: A design framework for sustainability. *Energy & Environmental Science*, *2*(10), 1038-1049. https://doi.org/10.1039/b904997p

14. Bertran-Llorens, S., Perondi, F., de Freitas, A. L. S., Chen, J., van Erven, G., & Deuss, P. J. (2024). Supercritical CO2 as effective wheat straw pretreatment for subsequent mild fractionation strategies. *Chemical Engineering Journal*, *497*, 154491. https://doi.org/10.1016/j.cej.2024.154491

15. Bohrpi, R., Nath, S., & Kango, N. (2026). Lignocellulosic Biomass Resources for Bioenergy and Valuable Platform Chemicals: A Circular Economy Concept. *Industrial Microbiology and Biotechnology: Trends in Microbial Biotechnology*, 821-843. https://doi.org/10.1007/978-981-95-5378-5_25

16. Brandt, A., Gräsvik, J., Hallett, J. P., & Welton, T. (2013). Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chemistry*, *15*(3), 550-583. https://doi.org/10.1039/c2gc36364j

17. Brandt, A., Ray, M. J., To, T. Q., Leak, D. J., Murphy, R. J., & Welton, T. (2011). Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid–water mixtures. *Green Chemistry*, *13*(9), 2489-2499. https://doi.org/10.1039/c1gc15374a

18. Buettner, C. S., Cognigni, A., Schröder, C., & Bica-Schröder, K. (2022). Surface-active ionic liquids: A review. *Journal of Molecular Liquids*, *347*, 118160. https://doi.org/10.1016/j.molliq.2021.118160

19. Cheah, W. Y., Sankaran, R., Show, P. L., Tg Ibrahim, T. N. B., Chew, K. W., Culaba, A., & Chang, J.-S. (2020). Pretreatment methods for lignocellulosic biofuels production: current advances, challenges and future prospects. *Biofuel Research Journal*, *7*(1), 1115-1127. https://doi.org/10.18331/BRJ2020.7.1.4

20. Chen, J., Ma, X., Liang, M., Guo, Z., Cai, Y., Zhu, C., Wang, Z., Wang, S., Xu, J., & Ying, H. (2024). Physical–chemical–biological pretreatment for biomass degradation and industrial applications: A review. Waste. https://doi.org/10.3390/waste2040024

21. Chen, J., Xu, Q., He, F., Yue, W., Hu, G., Gan, J., & Xie, H. (2022). Pretreatment of corn stover by levulinic acid-based protic ionic liquids for enhanced enzymatic hydrolysis. *ACS Sustainable Chemistry & Engineering*, *10*(21), 7134-7148. https://doi.org/10.1021/acssuschemeng.2c01339

22. Cheng, G., Varanasi, P., Li, C., Liu, H., Melnichenko, Y. B., Simmons, B. A., Kent, M. S., & Singh, S. (2011). Transition of cellulose crystalline structure and surface morphology of biomass as a function of ionic liquid pretreatment and its relation to enzymatic hydrolysis. *Biomacromolecules*, *12*(4), 933-941. https://doi.org/10.1021/bm101240z

23. Chopra, J., Rangarajan, V., Rathnasamy, S., & Dey, P. (2024). Life cycle assessment as a key decision tool for emerging pretreatment technologies of biomass-to-biofuel: unveiling challenges, advances, and future potential. *BioEnergy Research*, *17*(2), 857-876. https://doi.org/10.1007/s12155-024-10741-8

24. Choudhary, H., Pidatala, V. R., Mohan, M., Simmons, B. A., Gladden, J. M., & Singh, S. (2022). Renewable schiff-base ionic liquids for lignocellulosic biomass pretreatment. *Molecules*, *27*(19), 6278. https://doi.org/10.3390/molecules27196278

25. da Costa Lopes, A. M., João, K. G., Morais, A. R. C., Bogel-Łukasik, E., & Bogel-Łukasik, R. (2013). Ionic liquids as a tool for lignocellulosic biomass fractionation. *Sustainable Chemical Processes*, *1*(1), 3. https://doi.org/10.1186/2043-7129-1-3

26. de Jesus, S. S., & Maciel Filho, R. (2022). Are ionic liquids eco-friendly? *Renewable and Sustainable Energy Reviews*, *157*, 112039. https://doi.org/10.1016/j.rser.2021.112039

27. Devi, A., Bajar, S., Kour, H., Kothari, R., Pant, D., & Singh, A. (2022). Lignocellulosic biomass valorization for bioethanol production: a circular bioeconomy approach. *BioEnergy Research*, *15*(4), 1820-1841. https://doi.org/10.1007/s12155-022-10401-9

28. Dharaskar, S. A., Varma, M. N., Shende, D. Z., Yoo, C. K., & Wasewar, K. L. (2013). Research Article Synthesis, Characterization and Application of 1-Butyl-3 Methylimidazolium Chloride as Green Material for Extractive Desulfurization of Liquid Fuel. https://doi.org/10.1155/2013/395274

29. Diarsa, M., & Gupte, A. (2021). Preparation, characterization and its potential applications in Isoniazid drug delivery of porous microcrystalline cellulose from banana pseudostem fibers. *3 Biotech*, *11*(7), 334. https://doi.org/10.1007/s13205-021-02838-0

30. Dias, A. R., Costa-Rodrigues, J., Teixeira, C., Prudêncio, C., Gomes, P., & Ferraz, R. (2019). Ionic liquids for topical delivery in cancer. *Current medicinal chemistry*, *26*(41), 7520-7532. https://doi.org/10.2174/0929867325666181026110227

31. Dias, A. R., Costa-Rodrigues, J., Fernandes, M. H., Ferraz, R., & Prudêncio, C. (2017). The anticancer potential of ionic liquids. *ChemMedChem*, *12*(1), 11-18. https://doi.org/10.1002/cmdc.201600480

32. Ebner, G., Vejdovszky, P., Wahlström, R., Suurnäkki, A., Schrems, M., Kosma, P., Rosenau, T., & Potthast, A. (2014). The effect of 1-ethyl-3-methylimidazolium acetate on the enzymatic degradation of cellulose. *Journal of Molecular Catalysis B: Enzymatic*, *99*, 121-129. https://doi.org/10.1016/j.molcatb.2013.11.001

33. Espinosa, E., Sánchez, R., González, Z., Domínguez-Robles, J., Ferrari, B., & Rodríguez, A. (2017). Rapidly growing vegetables as new sources for lignocellulose nanofibre isolation: Physicochemical, thermal and rheological characterisation. *Carbohydrate polymers*, *175*, 27-37. https://doi.org/10.1016/j.carbpol.2017.07.055

34. Fougere, D., Nanda, S., Clarke, K., Kozinski, J. A., & Li, K. (2016). Effect of acidic pretreatment on the chemistry and distribution of lignin in aspen wood and wheat straw substrates. *Biomass and Bioenergy*, *91*, 56-68. https://doi.org/10.1016/j.biombioe.2016.03.027

35. Frink, L. A., Weatherly, C. A., & Armstrong, D. W. (2014). Water determination in active pharmaceutical ingredients using ionic liquid headspace gas chromatography and two different detection protocols. *Journal of pharmaceutical and biomedical analysis*, *94*, 111-117. https://doi.org/10.1016/j.jpba.2014.01.034

36. Fu, D., Mazza, G., & Tamaki, Y. (2010). Lignin extraction from straw by ionic liquids and enzymatic hydrolysis of the cellulosic residues. *Journal of agricultural and food chemistry*, *58*(5), 2915-2922. https://doi.org/10.1021/jf903616y

37. Gohain, P. B., & Borgohain, D. (2025). Lignocellulosic Biomass (LCB) for a Sustainable Circular Economy. *Agricultural Research Journal*, *62*(3), 246-255. https://doi.org/10.5958/2395-146X.2025.00031.2

38. Gowman, A. C., Picard, M. C., Rodriguez-Uribe, A., Misra, M., Khalil, H., Thimmanagari, M., & Mohanty, A. K. (2019). Physicochemical Analysis of Apple and Grape Pomaces. *BioResources*, *14*(2). https://doi.org/10.15376/biores.14.2.3210-3230

39. Gräsvik, J., Winestrand, S., Normark, M., Jönsson, L. J., & Mikkola, J.-P. (2014). Evaluation of four ionic liquids for pretreatment of lignocellulosic biomass. *BMC biotechnology*, *14*(1), 34. https://doi.org/10.1186/1472-6750-14-34

40. Hessel, V., Tran, N. N., Asrami, M. R., Tran, Q. D., Long, N. V. D., Escribà-Gelonch, M., Tejada, J. O., Linke, S., & Sundmacher, K. (2022). Sustainability of green solvents–review and perspective. *Green Chemistry*, *24*(2), 410-437. https://doi.org/10.1039/D1GC03662A

41. Hou, X. D., Li, N., & Zong, M. H. (2013). Renewable bio ionic liquids-water mixtures-mediated selective removal of lignin from rice straw: Visualization of changes in composition and cell wall structure. *Biotechnology and bioengineering*, *110*(7), 1895-1902. https://doi.org/10.1002/bit.24862

42. Hough, W. L., Smiglak, M., Rodríguez, H., Swatloski, R. P., Spear, S. K., Daly, D. T., Pernak, J., Grisel, J. E., Carliss, R. D., & Soutullo, M. D. (2007). The third evolution of ionic liquids: active pharmaceutical ingredients. *New Journal of Chemistry*, *31*(8), 1429-1436. https://doi.org/10.1039/b706677p

43. Imahori, T., Yamaguchi, R., & Kurihara, S. (2012). Azobenzene-tethered bis (trityl alcohol) as a photoswitchable cooperative acid catalyst for Morita-Baylis-Hillman reactions. *Chemistry (Weinheim an der Bergstrasse, Germany)*, *18*(35), 10802-10807. https://doi.org/10.1002/chem.201201383

44. Kamiya, N., Matsushita, Y., Hanaki, M., Nakashima, K., Narita, M., Goto, M., & Takahashi, H. (2008). Enzymatic in situ saccharification of cellulose in aqueous-ionic liquid media. *Biotechnology letters*, *30*(6), 1037-1040. https://doi.org/10.1007/s10529-008-9638-0

45. Karatzos, S. K., Edye, L. A., & Doherty, W. O. S. (2012). Sugarcane bagasse pretreatment using three imidazolium-based ionic liquids; mass balances and enzyme kinetics. *Biotechnology for biofuels*, *5*(1), 62. https://doi.org/10.1186/1754-6834-5-62

46. Kaur, G., Kumar, H., & Singla, M. (2022). Diverse applications of ionic liquids: A comprehensive review. *Journal of Molecular Liquids*, *351*, 118556. https://doi.org/10.1016/j.molliq.2022.118556

47. Kim, M., Saldarriaga-Hernandez, S., Rodriguez, A., Carrillo-Nieves, D., Simmons, B. A., Gladden, J. M., & Choudhary, H. (2026). A "Sweet" Biorefinery: Sugar-derived ionic liquids for the pretreatment of lignocellulosic biomass. *Journal of Ionic Liquids*, *6*(1), 100184. https://doi.org/10.1016/j.jil.2025.100184

48. Kumar, A. K., & Sharma, S. (2017). Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. *Bioresources and bioprocessing*, *4*(1), 7. https://doi.org/10.1186/s40643-017-0137-9

49. Lateef, H., Grimes, S., Kewcharoenwong, P., & Feinberg, B. (2009). Separation and recovery of cellulose and lignin using ionic liquids: a process for recovery from paper-based waste. *Journal of Chemical Technology & Biotechnology*, *84*(12), 1818-1827. https://doi.org/10.1002/jctb.2251

50. Lee, J.-Y., Lee, S.-E., & Lee, D.-W. (2022). Current status and future prospects of biological routes to bio-based products using raw materials, wastes, and residues as renewable resources. *Critical Reviews in Environmental Science and Technology*, *52*(14), 2453-2509. https://doi.org/10.1080/10643389.2021.1880259

51. Lee, S. H., Doherty, T. V., Linhardt, R. J., & Dordick, J. S. (2009). Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis. *Biotechnology and bioengineering*, *102*(5), 1368-1376. https://doi.org/10.1002/bit.22179

52. Li, P., Yang, C., Jiang, Z., Jin, Y., & Wu, W. (2023). Lignocellulose pretreatment by deep eutectic solvents and related technologies: A review. *Journal of Bioresources and Bioproducts*, *8*(1), 33-44. https://doi.org/10.1016/j.jobab.2022.11.004

53. Liang, X., Fu, Y., & Chang, J. (2017). Research on the quick and efficient recovery of 1-allyl-3-methylimidazolium chloride after biomass pretreatment with ionic liquid-aqueous alcohol system. *Bioresource technology*, *245*, 760-767. https://doi.org/10.1016/j.biortech.2017.08.145

54. Liu, Q.-P., Hou, X.-D., Li, N., & Zong, M.-H. (2012). Ionic liquids from renewable biomaterials: synthesis, characterization and application in the pretreatment of biomass. *Green Chemistry*, *14*(2), 304-307. https://doi.org/10.1039/C2GC16128A

55. Liu, Y.-R., Thomsen, K., Nie, Y., Zhang, S.-J., & Meyer, A. S. (2016). Predictive screening of ionic liquids for dissolving cellulose and experimental verification. *Green Chemistry*, *18*(23), 6246-6254. https://doi.org/10.1039/C6GC01827K

56. Liu, Y., Zheng, X., Tao, S., Hu, L., Zhang, X., & Lin, X. (2021). Process optimization for deep eutectic solvent pretreatment and enzymatic hydrolysis of sugar cane bagasse for cellulosic ethanol fermentation. *Renewable Energy*, *177*, 259-267. https://doi.org/10.1016/j.renene.2021.05.131

57. Maitra, M., Sruthi, S., Rao, P. M., Avanthi, V., & Radha, P. (2024). Lignocellulosic biomass for sustainable production of renewable fuels: embracing natural resources. In *Circular Bioeconomy Perspectives in Sustainable Bioenergy Production* (pp. 37-89). Springer. https://doi.org/10.1007/978-981-97-2523-6_3

58. Mohapatra, H. S., Dubey, P., Chatterjee, A., Kumar, P., & Ghosh, S. (2017). Development of a fibrous assembly from orange peel extract: characterization and antibacterial activity. *Cellul Chem Technol*, *51*(7-8), 601-608.

59. Montoya-Rosales, J., Peces, M., González-Rodríguez, L., Alatriste-Mondragón, F., & Villa-Gómez, D. (2020). A broad overview comparing a fungal, thermal and acid pretreatment of bean straw in terms of substrate and anaerobic digestion effect. *Biomass and Bioenergy*, *142*, 105775. https://doi.org/10.1016/j.biombioe.2020.105775

60. Moshikur, R. M., Chowdhury, M. R., Moniruzzaman, M., & Goto, M. (2020). Biocompatible ionic liquids and their applications in pharmaceutics. *Green Chemistry*, *22*(23), 8116-8139. https://doi.org/10.1039/D0GC02387F

61. Nakasu, P., Pin, T., Hallett, J., Rabelo, S., & Costa, A. (2021). In-depth process parameter investigation into a protic ionic liquid pretreatment for 2G ethanol production. *Renewable Energy*, *172*, 816-828. https://doi.org/10.1016/j.renene.2021.03.004

62. Neupane, B., Konda, N. M., Singh, S., Simmons, B. A., & Scown, C. D. (2017). Life-cycle greenhouse gas and water intensity of cellulosic biofuel production using cholinium lysinate ionic liquid pretreatment. *ACS Sustainable Chemistry & Engineering*, *5*(11), 10176-10185. https://doi.org/10.1021/acssuschemeng.7b02116

63. Ocreto, J. B., Chen, W.-H., Rollon, A. P., Ong, H. C., Pétrissans, A., Pétrissans, M., & De Luna, M. D. G. (2022). Ionic liquid dissolution utilized for biomass conversion into biofuels, value-added chemicals and advanced materials: A comprehensive review. *Chemical Engineering Journal*, *445*, 136733. https://doi.org/10.1016/j.cej.2022.136733

64. Okolie, J. A., Nanda, S., Dalai, A. K., & Kozinski, J. A. (2021). Chemistry and specialty industrial applications of lignocellulosic biomass. *Waste and Biomass Valorization*, *12*(5), 2145-2169. https://doi.org/10.1007/s12649-020-01123-0

65. Onwukamike, K. N., Grelier, S. p., Grau, E., Cramail, H., & Meier, M. A. (2018). Critical review on sustainable homogeneous cellulose modification: why renewability is not enough. *ACS Sustainable Chemistry & Engineering*, *7*(2), 1826-1840. https://doi.org/10.1021/acssuschemeng.8b04990

66. Ovejero-Pérez, A., Nakasu, P. Y., Hopson, C., Costa, J. M., & Hallett, J. P. (2024). Challenges and opportunities on the utilisation of ionic liquid for biomass pretreatment and valorisation. *npj Materials Sustainability*, *2*(1), 7. https://doi.org/10.1038/s44296-024-00015-x

67. Palliprath, S., Poolakkalody, N. J., Ramesh, K., & Manisseri, C. (2020). Lignocellulosic content and biofuel potential of post-harvest sugarcane leaves from commonly cultivated Indian varieties. *Sci Technol J*, *8*, 15-23. https://doi.org/10.22232/stj.2020.08.02.03

68. Payal, R. S., Bejagam, K. K., Mondal, A., & Balasubramanian, S. (2015). Dissolution of cellulose in room temperature ionic liquids: anion dependence. *The Journal of Physical Chemistry B*, *119*(4), 1654-1659. https://doi.org/10.1021/jp512240t

69. Pu, Y., Jiang, N., & Ragauskas, A. J. (2007). Ionic liquid as a green solvent for lignin. *Journal of Wood Chemistry and Technology*, *27*(1), 23-33. https://doi.org/10.1080/02773810701282330

70. Qasim, U., Rafiq, S., Jamil, F., Ahmed, A., Ali, T., Kers, J., Khurram, M. S., Hussain, M., Inayat, A., & Park, Y.-K. (2021). Processing of lignocellulose in ionic liquids: A cleaner and sustainable approach. *Journal of cleaner production*, *323*, 129189. https://doi.org/10.1016/j.jclepro.2021.129189

71. Rahman, M. M., Choudhary, H., Simmons, B. A., Gladden, J. M., & Rodriguez, A. (2025). Advances in ionic liquid recycling for lignocellulosic biomass pretreatment. *Green Chemistry*. https://doi.org/10.1039/D5GC03051J

72. Rashid, T., Kait, C. F., Regupathi, I., & Murugesan, T. (2016). Dissolution of kraft lignin using protic ionic liquids and characterization. *Industrial crops and products*, *84*, 284-293. https://doi.org/10.1016/j.indcrop.2016.02.017

73. Reza, N. A., Akhmal, N. H., Fadil, N. A., & Taib, M. F. M. (2021). A review on plants and biomass wastes as organic green corrosion inhibitors for mild steel in acidic environment. *Metals*, *11*(7), 1062. https://doi.org/10.3390/met11071062

74. Rodríguez, H. (2021). Ionic liquids in the pretreatment of lignocellulosic biomass. *Acta Innovations*(38), 23-36. https://doi.org/10.32933/ActaInnovations.38.3

75. Roy, S., & Chundawat, S. P. (2023). Ionic liquid–based pretreatment of lignocellulosic biomass for bioconversion: a critical review. *BioEnergy Research*, *16*(1), 263-278. https://doi.org/10.1007/s12155-022-10425-1

76. Salleh, A., Jalil, R., Jasmani, L., Abdullah, M. A. M., Mustapha, A., & Yusuf, Y. (2025). Exploring the versatility of ionic liquids in biomass utilization: A comprehensive review. *Journal of Molecular Liquids*, 128250. https://doi.org/10.1016/j.molliq.2025.128250

77. Sayyahi, S., Shabani, S., Ghasemi, S., Azin, A., & Hasani, S. M. (2015). Magnetic ionic liquid [bmim][FeCl4] as an efficient catalyst for the synthesis of 2-aryl benzimidazoles and 2-aryl benzothiazoles derivatives. *Oriental Journal of Chemistry*, *31*(3), 1773. https://doi.org/10.13005/ojc/310359

78. Sharma, P., Bano, A., Singh, S. P., & Tong, Y. W. (2024). Lignocellulosic biomass production: biodiversity benefits and threats. In *Biodiversity and Bioeconomy* (pp. 425-443). Elsevier. https://doi.org/10.1016/B978-0-323-95482-2.00019-5

79. Sharma, S., Ivanov, A. S., & Margulis, C. J. (2021). A brief guide to the structure of high-temperature molten salts and key aspects making them different from their low-temperature relatives, the ionic liquids. *The Journal of Physical Chemistry B*, *125*(24), 6359-6372. https://doi.org/10.1021/acs.jpcb.1c01065

80. Sharma, S., Pradhan, R., Manickavasagan, A., & Dutta, A. (2022). Characterization of ultrasonic-treated corn crop biomass using imaging, spectral and thermal techniques: a review. *Biomass conversion and biorefinery*, *12*(4), 1393-1408. https://doi.org/10.1007/s13399-020-00748-4

81. Sharma, V., Nargotra, P., Sharma, S., Sawhney, D., Vaid, S., Bangotra, R., Dutt, H. C., & Bajaj, B. K. (2023). Microwave irradiation-assisted ionic liquid or deep eutectic solvent pretreatment for effective bioconversion of sugarcane bagasse to bioethanol. *Energy, Ecology & Environment*, *8*(2), 141-156. https://doi.org/10.1007/s40974-022-00267-0

82. Sheldon, R. A. (2016). Biocatalysis and biomass conversion in alternative reaction media. *Chemistry–A European Journal*, *22*(37), 12984-12999. https://doi.org/10.1002/chem.201601940

83. Sheraz, M., Cao, L., Zhao, S., Gao, H., Dansawad, P., Xue, C., Li, Y., & Li, W. (2025). Lignocellulosic biomass pretreatment methods and application of extracted fractions. *Arabian Journal for Science and Engineering*, *50*(6), 3717-3736. https://doi.org/10.1007/s13369-024-09930-6

84. Silva, T. A. L., Varão, L. H. R., & Pasquini, D. (2024). Lignocellulosic biomass. In *Handbook of biomass* (pp. 105-142). Springer. https://doi.org/10.1007/978-981-99-6727-8_5

85. Singhvi, M. S., & Gokhale, D. V. (2019). Lignocellulosic biomass: hurdles and challenges in its valorization. *Applied microbiology and biotechnology*, *103*(23), 9305-9320. https://doi.org/10.1007/s00253-019-10212-7

86. Sitotaw, Y. W., Habtu, N. G., Gebreyohannes, A. Y., Nunes, S. P., & Van Gerven, T. (2023). Ball milling as an important pretreatment technique in lignocellulose biorefineries: a review. *Biomass conversion and biorefinery*, *13*(17), 15593-15616. https://doi.org/10.1007/s13399-021-01800-7

87. Stevulova, N., Cigasova, J., Estokova, A., Terpakova, E., Geffert, A., Kacik, F., Singovszka, E., & Holub, M. (2014). Properties characterization of chemically modified hemp hurds. *Materials*, *7*(12), 8131-8150. https://doi.org/10.3390/ma7128131

88. Sun, D., Lv, Z.-W., Rao, J., Tian, R., Sun, S.-N., & Peng, F. (2022). Effects of hydrothermal pretreatment on the dissolution and structural evolution of hemicelluloses and lignin: A review. *Carbohydrate polymers*, *281*, 119050. https://doi.org/10.1016/j.carbpol.2021.119050

89. Sun, N., Rahman, M., Qin, Y., Maxim, M. L., Rodríguez, H., & Rogers, R. D. (2009). Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. *Green Chemistry*, *11*(5), 646-655. https://doi.org/10.1039/b822702k

90. Sun, P., & Armstrong, D. W. (2010). Ionic liquids in analytical chemistry. *Analytica chimica acta*, *661*(1), 1-16. https://doi.org/10.1016/j.aca.2009.12.007

91. Sun, Y., & Cheng, J. (2002). Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource technology*, *83*(1), 1-11. https://doi.org/10.1016/S0960-8524(01)00212-7

92. Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellose with ionic liquids. *Journal of the American chemical society*, *124*(18), 4974-4975. https://doi.org/10.1021/ja025790m

93. Tomar, P., & Jain, D. (2022). A review of green solvent IONIC liquids: as a future solvent. *Journal of Advanced Scientific Research*, *13*(06), 1-16. https://doi.org/10.55218/JASR.202213601

94. Torriero, A. A. J., & Bond, A. M. (2008). Critical evaluation of dynamic electrochemistry in ionic liquids. In *Electroanalytical Chemistry Research Trends* (pp. 1-63). Nova Science Publishers.

95. Tsegaye, M., Chandravanshi, B., Feleke, S., & Redi, M. (2020). Chemical composition of yushania alpina (K. Schum.) WC Lin (1974)(highland bamboo) grown in Ethiopia. *World News of Natural Sciences*, *32*, 1-9.

96. Tufail, T., Saeed, F., Afzaal, M., Ain, H. B. U., Gilani, S. A., Hussain, M., & Anjum, F. M. (2021). Wheat straw: A natural remedy against different maladies. *Food Science & Nutrition*, *9*(4), 2335-2344. https://doi.org/10.1002/fsn3.2030

97. Umagiliyage, A. L., Choudhary, R., Liang, Y., Haddock, J., & Watson, D. G. (2015). Laboratory scale optimization of alkali pretreatment for improving enzymatic hydrolysis of sweet sorghum bagasse. *Industrial crops and products*, *74*, 977-986. https://doi.org/10.1016/j.indcrop.2015.05.044

98. Verdía Barbará, P., Choudhary, H., Nakasu, P. S., Al-Ghatta, A., Han, Y., Hopson, C., Aravena, R. I., Mishra, D. K., Ovejero-Pérez, A., & Simmons, B. A. (2025). Recent advances in the use of ionic liquids and deep eutectic solvents for lignocellulosic biorefineries and biobased chemical and material production. *Chemical Reviews*, *125*(12), 5461-5583. https://doi.org/10.1021/acs.chemrev.4c00754

99. Vieira, S., Barros, M. V., Sydney, A. C. N., Piekarski, C. M., de Francisco, A. C., de Souza Vandenberghe, L. P., & Sydney, E. B. (2020). Sustainability of sugarcane lignocellulosic biomass pretreatment for the production of bioethanol. *Bioresource technology*, *299*, 122635. https://doi.org/10.1016/j.biortech.2019.122635

100. Wang, W., Tan, X., Imtiaz, M., Wang, Q., Miao, C., Yuan, Z., & Zhuang, X. (2021). Rice straw pretreatment with KOH/urea for enhancing sugar yield and ethanol production at low temperature. *Industrial crops and products*, *170*, 113776. https://doi.org/10.1016/j.indcrop.2021.113776

101. Wang, X., Hu, X., Zhang, D., Zhang, Y., Xu, H., Sun, Y., Gu, X., Luo, J., & Gao, B. (2024). Environmental applications and toxicity of ionic liquids. *Journal of Environmental Chemical Engineering*, *12*(6), 114638. https://doi.org/10.1016/j.jece.2024.114638

102. Wei Kit Chin, D., Lim, S., Pang, Y. L., & Lam, M. K. (2020). Fundamental review of organosolv pretreatment and its challenges in emerging consolidated bioprocessing. *Biofuels, bioproducts and biorefining*, *14*(4), 808-829. https://doi.org/10.1002/bbb.2096

103. Wilkes, J. S. (2002). A short history of ionic liquids—from molten salts to neoteric solvents. *Green Chemistry*, *4*(2), 73-80. https://doi.org/10.1039/b110838g

104. Woźniak, A., Kuligowski, K., Świerczek, L., & Cenian, A. (2025). Review of lignocellulosic biomass pretreatment using physical, thermal and chemical methods for higher yields in bioethanol production. *Sustainability*, *17*(1), 287. https://doi.org/10.3390/su17010287

105. Xu, Z., Wang, Q., Jiang, Z., Yang, X.-x., & Ji, Y. (2007). Enzymatic hydrolysis of pretreated soybean straw. *Biomass and Bioenergy*, *31*(2-3), 162-167. https://doi.org/10.1016/j.biombioe.2006.06.015

106. Yang, Z.-Z., Zhao, Y.-N., & He, L.-N. (2011). CO2 chemistry: task-specific ionic liquids for CO2 capture/activation and subsequent conversion. *RSC advances*, *1*(4), 545-567. https://doi.org/10.1039/c1ra00307k

107. Yaylaci, C. (2025). Next Generation Solvents: A Sustainable Future with Green Chemistry Solvents. *Bilecik Şeyh Edebali Üniversitesi Fen Bilimleri Dergisi*, *12*(2), 763-780. https://doi.org/10.35193/bseufbd.1673341

108. Yoo, C. G., Pu, Y., & Ragauskas, A. J. (2017). Ionic liquids: Promising green solvents for lignocellulosic biomass utilization. *Current Opinion in Green and Sustainable Chemistry*, *5*, 5-11. https://doi.org/10.1016/j.cogsc.2017.03.003

109. Zhao, H., Baker, G. A., & Cowins, J. V. (2010). Fast enzymatic saccharification of switchgrass after pretreatment with ionic liquids. *Biotechnology Progress*, *26*(1), 127-133. https://doi.org/10.1002/btpr.331

110. Zhao, J., Yang, Y., Zhang, M., & Wang, D. (2021). Minimizing water consumption for sugar and lignin recovery via the integration of acid and alkali pretreated biomass and their mixed filtrate without post-washing. *Bioresource technology*, *337*, 125389. https://doi.org/10.1016/j.biortech.2021.125389

111. Zhu, S., Wu, Y., Chen, Q., Yu, Z., Wang, C., Jin, S., Ding, Y., & Wu, G. (2006). Dissolution of cellulose with ionic liquids and its application: a mini-review. *Green Chemistry*, *8*(4), 325-327. https://doi.org/10.1039/b601395c

112. Zhuang, W., Hachem, K., Bokov, D., Ansari, M. J., & Nakhjiri, A. T. (2022). Ionic liquids in pharmaceutical industry: A systematic review on applications and future perspectives. *Journal of Molecular Liquids*, *349*, 118145. https://doi.org/10.1016/j.molliq.2021.118145

113. Ziaei-Rad, Z., Fooladi, J., Pazouki, M., & Gummadi, S. N. (2021). Lignocellulosic biomass pre-treatment using low-cost ionic liquid for bioethanol production: an economically viable method for wheat straw fractionation. *Biomass and Bioenergy*, *151*, 106140. https://doi.org/10.1016/j.biombioe.2021.106140

PLANT WASTE MANAGEMENT THROUGH GREEN CHEMISTRY PRINCIPLES: CURRENT PRACTICES AND EMERGING TRENDS

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ABSTRACT

The increasing amount of vegetable waste and the environmentally harmful consequences of fossil fuel-based production processes increase the demand for sustainable and environmentally friendly technologies. In this context, biotechnological applications based on green chemistry principles create a great potential area for the appreciation of renewable raw material resources and the rise of the world bioeconomy. This chapter intensively evaluates existing and innovative approaches to evaluate the lignocellulosic composition of vegetable wastes of agricultural and industrial origin using green chemistry principles within an integrated biorefinery framework. In this context, the existing literature on biofuel production (especially bioethanol and biobutanol) and obtaining value-added biochemical products (such as platform chemicals and biopolymers) through enzymatic hydrolysis and fermentation processes has been evaluated in detail. Additionally, thermochemical conversion technologies, including pyrolysis, gasification, and hydrothermal liquefaction, are discussed as complementary pathways for waste valorization. This chapter evaluates the opportunities offered by enzymatic and thermal waste conversion processes based on green chemistry principles in terms of sustainable energy production and value-added product development, while critically discussing technical challenges, economic limitations, and providing implications for future research trends and potential application areas.

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1. INTRODUCTION

The rapid depletion of fossil fuel reserves, coupled with accelerating environmental degradation, has compelled a global paradigm shift toward sustainable, bio-based production models. Industrial and agricultural plant wastes, traditionally discarded or underutilized, represent a vast and renewable reservoir of carbon-rich lignocellulosic biomass capable of replacing petrochemical feedstocks. Efficiently managing and valorizing these green residues requires a holistic framework that integrates technological innovation with ecological responsibility. To establish this foundation, this introduction delineates the critical intersection between modern biotechnology, the twelve principles of green chemistry, and global sustainability targets, setting a conceptual stage for the advanced biorefinery and circular bioeconomy strategies explored throughout this chapter.

1.1. An Overview of Biotechnological Evaluation of Plant Waste within the Framework of Green Chemistry Principles and Sustainable Development Goals

Green chemistry is defined as sustainable alternatives to industrial chemicals, aiming to minimize the impact of chemical processes on the environment and human health through the use of hazardous substances (Kurul et al., 2025). The twelve principles of green chemistry are important for fundamental elements such as preventing waste production, using renewable raw material sources, saving energy, and creating safer chemical processes. While green chemistry principles directly support the Sustainable Development Goals (SDGs), the use of plant waste, especially that containing lignocellulose, is quite important. Plant waste (agricultural residues, forest waste, food processing by-products, etc.) are lignocellulosic biomass containing high levels of cellulose, hemicellulose, and lignin structures. When combined with modern biotechnologies, the use of waste can be a promising, renewable, and sustainable energy source, contributing to their conversion into sustainable energy and value-added products, and reducing gas emissions (Nath, 2024). Furthermore, the transformation of these wastes into new value-added products is a valuable element for the economic development of the region where it is implemented. The processes of creating energy from waste and value-added products from waste can significantly reduce the existing costs for the creation of a new product while minimizing ecological impact (Kover et al., 2022).

Energy consumption has increased considerably, especially due to many reasons such as industrialization, technological evolution, and urbanization, along with the continuous increase in population. Bioenergy significantly contributes to sustainable energy production and climate goals by overcoming all these negative effects (Bashiru et al., 2024). Biomass wastes have emerged as a promising potential as a sustainable energy source because they do not affect basic needs such as land, food, or water. Especially in recent years, physicochemical and biological methods for energy production from biomass have been developed.

Lignocellulosic biomass resources, which constitute a significant portion of all biomass on Earth, are important as a renewable carbon source. Generally considered waste or low-value resources, these can be transformed into organic acids, bioethanol, bioplastics, and other value-added products through biotechnological methods (Kaushik and Kataria, 2025). To reduce dependence on fossil fuels and minimize negative environmental impacts, conversion to value-added products is achieved through biocatalytic techniques such as enzymatic hydrolysis and fermentation.

The use of plant waste in value-added product production emphasizes both process optimization and product production from a green chemistry perspective. Green methods such as organosolv, hydrothermal processes, ionic liquids, and biological pretreatments are examples of environmentally friendly pretreatment technologies that increase the removal of lignin structure from biomass while reducing solvent consumption and hazardous byproduct production (Limeneh et al., 2025). Additionally, the use of enzymatic and catalytic processes in the hydrolysis steps allows reactions to occur at lower temperatures and pressures, minimizing energy consumption. These examples can be said to be directly related to Sustainable Development Goals 12 (Responsible Production and Consumption) and 7 (Accessible and Clean Energy). The conceptual framework intersecting the selected principles of green chemistry with global Sustainable Development Goals (specifically SDG 7 and SDG 12) through effective plant waste management strategies is systematically illustrated in Figure 1.

The concept of circular bioeconomy is also based on biotechnological evaluation procedures. Circular bioeconomy aims to reduce waste production and use biological resources in the most efficient way (Devi et al., 2022). The biorefining approach, which involves converting lignocellulosic biomass into various products, supports both environmental and economic sustainability by enabling the production of multiple products from a single raw material. This strategy is crucial for reducing greenhouse gas emissions and increasing resource efficiency. According to recent research, integrating green chemistry concepts into biomass conversion processes increases process efficiency and economic viability while also benefiting the environment (Sharma et al., 2022). However, technical and financial challenges such as the challenging structure of lignin, pre-processing costs, and enzyme costs remain significant research areas. Overall, the biotechnological use of plant waste is a potential tool for achieving sustainable development goals in line with green chemistry principles. This strategy makes it possible to produce high value-added products using renewable resources while minimizing environmental impacts. Future advancements in fields such as enzyme engineering, process integration, and AI-powered optimization are expected to further enhance the industrial applicability of these systems.

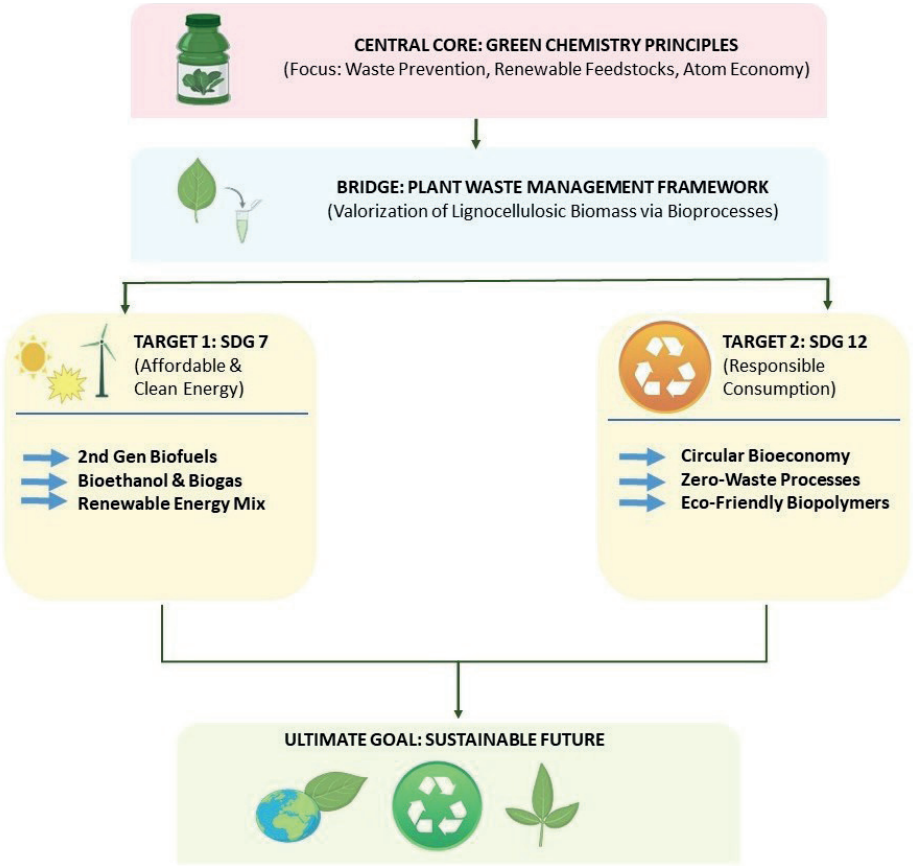


Figure 1. *Conceptual mapping of green chemistry initiatives and Sustainable Development Goal (SDG) targets within the framework of biomass waste management. The diagram illustrates the synergistic bridge between core green chemistry principles (waste prevention, renewable feedstocks, and atom economy) and plant waste valorization bioprocesses. It outlines the specific parallel pathways contributing directly to Target 1 (SDG 7: Affordable and Clean Energy) via second-generation biofuels, and Target 2 (SDG 12: Responsible Consumption and Production) via zero-waste circular bioeconomy systems, culminating in a sustainable environmental future.*

2. LIGNOCELLULOSE COMPOSITION AND MORPHOLOGICAL-CHEMICAL PROPERTIES OF GREEN WASTE FROM THE PERSPECTIVE OF SUSTAINABLE RESOURCE MANAGEMENT

Lignocellulosic biomass (LCB) is the most abundant and easily accessible sustainable resource on Earth. Lignocellulose has perfect properties for industrial applications and research. One of the basic criteria for value-added product production is the accessibility of the material to be used. LCB meets this requirement with its abundance, cost-effectiveness, quick availability, and ease of production. LCB is the most sustainable alternative source in the conversion to biofuels that can replace fossil fuels. Since it can be converted into both liquid and gaseous fuels, it offers a green alternative to petrochemical energy sources (Deivayanai et al., 2022). In

addition to all these positive features, LCB offers an important bioenergy source alternative for existing energy sources due to its low cost, minimization of harmful greenhouse gases, and ease of processing (Olatunji et al., 2020).

LCB consists of three main polymer structures called cellulose, hemicellulose, and lignin, which form the basic structure of the plant cell wall. This complex structure helps plants to be strong and flexible, and prevents biotic/abiotic stresses in the environment. In the literature, it is reported that approximately 90% of LCB consists of these three organic macromolecules, and the remaining part consists of low molecular weight compounds called extractive substances (Tamo et al., 2025).

Cellulose, the main component of LCB, is a structure consisting of unbranched D-glucose subunits linked by β-1,4-glycosidic bonds. Cellulose, which has a homopolysaccharide structure, is known as the most abundant biopolymer in nature. The intense hydrogen bonds between cellulose chains are one of the main reasons for its high strength, giving the biomass a rigid structure and providing resistance to degradation (Kumar et al., 2008). Hemicellulose is the second most important component in biomass after cellulose. Unlike cellulose, it has an amorphous, branched, and heteropolysaccharide structure. It can consist of various sugar monomers such as xylose, arabinose, mannose, and galactose. Although the heterogeneous structure of hemicellulose makes it easier to hydrolyse, the covalent bonding of hemicellulose to lignin significantly complicates biomass processing (Zhao et al., 2012). Lignin, which is generally considered a by-product of biomass, is a complex, amorphous aromatic polymer composed of phenylpropanoid units that provide structural support and hydrophobicity to plant cell walls. Lignin acts as a 'binding matrix' between cellulose and hemicellulose structures, providing structural integrity. Thanks to its hydrophobic and cross-linked structure, it also supports the resistance of lignocellulosic biomass to environmental stresses (Shah et al., 2022).

Furthermore, lignin plays a crucial role in regulating water transport in plants and protecting against potential microbial attacks. LCBs show great variability among themselves depending on their biological origin and species. For instance, agricultural waste typically contains 40–50% cellulose, 20–30% hemicellulose and 10–25% lignin (Shahzadi et al., 2014), whereas these structural proportions differ substantially in woody biomass, as systematically summarized in Table 1. In hardwoods, the cellulose content ranges between 43–47%, while the lignin content is 16–24%; in softwoods, however, the lignin fraction can reach up to 30–60% (Díez et al., 2020). These compositional differences directly affect the processability of biomass in the production of value-added products and the overall efficiency of downstream biotechnological conversion pathways.

Table 1. *Structural Lignocellulosic Composition of Major Plant Waste Feedstocks*

Biomass Category	Cellulose (%)	Hemicellulose	(%) Lignin	Key Reference
Agricultural Residues (*e.g., Straw, Bagasse*)	40–50%	20–30%	10–25%	Shahzadi et al., 2014
Hardwoods (*e.g., Beech, Poplar*)	43–47%	25–35%	16–24%	Díez et al., 2020
Softwoods (*e.g., Pine, Spruce*)	40–45%	20–30%	30–60%	Díez et al., 2020

The plant cell wall generally consists of different layers, including primary and secondary structures, which contain varying amounts of cellulose, hemicellulose and lignin (Silva et al., 2024). Cellulose structures are arranged either parallel or at an angle within the cell wall, providing high tensile strength. The cellulose structure is embedded within a matrix of hemicellulose and lignin. The presence of crystalline and amorphous regions in cellulose structures directly affects the enzymatic hydrolysis stages. Crystalline portions resist enzymatic hydrolysis, while amorphous portions are easily broken down. Thus, the degree of crystallinity of biomass is a significant determinant in biological transformation processes. Hemicellulose, on the other hand, plays a binding role by increasing the interaction between cellulose structures and contributes to increased structural stability. Lignin forms a three-dimensional network of fibrils surrounding these structures, making the cell wall hydrophobic. The binding of water and enzymes to the cell wall is restricted, thus increasing the resistance property of the biomass (Balk et al., 2023) (Figure 2).

The chemical properties of LCBs are generally determined by the functional groups they contain, the types of bonds they possess, and polymer interactions. Interactions between cellulose, hemicellulose, and lignin form structures called lignin-carbohydrate complexes (LCCs). The biggest disadvantage of these structures in biomass is that they make chemical and enzymatic degradation difficult (Beck et al., 2022). At the same time, the irregular and cross-linked structure of lignin is quite difficult to separate.

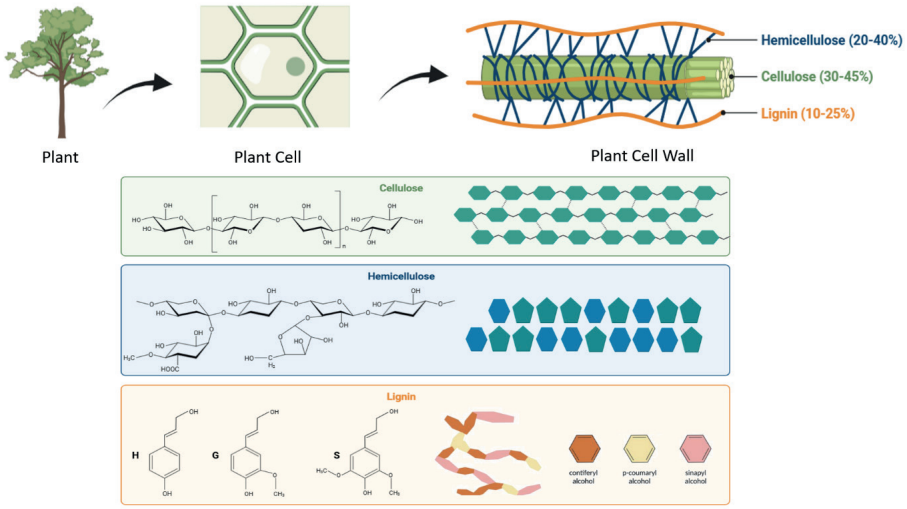


Figure 2. *Structural and chemical architecture of the lignocellulosic plant cell wall matrix. The schematic illustrates the hierarchical organization from macro-scale plant tissues down to the micro-fibrillar arrangement within the cell wall layers, highlighting the interlocking network of cellulose (30–45%), hemicellulose (20–40%), and lignin (10–25%). The lower panels detail the fundamental chemical compositions: the linear homopolysaccharide chains of cellulose; the branched, heterogeneous polymer structure of hemicellulose; and the complex three-dimensional aromatic network of lignin synthesized from p-coumaryl (H), coniferyl (G), and sinapyl (S) alcohol phenylpropanoid monolignol units.*

When examined physicochemically, the LCB structure possesses many properties such as high mechanical strength, low solubility, and heterogeneous surface morphology. These properties highlight the need for pretreatment in order to utilize biomass in various industrial fields. The main purpose of pretreatment is to break down and remove the complex lignin structure, partially dissolve the hemicellulose structure, and increase the accessibility of cellulose (Zhang et al., 2025).

To evaluate the LCB structure, a thorough understanding of the structural and chemical properties of cellulose, hemicellulose, and lignin, and investigation of existing methods according to their intended use in industries are necessary. Thus, future studies are expected to contribute to the development of sustainable biomass conversion technologies by revealing structure-property relationships in more detail.

3. CURRENT, INNOVATIVE AND ENVIRONMENTALLY FRIENDLY TECHNOLOGIES FOR THE USE OF PLANT WASTE IN ACCORDANCE WITH GREEN CHEMISTRY APPROACHES

The systematic valorization of plant waste requires a diverse array of advanced technological pathways capable of deconstructing complex biomass with minimal ecological disruption. To satisfy the stringent criteria of green chemistry, these emerging methodologies must prioritize resource circularity, low energy consumption, and the elimination of hazardous secondary waste streams. This section delivers a comprehensive evaluation of the core technical platforms driving sustainable waste management today. The discussion spans from the structural fractionation of the integrated biorefinery framework to clean biotechnological conversions and highly efficient thermochemical processes, highlighting how each approach redefines agricultural and industrial residues as high-value chemical and energetic assets.

3.1. Biorefinery Approaches

One of the highly valuable sustainable technologies that has been the subject of intensive research recently is the biorefinery approach. Briefly, the concept of biorefinery is a technology that converts biomass into biofuels and chemical products. Many raw material sources are used in biorefinement systems. The separation of LCB into different fractions and the separate evaluation of each fraction is important from the perspective of the biorefinery concept (Kn et al., 2023). For example, while the cellulose and hemicellulose parts of LCB can be used to produce bioethanol using enzymatic hydrolysis and fermentation methods, the lignin parts can be used in the production of aromatic chemicals or biomaterials.

The integrated biorefinery concept represents one of the most effective strategies for maximizing resource efficiency within the framework of green chemistry. Rather than focusing on a single product stream, modern biorefineries aim to fractionate lignocellulosic biomass into cellulose, hemicellulose, and lignin components, enabling the parallel production of biofuels, platform chemicals, biomaterials, and bio-based products. This cascading utilization approach minimizes waste generation, improves economic feasibility, and supports circular bioeconomy principles by ensuring that each biomass fraction is valorized through the most appropriate conversion pathway. Figure 3 illustrates the general flow of an integrated biorefinery system for sustainable plant waste management.

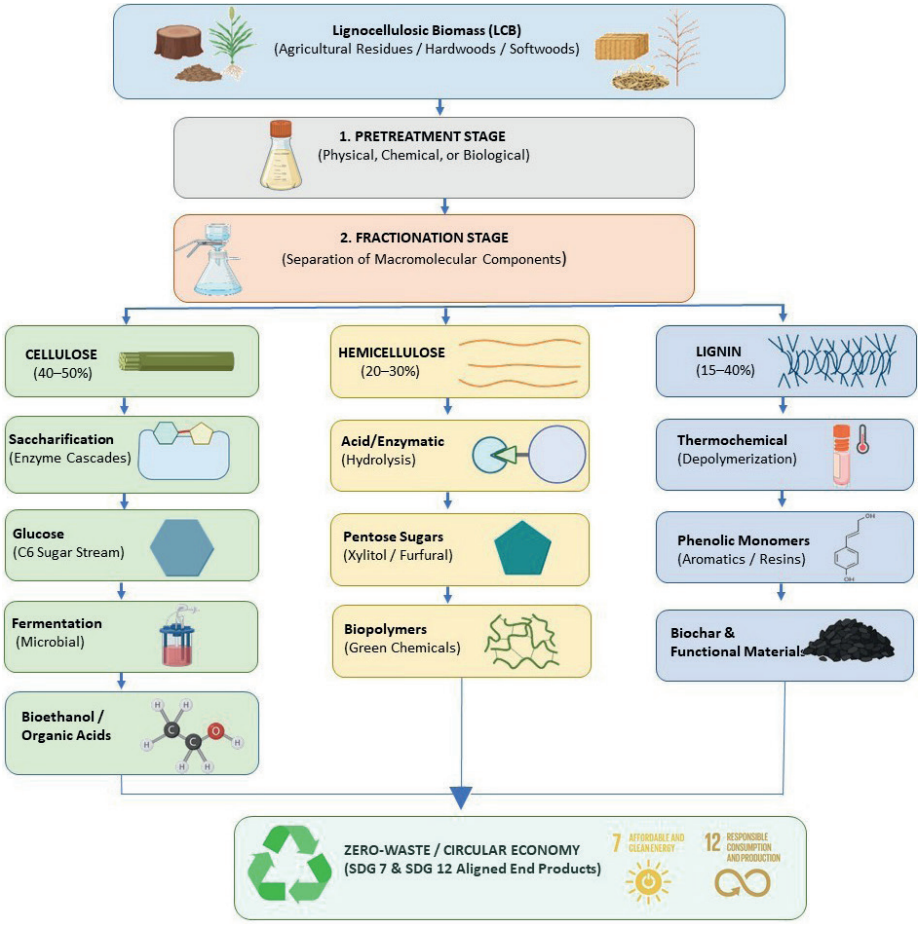


Figure 3. *Integrated biorefinery framework for the multi-product conversion of plant waste in accordance with green chemistry principles. The flowchart systematically details the cascading fractionation of lignocellulosic biomass (LCB) following physical, chemical, or biological pretreatment. It outlines the downstream processing technologies designed to separate and valorize individual macromolecular components: saccharification and fermentation of cellulose into bioethanol/organic acids; hydrolysis of hemicellulose into pentose sugars and green chemicals; and thermochemical depolymerization of lignin into phenolic monomers, biochar, and functional materials to secure a closed-loop circular bioeconomy.*

3.2. Biotechnological Transformation Technologies

Biotechnological transformation technologies offer sustainable pathways that closely align with the principles of green chemistry by minimizing hazardous chemical usage and operating under mild environmental conditions. Utilizing microbial and enzymatic systems to valorize plant waste not only mitigates ecological burdens but also strengthens the global bioeconomy through the synthesis of renewable biofuels and bio-based platform chemicals (Vasić et al., 2021). For instance, solid-state fermentation (SSF) exemplifies an energy-efficient, low-water approach to harvesting diverse enzymes, organic acids, and bioactive compounds from agricultural

residues (Karimi et al., 2025). This subsection outlines the fundamental biological steps involved in biomass conversion, establishing a conceptual foundation for the advanced process configurations detailed in later sections of this chapter.

Pretreatment and Enzymatic Hydrolysis of Lignocellulosic Biomass

The complex and recalcitrant matrix of lignocellulosic biomass (LCB) requires a sequential deconstruction approach to unlock its inner sugars. Initially, physical, chemical, or biological pretreatment methods are deployed to disrupt the cell wall structure, remove the protective lignin shield, and enhance substrate accessibility for downstream biocatalysts (Vasić et al., 2021). Following pretreatment, a consortium of cellulolytic and hemicellulolytic enzymes works synergistically to cleave complex carbohydrate polymers into fermentable monomeric sugars (Kumar et al., 2021). While traditional chemical pathways like concentrated acid hydrolysis exist, they diverge significantly from green chemistry objectives due to their high energy demands, equipment corrosion, and toxic inhibitor generation, leaving enzymatic hydrolysis as the preferred sustainable route.

Enzyme Production and Process Optimization

The industrial and economic viability of biomass saccharification is heavily governed by the cost and catalytic efficiency of the enzymes utilized. Current biotechnological trends focus on screening hyper-producing microbial strains and applying genetic engineering to enhance enzyme stability, specificity, and tolerance (Sharma et al., 2021). Achieving optimal sugar yields requires a delicate balance of critical operational variables—such as pH, temperature, enzyme-to-substrate loading, and the mitigation of degradation inhibitors (Kristensen et al., 2009). A holistic optimization of these bioprocess parameters is vital to maximizing both economic returns and environmental benefits.

Fermentation and Biofuel Production

Once the biomass polymers are successfully saccharified into constituent monomeric sugars, microorganisms act as biological factories to convert these carbohydrate streams into renewable biofuels like bioethanol, biobutanol, and biohydrogen. Traditional fermentation processes often rely on classic strains like Saccharomyces cerevisiae for hexose utilization; however, comprehensive waste valorization demands the efficient processing of both pentose and hexose fractions derived from the plant cell wall (Xiong et al., 2018). This is increasingly achieved through robust microbial co-cultures or metabolically engineered strains capable of simultaneous sugar utilization.

3.3. Thermochemical Conversion Technologies and Production of Value-Added Biochemical Products

Thermochemical methods are one of the important methods used in the process of converting plant waste into products. Using processes such as pyrolysis,

gasification, and hydrothermal liquefaction, which are among the leading methods, value-added products such as biooil, synthesis gas, and biochar can be obtained from waste (Pelagalli et al., 2024). Thanks to co-liquefaction technology, which has been used and developed especially in recent years under thermochemical conversion methods, the quality of biooil obtained by processing lignocellulosic biomass waste and plastic waste together is achieved at higher levels. In addition to this method, biochar produced from waste subjected to pyrolysis is used as a soil conditioner and contributes to carbon sequestration, in addition to energy production (Lee et al., 2017). The positive environmental features it offers make this technology an important tool in preventing climate change and greenhouse gas production. Lignocellulosic biomass and waste not only contribute to energy production but also to the production of value-added chemicals, resulting in products such as phenolic compounds, antioxidants, and bioplastic raw materials (Blasi et al., 2023). These products can be used in the food and cosmetics sectors, offering significant economic opportunities. In conclusion, obtaining various products from lignocellulosic biomass and waste using diverse methods is a promising approach for many sectors. Recent advancements in enzyme technology, biotechnology, genetic engineering applications, and process integration significantly contribute to achieving higher levels of efficiency in this field. In the near future, the development of low-cost enzyme production systems and integrated biorefinery approaches is expected to play a crucial role in the widespread adoption of this technology.

4. ENZYMATIC CONVERSION PROCESSES TO REDUCE ENVIRONMENTAL IMPACT: A GREEN CHEMISTRY-BASED AND SUSTAINABLE BIOCATALYTIC APPROACH

Enzymatic conversion processes represent a cornerstone paradigm shift in sustainable manufacturing, fundamentally restructuring industrial chemistry by maximizing atom economy and minimizing environmental burdens. By operating under benign conditions, biocatalytic systems drastically reduce byproduct formation while escalating process safety and kinetic selectivity. This innate precision bypasses the need for protecting groups and intermediate isolation steps typical of multi-step organic synthesis, thereby shrinking both energy footprints and cumulative waste streams. Beyond natural pathways, contemporary biocatalysis can be systematically tailored to transform synthetic targets as well (Sheldon, 2016). Recent breakthroughs in directed evolution and protein engineering have substantially elevated the thermal and chemical robustness of industrial enzymes (Grigorakis et al., 2025). Consequently, novel biocatalysts engineered to withstand extreme pH, elevated temperatures, and non-aqueous organic media are expanding the industrial scalability of green chemistry across diverse sectors (Li et al., 2025).

When applied to renewable resources, biocatalytic deconstruction serves as an ecologically superior alternative to conventional chemical processing. Transitioning from fossil feedstocks to agricultural and industrial plant residues allows biocatalysis to facilitate a closed-loop carbon cycle (Akash et al., 2023). Utilizing complex

matrices like lignocellulosic biomass through selective enzymatic arrays provides a low-emission pathway for extracting structural components without generating the corrosive and toxic effluents associated with thermo-chemical approaches (Dwivedi et al., 2022). Rather than evaluating downstream product synthesis, the focus here remains strictly on the environmental and thermodynamic superiority of utilizing these biological catalysts.

Process intensification via multi-step enzyme cascade reactions further enhances the environmental performance of biocatalytic networks. By establishing systems where the product of an upstream reaction serves as the immediate substrate for the subsequent enzyme, these cascade architectures eliminate energy-intensive intermediate purification steps, compress processing times, and maximize overall space-time yields (Benítez-Mateos et al., 2022). Furthermore, the integration of advanced enzyme immobilization technologies drastically extends catalyst operational lifecycles. Although matrix synthesis introduces an initial environmental footprint, the multi-cycle reusability of immobilized enzymes, coupled with streamlined product-catalyst separation and continuous-flow configurations, yields significant net reductions in both process E-factors and operational expenditures (Alcalde et al., 2006).

The environmental virtues of biocatalysis are thoroughly validated by rigorous quantitative metrics, including Life Cycle Assessments (LCA). Empirically, transitioning from conventional chemical synthesis to enzymatic routes has been shown to decrease overall environmental impacts by 7–13%, primarily driven by reduced primary energy demands and diminished hazardous waste streams (Nachtergaele et al., 2024). In sum, biocatalytic systems provide a quantifiable, metrics-driven approach to green manufacturing by balancing maximum selectivity with minimized ecological footprints.

5. RENEWABLE BIOFUEL PRODUCTION THROUGH ENZYMATIC HYDROLYSIS AND FERMENTATION PROCESSES: CONTRIBUTIONS TO SUSTAINABLE ENERGY SYSTEMS

In the utilization of lignocellulosic biomass (LCB) for biofuel production, enzymatic hydrolysis and fermentation represent the foundational pillars that dictate overall process efficiency and economic viability. Recent advancements in bioreactor design and enzyme technologies have demonstrated that maximizing the deconstruction efficiency of complex carbohydrate matrices is critical to escalating the sustainability and market competitiveness of bio-based energy systems (Srivastava et al., 2023).

The primary objective of the enzymatic hydrolysis stage is the systematic depolymerization of cellulose and hemicellulose fractions into fermentable monomeric sugars. The crystalline structure of cellulose is synergistically cleaved into glucose monomers through a multi-enzyme cocktail comprising:

- **Endoglucanases (EC 3.2.1.4)**, which randomly cleave internal amorphous regions,

- **Exoglucanases / Cellobiohydrolases (EC 3.2.1.91)**, which progressively release cellobiose units from both the reducing and non-reducing ends of the polymer chain,
- **β-glucosidases (EC 3.2.1.21)**, which hydrolyze cellobiose into final glucose molecules to prevent feedback inhibition.

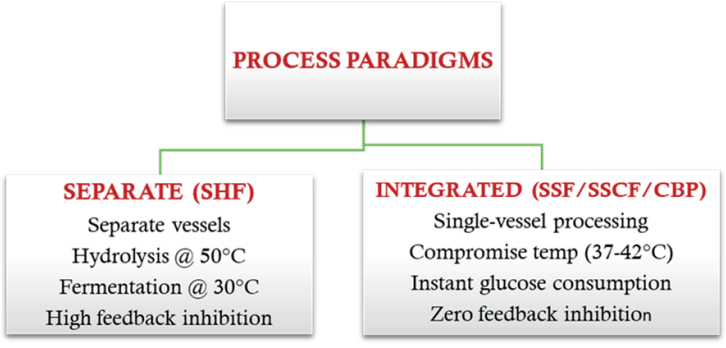
Concurrently, the highly branched and amorphous structure of hemicellulose demands an array of auxiliary enzymes—including xylanases, β-xylosidases, arabinofuranosidases, acetyl xylan esterases, and feruloyl esterases—to ensure complete degradation. Given that agricultural and industrial plant wastes possess substantial xylan fractions, optimizing these hemicellulolytic enzyme arrays is paramount to maximizing total carbohydrate recovery and ensuring high-yield sugar streams (Kocabaş et al., 2015).

The operational success of this enzymatic saccharification is strictly governed by a delicate interplay of reaction parameters, including enzyme loading, incubation time, pH, temperature, and substrate concentration. Biocatalysts must be meticulously screened or designed to operate within precise optimal pH and temperature ranges. A major bottleneck in industrial scaling is the transition to high solids loading (>10–15% w/v); while economically attractive, it drastically increases medium viscosity, induces mass transfer limitations, impairs rheological control, and triggers severe product inhibition due to localized sugar accumulation (da Silva et al., 2020).

5.1. Advanced Bioprocess Configurations and Fermentation Kinetics

The integration of enzymatic hydrolysis and subsequent fermentation steps is executed through distinct operational configurations, each presenting unique thermodynamic and economic trade-offs. The holistic pathway transforming raw plant biomass into functional green fuels through these integrated steps is systematically illustrated in Figure 4.

The fundamental operational divergence between these key bioprocess configurations and manufacturing pathways is further conceptualized in the schematic flow below:



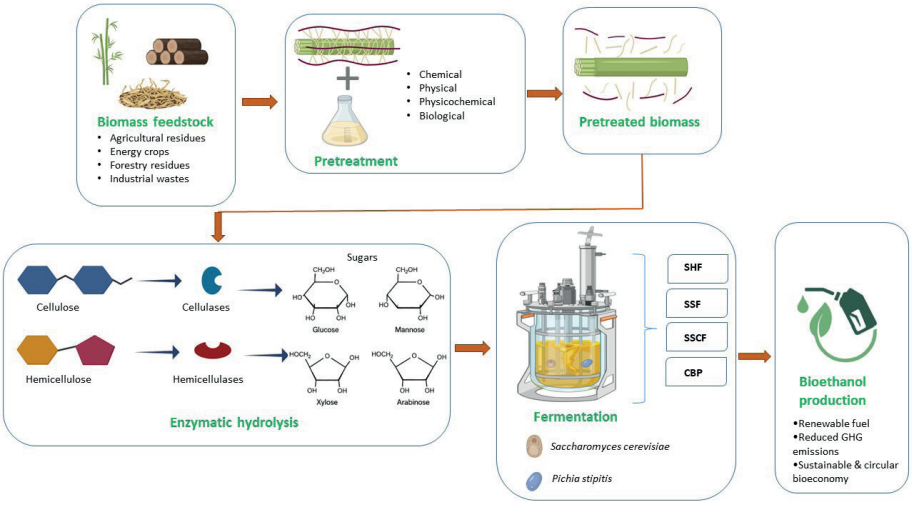


Figure 4. *Comprehensive bioprocess workflow for the biotechnological conversion of diverse plant biomass feedstocks into second-generation bioethanol. The diagram delineates the sequential stages starting from raw residue processing (agricultural, forestry, and industrial wastes) and shifting through various pretreatment modalities (chemical, physical, physicochemical, and biological). It details the continuous pathway of enzymatic hydrolysis using tailored cellulase and hemicellulase cocktails to liberate fermentable monomeric sugars (glucose, mannose, xylose, arabinose), followed by industrial fermentation configurations (including SHF, SSF, SSCF, and CBP) utilizing specialized yeast strains to achieve sustainable, low-emission biofuel production.*

Historically, Separate Hydrolysis and Fermentation (SHF) has been favored due to its capacity to run both stages under their respective, absolute optimal conditions (typically 50°C for cellulases and 30°C for conventional yeasts). However, the accumulation of liberated glucose in the reaction medium exerts strong feedback inhibition on cellobiohydrolases and β-glucosidases, arresting hydrolysis rates over time.

To circumvent this kinetic barrier, modern green processes utilize Simultaneous Saccharification and Fermentation (SSF), where both hydrolysis and microbial fermentation occur concurrently in a single bioreactor. In an SSF configuration, the fermenting microorganisms immediately consume the released monomeric sugars, virtually eliminating enzyme product inhibition, compressing processing times, and minimizing contamination risks and capital footprint costs (Olofsson et al., 2008).

Further process intensification is realized via Simultaneous Saccharification and Co-Fermentation (SSCF), which expands the system's capability to process hexose and pentose sugars simultaneously. The ultimate frontier in bioprocess consolidation is the Consolidated Bioprocessing (CBP) model. CBP streamlines enzyme expression, substrate saccharification, and multi-sugar fermentation within a unified microbial factory using a single hyper-producing strain or synthetic microbial consortium. Although CBP requires further research to achieve full commercial maturity and overcome genetic stability limits, it remains one of the most promising, cost-reductive strategies for next-generation bioeconomies (Singhania et al., 2022).

The comparative techno-environmental dynamics, operational boundaries, and green chemistry metrics of all these major bioprocess configurations are systematically structured and evaluated in Table 2.

Table 2. *Techno-Environmental Matrix of Main Bioprocess Configurations for LCB Valorization*

Configuration	Major Engineering Advantage	Primary Operational Limitation	Green Chemistry Alignment Metrics
SHF	Independent parameter control; allows distinct thermal optima	Severe enzymatic feedback inhibition; high risk of system contamination	Moderate (High energy & equipment footprint)
SSF	Eradicates glucose inhibition; lowers total capital expenditures	Requires a thermal compromise (37–40°C), restricting initial hydrolysis rates	High (Process intensification, minimized solvent usage)
SSCF	Maximizes atom economy by co-utilizing hexose and pentose streams	Extreme kinetic complexity in balancing multi-substrate consumption	Very High (Zero waste generation from structural fractions)
CBP	Eliminates external enzyme production and purification costs	Low ethanol tolerance of wild strains; high genetic engineering barriers	Outstanding (Ultimate closed-loop circular economy paradigm)

Biobutanol production is primarily achieved via Acetone-Butanol-Ethanol (ABE) fermentation using strictly anaerobic bacteria like *Clostridium acetobutylicum* and *Clostridium beijerinckii* (Lin et al., 2023). These specialized metabolic factories convert both hexose and pentose hydrolysates into valuable solvent streams, converting underutilized agricultural residues into premium-tier biochemical assets (Chen et al., 2024).

Looking forward, the economic viability of these renewable fuel systems is being transformed by radical innovations in enzyme engineering. The integration of artificial intelligence (AI-assisted enzyme design) and computational protein modeling allows for the de novo creation of synthetic biocatalysts with unprecedented thermal stability, extreme pH tolerance, and resistance to degradation inhibitors. By coupling predictive machine learning algorithms with automated directed evolution, researchers are drastically reducing the enzyme-to-substrate loading ratios required for saccharification. These emerging digital trends provide a definitive pathway toward minimizing operational expenditures, driving down the minimum selling price (MSP) of biofuels, and enabling green energy systems to aggressively compete with traditional fossil fuel infrastructures on a global industrial scale.

6. OBTAINING VALUE-ADDED BIOCHEMICAL PRODUCTS THROUGH ENZYMATIC PROCESSES IN ACCORDANCE WITH GREEN CHEMISTRY PRINCIPLES AND THEIR INDUSTRIAL POTENTIAL

Within the operational framework of industrial biotechnology, biocatalysis serves as the primary engine driving the clean synthesis of high-purity biochemicals, functional ingredients, and specialty macromolecules. By utilizing the molecular specificity of engineered enzymes, modern biorefineries can selectively target complex structural transformations without the need for extensive protecting-group chemistry or heavy infrastructure for downstream trace purification. This chemical precision delivers immense economic and qualitative advantages, particularly in sectors where structural isomerism, enantiomeric purity, and non-toxic processing are mandatory for market approval (Sheldon and Brady, 2022). Currently, the global fine chemical and pharmaceutical sectors rely heavily on tailored enzyme classes—such as transaminases, ketoreductases, and lipases—to synthesize core active pharmaceutical ingredients (APIs) and advanced chiral intermediates under benign, aqueous conditions (Schwarz et al., 2024).

Among these industrial biocatalysts, lipases (EC 3.1.1.3) represent one of the most versatile tools for manufacturing high-value oleochemicals and cosmetic formulations. By executing highly selective esterification and transesterification pathways, lipases facilitate the synthesis of structural aroma compounds, specialized functional lipids, and emollient esters from renewable plant fats. Because these reactions bypass traditional harsh chemical catalysts, the resulting products maintain structural integrity and can be legally certified and marketed as "all-natural" components—a designation that carries substantial premium value in contemporary consumer markets (Sharma et al., 2025).

Similarly, carbohydrate-transforming enzymes have fundamentally redefined large-scale agro-industrial processing. The landmark deployment of glucose isomerase for manufacturing high-fructose corn syrup stands as a foundational success story in industrial enzymology, balancing macro-scale efficiency with predictable kinetic control. In modern dairy and food technology, galactosidases are extensively utilized to engineer specialized lactose-free matrices and prebiotic galacto-oligosaccharides, while highly stable amylases dictate efficiency in starch liquefaction and processing sectors (Kognou et al., 2022; Li et al., 2023).

Beyond conventional food ingredients, current research focuses heavily on using enzymatic systems to polymerize next-generation biomaterials and synthesize versatile platform chemicals from green sugar platforms, as structured in Table 3.

Enzymatic polymerization represents a rapidly expanding frontier in green materials science, enabling the synthesis of tailored, biodegradable polyesters, functional oligomers, and biocompatible hydrogels. Conventional chemical polymerizations demand toxic, heavy-metal catalysts (such as organotin compounds) that often leave hazardous residues embedded within the plastic matrix, restricting their biomedical

or food-contact viability. Biocatalytic synthesis completely eliminates these eco-toxicological barriers, yielding pristine, fully circular biomaterials (Qadir et al., 2026).

Furthermore, the fermentable sugar streams extracted from plant residues can be enzymatically converted into major platform chemicals like 5-hydroxymethylfurfural (5-HMF) and furfural. These bio-based building blocks serve as direct, drop-in replacements for petroleum derivatives in manufacturing bioplastics, structural resins, and sustainable fuel additives (Jiang et al., 2023).

Concurrently, there is surging commercial interest in the biocatalytic synthesis of rare sugars, including D-allulose (D-psychose), D-tagatose, and L-ribose via precise epimerization cascades (Dai and Jin, 2024). These rare carbohydrates serve as premium, ultra-low-calorie functional sweeteners possessing intrinsic prebiotic and therapeutic properties.

Table 3. *Industrial Portfolio of Value-Added Biochemicals Synthesized via Biocatalytic Pathways*

Target Biochemical Category	Key Enzyme System(s)	Primary Industrial Application	Green Technology Advantage Over Chemical Routes
Pharmaceutical Intermediates	Transaminases, Lipases, Ketoreductases	Chiral APIs, enantiopure drug synthesis, cosmetics.	Eliminates hazardous organic solvents; ultra-high enantioselectivity (Schwarz et al., 2024).
Functional Food & Sweeteners	Glucose Isomerase, Galactosidases	High-fructose syrups, lactose-free dairy, prebiotics.	Mild operational temperatures; zero toxic byproduct formation (Li et al., 2023).
Biopolymers & Biomaterials	Lipases, Cutinases (Enzymatic Polymerization)	Biodegradable polyesters, eco-friendly packaging, biomedical resins.	Replaces toxic, heavy-metal catalysts; ensures biocompatibility (Qadir et al., 2026).
Platform Building Blocks	Dehydratases, Isomerases	5-HMF, Furfural, bio-resins, green solvents, plasticizers.	Direct valorization of waste-derived hexose/pentose fractions (Jiang et al., 2023).
Rare Sugars (Prebiotics)	Epimerases, Dehydrogenases	D-allulose, D-tagatose, L-ribose (Low-calorie sweeteners).	Bypasses highly complex, multi-step chemical synthesis barriers (Dai and Jin, 2024).

Ultimately, transitioning the production of these complex molecules to multi-enzyme closed loops satisfies the core mandates of the bioeconomy: maximizing atom economy, substituting fossil feedstocks with agricultural plant waste, and securing a non-toxic, economically viable industrial future.

7. CHALLENGES, LIMITATIONS, AND FUTURE RESEARCH TRENDS IN ENZYMATIC HYDROLYSIS AND FERMENTATION PROCESSES FROM A SUSTAINABLE WASTE MANAGEMENT PERSPECTIVE

While enzymatic hydrolysis and fermentation offer highly sustainable and eco-friendly alternatives to petroleum-based processing, transitioning these biocatalytic frameworks from bench-scale assays to continuous industrial-scale operations introduces formidable technical, economic, and rheological boundaries. The inherent recalcitrance of the plant cell wall matrix, coupled with thermodynamic limitations in microbial mass transfer, remains the primary hurdle restricting high-efficiency waste valorization (Pragya and Kumar, 2025).

7.1. Upstream and Rheological Bottlenecks in Saccharification

The initial limitation in the enzymatic saccharification stage stems from the highly complex, naturally evolved structural resistance of lignocellulosic biomass (LCB). The dense, cross-linked network of hydrophobic lignin and amorphous hemicellulose physically shields crystalline cellulose microfibrils, drastically restricting downstream enzyme accessibility. Furthermore, non-productive binding of cellulases onto the exposed lignin surfaces induces irreversible enzyme immobilization and denaturation, triggering substantial catalytic losses that depress final glucose yields far below theoretical limits, particularly in forestry and high-lignin agricultural residues (Gohain and Borgohain, 2025).

This structural resistance is compounded by severe economic and operational constraints. Achieving commercial viability requires minimizing the high purchasing costs of complex enzyme cocktails. Industrial saccharification demands massive enzyme dosages containing balanced cellulolytic and hemicellulolytic arrays. However, as these enzymes cleave the matrix, the rapid accumulation of cellobiose and glucose triggers intense feedback inhibition, repressing cellobiohydrolase and β-glucosidase activities over time (Chauhan et al., 2024).

Moreover, operating under high solids loading (>15% w/v)—a mandate for ensuring economically viable, highly concentrated downstream product streams—dramatically escalates medium viscosity. This non-Newtonian fluid behavior induces severe mass transfer limitations, localized temperature gradients, and high power requirements for bioreactor agitation (Singhania et al., 2022).

These rheological constraints are further complicated by regional and seasonal substrate heterogeneity. The chemical composition of agricultural residues fluctuates constantly based on crop genus, soil quality, harvesting seasons, and post-harvest storage conditions, making the standardization of macro-scale industrial process parameters highly volatile (Šelo et al., 2021).

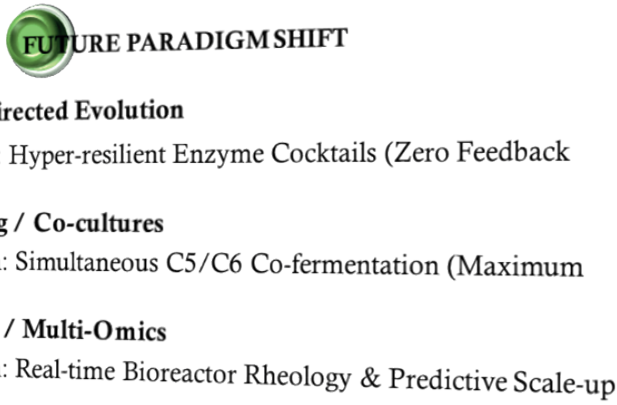
7.2. Downstream Metabolic Barriers and Inhibitor Toxicity

Following saccharification, the resulting crude hydrolysate presents an intricate chemical mixture that complicates fermentation kinetics. Unlike pure starch-derived glucose streams, LCB hydrolysates contain a combination of hexose (C6) and pentose (C5) sugars, such as xylose and arabinose. The industrial workhorse strains conventionally deployed in large-scale fermentations lack native metabolic pathways to simultaneously and efficiently co-utilize both sugar fractions, often leading to sequential consumption, slow kinetics, and unassimilated pentose streams that drastically reduce overall plant atom economy (Peters, 2006).

Compounding this metabolic limitation is the severe toxicity of degradation inhibitors generated during upstream processing. Complex matrix disruption inevitably releases a barrage of microbial toxins—including furan derivatives (furfural and 5-hydroxymethylfurfural), aliphatic organic acids (acetic, formic, and levulinic acids), and low-molecular-weight phenolic fragments (Soares et al., 2023). These toxic effluents synergistically disrupt microbial cell membrane integrity, inhibit key glycolytic enzymes, deplete intracellular ATP pools, and severely lower final biofuel and biochemical yields.

7.3. Future Horizons: Synthetic Biology, Multi-Omics, and Process Intensification

To overcome these multi-tiered barriers, future research trends are rapidly shifting toward advanced molecular engineering, process consolidation, and digital optimization tools. The core technological paradigm shifts driving these upcoming sustainable breakthroughs are conceptualized in the schematic flow below:



In enzyme technology, the integration of protein engineering, recombinant DNA architectures, and high-throughput directed evolution is facilitating the design of de novo synthetic biocatalysts tailored to operate under high temperatures, extreme pH environments, and elevated sugar concentrations with zero product inhibition (Khan, 2025).

Concurrently, synthetic biology and CRISPR-Cas9 genetic editing are being deployed to rewire the metabolic networks of industrial yeasts and bacteria. Researchers are successfully constructing robust, multi-sugar-utilizing phenotypes capable of simultaneous C5/C6 fermentation while introducing heterologous pathways that actively detoxify furan and phenolic inhibitors in real time.

Complementing single-strain modifications, the engineering of synthetic microbial consortia and co-culture systems offers a powerful framework for mimicking natural ecosystems, where diverse microbial specialists collaborate to digest complex hydrolysates without catabolite repression (Khedkar et al., 2024).

Ultimately, integrating these bio-engineered systems with predictive machine learning algorithms and multi-omics analytical platforms (genomics, transcriptomics, and metabolomics) will allow for real-time adjustments to substrate heterogeneity, unlocking the full commercial potential of circular bioeconomies on a global scale.

CONCLUSION

For decades, the massive volumes of biomass waste generated globally from agricultural production, food processing activities, and forestry management were universally defined as low-value byproducts or operational liabilities requiring costly disposal. However, the recent maturation of the circular bioeconomy paradigm has triggered a profound shift, redefining these complex waste matrices as premium renewable feedstocks capable of generating high-value commercial portfolios. Implementing green chemistry principles serves as the definitive roadmap for these conversion pathways, ensuring that resource efficiency is maximized while minimizing long-term ecological footprints.

At the heart of this plant-based transformation is lignocellulosic biomass (LCB). Thanks to its intrinsic composition of structural cellulose, hemicellulose, and cross-linked lignin networks, LCB provides an abundant carbon platform for the synthesis of advanced biofuels, functional biopolymers, and rare biochemical entities. The modern extraction of these structural fractions has been immensely improved by substituting harsh chemical methods with eco-friendly alternatives. Integrating advanced green solvents (such as ionic liquids and deep eutectic solvents) for selective delignification has dramatically minimized hazardous effluents, directly advancing environmental and occupational health.

Concurrently, enzymatic conversion processes have emerged as the most technologically aligned approach with green chemistry doctrines. The extreme substrate specificity of biological catalysts, their ability to operate under benign, low-energy conditions, and their lack of toxic byproduct formation offer undeniable advantages over traditional, corrosive chemical synthesis.

The technological insights synthesized throughout this chapter demonstrate that plant waste is no longer restricted to low-tier energy generation. Instead, engineered biocatalysis enables the precise transformation of waste carbohydrates into structural bioplastics, organic platform acids, specialty cosmetic esters, and health-promoting prebiotic sweeteners. By shifting the waste management philosophy from simple disposal to a secondary raw material supply chain, this framework perfectly embodies the circular economy model—simultaneously lowering industrial waste generation, maximizing atom economy, and securing thermodynamic sustainability.

Despite this immense potential, expanding these technologies to global industrial scales demands a rigorous evaluation of existing socio-economic and engineering barriers. Substrate heterogeneity, high purchasing and recycling costs of enzyme cocktails, high-solids rheological constraints, and complex downstream product recovery loops remain the primary focus of active industrial research. To ensure that these biological advancements genuinely fulfill global sustainability targets, quantitative tools such as Life Cycle Assessments (LCA), cumulative E-factor analyses, and techno-economic modeling must be seamlessly integrated into the earliest stages of bioprocess design rather than treated as late-stage academic reviews.

Looking toward the future, the global scalability of plant waste valorization will be dictated by radical innovations at the intersection of biology and digital technology. The commercial integration of next-generation enzyme engineering, CRISPR-mediated synthetic biology, multi-omics analytical monitoring, and AI-driven bioreactor optimization is poised to deliver highly automated, cost-efficient manufacturing hubs. Furthermore, the development of consolidated biorefinery models—where process intensification frameworks like Simultaneous Saccharification and Fermentation (SSF) or Consolidated Bioprocessing (CBP) are linked with zero-waste cascading configurations—will maximize the economic extraction of every biomass fraction. Supported by progressive environmental policies and rising industrial investments, these enzymatic waste-to-wealth technologies are destined to become the foundational infrastructure of tomorrow's low-carbon, resource-efficient, and fully sustainable global bioeconomy.

SONUÇ

Tarımsal üretim, gıda işleme faaliyetleri ve ormancılık yönetiminden küresel ölçekte açığa çıkan devasa miktardaki biyokütle atıkları, onlarca yıldır ekonomik değeri düşük yan ürünler veya maliyetli bertaraf süreçleri gerektiren operasyonel yükümlülükler olarak tanımlanmıştır. Ancak son yıllarda döngüsel biyoekonomi yaklaşımının olgunlaşması, bu karmaşık atık matrislerini yüksek katma değerli ticari portföyler üretebilen birinci sınıf yenilenebilir ham maddeler olarak yeniden tanımlayarak köklü bir paradigma değişimini tetiklemiştir. Yeşil kimya ilkelerinin uygulanması, bu dönüşüm süreçleri için nihai yol haritasını sunmakta; uzun vadeli ekolojik ayak izlerini en aza indirirken kaynak verimliliğinin en üst düzeye çıkarılmasını garanti altına almaktadır.

Bu bitki tabanlı dönüşümün kalbinde lignoselülozik biyokütle (LSB) yer almaktadır. Selüloz, hemiselüloz ve çapraz bağlı lignin ağlarından oluşan doğal yapısı sayesinde LSB; gelişmiş biyoyakıtların, fonksiyonel biyopolimerlerin ve nadir biyokimyasal bileşiklerin sentezi için bol miktarda karbon platformu sağlamaktadır. Bu yapısal fraksiyonların modern yöntemlerle ekstrakte edilmesi, sert kimyasal metodolojilerin yerini çevre dostu alternatiflerin almasıyla muazzam bir şekilde gelişmiştir. Seçici delignifikasyon için derin ötektik çözücüler ve iyonik sıvılar gibi gelişmiş yeşil çözücülerin sürece dahil edilmesi, tehlikeli atık suları önemli ölçüde minimize ederek çevre ve çalışan sağlığına doğrudan katkı sağlamıştır. Eş zamanlı olarak, enzimatik dönüşüm süreçleri, yeşil kimya doktrinleriyle teknolojik açıdan en uyumlu yaklaşım olarak öne çıkmıştır. Biyolojik katalizörlerin yüksek substrat özgüllüğü, ılıman ve düşük enerjili koşullar altında çalışabilme yetenekleri ve toksik yan ürün oluşturmamaları, geleneksel, aşındırıcı kimyasal sentezlere kıyasla yadsınamaz avantajlar sunmaktadır.

Bu kitap bölümü boyunca sentezlenen teknolojik çıktılar, bitkisel atıkların artık sadece düşük seviyeli enerji üretimiyle sınırlı kalmadığını açıkça göstermektedir. Aksine, mühendislik ürünü biyokataliz, atık karbonhidratların yapısal biyoplastiklere, organik platform asitlerine, özel kozmetik esterlerine ve sağlığı destekleyen prebiyotik tatlandırıcılara hassas bir şekilde dönüştürülmesini sağlamaktadır. Atık yönetimi felsefesini basit bir bertaraftan ikincil bir ham madde tedarik zincirine kaydıran bu çerçeve; atık oluşumunu azaltarak, atom ekonomisini maksimuma çıkararak ve termodinamik sürdürülebilirliği güvence altına alarak döngüsel ekonomi modelini mükemmel bir şekilde somutlaştırmaktadır.

Bu devasa potansiyele rağmen, söz konusu teknolojilerin küresel endüstriyel ölçeklere taşınması; mevcut sosyo-ekonomik ve mühendislik engellerinin titizlikle değerlendirilmesini gerektirmektedir. Ham madde heterojenliği, enzim kokteyllerinin yüksek satın alma ve geri dönüşüm maliyetleri, yüksek katı yüklemesinden kaynaklanan reolojik kısıtlamalar ve karmaşık aşağı akış (downstream) ürün geri kazanım döngüleri, aktif endüstriyel araştırmaların odak noktası olmaya devam etmektedir. Bu biyolojik gelişmelerin küresel sürdürülebilirlik hedeflerini gerçekten karşılamasını sağlamak amacıyla; Yaşam Döngüsü Analizi (LCA), kümülatif

E-faktörü analizleri ve tekno-ekonomik modelleme gibi kantitatif araçlar, proses tasarımının geç aşama akademik incelemeleri olarak değil, en erken aşamalarına sorunsuz bir şekilde entegre edilmelidir.

Geleceğe bakıldığında, bitkisel atıkların katma değere dönüştürülmesinin küresel ölçeklenebilirliği, biyoloji ve dijital teknolojinin kesiştiği noktadaki radikal yenilikler tarafından şekillendirilecektir. Yeni nesil enzim mühendisliği, CRISPR aracılı sentetik biyoloji, multi-omiks analitik izleme ve yapay zeka destekli biyoreaktör optimizasyonunun ticari entegrasyonu, son derece otomatize ve maliyet etkin üretim merkezleri sunmaya adaydır. Ayrıca, Eş Zamanlı Sakkarifikasyon ve Fermantasyon (SSF) veya Konsolide Biyoproses (CBP) gibi proses yoğunlaştırma çerçevelerinin sıfır atıklı kaskat konfigürasyonlarla bağlandığı entegre biyorefineri modellerinin geliştirilmesi, her bir biyokütle fraksiyonundan elde edilen ekonomik kazanımı maksimuma çıkaracaktır. İleri görüşlü çevre politikaları ve artan endüstriyel yatırımlarla desteklenen bu enzimatik atıktan servete (waste-to-wealth) teknolojileri, yarının düşük karbonlu, kaynak verimli ve tamamen sürdürülebilir küresel biyoekonomisinin temel altyapısı olmaya adaydır.

REFERENCES

1. Akash, S., Sivaprakash, B., Rajamohan, N., & Vo, D. V. N. (2023). Biotechnology to convert carbon dioxide into biogas, bioethanol, bioplastic and succinic acid using algae, bacteria and yeast: a review. *Environmental Chemistry Letters*, *21*(3), 1477-1497. https://doi.org/10.1007/s10311-023-01569-3
2. Alcalde, M., Ferrer, M., Plou, F. J., & Ballesteros, A. (2006). Environmental biocatalysis: from remediation with enzymes to novel green processes. *TRENDS in Biotechnology*, *24*(6), 281-287. https://doi.org/10.1016/j.tibtech.2006.04.002
3. Balk, M., Sofia, P., Neffe, A. T., & Tirelli, N. (2023). Lignin, the lignification process, and advanced, lignin-based materials. *International Journal of Molecular Sciences*, *24*(14), 11668. https://doi.org/10.3390/ijms241411668
4. Bashiru, O., Ochem, C., Enyejo, L. A., Manuel, H. N. N., & Adeoye, T. O. (2024). The crucial role of renewable energy in achieving the sustainable development goals for cleaner energy. *Global Journal of Engineering and Technology Advances*, *19*(3), 011-036. https://doi.org/10.30574/gjeta.2024.19.3.0099
5. Beck, S., Choi, P., & Mushrif, S. H. (2022). Physico-chemical interactions within lignocellulosic biomass and their importance in developing solvent based deconstruction methods. *Reaction Chemistry & Engineering*, *7*(12), 2471-2487. https://doi.org/10.1039/D2RE00374K
6. Benítez-Mateos, A. I., Roura Padrosa, D., & Paradisi, F. (2022). Multistep enzyme cascades as a route towards green and sustainable pharmaceutical syntheses. *Nature chemistry*, *14*(5), 489-499. https://doi.org/10.1038/s41557-022-00931-2
7. Blasi, A., Verardi, A., Lopresto, C. G., Siciliano, S., & Sangiorgio, P. (2023). Lignocellulosic agricultural waste valorization to obtain valuable products: An overview. *Recycling*, *8*(4), 61. https://doi.org/10.3390/recycling8040061
8. Chauhan, A. S., Patel, A. K., Chen, C. W., Dong, C. D., & Singhania, R. R. (2024). Strategies for Overcoming the Inhibition of Cellulose Hydrolysis. In *Handbook of Biorefinery Research and Technology: Biomass Logistics to Saccharification* (pp. 1001-1021). Dordrecht: Springer Netherlands. https://doi.org/10.1007/978-94-007-6308-1_70
9. Chen, C. W., Yu, W. S., Zheng, Z. X., Cheng, Y. S., & Li, S. Y. (2024). Waste valorization through acetone-butanol-ethanol (ABE) fermentation. *Journal of the Taiwan Institute of Chemical Engineers*, *160*, 105280. https://doi.org/10.1016/j.jtice.2023.105280
10. da Silva, A. S. A., Espinheira, R. P., Teixeira, R. S. S., de Souza, M. F., Ferreira-Leitão, V., & Bon, E. P. (2020). Constraints and advances in high-solids enzymatic hydrolysis of lignocellulosic biomass: a critical review. *Biotechnology for Biofuels*, *13*(1), 58. https://doi.org/10.1186/s13068-020-01697-w
11. Dai, D., & Jin, Y. S. (2024). Rare sugar bioproduction: Advantages as sweeteners, enzymatic innovation, and fermentative frontiers. *Current Opinion in Food Science*, *56*, 101137. https://doi.org/10.1016/j.cofs.2024.101137
12. Deivayanai, V. C., Yaashikaa, P. R., Kumar, P. S., & Rangasamy, G. (2022). A comprehensive review on the biological conversion of lignocellulosic biomass into hydrogen: Pretreatment strategy, technology advances and perspectives. *Bioresource Technology*, *365*, 128166. https://doi.org/10.1016/j.biortech.2022.128166

13. Devi, A., Bajar, S., Kour, H., Kothari, R., Pant, D., & Singh, A. (2022). Lignocellulosic biomass valorization for bioethanol production: a circular bioeconomy approach. *Bioenergy Research*, *15*(4), 1820-1841. https://doi.org/10.1007/s12155-022-10401-9

14. Díez, D., Urueña, A., Piñero, R., Barrio, A., & Tamminen, T. (2020). Determination of hemicellulose, cellulose, and lignin content in different types of biomasses by thermogravimetric analysis and pseudocomponent kinetic model (TGA-PKM method). *Processes*, *8*(9), 1048. https://doi.org/10.3390/pr8091048

15. Dwivedi, S., Tanveer, A., Yadav, S., Anand, G., & Yadav, D. (2022). Agro-wastes for cost effective production of industrially important microbial enzymes: an overview. *Microbial biotechnology: role in ecological sustainability and research*, 435-460. https://doi.org/10.1002/9781119834489.ch23

16. Gohain, P. B., & Borgohain, D. (2025). Lignocellulosic Biomass (LCB) for a Sustainable Circular Economy. *Agricultural Research Journal*, *62*(3), 246-255. https://doi.org/10.5958/2395-146X.2025.00031.2

17. Grigorakis, K., Ferousi, C., & Topakas, E. (2025). Protein engineering for industrial biocatalysis: principles, approaches, and lessons from engineered PETases. *Catalysts*, *15*(2), 147. https://doi.org/10.3390/catal15020147

18. Jhariya, U., Dafale, N. A., Srivastava, S., Bhende, R. S., Kapley, A., & Purohit, H. J. (2021). Understanding ethanol tolerance mechanism in Saccharomyces cerevisiae to enhance the bioethanol production: current and future prospects. *BioEnergy Research*, *14*(2), 670-688. https://doi.org/10.1007/s12155-020-10228-2

19. Jiang, Z., Zeng, Y., Hu, D., Guo, R., Yan, K., & Luque, R. (2023). Chemical transformations of 5-hydroxymethylfurfural into highly added value products: present and future. *Green Chemistry*, *25*(3), 871-892. https://doi.org/10.1039/D2GC03444A

20. Karimi, F., Mazaheri, D., Saei Moghaddam, M., Mataei Moghaddam, A., Sanati, A. L., & Orooji, Y. (2025). Solid-state fermentation as an alternative technology for cost-effective production of bioethanol as useful renewable energy: a review. *Biomass Conversion and Biorefinery*, *15*(23), 29523-29539. https://doi.org/10.1007/s13399-021-01875-2

21. Kaushik, V., & Kataria, R. (2025). Non-conventional strategies for pretreatment of lignocellulosic biomass for production of value-added products: a sustainable and circular economy approach. *Biomass Conversion and Biorefinery*, *15*(10), 14697-14727. https://doi.org/10.1007/s13399-024-06388-2

22. Khan, M. F. (2025). Enhancing stability of enzymes for industrial applications: Molecular insights and emerging approaches. *World Journal of Microbiology and Biotechnology*, *41*(10), 362. https://doi.org/10.1007/s11274-025-04568-4

23. Khedkar, M., Bedade, D., Singhal, R. S., & Bankar, S. B. (2024). Mixed culture cultivation in microbial bioprocesses. *Mixed Cultures in Industrial Bioprocesses*, 9-69. https://doi.org/10.1007/10_2023_248

24. Kn, Y., TM, M. U., S, K., Sachdeva, S., Thakur, S., & S, A. K. (2023). Lignocellulosic biorefinery technologies: a perception into recent advances in biomass fractionation, biorefineries, economic hurdles and market outlook. *Fermentation*, *9*(3), 238. https://doi.org/10.3390/fermentation9030238

25. Kocabaş, D. S., Güder, S., & Özben, N. (2015). Purification strategies and properties of a low-molecular weight xylanase and its application in agricultural waste biomass hydrolysis. *Journal of Molecular Catalysis B: Enzymatic*, *115*, 66-75. https://doi.org/10.1016/j.molcatb.2015.01.012

26. Kognou, A. L. M., Shrestha, S., Jiang, Z., Xu, C. C., Sun, F., & Qin, W. (2022). High-fructose corn syrup production and its new applications for 5-hydroxymethylfurfural and value-added furan derivatives: Promises and challenges. *Journal of Bioresources and Bioproducts*, *7*(3), 148-160. https://doi.org/10.1016/j.jobab.2022.03.004

27. Kover, A., Kraljić, D., Marinaro, R., & Rene, E. R. (2022). Processes for the valorization of food and agricultural wastes to value-added products: recent practices and perspectives. *Systems Microbiology and Biomanufacturing*, *2*(1), 50-66. https://doi.org/10.1007/s43393-021-00042-y

28. Kristensen, J. B., Felby, C., & Jørgensen, H. (2009). Yield-determining factors in high-solids enzymatic hydrolysis of lignocellulose. *Biotechnology for biofuels*, *2*(1), 11. https://doi.org/10.1186/1754-6834-2-11

29. Kumar, A., Aggarwal, D., Bharti, A. K., & Ram, C. (2021). Lignocellulosic biomass wastes to bioenergy: role of microbial enzymes for second generation biofuels. In *Nanobiotechnology for Green Environment* (pp. 115-138). CRC Press. https://doi.org/10.1201/9780367461362-5

30. Kumar, R., Singh, S., & Singh, O. V. (2008). Bioconversion of lignocellulosic biomass: biochemical and molecular perspectives. *Journal of industrial microbiology and biotechnology*, *35*(5), 377-391. https://doi.org/10.1007/s10295-008-0327-8

31. Kurul, F., Doruk, B., & Topkaya, S. N. (2025). Principles of green chemistry: building a sustainable future. *Discover Chemistry*, *2*(1), 68. https://doi.org/10.1007/s44371-025-00152-9

32. Lee, J., Yang, X., Cho, S. H., Kim, J. K., Lee, S. S., Tsang, D. C., ... & Kwon, E. E. (2017). Pyrolysis process of agricultural waste using CO2 for waste management, energy recovery, and biochar fabrication. *Applied energy*, *185*, 214-222. https://doi.org/10.1016/j.apenergy.2016.10.092

33. Li, A., Zheng, J., Han, X., Yang, S., Cheng, S., Zhao, J., ... & Lu, Y. (2023). Advances in low-lactose/lactose-free dairy products and their production. *Foods*, *12*(13), 2553. https://doi.org/10.3390/foods12132553

34. Li, J., Sun, L., & Huo, Y. X. (2025). High-temperature catalytic platform powered by thermophilic microorganisms and thermozymes. *Synthetic Biology and Engineering*, *3*(1), 10001. https://doi.org/10.70322/sbe.2025.10001

35. Limeneh, D. Y., Abate, M. T., & Yilma, K. T. (2025). Lignocellulosic biomass pretreatment technologies: a review of recent advancements and emerging technologies. *Lignocellulosic biomass and enzymes: fundamentals, emerging technologies and applications*, 3-31. https://doi.org/10.1007/978-981-96-3037-0_1

36. Lin, Z., Cong, W., & Zhang, J. A. (2023). Biobutanol production from acetone–butanol–ethanol fermentation: developments and prospects. *Fermentation*, *9*(9), 847. https://doi.org/10.3390/fermentation9090847

37. Nachtergaele, P., Kocak, O., Escobar, Y. R., Motte, J., Gabriels, D., Mottet, L., & Dewulf, J. (2024). Does enzymatic catalysis lead to more sustainable chemicals production? A life cycle sustainability assessment of isopropyl palmitate. *Green Chemistry*, *26*(23), 11662-11672. https://doi.org/10.1039/D4GC04514A

38. Nath, S. (2024). Biotechnology and biofuels: paving the way towards a sustainable and equitable energy for the future. *Discover Energy*, *4*(1), 8. https://doi.org/10.1007/s43937-024-00032-w

39. Olatunji, O., Akinlabi, S., & Madushele, N. (2020). Application of lignocellulosic biomass (LCB). In *Valorization of biomass to value-added commodities: Current trends, challenges, and future prospects* (pp. 3-19). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-030-38032-8_1

40. Olofsson, K., Bertilsson, M., & Lidén, G. (2008). A short review on SSF–an interesting process option for ethanol production from lignocellulosic feedstocks. *Biotechnology for biofuels*, *1*(1), 7. https://doi.org/10.1186/1754-6834-1-7

41. Pelagalli, V., Langone, M., Matassa, S., Race, M., Tuffi, R., Papirio, S., ... & Esposito, G. (2024). Pyrolysis of municipal sewage sludge: Challenges, opportunities and new valorization routes for biochar, bio-oil, and pyrolysis gas. *Environmental Science: Water Research & Technology*, *10*(10), 2282-2312. https://doi.org/10.1039/D4EW00278D

42. Peters, D. (2006). Carbohydrates for fermentation. *Biotechnology Journal: Healthcare Nutrition Technology*, *1*(7-8), 806-814. https://doi.org/10.1002/biot.200600041

43. Pragya, & Kumar, P. (2025). Microbial enzymes acting on lignocellulosic biomass: an overview. *Lignocellulosic Biomass and Enzymes: Fundamentals, Emerging Technologies and Applications*, 177-209. https://doi.org/10.1007/978-981-96-3037-0_8

44. Qadir, M. L., Arshad, S., Hussain, N., Hafsa, Javed, M. A., Ashfaq, M., & Ali, Q. (2026). Polymer-Based Nanoparticles and Nano-Biocatalytic Systems for the Mitigation of Environmental Pollutants. *Geomicrobiology Journal*, *43*(3), 259-281. https://doi.org/10.1080/01490451.2025.2580963

45. Schwarz, J., Volmer, J., & Lütz, S. (2024). Enzymes in the Chemical and Pharmaceutical Industry. In *Introduction to Enzyme Technology* (pp. 289-314). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-031-42999-6_14

46. Šelo, G., Planinić, M., Tišma, M., Tomas, S., Koceva Komlenić, D., & Bucić-Kojić, A. (2021). A comprehensive review on valorization of agro-food industrial residues by solid-state fermentation. *Foods*, *10*(5), 927. https://doi.org/10.3390/foods10050927

47. Serrano-Echeverry, V. A., Guerrero-Fajardo, C. A., & Castro-Tibabisco, K. T. (2025). A Review of Biobutanol: Eco-Friendly Fuel of the Future—History, Current Advances, and Trends. *Fuels*, *6*(3), 55. https://doi.org/10.3390/fuels6030055

48. Shah, T. A., Zhihe, L., Zhiyu, L., & Andong, Z. (2022). Composition and role of lignin in biochemicals. In *Lignin-chemistry, structure, and application*. IntechOpen. https://doi.org/10.5772/intechopen.106527

49. Shahzadi, T., Mehmood, S., Irshad, M., Anwar, Z., Afroz, A., Zeeshan, N., ... & Sughra, K. (2014). Advances in lignocellulosic biotechnology: A brief review on lignocellulosic biomass and cellulases. *Advances in Bioscience and Biotechnology*, *5*(3), 246. https://doi.org/10.4236/abb.2014.53031

50. Sharma, A., Gupta, G., Ahmad, T., Mansoor, S., & Kaur, B. (2021). Enzyme engineering: current trends and future perspectives. *Food Reviews International*, *37*(2), 121-154. https://doi.org/10.1080/87559129.2019.1695835

51. Sharma, N., Ahlawat, Y. K., Stalin, N., Mehmood, S., Morya, S., Malik, A., ... & Bhanot, D. (2025). Microbial enzymes in industrial biotechnology: Sources, production, and significant applications of lipases. *Journal of Industrial Microbiology and Biotechnology*, *52*, kuaf010. https://doi.org/10.1093/jimb/kuaf010

52. Sharma, S., Tsai, M. L., Sharma, V., Sun, P. P., Nargotra, P., Bajaj, B. K., ... & Dong, C. D. (2022). Environment friendly pretreatment approaches for the bioconversion of lignocellulosic biomass into biofuels and value-added products. *Environments*, *10*(1), 6. https://doi.org/10.3390/environments10010006

53. Sheldon, R. A. (2016). Biocatalysis and green chemistry. *Green biocatalysis*, 1-15. https://doi.org/10.1002/9781118828083.ch1

54. Sheldon, R. A., & Brady, D. (2022). Green chemistry, biocatalysis, and the chemical industry of the future. *ChemSusChem*, *15*(9), e202102628. https://doi.org/10.1002/cssc.202102628

55. Silva, T. A. L., Varão, L. H. R., & Pasquini, D. (2024). Lignocellulosic biomass. In *Handbook of biomass* (pp. 105-142). Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-99-6727-8_5

56. Singhania, R. R., Patel, A. K., Raj, T., Tsai, M. L., Chen, C. W., & Dong, C. D. (2022). Advances and challenges in biocatalysts application for high solid-loading of biomass for 2nd generation bio-ethanol production. *Catalysts*, *12*(6), 615. https://doi.org/10.3390/catal12060615

57. Singhania, R. R., Patel, A. K., Singh, A., Haldar, D., Soam, S., Chen, C. W., ... & Dong, C. D. (2022). Consolidated bioprocessing of lignocellulosic biomass: technological advances and challenges. *Bioresource technology*, *354*, 127153. https://doi.org/10.1016/j.biortech.2022.127153

58. Soares, L. B., da Silveira, J. M., Biazi, L. E., Longo, L., de Oliveira, D., Furigo Junior, A., & Ienczak, J. L. (2023). An overview on fermentation strategies to overcome lignocellulosic inhibitors in second-generation ethanol production using cell immobilization. *Critical Reviews in Biotechnology*, *43*(8), 1150-1171. https://doi.org/10.1080/07388551.2022.2109452

59. Srivastava, N., Singh, R., Singh, P., Ahmad, I., Singh, R. P., Rai, A. K., ... & Gupta, V. K. (2023). Recent advances on lignocellulosic bioresources and their valorization in biofuels production: Challenges and viability assessment. *Environmental Technology & Innovation*, *29*, 103037. https://doi.org/10.1016/j.eti.2023.103037

60. Tamo, A. K., Doench, I., Deffo, G., Jiokeng, S. L. Z., Doungmo, G., Fotsop, C. G., ... & Osorio-Madrazo, A. (2025). Lignocellulosic biomass and its main structural polymers as sustainable materials for (bio) sensing applications. *Journal of Materials Chemistry A*, *13*(30), 24185-24253. https://doi.org/10.1039/D5TA02900G

61. Vasić, K., Knez, Ž., & Leitgeb, M. (2021). Bioethanol production by enzymatic hydrolysis from different lignocellulosic sources. *Molecules*, *26*(3), 753. https://doi.org/10.3390/molecules26030753

62. Xiong, W., Reyes, L. H., Michener, W. E., Maness, P. C., & Chou, K. J. (2018). Engineering cellulolytic bacterium Clostridium thermocellum to co-ferment cellulose- and hemicellulose-derived sugars simultaneously. *Biotechnology and bioengineering*, *115*(7), 1755-1763. https://doi.org/10.1002/bit.26590

63. Zhang, X., Liu, A., Li, X., Xu, W., Duan, X., Shi, J., & Li, X. (2025). Research progress of deep eutectic solvents in lignocellulosic biomass pretreatment. *Cellulose*, *32*(8), 4637-4650. https://doi.org/10.1007/s10570-025-06553-4

64. Zhao, X., Zhang, L., & Liu, D. (2012). Biomass recalcitrance. Part I: the chemical compositions and physical structures affecting the enzymatic hydrolysis of lignocellulose. *Biofuels, bioproducts and biorefining*, *6*(4), 465-482. https://doi.org/10.1002/bbb.1331

GREEN CHEMISTRY AND TECHNOLOGIES FOR AIR POLLUTION CONTROL AND ATMOSPHERIC SUSTAINABILITY

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ABSTRACT

Air pollution remains one of the most significant environmental challenges worldwide, with volatile organic compounds (VOCs) playing a critical role in the formation of ground-level ozone, secondary organic aerosols, and adverse human health impacts. This chapter examines the application of green chemistry principles and sustainable technologies to control VOC emissions and advance atmospheric sustainability. Conventional abatement technologies, including adsorption, absorption, thermal oxidation, catalytic oxidation, photocatalytic oxidation, and biological treatment systems, are evaluated from both technical and environmental perspectives. Particular emphasis is placed on resource consumption, energy demand, water use, chemical requirements, secondary waste generation, and life-cycle environmental impacts. Emerging green alternatives, such as bio-based adsorbents, low-temperature catalysts, renewable-energy-assisted systems, circular-economy approaches, and digital process optimization, are also discussed. Furthermore, environmental sustainability indicators and life-cycle assessment frameworks are presented as essential tools for evaluating the overall performance of VOC control technologies. The chapter highlights the need to move beyond pollutant removal efficiency toward integrated environmental sustainability and resource-efficient air pollution management strategies.

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1. INTRODUCTION

Integration of the twelve principles of green chemistry into industrial process design to minimize hazardous emissions (Fantozzi & Buratti, 2011; Sharma et al., 2022). This strategy facilitates the transition from reactive, end-of-pipe treatment technologies to proactive molecular engineering, thereby enhancing resource efficiency and reducing the environmental footprint of volatile organic compound abatement (More, 2026). By prioritizing the design of safer chemicals and catalytic processes, industries can fundamentally reduce the generation of precursors to atmospheric pollutants at their source rather than relying solely on filtration (Beach et al., 2009; Weller et al., 2025). This paradigm shift uses quantitative sustainability metrics—such as atom economy and life-cycle assessment—to objectively evaluate and optimize chemical pathways for cleaner atmospheric emissions (More, 2026).

Volatile organic compounds serve as critical precursors in the formation of ground-level ozone and secondary organic aerosols, significantly complicating regional air quality management (Ch et al., 2025). The widespread release of these pollutants, largely driven by rapid industrialization and urbanization, necessitates the implementation of advanced heterogeneous catalysis to effectively mitigate hazardous waste streams before they enter the atmosphere (He et al., 2019). Specifically, catalytic oxidation technologies offer a robust solution for abating these emissions, enabling high destruction efficiencies at lower operational temperatures than traditional incineration methods (Silva et al., 2016). These advanced catalytic systems leverage high-performance materials to enhance reaction kinetics and lower activation energy, ensuring pollutant degradation occurs under milder, energy-efficient conditions (Liu et al., 2024).

Major contributors include the chemical manufacturing, petroleum refining, and automotive painting sectors, where excessive fossil fuel consumption and raw material processing result in the continuous release of harmful organic vapors (Hoàng et al., 2025). Projections indicate that global VOC emissions may reach 135.5 Tg/year by 2050, underscoring the urgent need for stringent emission standards and for adopting more sustainable industrial practices (Baskaran et al., 2024; Yang et al., 2019). Furthermore, adopting circular economy principles facilitates the recovery and regeneration of spent catalysts, thereby mitigating the significant environmental impacts associated with their production and disposal (Afolabi et al., 2024). Beyond catalyst longevity, the implementation of wet scrubbers and specialized particulate filtration systems remains essential for capturing auxiliary pollutants and residues that bypass catalytic conversion (Bhat et al., 2024).

The formation of water vapor during catalytic combustion represents a significant technical challenge, as it can inadvertently poison active sites and diminish long-term catalytic performance (Hosseini et al., 2019). Additionally, the presence of sulfur-containing impurities often leads to the irreversible deactivation of active metal centers, necessitating the development of catalysts with enhanced tolerance to such chemical poisons (Zhang et al., 2025). Moreover, the complex composition of industrial flue gases often comprises a mixture of halogenated and oxygenated hydrocarbons,

which complicates substrate selectivity and necessitates advanced structure-activity relationships to maintain structural integrity (Zhao et al., 2025). To address these challenges, current research is shifting toward the development of multifunctional catalytic systems capable of simultaneously removing pollutants and maintaining high stability in complex exhaust streams (Lei et al., 2024; Yang et al., 2025).

The application of these principles prioritizes the synthesis of noble-metal-free catalysts, such as mechanically activated hydroxyapatites, which offer a non-toxic, cost-effective alternative to precious-metal-based systems (Xin et al., 2021). These innovative materials demonstrate remarkable activity for VOC degradation while mitigating the economic and supply chain constraints associated with palladium or platinum (Pan et al., 2017).

Life cycle assessment must be integrated into the developmental phase to quantify the net ecological impact of synthesis routes, ensuring that the energy expended during catalyst production does not outweigh the benefits of emission abatement (Liu et al., 2023). This comprehensive evaluation further necessitates investigation of by-product formation, as incomplete oxidation can inadvertently generate secondary pollutants that are more toxic than the original gas-phase reagents (Zhao et al., 2025). Furthermore, the industrial implementation of these oxidation processes requires addressing catalyst deactivation due to surface chlorination, particularly when handling halogenated organic compounds (Weng et al., 2018). High VOC removal efficiency does not necessarily indicate environmental sustainability if the process requires intensive water consumption, activated carbon replacement, chemical inputs, energy demand, and secondary waste management.

Consequently, future research must prioritize the development of highly active, poison-resistant catalysts capable of maintaining performance despite the co-existence of moisture and sulfur-containing compounds (He et al., 2019; Song et al., 2020). Beyond performance stability, research must focus on deciphering interfacial reaction mechanisms through time-resolved spectroscopic analysis to prevent the accumulation of toxic intermediates (Deng et al., 2023). Furthermore, the integration of cascade processes -where multiple pollutants such as NOx, N2O, and NH3 are abated simultaneously- offers a promising pathway toward achieving zero-emission industrial operations (Galloni et al., 2020). Ultimately, the transition toward atmospheric sustainability requires a shift from evaluating VOC abatement technologies solely on removal efficiency to assessing their overall environmental performance across the life cycle. Future air pollution control strategies must therefore integrate green chemistry principles, life cycle assessment, resource efficiency, and circular economy approaches to minimize not only VOC emissions but also the associated consumption of energy, water, chemicals, and materials. In this context, atmospheric sustainability indicators -including carbon footprint, water footprint, secondary waste generation, resource depletion, and human health impacts-should be considered alongside pollutant removal efficiency when designing and selecting VOC control technologies. Such a holistic framework will support the development of next-generation air pollution mitigation systems capable of delivering both effective emission reduction and long-term environmental sustainability.

2. VOLATILE ORGANIC COMPOUNDS (VOCS): SOURCES, CHARACTERISTICS, AND ENVIRONMENTAL IMPACTS

Chemical structures are typically categorized by their vapor pressure and boiling points, encompassing a broad range of hydrocarbons, including alkanes, aromatics, and oxygenated compounds. These substances contribute significantly to the formation of ground-level ozone and fine particulate matter through complex atmospheric photochemical reactions. These gaseous precursors also serve as primary drivers of secondary organic aerosol formation, which exacerbate respiratory health risks and impair regional visibility (Yang et al., 2019).

2.1. Major industrial emission sources:

- Petroleum Refining: Distillation, storage tank breathing losses, and wastewater treatment units release volatile hydrocarbons, including benzene and toluene, which necessitate advanced recovery and abatement strategies (Tomatis et al., 2016).
- Chemical industry: Processes such as solvent extraction, monomer production, and synthetic resin manufacturing generate substantial quantities of fugitive emissions (Ma et al., 2021).
- Automotive manufacturing: Surface coating and spray painting operations utilize high-volume solvent applications that release complex mixtures of aromatics and oxygenated hydrocarbons, requiring specialized photocatalytic or regenerative thermal oxidation systems for effective capture (El Khawaja et al., 2022; M. Li & Wang, 2025).
- Textile finishing: Dyeing and finishing processes involve large-scale utilization of organic solvents and chemical fixatives, leading to the discharge of hazardous gaseous emissions that demand high-efficiency adsorption and oxidative treatment systems (Liu et al., 2025).
- Petrochemical facilities: Distillation, storage tank breathing losses, and wastewater treatment units release volatile hydrocarbons, including benzene and toluene, which necessitate advanced recovery and abatement strategies (Tomatis et al., 2016).
- Waste treatment plants: Biological decomposition and landfill gas management often release fugitive methane and non-methane VOCs, requiring integration of adsorption or thermal oxidation to mitigate odor and greenhouse gas potential (Baskaran et al., 2024; Schick et al., 2019).
- Surface coating and painting: These operations involve high-volume solvent utilization and curing processes, emitting complex mixtures of aromatics and oxygenated compounds that necessitate advanced photocatalytic or regenerative thermal oxidation systems for effective capture (Chen et al., 2020; Wróblewska & Jeong, 2021).

2.2. Environmental consequences:

- Ground-level ozone formation
- Secondary organic aerosol (SOA)
- Human toxicity
- Climate impacts
- Odor pollution

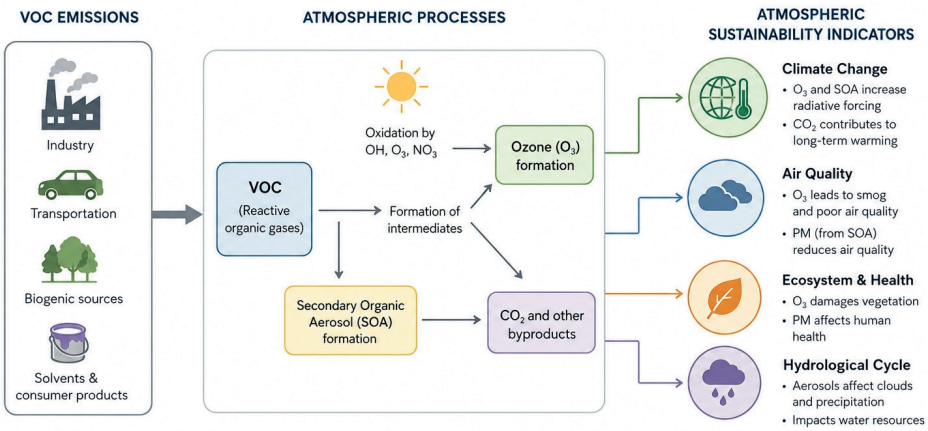

Figure 1. *Relationship between VOC emissions and atmospheric sustainability indicators (Illustrated using NotebookLM)*

3. CONVENTIONAL VOC ABATEMENT TECHNOLOGIES AND THEIR ENVIRONMENTAL BURDENS

Thermal incineration, while effective for high-concentration streams, frequently incurs substantial carbon footprints due to intense energy consumption and the potential for secondary pollutant generation (Ma et al., 2021). Similarly, activated carbon adsorption provides a versatile recovery method but is inherently limited by the downstream management of hazardous spent materials, which often requires further incineration and risks contaminant transfer into auxiliary waste streams (Oliva et al., 2022). Conversely, while absorption and condensation techniques facilitate the potential recovery of solvents, they often fail to achieve the high destruction efficiencies required for dilute, complex industrial gas streams (Gao et al., 2022; Parmar et al., 2008).

3.1. Adsorption-Based VOC Removal Systems

These systems utilize porous materials with high surface areas to selectively capture VOCs, yet their efficacy is often constrained by the competitive adsorption of atmospheric moisture and by the challenges of regenerating saturated media (Y. Li, 2024; Subrahmanyam et al., 2006). To mitigate these operational limitations, integrated systems that combine adsorption with subsequent catalytic oxidation

have emerged as a robust strategy, allowing for the concentration of dilute emissions prior to efficient mineralization (El Khawaja et al., 2022).

Conventional Technologies

Activated carbon adsorption: Zeolite molecular sieves, which provide superior thermal stability and moisture resistance compared to carbonaceous media (He et al., 2021).

- These hydrophobic zeolitic frameworks offer improved performance in high-humidity environments, effectively preventing pore blockage that otherwise hinders the capture efficiency of traditional activated carbon (Wang et al., 2021).
- Zeolite adsorption: These crystalline aluminosilicates facilitate shape-selective adsorption, enabling the targeted recovery of specific hydrocarbons while maintaining structural integrity during high-temperature thermal regeneration (Wu et al., 2023; Yu et al., 2022). Furthermore, the implementation of Metal-Organic Frameworks offers a cutting-edge alternative, demonstrating exceptional recovery capabilities that warrant further investigation to address current challenges in structural stability and regeneration efficiency (Baskaran et al., 2024).
- Polymer-based adsorbents: These synthetic materials provide tunable surface chemistry and pore architectures, allowing for enhanced selectivity toward specific VOC species compared to traditional carbonaceous sorbents (R. Li et al., 2019). Additionally, microporous materials such as silica gel and super-crosslinked polymerization resins are increasingly used as noncombustible alternatives to conventional carbon adsorbents, effectively addressing concerns about the flammability and regeneration difficulties inherent in carbonaceous media (Valdés et al., 2021; Y. Yuan et al., 2023).

Environmental footprint indicators

To evaluate the comparative environmental performance of various VOC abatement technologies, the following table summarizes key metrics, including energy intensity, waste generation, and overall lifecycle sustainability.

- Activated carbon consumption: High volumes of spent media necessitate energy-intensive thermal regeneration processes or hazardous waste incineration, which contribute to the overall carbon footprint and lifecycle toxicity of the system (Vellingiri et al., 2016; Y. Yuan et al., 2023).
- Metal-Zeolite Composites: These multifunctional materials leverage dispersed metal nanoparticles within zeolitic frameworks to enable simultaneous adsorption and catalytic mineralization, thereby reducing the energy requirements and operational stages typical of segregated removal processes (Xue & Yang, 2021).
- Carbon regeneration requirements: Furthermore, the transition toward advanced materials like MOFs and biochar leverages superior surface areas

and tunable pore structures to achieve higher removal capacities, potentially minimizing the frequency of regeneration cycles and associated energy penalties (Talaie et al., 2025; Vellingiri et al., 2016).

- Water demand: High-temperature steam usage for desorbing captured VOCs from activated carbon significantly elevates process energy demands, whereas zeolites allow for more efficient thermal regeneration due to their superior stability (Cramer & Cole, 2017; Valdés et al., 2021).
- Secondary waste generation: Solvent-based absorption processes often necessitate the management of contaminated aqueous effluents, whereas integrated catalytic systems minimize liquid waste by converting hazardous pollutants into benign atmospheric components (Wang et al., 2021; Zhou et al., 2019).
- Disposal requirements: The utilization of metal-organic frameworks and specialized zeolites reduces the accumulation of hazardous spent media compared to traditional activated carbons, as their enhanced thermal stability and regenerative capacity extend the material's operational lifespan (J. Li et al., 2023; Vellingiri et al., 2016).
- Operating cost: While activated carbon requires frequent and costly replacement due to regeneration issues and flammability risks (Saidi et al., 2021; Valdés et al., 2021), advanced crystalline materials provide lower long-term expenditures by extending adsorbent service life and reducing the necessity for energy-intensive waste management (Razali et al., 2015).

Green alternatives

The adoption of bio-based sorbents, such as those derived from agricultural waste, represents a sustainable shift that minimizes the ecological footprint associated with material production and disposal (Ketabchi et al., 2023; Osman et al., 2023). Furthermore, the valorization of precursors such as spent coffee grounds into high-performance carbonaceous adsorbents exemplifies a circular economy approach that simultaneously diverts organic waste from landfills while providing cost-effective solutions for gas purification (Plaza et al., 2012).

- Biochar-based adsorbents: These materials utilize biomass-derived porous frameworks that provide competitive surface area for VOC capture while offering a carbon-neutral lifecycle and significantly lower production costs compared to synthetic zeolites or traditional activated carbons. By incorporating functional groups during pre- or post-synthesis, these bio-based media can be further optimized to increase selectivity and capacity, mirroring the tailored performance of advanced metal-organic frameworks (Vellingiri et al., 2016).
- Waste-derived adsorbents: These substrates utilize industrial and agricultural residues, such as fly ash or husks, to create low-cost porous supports that alleviate the economic burden of sourcing high-purity synthetic precursors for atmospheric remediation (Valdés et al., 2021).

- Regenerative adsorption systems: These systems focus on optimizing adsorption-desorption cycling through precise control of pressure or temperature swings, which minimizes structural fatigue and maintains the adsorbent's capacity over prolonged operational lifespans. Additionally, the integration of computational modeling for the rational design of these porous frameworks allows for the fine-tuning of adsorbent-adsorbate energetics, thereby reducing the energy penalty associated with excessive binding affinities (Pardakhti et al., 2019).
- Low-carbon sorbent production: This approach prioritizes green synthesis pathways—such as solvent-free, mechanochemical, and microwave-assisted methods—to align the fabrication of metal-organic frameworks and other porous materials with the principles of sustainable chemistry. By using renewable precursors such as biomass and waste biochar, these synthetic strategies significantly reduce reliance on fossil-fuel-derived materials and hazardous activation agents (Titirici et al., 2015).

Indicators

To comprehensively assess the viability of these emerging materials, a life-cycle perspective is essential for quantifying environmental impacts, including cumulative CO_2 emissions from sample preparation and the energy consumption associated with regeneration processes (X. Yuan et al., 2022).

- kg adsorbent/kg VOC removed
- kg waste/kg VOC removed
- m^3 water/kg VOC removed
- kg CO_2-eq/kg VOC removed

3.2. Absorption and Wet Scrubbing Technologies

While traditional amine-based systems have long dominated industrial gas treatment, they often face challenges due to high solvent degradation rates and the resulting emissions of secondary volatile organic compounds (Zhang et al., 2024). Consequently, researchers are pivoting toward hybrid membranes and supported ionic liquid configurations that offer enhanced chemical stability and reduced volatility, thereby mitigating the environmental risks posed by solvent carryover (Pudi et al., 2022). Moreover, the development of switchable solvents and task-specific ionic liquids presents an opportunity to improve capture efficiency while concurrently lowering the energy intensity of regeneration cycles (Ume Onwuka & Adu, 2024).

Conventional technologies

- Water scrubbing: This technique utilizes the high solubility of specific pollutants to facilitate mass transfer from the gas to the liquid phase, though it is often limited by its low efficiency for hydrophobic compounds (Severino et al., 2023).

- Alkaline scrubbing: This process employs basic aqueous solutions to neutralize acidic gaseous pollutants like SOx and HCl, yet it frequently produces substantial volumes of hazardous saline wastewater that demand intensive downstream treatment (Iroegbu et al., 2025).
- Chemical scrubbing: This method employs reactive reagents -typically aqueous amines or ammonia- to enhance pollutant uptake through chemisorption, though it remains burdened by significant energy penalties during solvent regeneration (Fisher et al., 2023). To address these inherent limitations, recent advancements have focused on bioregenerative materials and ionic liquids that offer superior environmental profiles and potential for lower-energy, sustainable gas capture (Abdullatif et al., 2023).
- Alkali absorption: By utilizing biodegradable alkaline agents derived from waste streams, this method significantly reduces the accumulation of low-value gypsum and hazardous saline by-products commonly generated by traditional limestone scrubbing (Siami et al., 2023).
- Solvent-based scrubbing: Utilizing specialized organic solvents such as polyethylene glycol dimethyl ether can improve CO2 solubility compared to water, allowing for smaller column sizes and reduced operating pressures (Nguyen et al., 2021).

Environmental concerns

The widespread deployment of chemical scrubbing agents is frequently constrained by the risks of solvent degradation and the potential release of volatile organic compounds into the atmosphere (Mikulčić et al., 2019; Seoane et al., 2015). To mitigate these challenges, ionic liquids are increasingly being investigated as non-volatile alternatives with low vapor pressure and exceptional thermal stability, effectively eliminating solvent loss during operation (Osman et al., 2021).

- High water demand: Many conventional amine-based systems necessitate substantial aqueous volumes for cooling and solvent make-up, a burden that ionic liquid applications significantly alleviate due to their negligible volatility and tunable stability (Bui et al., 2018).
- Wastewater generation: The reliance on aqueous alkali hydroxide solutions often results in significant salt-laden effluent, whereas systems utilizing ionic liquids or bipolar membrane electrodialysis can facilitate efficient solvent regeneration while drastically minimizing the volume of waste discharge (Aminuddin et al., 2024).
- Chemical consumption: Traditional systems often require continuous make-up of hazardous reagents to compensate for losses through thermal degradation, oxidation, or evaporative stripping (Ahmed et al., 2021).
- Sludge production: The use of conventional scrubbers often generates significant solid residues through the precipitation of carbonates or lime-based by-products, whereas emerging strategies like bipolar membrane electrodi-

alysis enable closed-loop regeneration that avoids such sludge formation entirely (Erans et al., 2022).

- Disposal burden: Traditional scrubbing processes often necessitate complex treatment protocols for heat-stable salts and hazardous degradation products, whereas non-aqueous ionic liquid systems minimize these waste streams by ensuring long-term chemical resilience and reduced chemical reagent consumption (Santos & Hanak, 2022).

Green alternatives

The investigation into ionic liquids has intensified due to their negligible volatility, broad liquid range, and tunable molecular structures, which facilitate superior carbon dioxide absorption compared to conventional aqueous amines (Abdrabou et al., 2023). Furthermore, integrating these ionic liquids with amines creates hybrid media that combine enhanced capture capacity with lower regeneration energy requirements.

- Closed-loop water systems: These frameworks minimize freshwater consumption by recycling process streams, directly addressing the high water-intensity inherent in conventional amine-based cooling and scrubbing operations (Bui et al., 2018).
- Solvent recovery: These innovative processes leverage the negligible vapor pressure and high thermal stability of ionic liquids to enable efficient solvent regeneration with significantly lower energy penalties than those observed in traditional amine-based stripping (Shukla et al., 2019).
- Green solvents: These ionic liquids and deep eutectic solvents offer tunable properties by varying cation-anion combinations, allowing for customized performance in both physical and chemical CO2 absorption processes (Cheng et al., 2023).
- Membrane-assisted absorption: This approach utilizes porous hydrophobic contactors to decouple gas and liquid flow, preventing solvent flooding and enhancing mass transfer kinetics for selective acid gas separation (Keerio et al., 2026).

Indicators

- m^3 water/kg VOC
- kg chemical/kg VOC
- wastewater generation rate

3.3. Thermal and Catalytic Oxidation Technologies

These processes utilize high-temperature combustion or specialized catalysts to mineralize volatile organic compounds into carbon dioxide and water vapor. However, these methods typically impose a substantial energy demand because they require auxiliary fuel to sustain the necessary reaction temperatures. To circumvent these thermal requirements, catalytic oxidation strategies employ transition metal

oxides or noble metal catalysts, which effectively lower the activation energy and enable complete mineralization at significantly reduced operating temperatures (Foorginezhad et al., 2025).

Conventional Technologies

- Thermal oxidation: This method relies on high-temperature incineration, typically between 800°C and 1200°C, to ensure the complete destruction of pollutants through rapid thermal decomposition.
- Regenerative thermal oxidation (RTO): This approach utilizes ceramic heat-exchange media to recapture thermal energy from exhaust streams, achieving high pollutant destruction efficiency while drastically reducing auxiliary fuel consumption (Wilberforce et al., 2018).
- Catalytic oxidation: By employing transition metal catalysts such as manganese or copper oxides, this approach facilitates the mineralization of volatile organic compounds at significantly lower temperatures, thereby optimizing energy efficiency and reducing operational costs compared to non-catalytic incineration (Ekemezie et al., 2024).

Environmental footprint

The assessment of these technologies requires a holistic evaluation of environmental and human health indices to ensure that localized pollutant reduction does not inadvertently increase secondary impacts (Shonnard et al., 2000). Specifically, life-cycle assessments must account for the carbon footprint associated with catalyst manufacturing and the potential for residual emissions during process start-up and shutdown cycles (Chen et al., 2024). Moreover, process control must address the risk of incomplete combustion, which can lead to the formation of harmful by-products such as nitrogen oxides, dioxins, or multi-ring aromatic hydrocarbons (Wysocka et al., 2019).

- Natural gas demand: The energy-intensive nature of traditional thermal oxidation necessitates a continuous supply of auxiliary fuel to maintain combustion temperatures, a requirement that significantly inflates the operational carbon footprint (Abdallah & G., 2021).
- CO_2 emissions: The combustion of supplemental fossil fuels to maintain oxidation temperatures contributes to direct greenhouse gas releases, often negating a portion of the environmental benefits gained from VOC abatement (Berenjian et al., 2012).
- NOx formation: High-temperature thermal oxidation often facilitates the thermal fixation of atmospheric nitrogen, resulting in the generation of nitrogen oxides as undesirable secondary pollutants (Abdallah & G., 2021).
- Catalyst replacement: Frequent deactivation of specialized catalysts necessitates regular replacement cycles, which pose logistical and environmental burdens due to the hazardous nature of spent metal-based materials (Urashima et al., 2000).

Green alternatives

Biofiltration units: These systems leverage microbial degradation to convert organic pollutants into harmless end-products at ambient temperatures, effectively circumventing the reliance on fuel-intensive thermal or noble-metal-based processes (Berenjian et al., 2012).

Photocatalytic oxidation: Utilizing renewable energy, this emerging technology enables the mineralization of volatile organic compounds into innocuous species at room temperature, though careful design is required to mitigate the formation of harmful by-products (Rosset et al., 2021).

- Low-temperature catalysts: These materials facilitate the mineralization of pollutants under mild thermal conditions, thereby minimizing energy consumption and reducing the risk of thermal nitrogen fixation (Wu et al., 2023).
- Electrified oxidation: This approach utilizes electrical energy, such as non-thermal plasma or resistive heating, to drive oxidation reactions directly, effectively decoupling the process from fossil-fuel-based auxiliary heating requirements (Ye et al., 2022).
- Waste heat recovery: This strategy integrates heat exchangers to capture thermal energy from treated exhaust streams, which is subsequently repurposed to preheat incoming process air, thereby enhancing the overall thermodynamic efficiency of the abatement system.
- Renewable-energy-assisted systems: These configurations leverage solar or wind energy to power auxiliary components or direct heating elements, further minimizing the reliance on carbon-intensive grid electricity for pollution control operations (Fayyazbakhsh et al., 2022).

Indicators

- MJ/kg VOC
- kg CO_2-eq/kg VOC

3.4. Photocatalytic and Advanced Oxidation Technologies

These processes leverage high-energy photons or radical species to drive the degradation of recalcitrant pollutants at ambient conditions, effectively bypassing the thermodynamic limitations inherent in conventional incineration (Tran et al., 2023). By utilizing reactive oxygen species generated through light-harvesting semiconductor materials, these systems facilitate the mineralization of pollutants while significantly reducing auxiliary energy inputs (Osman et al., 2023). Furthermore, the integration of solar-driven photocatalysis with bio-electrochemical systems, such as microbial fuel cells, offers a synergistic pathway to enhance pollutant degradation while simultaneously recovering electricity, thereby improving the net environmental balance compared to traditional thermal or chemical oxidation methods (Bashir et al., 2023).

Convnetional Technologies

- TiO_2 photocatalysis: This process utilizes ultraviolet or visible light to activate the semiconductor, generating electron–hole pairs that catalyze the decomposition of persistent pollutants such as acetaldehyde, VOCs, and sulfur oxides into non-toxic gases (Asghar et al., 2024).
- Plasma-assisted oxidation: This method employs non-thermal plasma, such as dielectric barrier discharge, to generate highly reactive species at ambient temperatures, enabling the efficient degradation of aromatics, aldehydes, and various inorganic compounds (Abou Saoud et al., 2018).
- UV oxidation: This technique employs high-intensity ultraviolet radiation, often in combination with chemical oxidants like hydrogen peroxide or ozone, to generate hydroxyl radicals that facilitate the rapid mineralization of biorefractory organic micro-pollutants (Ite & Ite, 2024).

Environmental challenges

Operational constraints include the limited visible light absorption of standard photocatalysts like TiO_2, which necessitates broader spectral activation strategies to achieve practical large-scale deployment.

- Electricity demand: High energy consumption remains a primary driver of the global warming potential for advanced oxidation, particularly when relying on electrical grid supply for ozonizers, ultraviolet lamps, and pumps (Chatzisymeon et al., 2013).
- Catalyst production: The synthesis of sophisticated photocatalysts often involves resource-intensive chemical vapor deposition or solvothermal methods, which frequently utilize toxic solvents and precursors that contribute to an unfavorable environmental life-cycle profile (Jari et al., 2025).
- By-product formation: Incomplete degradation of complex organic precursors during photocatalytic treatment can lead to the persistence of intermediate transformation products, which may exhibit higher toxicity or mobility than the parent compounds (Amaya Santos et al., 2025).

Green alternatives

- Phase-engineered catalysts: Implementing crystal facet control can optimize the surface electronic structure of semiconductors, enhancing charge carrier separation and reaction selectivity to ensure complete mineralization (Uddin et al., 2020).
- Solar-responsive semiconductors: Integrating visible-light-active materials, such as green-synthesized metal oxide nanocomposites, can significantly reduce reliance on artificial UV sources while maintaining high oxidative capacity for pollutant degradation (Osman et al., 2023).
- Solar photocatalysis: By utilizing concentrated sunlight or optimized compound parabolic collectors, this approach minimizes artificial energy depen-

dence and enables the efficient excitation of wide-bandgap photocatalysts for atmospheric remediation (Satyam & Patra, 2025).

- Metal-free catalysts: These materials, such as graphitic carbon nitride or doped biochars, offer sustainable and cost-effective alternatives to conventional metal-based semiconductors, circumventing issues related to catalyst toxicity and environmental persistence (Oluwole et al., 2020).
- Visible-light activation: Developing photocatalysts responsive to the visible spectrum is critical, as natural solar radiation contains only a small fraction of ultraviolet light, necessitating the use of narrow bandgap materials or the chemical modification of conventional metal oxides (Parvulescu et al., 2022).

3.5. Biological VOC Treatment Technologies

These systems utilize microbial metabolic pathways -such as those found in biofilters, biotrickling filters, and bioscrubbers- to oxidize volatile organic compounds into carbon dioxide, water, and biomass under ambient conditions. By leveraging the metabolic diversity of specialized microorganisms, these bio-remediation systems provide a low-impact alternative to energy-intensive thermal oxidation, particularly for streams with low pollutant concentrations (Parvulescu et al., 2022).

Conventional Technologies

- Biofilters: These systems rely on a porous filter bed, typically comprised of organic materials like compost or wood chips, which support a biofilm that absorbs and degrades contaminants as the gas stream passes through the media.
- Bioscrubbers: These units utilize a liquid phase to absorb gaseous pollutants, which are subsequently degraded in a separate bioreactor vessel containing suspended microorganisms, allowing for precise control over pH and nutrient concentrations.
- Biotrickling filters: These systems employ a fixed-film packing material over which a nutrient-rich aqueous phase is continuously recirculated, enabling efficient mass transfer and microbial biodegradation of water-soluble pollutants (Shayegan et al., 2018).

Environmental considerations

Operational stability is often challenged by fluctuations in contaminant loading and environmental factors, which can inhibit microbial activity and compromise degradation efficiency (Silva et al., 2025). Moreover, the generation of metabolic waste products requires appropriate secondary treatment or disposal protocols to prevent secondary environmental impacts, further complicating the design of robust full-scale systems (Schiavon et al., 2017).

- Moisture requirements: Maintaining optimal humidity within the filter bed is essential for sustaining active biofilm growth, as desiccation can rapidly lead

to microbial stress and a significant decline in pollutant removal efficiency (Shihab et al., 2022).

- Nutrient inputs: Sustaining microbial metabolic activity requires a continuous supply of essential macronutrients and micronutrients in the recirculated aqueous phase to prevent nutrient limitation (Delhoménie & Heitz, 2005).
- Biomedia replacement: Over time, the accumulation of inert biomass and degradation products can cause clogging and increased pressure drops, necessitating the periodic replacement of organic packing materials to restore hydrodynamic performance (Wambugu et al., 2017).
- Biological residue disposal: The accumulation of spent filter media and excess sludge necessitates sustainable management strategies, as these materials may contain concentrated pollutants or metabolic by-products that require careful handling to avoid secondary environmental degradation (Lamprea-Pineda et al., 2024).

Green alternatives

- Process intensification: Optimizing the hydrodynamic properties of packing materials and utilizing computational fluid dynamics can improve gas-liquid mass transfer efficiency, thereby reducing the residence time required for degradation (Moreno-Casas et al., 2020). Additionally, transitioning from fixed-film media to suspended-growth configurations can mitigate traditional clogging issues while enhancing the selective use of microorganisms for more robust pollutant abatement (Struk et al., 2023).
- Self-regenerating biofilms: These engineered systems leverage controlled metabolic feedback loops to modulate extracellular polymeric substance production, ensuring sustained pollutant degradation capacity without the need for periodic media replacement or extensive maintenance (Das & Bhattarai, 2025).
- Circular nutrient utilization: Integrating waste-derived substrates and recovered nitrogen from aqueous effluent streams as supplementary nutrient sources can close the loop in biological treatment cycles, thereby minimizing dependence on synthetic chemical inputs (Jagaba et al., 2021).
- Hybrid biological systems: These configurations synergize photocatalytic oxidation and biofiltration to achieve the degradation of recalcitrant compounds that are otherwise resistant to purely biological pathways (Kraakman et al., 2011).

4. ENVIRONMENTAL FOOTPRINT ASSESSMENT OF VOC ABATEMENT TECHNOLOGIES

Evaluating the environmental impact of these abatement strategies requires a comprehensive life-cycle assessment to quantify inputs such as energy consumption,

chemical reagent usage, and the mitigation of secondary pollutant formation (Lamprea-Pineda et al., 2024; Shihab et al., 2022). Furthermore, while biotechnologies are recognized for their low energy consumption and minimal by-product generation compared to traditional thermal processes, their overall sustainability depends heavily on the pollutant's physical-chemical characteristics and specific operational conditions (Pineda et al., 2022). Shifting toward low-emission technologies necessitates a critical re-evaluation of how municipal and industrial waste gas treatment aligns with international climate-relevant emission targets (Dobslaw et al., 2020).

Table 1. *Environmental Sustainability Indicators for the Assessment of VOC Abatement Technologies*

Assessment dimension	Indicator	Unit	Typical literature range	Main basis / interpretation
Water footprint	Water consumption	m^3/kg VOC	0–0.02 (thermal oxidation) / 0.05–1.5 (scrubber, biotrickling)	Cooling, humidification, scrubbing liquid make-up
Carbon footprint	Climate impact	kg CO_2-eq/ kg VOC	0.3–12	Electricity, natural gas, adsorbent production
Chemical consumption	Chemical reagent demand	kg/kg VOC	0–3.0	NaOH, oxidants, nutrient addition
Adsorbent consumption	Adsorbent use	kg/kg VOC	0–0.5 (regenerated AC) / 0.5–5 (single-use)	Activated carbon replacement/ regeneration
Secondary waste generation	Waste produced	kg/kg VOC	0.05–3.0	Spent carbon, sludge, concentrated waste
Disposal burden	Disposal cost	$/kg VOC	0.05–8.0	Hazardous waste and media handling
Energy intensity	Energy demand	MJ/kg VOC	1–80	Fans, heating, regeneration energy

5. LIFE CYCLE THINKING AND CIRCULAR APPROACHES FOR VOC CONTROL

Integrating microbial bioremediation into broader circular economy models facilitates the transformation of pollution control from a liability into a resource-recovery mechanism, such as the generation of renewable energy from waste streams (Thirumalaivasan et al., 2024; Ummah, 2019). Innovative algae-bacteria consortia have demonstrated significant potential in this regard, facilitating the efficient conversion of captured volatile organic compounds into algal biomass while simultaneously serving as robust emission control agents. These synergistic consortia utilize carbon dioxide for organic compound production, further enhancing the bioremediation of nutrient-rich waste streams while yielding secondary metabolites of industrial value (Sharma et al., 2022).

5.1. Environmental assessment methods:

- Life Cycle Assessment (LCA): A standardized methodology that quantifies cradle-to-grave impacts, enabling the benchmarking of novel algae-bacteria consortia against traditional thermal oxidation systems (Cai et al., 2024).
- Water Footprint Assessment: A critical metric for quantifying the direct and indirect consumption of water resources throughout the pollutant removal process, accounting for both upstream production and operational losses in closed-loop configurations (Egedy et al., 2020).
- Material Flow Analysis (MFA): A methodology to map the movement of hazardous substances and secondary waste streams through the treatment facility, identifying recovery pathways that reduce the final disposal burden (Oliva et al., 2018).
- Techno-Economic Assessment (TEA): This framework evaluates the economic viability of abatement technologies by analyzing capital expenditures, operational costs, and the potential value generated from recovered by-products (Zhao et al., 2025).
- Multi-Criteria Decision Analysis (MCDA): This framework systematically evaluates conflicting sustainability objectives by weighing technical, environmental, and social indicators—such as resource depletion, waste generation, and regional socio-economic impacts—to optimize decision-making within complex biorefinery and pollution control contexts (Parajuli et al., 2015).

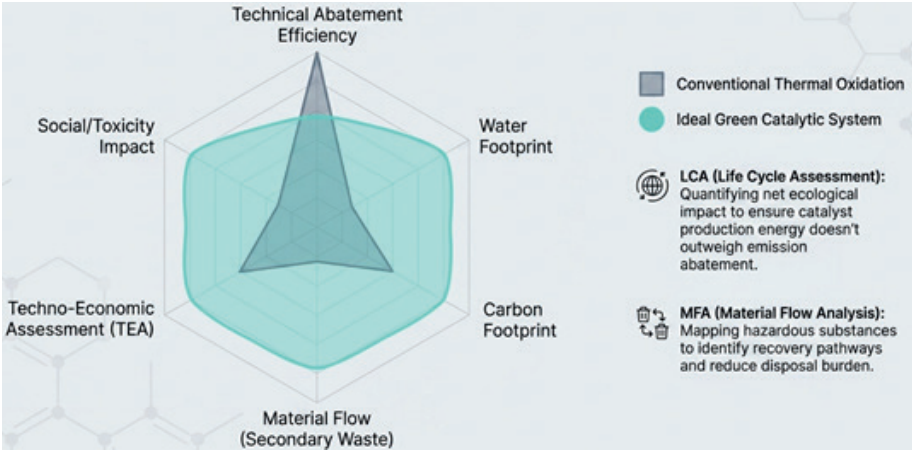

Figure 2. *Multidimensional Life-Cycle Assessment Framework for Sustainable VOC Abatement Technologies (Illustrated using NotebookLm)*

5.2. Green Chemistry Principles for Sustainable Air Pollution Control

Applying these principles shifts the paradigm toward inherently safer molecular design, prioritizing the substitution of hazardous solvent-based VOC scrubbers with renewable, bio-based alternatives that minimize toxicity (Xiong et al., 2019).

Furthermore, the utilization of genetically engineered algal and microbial strains can enhance resistance to the inherent toxicity of industrial flue gases while optimizing the capture of CO2 and other hazardous pollutants (Das & Bhattarai, 2025). By optimizing these biological platforms through AI-driven systems biology, researchers can further diminish land and water requirements while maximizing the overall efficiency of the carbon-neutral bioeconomy (Nneoma et al., 2025).

Prevention of waste, Atom economy, Safer chemicals, Energy efficiency, Renewable feedstocks, Process intensification, and Real-time monitoring principles have been used efficiently to overcome long-standing regulatory, technological, and institutional barriers to implementation (Shah et al., 2023).

These principles collectively foster a strategic transition from end-of-pipe mitigation to the inherent reduction of pollution at the source, effectively integrating regulatory compliance with corporate sustainability objectives (Shah et al., 2023). This systemic approach aligns industrial air quality management with broader circular economy frameworks, ensuring that atmospheric sustainability is achieved through resource-efficient, low-impact technological innovation (Gargalo et al., 2024; More, 2026). Furthermore, the adoption of green chemistry metrics such as the E-factor and process mass intensity provides the quantitative rigor necessary to validate the transition toward these environmentally benign synthetic and operational pathways (Chauth et al., 2026; More, 2026).

5.3. Future Perspectives: Toward Net-Positive VOC Abatement Systems

The transition toward these systems necessitates the development of self-regenerative abatement platforms that function as carbon sinks while simultaneously producing high-value biochemicals from captured pollutants (Sah et al., 2025; Sheldon, 2023). Such closed-loop architectures leverage process intensification and biocatalysis to transform hazardous atmospheric emissions into renewable feedstocks, effectively decoupling industrial growth from environmental degradation (Ch et al., 2025). Furthermore, the deployment of advanced catalysis and AI-optimized operational protocols can facilitate the scalable adoption of these net-positive models, enabling industries to meet stringent 2030 sustainability targets while fostering collaborative innovation between public and private sectors (Lozano-Onrubia et al., 2025). Additionally, the integration of visible-light-responsive catalysts and self-regenerating supports, such as HZSM-5, will be essential to extend operational durability and enhance the scalability of these advanced abatement Technologies (Talaie et al., 2025).

Future directions in sustainable VOC abatement include the development of carbon-negative treatment systems, water-neutral air pollution control technologies, reusable adsorbents, AI-assisted process optimization, circular economy integration, and the implementation of digital twins and predictive control frameworks. These advanced digital approaches, supported by in situ characterization techniques such as proton transfer reaction–mass spectrometry (PTR-MS), enable precise correlations between catalyst surface chemistry and degradation mechanisms, thereby improving process efficiency and supporting data-driven optimization of VOC removal systems (He et al., 2019).

CONCLUSION

Future air pollution control technologies should no longer be evaluated solely on the basis of volatile organic compound (VOC) removal efficiency. Instead, they should be assessed through integrated environmental performance criteria encompassing water consumption, adsorbent requirements, chemical dependency, secondary waste generation, disposal impacts, and overall life-cycle sustainability. Achieving this objective requires the adoption of a holistic approach to the design of composite catalytic materials that incorporate multiple active sites capable of synergistically removing complex mixtures of pollutants.

This transformation in catalyst engineering must be supported by the development of environmentally friendly and scalable synthesis strategies that minimize reliance on organic reagents and strong acidic or basic precursors. Furthermore, comprehensive life-cycle assessments of these materials should incorporate energy consumption and total greenhouse gas emissions to ensure that the environmental footprint associated with catalyst production does not outweigh the pollution mitigation benefits achieved during their application.

In addition, the successful translation of laboratory-scale innovations into robust and commercially viable industrial solutions necessitates the development of advanced hybrid systems and the execution of detailed techno-economic feasibility studies. Future research should also prioritize the design of durable and long-lasting catalysts capable of maintaining high performance even in complex industrial gas streams containing trace contaminants such as sulfur compounds and ammonia.

In conclusion, sustainable air pollution control requires moving beyond the sole pursuit of high removal efficiencies and embracing integrated approaches that simultaneously consider environmental, economic, and life-cycle-based criteria. Next-generation catalytic systems developed within this framework will contribute significantly to the effective reduction of industrial emissions while advancing the objectives of green chemistry and sustainable development.

SONUÇ

Geleceğin hava kirliliği kontrol teknolojileri artık yalnızca uçucu organik bileşiklerin (VOC) giderim verimliliği temelinde değil; su tüketimi, adsorban ihtiyacı, kimyasal bağımlılık, ikincil atık oluşumu, bertaraf etkileri ve yaşam döngüsü sürdürülebilirliğini kapsayan bütünleşik çevresel performans ölçütleri çerçevesinde değerlendirilmelidir. Bu hedefe ulaşabilmek için, karmaşık kirletici karışımlarının sinerjik biçimde giderilmesini sağlayacak çoklu aktif merkezleri bünyesinde barındıran kompozit katalitik malzemelerin tasarımına yönelik bütüncül bir yaklaşım benimsenmesi gerekmektedir.

Katalizör mühendisliğindeki bu dönüşümün, organik reaktiflere ve güçlü asidik veya bazik öncüllere olan bağımlılığı en aza indiren, çevre dostu ve ölçeklenebilir sentez yöntemlerinin geliştirilmesiyle desteklenmesi zorunludur. Ayrıca, bu malzemelerin yaşam döngüsü değerlendirmelerinin; enerji tüketimi ve toplam sera gazı emisyonları da dikkate alınarak yapılması, katalizör üretiminin çevresel ayak izinin, sonrasında sağlanan kirlilik azaltım faydalarını ortadan kaldırmamasını güvence altına almak açısından kritik öneme sahiptir.

Bunun yanı sıra, laboratuvar ölçeğindeki yeniliklerin sağlam ve ticari açıdan uygulanabilir endüstriyel çözümlere dönüştürülebilmesi için kapsamlı hibrit sistemlerin geliştirilmesi ve ayrıntılı teknik-ekonomik fizibilite çalışmalarının yürütülmesi gerekmektedir. Gelecekteki araştırmalar ayrıca, kükürtlü bileşikler ve amonyak gibi iz miktardaki kirleticileri içeren karmaşık endüstriyel gaz akımlarında dahi yüksek performansını koruyabilen, uzun ömürlü ve dayanıklı katalizörlerin tasarımına öncelik vermelidir.

Sonuç olarak, sürdürülebilir hava kirliliği kontrolü; yüksek giderim verimliliğinin ötesine geçerek çevresel, ekonomik ve yaşam döngüsü temelli ölçütlerin birlikte değerlendirildiği bütünleşik yaklaşımların benimsenmesini gerektirmektedir. Bu doğrultuda geliştirilecek yeni nesil katalitik sistemler, hem endüstriyel emisyonların etkin biçimde azaltılmasına hem de yeşil kimya ve sürdürülebilir kalkınma hedeflerinin gerçekleştirilmesine önemli katkılar sağlayacaktır.

REFERENCES

1. Abdallah, & G. (2021). *Comprehensive approach of post-plasma catalytic process for trichloroethylene abatement in air on Cerium doped Birnessite-like MnO2 through the study of O3 and HCHO catalytic elimination*.
2. Abdrabou, H. K., AlNashef, I., Zahra, M. A., Mokraoui, S., Ali, E., & Hadj-Kali, M. K. (2023). Experimental investigation of novel ternary amine-based deep eutectic solvents for CO2 capture. *PLoS ONE*, *18*(6 June), 1–19. https://doi.org/10.1371/journal.pone.0286960
3. Abdullatif, Y., Sodiq, A., Mir, N., Bicer, Y., Al-Ansari, T., El-Naas, M. H., & Amhamed, A. I. (2023). Emerging trends in direct air capture of CO2: a review of technology options targeting net-zero emissions. *RSC Advances*, *13*(9), 5687–5722. https://doi.org/10.1039/d2ra07940b
4. Abou Saoud, W., Assadi, A. A., Guiza, M., Bouzaza, A., Aboussaoud, W., Soutrel, I., Ouederni, A., Wolbert, D., & Rtimi, S. (2018). Abatement of ammonia and butyraldehyde under non-thermal plasma and photocatalysis: Oxidation processes for the removal of mixture pollutants at pilot scale. *Chemical Engineering Journal*, *344*(March), 165–172. https://doi.org/10.1016/j.cej.2018.03.068
5. Afolabi, M., Chukwuemeka, O., Igunma, & T. (2024). *Sustainable catalysis: A holistic framework for lifecycle analysis and circular economy integration in catalyst design*. https://doi.org/10.51594/estj.v5i12.1754
6. Ahmed, S. F., Mofijur, M., Tarannum, K., Chowdhury, A. T., Rafa, N., Nuzhat, S., Kumar, P. S., Vo, D. V. N., Lichtfouse, E., & Mahlia, T. M. I. (2021). Biogas upgrading, economy and utilization: a review. *Environmental Chemistry Letters*, *19*(6), 4137–4164. https://doi.org/10.1007/s10311-021-01292-x
7. Amaya Santos, G., Ali, A. Z., & Lettieri, P. (2025). Sustainable advanced wastewater treatment via photoelectrocatalytic oxidation: insights from life cycle assessment. *Npj Clean Water*, *8*(1). https://doi.org/10.1038/s41545-025-00522-x
8. Aminuddin, M. S., Bustam, M. A., & Johari, K. (2024). Latest technological advances and insights into capture and removal of hydrogen sulfide: a critical review. *RSC Sustainability*, *2*(4), 757–803. https://doi.org/10.1039/d3su00484h
9. Asghar, N., Hussain, A., Nguyen, D. A., Ali, S., Hussain, I., Junejo, A., & Ali, A. (2024). Advancement in nanomaterials for environmental pollutants remediation: a systematic review on bibliometrics analysis, material types, synthesis pathways, and related mechanisms. *Journal of Nanobiotechnology, 22*(1). https://doi.org/10.1186/s12951-023-02151-3
10. Bashir, Y., Raj, R., Ghangrekar, M. M., Nema, A. K., & Das, S. (2023). Critical assessment of advanced oxidation processes and bio-electrochemical integrated systems for removing emerging contaminants from wastewater. *RSC Sustainability*, *1*(8), 1912–1931. https://doi.org/10.1039/d3su00112a
11. Baskaran, D., Dhamodharan, D., Behera, U., Byun, & H.-S. (2024). *A comprehensive review and perspective research in technology integration for the treatment of gaseous volatile organic compounds*. https://doi.org/10.1016/j.envres.2024.118472
12. Beach, E. S., Cui, Z., & Anastas, P. T. (2009). Green Chemistry: A design framework for sustainability. *Energy and Environmental Science*, *2*(10), 1038–1049. https://doi.org/10.1039/b904997p
13. Berenjian, A., Chan, N.-C., Malmiri, & H. (2012). *VOLATILE ORGANIC COMPOUNDS REMOVAL METHODS: A REVIEW*. https://doi.org/10.3844/ajbbsp.2012.220.229

14. Bhat, R., Jain, A., Rakesh, C., Khan, I., Pahwa, S., Abood, & A. (2024). *Improvement of the Quality of Air and the Implementation of Sustainable Technologies in Green Technological Innovation*. https://doi.org/10.1051/e3sconf/202450503011

15. Bui, M., Adjiman, C. S., Bardow, A., Anthony, E. J., Boston, A., Brown, S., Fennell, P. S., Fuss, S., Galindo, A., Hackett, L. A., Hallett, J. P., Herzog, H. J., Jackson, G., Kemper, J., Krevor, S., Maitland, G. C., Matuszewski, M., Metcalfe, I. S., Petit, C., … Mac Dowell, N. (2018). Carbon capture and storage (CCS): The way forward. *Energy and Environmental Science*, *11*(5), 1062–1176. https://doi.org/10.1039/c7ee02342a

16. Cai, Z., Karunakaran, E., & Pandhal, J. (2024). Bottom-up construction and screening of algae-bacteria consortia for pollutant biodegradation. *Frontiers in Microbiology*, *15*(February), 1–16. https://doi.org/10.3389/fmicb.2024.1349016

17. Ch, H., Kamala, & G. (2025). *Molecular Design Principles and Applications of Green Chemistry*. https://doi.org/10.69613/mxabpe83

18. Chatzisymeon, E., Foteinis, S., Mantzavinos, D., & Tsoutsos, T. (2013). Life cycle assessment of advanced oxidation processes for olive mill wastewater treatment. *Journal of Cleaner Production*, *54*, 229–234. https://doi.org/10.1016/j.jclepro.2013.05.013

19. Chauth, V., Shaik, M., Jadhav, A., & Echale, K. (2026). *Green Chemistry : A Sustainable Approach*. *4*(1), 719–731. https://doi.org/10.5281/zenodo.18186449

20. Chen, G. F., Lai, C. H., & Chen, W. H. (2020). Principal component analysis and mapping to characterize the emission of volatile organic compounds in a typical petrochemical industrial park. *Aerosol and Air Quality Research*, *20*(3), 465–476. https://doi.org/10.4209/aaqr.2019.07.0365

21. Chen, Y., Xie, & G. (2024). *Novel technology for industrial VOCs exhaust treatment under dual-carbon target based on multivariate statistical analysis*. https://doi.org/10.2478/amns-2024-0538

22. Cheng, J., Xie, K., Guo, P., Qin, H., Deng, L., Qi, Z., & Song, Z. (2023). Capturing CO2 by ionic liquids and deep eutectic solvents: A comparative study based on multi-level absorbent screening. *Chemical Engineering Science*, *281*(May), 119133. https://doi.org/10.1016/j.ces.2023.119133

23. Cramer, A. J., & Cole, J. M. (2017). Removal or storage of environmental pollutants and alternative fuel sources with inorganic adsorbents: Via host-guest encapsulation. *Journal of Materials Chemistry A*, *5*(22), 10746–10771. https://doi.org/10.1039/c7ta02401k

24. Das, B. D., & Bhattarai, A. (2025). The versatility of algae in addressing the global sustainability challenges. *Frontiers in Bioengineering and Biotechnology*, *13*(October), 1–13. https://doi.org/10.3389/fbioe.2025.1621817

25. Delhoménie, M. C., & Heitz, M. (2005). Biofiltration of air: A review. *Critical Reviews in Biotechnology*, *25*(1–2), 53–72. https://doi.org/10.1080/07388550590935814

26. Deng, M., Sun, J., Chakraborty, J., Zhou, M., & Voort: (2023). *From Design to Applications: A Comprehensive Review on Porous Frameworks for Photocatalytic Volatile Organic Compounds (VOCs) Removal*. https://doi.org/10.1002/cctc.202300783

27. Dobslaw, D., Ortlinghaus, & O. (2020). *Biological Waste Air and Waste Gas Treatment: Overview, Challenges, Operational Efficiency, and Current Trends*. https://doi.org/10.3390/su12208577

28. Egedy, A., Gyurik, L., Ulbert, Z., & Rado, A. (2020). CFD modeling and environmental assessment of a VOC removal silo. *International Journal of Environmental Science and Technology*, *18*(1), 141–150. https://doi.org/10.1007/s13762-020-02833-7

29. Ekemezie, I., Digitemie, & W. (2024). *CARBON CAPTURE AND UTILIZATION (CCU): A REVIEW OF EMERGING APPLICATIONS AND CHALLENGES*. https://doi.org/10.51594/estj.v5i3.949

30. El Khawaja, R., Veerapandian, S. K. P., Bitar, R., De Geyter, N., Morent, R., Heymans, N., De Weireld, G., Barakat, T., Ding, Y., Abdallah, G., Sonar, S., Löfberg, A., Giraudon, J. M., Poupin, C., Cousin, R., Cazier, F., Dewaele, D., Genevray, P., Landkocz, Y., … Siffert, S. (2022). Boosting VOCs elimination by coupling different techniques. *Chemical Synthesis*, *2*(2). https://doi.org/10.20517/cs.2022.10

31. Erans, M., Sanz-Pérez, E. S., Hanak, D. P., Clulow, Z., Reiner, D. M., & Mutch, G. A. (2022). Direct air capture: process technology, techno-economic and socio-political challenges. *Energy and Environmental Science*, *15*(4), 1360–1405. https://doi.org/10.1039/d1ee03523a

32. Fantozzi, F., & Buratti, C. (2011). Anaerobic digestion of mechanically treated OFMSW: Experimental data on biogas/methane production and residues characterization. *Bioresource Technology*, *102*(19), 8885–8892. https://doi.org/10.1016/j.biortech.2011.06.077

33. Fayyazbakhsh, A., Bell, M., Zhu, X., Mei, X., Koutný, M., Hajinajaf, N., Zhang, & Y. (2022). *Engine emissions with air pollutants and greenhouse gases and their control technologies*. https://doi.org/10.1016/j.jclepro.2022.134260

34. Fisher, O. J., Xing, L., Tian, X., Tai, X. Y., & Xuan, J. (2023). Responsive CO2 capture: predictive multi-objective optimisation for managing intermittent flue gas and renewable energy supply. *Reaction Chemistry and Engineering*, *9*(2), 235–250. https://doi.org/10.1039/d3re00544e

35. Foorginezhad, S., Ji, & X. (2025). *Immobilized ionic liquids/deep eutectic solvents in carbon capture: current progress and future potential*. https://doi.org/10.1007/s10098-025-03276-9

36. Galloni, M., Campisi, S., Marchetti, S., Gervasini, & A. (2020). *Environmental Reactions of Air-Quality Protection on Eco-Friendly Iron-Based Catalysts*. https://doi.org/10.3390/catal10121415

37. Gao, M., Mao, M., Shi, J., Liu, Y., Chen, Q., Li, & J. (2022). *A review of the treatment techniques of VOC*. https://doi.org/10.2478/amns.2021.2.00131

38. Gargalo, C. L., Yu, H., Vollmer, N., Arabkoohsar, A., Gernaey, K. V., & Sin, G. (2024). A process systems engineering view of environmental impact assessment in renewable and sustainable energy production: Status and perspectives. *Computers and Chemical Engineering*, *180*(January 2022), 108504. https://doi.org/10.1016/j.compchemeng.2023.108504

39. He, C., Cheng, J., Zhang, X., Douthwaite, M., Pattisson, S., Hao, & Z. (2019). *Recent Advances in the Catalytic Oxidation of Volatile Organic Compounds: A Review Based on Pollutant Sorts and Sources*. https://doi.org/10.1021/acs.chemrev.8b00408

40. He, F., Jeon, W., & Choi, W. (2021). Photocatalytic air purification mimicking the self-cleaning process of the atmosphere. *Nature Communications*, *12*(1), 10–13. https://doi.org/10.1038/s41467-021-22839-0

41. Hoàng, L., Quynh, H., Nghi, M., Phương, N., Duong, N., Long, & N. (2025). *Green Synthesis of Chitosan-Assisted ZnO Nanoparticles and Their Photocatalytic Application in ZnO/TiO₂ Composites for Isopropanol Degradation*. https://doi.org/10.9767/bcrec.20431

42. Hosseini, S., Moghaddas, H., Soltani, S., Kheawhom, & S. (2019). *Technological Applications of Honeycomb Monoliths in Environmental Processes: A review*. https://doi.org/10.1016/j.psep.2019.11.020

43. Iroegbu, A. O. C., Teffo, M. L., Sadiku, E. R., Meijboom, R., & Hlangothi, S. P. (2025). Advancing wastewater treatment with green and scalable metal–organic frameworks: from synthetic strategies to real-world deployment. *Npj Clean Water*, *8*(1). https://doi.org/10.1038/s41545-025-00514-x

44. Ite, A. E., & Ite, I. A. (2024). Organic Micropollutants in the Air: Origin and Occurence, Environmental and Health Effects, and Mitigation Strategies. *Environment & Ecosystem Science*, *8*(1), 36–52. https://doi.org/10.26480/ees.01.2024.36.52

45. Jagaba, A. H., Kutty, S. R. M., Noor, A., Birniwa, A. H., Affam, A. C., Lawal, I. M., Kankia, M. U., & Kilaco, A. U. (2021). A systematic literature review of biocarriers: Central elements for biofilm formation, organic and nutrients removal in sequencing batch biofilm reactor. *Journal of Water Process Engineering*, *42*(March), 102178. https://doi.org/10.1016/j.jwpe.2021.102178

46. Jari, Y., Najid, N., Necibi, M. C., Gourich, B., Vial, C., Elhalil, A., Kaur, P., Mohdeb, I., Park, Y., Hwang, Y., Garcia, A. R., Roche, N., & El Midaoui, A. (2025). A comprehensive review on TiO2-based heterogeneous photocatalytic technologies for emerging pollutants removal from water and wastewater: From engineering aspects to modeling approaches. *Journal of Environmental Management*, *373*(July 2024). https://doi.org/10.1016/j.jenvman.2024.123703

47. Keerio, H. A., Panhwar, S., Alnadish, A. M., Chandio, T. A., Memon, T. A., Kumar, S., Shah, S. A., Ahmed, F., & Muqeet, M. (2026). Molecular solutions to carbon pollution: innovations, mechanisms, and challenges in solvent-based carbon capture. *Water Science and Technology : A Journal of the International Association on Water Pollution Research*, *93*(6), 849–874. https://doi.org/10.2166/wst.2026.238

48. Ketabchi, M. R., Babamohammadi, S., Davies, W. G., Gorbounov, M., & Masoudi Soltani, S. (2023). Latest advances and challenges in carbon capture using bio-based sorbents: A state-of-the-art review. *Carbon Capture Science and Technology*, *6*(November 2022), 100087. https://doi.org/10.1016/j.ccst.2022.100087

49. Kraakman, N. J. R., Rocha-Rios, J., & Van Loosdrecht, M. C. M. (2011). Review of mass transfer aspects for biological gas treatment. *Applied Microbiology and Biotechnology*, *91*(4), 873–886. https://doi.org/10.1007/s00253-011-3365-5

50. Lamprea-Pineda, P., Demeestere, K., González-Cortés, J., Boon, N., Devlieghere, F., Langenhove, H., Walgraeve, & C. (2024). *Addition of (bio)surfactants in the biofiltration of hydrophobic volatile organic compounds in air*. https://doi.org/10.1016/j.jenvman.2024.120132

51. Lei, S., Wang, L., Xu, L., Wang, B., Sun, & L. (2024). *Experimental and theoretical studies on effective synergistic low-temperature removal of NO and typical volatile organic compounds (VOCs) from flue gas based on Cu@VWTi catalyst*. https://doi.org/10.1016/j.jclepro.2024.142567

52. Li, J., Gao, Z. R., Lin, Q.-F., Liu, C., Gao, F., Lin, C., Zhang, S., Deng, H., Mayoral, A., Fan, W., Luo, S., Chen, X., He, H., Camblor, M. A., Chen, F.-J., & Yu, J. (2023). A 3D extra-large-pore zeolite enabled by 1D-to-3D topotactic condensation of a chain silicate. *Science*, *379*(6629), 283–287. https://doi.org/10.1126/science.ade1771

53. Li, M., & Wang, R. (2025). Combined Catalytic Conversion of NOx and VOCs: Present Status and Prospects. *Materials*, *18*(1), 1–20. https://doi.org/10.3390/ma18010039

54. Li, R., Chong, S., Altaf, N., Gao, Y., Louis, B., & Wang, Q. (2019). Synthesis of ZSM-5/Siliceous Zeolite Composites for Improvement of Hydrophobic Adsorption of Volatile Organic Compounds. *Frontiers in Chemistry*, *7*(July), 1–10. https://doi.org/10.3389/fchem.2019.00505

55. Li, Y. (2024). Advanced Technologies for Volatile Organic Compound (VOC) Emission Treatment: An Overview. *Journal of Electronic Research and Application*, *8*(2), 1–7. https://doi.org/10.26689/jera.v8i2.6051

56. Liu, J., Burciaga, R., Tang, S., Ding, S., Ran, H., Zhao, W., Zhu, & W. (2024). *Heterogeneous catalysis for the environment*. https://doi.org/10.59717/j.xinn-mater.2024.100090

57. Liu, J., Wang, Y., Dai, Z., Jia, C., Yang, L., Liu, J., Jiang, & W. (2023). *Recent advances in Zeolite-Based catalysts for volatile organic compounds decontamination by thermal catalytic oxidation*. https://doi.org/10.1016/j.seppur.2023.125339

58. Liu, J., Wu, Y., Zheng, C., Tian, M., Jiang, Z., Albilali, R., & He, C. (2025). Recent Advances in Engineering Functional Catalysts toward Multicomponent VOC Purification under Reality. *ACS ES&T Engineering*, *5*(6), 1316–1337. https://doi.org/10.1021/acsestengg.5c00159

59. Lozano-Onrubia, G., Castillo-Pazos, D. J., Grieger, K., Wheeler, M., Grignon, E., Pazoki, F., Gallenstein, R., Castilla-Acevedo, S. F., Fan, F., Musa, E. N., Beena, N. C., Ahuja, H., Popoola, O., Battaglia, A. M., Kaur, G., Alahakoon, I., Chipangura, Y. E., Aransiola, E., Moumbogno Tchodimo, F. C., … Moores, A. (2025). Industry's Path to a Greener Future: A Perspective on Current Sustainable Practices and Areas of Opportunity. *ACS Sustainable Chemistry & Engineering*, *13*(19), 6849–6874. https://doi.org/10.1021/acssuschemeng.5c00741

60. Ma, X., Yang, L., Wu, & H. (2021). *Removal of volatile organic compounds from the coal-fired flue gas by adsorption on activated carbon*. https://doi.org/10.1016/j.jclepro.2021.126925

61. Mikulčić, H., Skov, I. R., Dominković, D. F., Wan Alwi, S. R., Manan, Z. A., Tan, R., Duić, N., Hidayah Mohamad, S. N., & Wang, X. (2019). Flexible Carbon Capture and Utilization technologies in future energy systems and the utilization pathways of captured CO2. *Renewable and Sustainable Energy Reviews*, *114*(July). https://doi.org/10.1016/j.rser.2019.109338

62. More, D. (2026). *PHARMACEUTICAL SCIENCES PRINCIPLES OF GREEN CHEMISTRY AND THEIR INDUSTRIAL AND ENVIRONMENTAL APPLICATIONS*. *13*(02), 94–104.

63. Moreno-Casas, P. A., Scott, F., Delpiano, J., Abell, J. A., Caicedo, F., Muñoz, R., & Vergara-Fernández, A. (2020). Mechanistic Description of Convective Gas–Liquid Mass Transfer in Biotrickling Filters Using CFD Modeling. *Environmental Science & Technology*, *54*(1), 419–426. https://doi.org/10.1021/acs.est.9b02662

64. Nguyen, L. N., Kumar, J., Vu, M. T., Mohammed, J. A. H., Pathak, N., Commault, A. S., Sutherland, D., Zdarta, J., Tyagi, V. K., & Nghiem, L. D. (2021). Biomethane production from anaerobic co-digestion at wastewater treatment plants: A critical review on development and innovations in biogas upgrading techniques. *Science of the Total Environment*, *765*, 142753. https://doi.org/10.1016/j.scitotenv.2020.142753

65. Nneoma, U. C., Chukwudi, O. F., Nnenna, U. J., & Paul-Chima, U. O. (2025). Hybrid biofactories: integrating microalgae and engineered microbiomes for enhanced biofuel production in circular carbon systems. *Frontiers in Energy Research*, *13*(September), 1–16. https://doi.org/10.3389/fenrg.2025.1654079

66. Oliva, G., Comia, J., Senatore, V., Zarra, T., Ballestreros, F., Belgiorno, V., Naddeo, & V. (2022). *Degradation of gaseous volatile organic compounds (VOCs) by a novel UV-ozone technology*. https://doi.org/10.1038/s41598-022-14191-0

67. Oliva, G., Zarra, T., Naddeo, V., Munoz, R., Lebrero, R., Ángeles, R., & Belgiorno, V. (2018). Comparative analysis of AOPs and biological processes for the control of VOCs industrial emissions. *Chemical Engineering Transactions*, *68*, 451–456. https://doi.org/10.3303/CET1868076

68. Oluwole, A. O., Omotola, E. O., & Olatunji, O. S. (2020). Pharmaceuticals and personal care products in water and wastewater: a review of treatment processes and use of photocatalyst immobilized on functionalized carbon in AOP degradation. *BMC Chemistry*, *14*(1), 1–29. https://doi.org/10.1186/s13065-020-00714-1

69. Osman, A. I., El-Monaem, E. M. A., Elgarahy, A. M., Aniagor, C. O., Hosny, M., Farghali, M., Rashad, E., Ejimofor, M. I., López-Maldonado, E. A., Ihara, I., Yap, P. S., Rooney, D. W., & Eltaweil, A. S. (2023). Methods to prepare biosorbents and magnetic sorbents for water treatment: a review. In *Environmental Chemistry Letters* (Vol. 21, Issue 4). Springer International Publishing. https://doi.org/10.1007/s10311-023-01603-4

70. Osman, A. I., Hefny, M., Abdel Maksoud, M. I. A., Elgarahy, A. M., & Rooney, D. W. (2021). Recent advances in carbon capture storage and utilisation technologies: a review. In *Environmental Chemistry Letters* (Vol. 19, Issue 2). Springer International Publishing. https://doi.org/10.1007/s10311-020-01133-3

71. Pan, H., Jian, Y., Chen, C., He, C., Hao, Z., Shen, Z., Liu, & H. (2017). *Sphere-Shaped Mn3O4 Catalyst with Remarkable Low-Temperature Activity for Methyl–Ethyl–Ketone Combustion*. https://doi.org/10.1021/acs.est.7b00136

72. Parajuli, R., Dalgaard, T., Jørgensen, U., Adamsen, A. P. S., Knudsen, M. T., Birkved, M., Gylling, M., & Schjørring, J. K. (2015). Biorefining in the prevailing energy and materials crisis: A review of sustainable pathways for biorefinery value chains and sustainability assessment methodologies. *Renewable and Sustainable Energy Reviews*, *43*, 244–263. https://doi.org/10.1016/j.rser.2014.11.041

73. Pardakhti, M., Jafari, T., Tobin, Z., Dutta, B., Moharreri, E., Shemshaki, N. S., Suib, S., & Srivastava, R. (2019). Trends in Solid Adsorbent Materials Development for CO2 Capture. *ACS Applied Materials & Interfaces*, *11*(38), 34533–34559. https://doi.org/10.1021/acsami.9b08487

74. Parmar, G., Rao, & N. (2008). *Emerging Control Technologies for Volatile Organic Compounds*. https://doi.org/10.1080/10643380701413658

75. Parvulescu, V. I., Epron, F., Garcia, H., & Granger, P. (2022). Recent Progress and Prospects in Catalytic Water Treatment. *Chemical Reviews*, *122*(3), 2981–3121. https://doi.org/10.1021/acs.chemrev.1c00527

76. Pineda, P., Demeestere, K., Sabbe, M., Bruneel, J., Langenhove, H., Walgraeve, & C. (2022). *Effect of (bio)surfactant type and concentration on the gas-liquid equilibrium partitioning of hydrophobic volatile organic compounds*. https://doi.org/10.1016/j.jhazmat.2022.130320

77. Plaza, M. G., González, A. S., Pevida, C., Pis, J. J., & Rubiera, F. (2012). Valorisation of spent coffee grounds as CO2 adsorbents for postcombustion capture applications. *Applied Energy*, *99*, 272–279. https://doi.org/10.1016/j.apenergy.2012.05.028

78. Pudi, A., Rezaei, M., Signorini, V., Andersson, M. P., Baschetti, M. G., & Mansouri, S. S. (2022). Hydrogen sulfide capture and removal technologies: A comprehensive review of recent developments and emerging trends. *Separation and Purification Technology*, *298*(June), 121448. https://doi.org/10.1016/j.seppur.2022.121448

79. Razali, M., Kim, J. F., Attfield, M., Budd, P. M., Drioli, E., Lee, Y. M., & Szekely, G. (2015). Sustainable wastewater treatment and recycling in membrane manufacturing. *Green Chemistry*, *17*(12), 5196–5205. https://doi.org/10.1039/c5gc01937k

80. Rosset, A., Bartolomei, V., Laisney, J., Shandilya, N., Voisin, H., Morin, J., Artous, & S. (2021). *Towards the development of safer by design TiO2-based photocatalytic paint: impacts and performances*. https://doi.org/10.1039/d0en01232g

81. Sah, M. K., Ettarhouni, Z. O., Pathak, R., Gawad, J., Bonde, C., Arya, S. P., & Bhattarai, A. (2025). Green Chemistry: Strategies and Sustainable Approaches for Bridging UN SDGS. *ChemistrySelect*, *10*(25), 1–37. https://doi.org/10.1002/slct.202500847

82. Saidi, M., Ho, P. H., Yadav, P., Salles, F., Charnay, C., Girard, L., Boukli-hacene, L., & Trens, P. (2021). Carbon Dioxide and Ethanol Vapour . A Comparative Study. *Molecules*, *26*(24), 7620.

83. Santos, M. P. S., & Hanak, D. P. (2022). Carbon capture for decarbonisation of energy-intensive industries: a comparative review of techno-economic feasibility of solid looping cycles. *Frontiers of Chemical Science and Engineering*, *16*(9), 1291–1317. https://doi.org/10.1007/s11705-022-2151-5

84. Satyam, S., & Patra, S. (2025). The Evolving Landscape of Advanced Oxidation Processes in Wastewater Treatment: Challenges and Recent Innovations. *Processes*, *13*(4). https://doi.org/10.3390/pr13040987

85. Schiavon, M., Schiorlin, M., Torretta, V., Brandenburg, R., & Ragazzi, M. (2017). Non-thermal plasma assisting the biofiltration of volatile organic compounds. *Journal of Cleaner Production*, *148*, 498–508. https://doi.org/10.1016/j.jclepro.2017.02.008

86. Schick, L., Sanchis, R., González-Alfaro, V., Agouram, S., López, J. M., Torrente-Murciano, L., García, T., & Solsona, B. (2019). Size-activity relationship of iridium particles supported on silica for the total oxidation of volatile organic compounds (VOCs). *Chemical Engineering Journal*, *366*(February), 100–111. https://doi.org/10.1016/j.cej.2019.02.087

87. Seoane, B., Coronas, J., Gascon, I., Benavides, M. E., Karvan, O., Caro, J., Kapteijn, F., & Gascon, J. (2015). Metal-organic framework based mixed matrix membranes: A solution for highly efficient CO2 capture? *Chemical Society Reviews*, *44*(8), 2421–2454. https://doi.org/10.1039/c4cs00437j

88. Severino, M. I., Al Mohtar, A., Vieira Soares, C., Freitas, C., Sadovnik, N., Nandi, S., Mouchaham, G., Pimenta, V., Nouar, F., Daturi, M., Maurin, G., Pinto, M. L., & Serre, C. (2023). MOFs with Open Metal(III) Sites for the Environmental Capture of Polar Volatile Organic Compounds. *Angewandte Chemie - International Edition*, *62*(6). https://doi.org/10.1002/anie.202211583

89. Shah, K. J., Jiang, A., You, Z., & Li, J. (2023). *Perspective Chapter: Implementing Green Chemistry Principles for Pollution Control to Achieve Environmental Sustainability – A Review* (K. J. Shah (ed.)). IntechOpen. https://doi.org/10.5772/intechopen.1003627

90. Sharma, P., Gaur, V. K., Gupta, S., Varjani, S., Pandey, A., Gnansounou, E., You, S., Ngo, H. H., & Wong, J. W. C. (2022). Trends in mitigation of industrial waste: Global health hazards, environmental implications and waste derived economy for environmental sustainability. *Science of the Total Environment*, *811*, 152357. https://doi.org/10.1016/j.scitotenv.2021.152357

91. Shayegan, Z., Lee, C. S., & Haghighat, F. (2018). TiO2 photocatalyst for removal of volatile organic compounds in gas phase – A review. *Chemical Engineering Journal*, *334*(August 2017), 2408–2439. https://doi.org/10.1016/j.cej.2017.09.153

92. Sheldon, R. A. (2023). The E factor at 30: a passion for pollution prevention. *Green Chemistry*, *25*(5), 1704–1728. https://doi.org/10.1039/d2gc04747k

93. Shihab, M., Mhemid, R., Saeed, L., Ismail, H., Alp, & K. (2022). *Reducing Volatile Organic Compound Emissions Using Biotrickling Filters and Bioscrubber Systems*. https://doi.org/10.12911/22998993/152460

94. Shonnard, D., Hiew, & D. (2000). *Comparative Environmental Assessments of VOC Recovery and Recycle Design Alternatives for a Gaseous Waste Stream*. https://doi.org/10.1021/es0010857

95. Shukla, S. K., Khokarale, S. G., Bui, T. Q., & Mikkola, J. P. T. (2019). Ionic liquids: Potential materials for carbon dioxide capture and utilization. *Frontiers in Materials*, *6*(March), 1–8. https://doi.org/10.3389/fmats.2019.00042

96. Siami, H., Razmkhah, M., & Moosavi, F. (2023). Cation functional group effect on SO2 absorption in amino acid ionic liquids. *Frontiers in Chemistry*, *11*(February), 1–12. https://doi.org/10.3389/fchem.2023.1113394

97. Silva, B., Neves, I., Tavares, & T. (2016). *A sustained approach to environmental catalysis: Reutilization of chromium from wastewater*. https://doi.org/10.1080/10643389.2016.1255505

98. Silva, J. R., Quinta-Ferreira, R. M., & Castro, L. M. (2025). Biological Treatments for VOC-Contaminated Off-Gas: Advances, Challenges, and Energetic Valorization Opportunities. *Sustainability (Switzerland)*, *17*(11), 1–51. https://doi.org/10.3390/su17114802

99. Song, S., Zhang, S., Zhang, X., Verma, P., Wen, & M. (2020). *Advances in Catalytic Oxidation of Volatile Organic Compounds over Pd-Supported Catalysts: Recent Trends and Challenges*. https://doi.org/10.3389/fmats.2020.595667

100. Struk, M., Sepúlveda-Muñoz, C. A., Kushkevych, I., & Muñoz, R. (2023). Photoautotrophic removal of hydrogen sulfide from biogas using purple and green sulfur bacteria. *Journal of Hazardous Materials*, *443*(June 2022). https://doi.org/10.1016/j.jhazmat.2022.130337

101. Subrahmanyam, C., Magureanu, M., Renken, A., & Kiwi-Minsker, L. (2006). Catalytic abatement of volatile organic compounds assisted by non-thermal plasma. Part 1. A novel dielectric barrier discharge reactor containing catalytic electrode. *Applied Catalysis B: Environmental*, *65*(1–2), 150–156. https://doi.org/10.1016/j.apcatb.2006.01.006

102. Talaie, A., Fulazzaky, M. A., Rezania, S., & Tamadon, A. (2025). Adsorption, catalytic oxidation, and phytoremediation for air pollution control: a comprehensive review. *Environmental Science: Atmospheres*, 27–46. https://doi.org/10.1039/d5ea00079c

103. Thirumalaivasan, N., Gnanasekaran, L., Kumar, S., Durvasulu, R., Sundaram, T., Rajendran, S., Nangan, S., & Kanagaraj, K. (2024). Utilization of fungal and bacterial bioremediation techniques for the treatment of toxic waste and biowaste. *Frontiers in Materials*, *11*(July), 1–20. https://doi.org/10.3389/fmats.2024.1416445

104. Titirici, M. M., White, R. J., Brun, N., Budarin, V. L., Su, D. S., Del Monte, F., Clark, J. H., & MacLachlan, M. J. (2015). Sustainable carbon materials. *Chemical Society Reviews*, *44*(1), 250–290. https://doi.org/10.1039/c4cs00232f

105. Tomatis, M., Xu, H. H., He, J., & Zhang, X. D. (2016). Recent Development of Catalysts for Removal of Volatile Organic Compounds in Flue Gas by Combustion: A Review. *Journal of Chemistry*, *2016*(x). https://doi.org/10.1155/2016/8324826

106. Tran, N. N., Escribà-Gelonch, M., Sarafraz, M. M., Pho, Q. H., Sagadevan, S., & Hessel, V. (2023). Process Technology and Sustainability Assessment of Wastewater Treatment. *Industrial & Engineering Chemistry Research*, *62*(3), 1195–1214. https://doi.org/10.1021/acs.iecr.2c03471

107. Uddin, N., Zhang, H., Du, Y., Jia, G., Wang, S., & Yin, Z. (2020). Structural-Phase Catalytic Redox Reactions in Energy and Environmental Applications. *Advanced Materials*, *32*(9), 1–54. https://doi.org/10.1002/adma.201905739

108. Ume Onwuka, O., & Adu, A. (2024). Sustainable Strategies in Onshore Gas Exploration: Incorporating Carbon Capture for Environmental Compliance. *Engineering Science & Technology Journal*, *5*(4), 1184–1202. https://doi.org/10.51594/estj/v5i4.995

109. Ummah, M. S. (2019). No 主観的健康感を中心とした在宅高齢者における 健康関連指標に関する共分散構造分析Title. *Sustainability (Switzerland)*, *11*(1), 1–14. http://scioteca.caf.com/bitstream/handle/123456789/1091/RED2017-Eng8ene.pdf?sequence=12&isAllowed=y%0Ahttp://dx.doi.org/10.1016/j.regsciurbeco.2008.06.005%0Ahttps://www.researchgate.net/publication/305320484_SISTEM_PEMBETUNGAN_TERPUSAT_STRATEGI_MELESTARI

110. Urashima, K., Chang, & J.-S. (2000). *Removal of Volatile Organic Compounds from Air Streams and Industrial Flue Gases*.

111. Valdés, H., Riquelme, A. L., Solar, V. A., Azzolina-Jury, F., & Thibault-Starzyk, F. (2021). Removal of chlorinated volatile organic compounds onto natural and Cu-modified zeolite: The role of chemical surface characteristics in the adsorption mechanism. *Separation and Purification Technology*, *258*(November 2020). https://doi.org/10.1016/j.seppur.2020.118080

112. Vellingiri, K., Szulejko, J. E., Kumar, P., Kwon, E. E., Kim, K. H., Deep, A., Boukhvalov, D. W., & Brown, R. J. C. (2016). Metal organic frameworks as sorption media for volatile and semi-volatile organic compounds at ambient conditions. *Scientific Reports*, *6*(April), 1–11. https://doi.org/10.1038/srep27813

113. Wambugu, C., Danso Marvins, A., Das, J., & R. Rene, E. (2017). Conventional bioprocesses for the removal of gas-phase contaminants. *Research and Review Insights*, *1*(1), 1–2. https://doi.org/10.15761/rri.1000101

114. Wang, X., Wu, Y., Yang, X., Chen, H., Zhang, J., & Ma, X. (2021). Review of adsorptive removal of volatile organic compounds by zeolite. *Huagong Jinzhan/Chemical Industry and Engineering Progress*, *40*(5), 2813–2826. https://doi.org/10.16085/j.issn.1000-6613.2020-1145

115. Weller, M., Rourke, J., Armstrong, F., Lancaster, S., Overton, T., Weller, M., Rourke, J., Armstrong, F., Lancaster, S., & Overton, T. (2025). Inorganic Chemistry. In *Green chemistry* (8th ed.). Oxford University Press. https://doi.org/10.1093/hesc/9780198866916.001.0001

116. Weng, X., Meng, Q., Liu, J., Jiang, W., Pattisson, S., Wu, & Z. (2018). *Catalytic Oxidation of Chlorinated Organics over Lanthanide Perovskites: Effects of Phosphoric Acid Etching and Water Vapor on Chlorine Desorption Behavior*. https://doi.org/10.1021/acs.est.8b04582

117. Wilberforce, T., Baroutaji, A., Soudan, B., Alami, A., Olabi, & A. (2018). *Outlook of carbon capture technology and challenges*. https://doi.org/10.1016/j.scitotenv.2018.11.424

118. Wróblewska, K., & Jeong, B. R. (2021). Effectiveness of plants and green infrastructure utilization in ambient particulate matter removal. *Environmental Sciences Europe*, *33*(1). https://doi.org/10.1186/s12302-021-00547-2

119. Wu, X., Lin, Y., Wang, Y., Wu, S., Yang, & C. (2023). *Volatile organic compound removal via biofiltration: Influences, challenges, and strategies*. https://doi.org/10.1016/j.cej.2023.144420

120. Wysocka, I., Gębicki, J., Namieśnik, & J. (2019). *Technologies for deodorization of malodorous gases*. https://doi.org/10.1007/s11356-019-04195-1

121. Xin, Y., Shirai, & T. (2021). *Noble-metal-free hydroxyapatite activated by facile mechanochemical treatment towards highly-efficient catalytic oxidation of volatile organic compound*. https://doi.org/10.1038/s41598-021-86992-8

122. Xiong, X., Yu, I. K. M., Tsang, D. C. W., Bolan, N. S., Sik Ok, Y., Igalavithana, A. D., Kirkham, M. B., Kim, K. H., & Vikrant, K. (2019). Value-added chemicals from food supply chain wastes: State-of-the-art review and future prospects. *Chemical Engineering Journal*, *375*(June), 121983. https://doi.org/10.1016/j.cej.2019.121983

123. Xue, T., & Yang, L. (2021). Zeolite-Based Materials for the Catalytic Oxidation of VOCs: A Mini Review. *Frontiers in Chemistry*, *9*(October), 1–6. https://doi.org/10.3389/fchem.2021.751581

124. Yang, C., Miao, G., Pi, Y., Xia, Q., Wu, J., Li, Z., Xiao, & J. (2019). *Abatement of various types of VOCs by adsorption/catalytic oxidation: A review*. https://doi.org/10.1016/j.cej.2019.03.232

125. Yang, P., Zhang, T., Ling, Z., Liu, M., Zeng, & X. (2025). *Regenerative Oxidation Technology for VOC Treatment: A Review*. https://doi.org/10.3390/en18133430

126. Ye, B., Jeong, B., Lee, M.-j., Kim, T., Park, S.-S., Jung, J.-i., Kim, & H.-D. (2022). *Recent trends in vanadium-based SCR catalysts for NOx reduction in industrial applications: stationary sources*. https://doi.org/10.1186/s40580-022-00341-7

127. Yu, H. C., You, S. W., Wang, C., Deng, J. G., & Hsi, H. C. (2022). Regeneration of beaded activated carbon saturated with volatile organic compounds by a novel electrothermal swing adsorption system. *Sustainable Environment Research*, *32*(1). https://doi.org/10.1186/s42834-022-00162-7

128. Yuan, X., Wang, J., Deng, S., Dissanayake, P. D., Wang, S., You, S., Yip, A. C. K., Li, S., Jeong, Y., Tsang, D. C. W., & Ok, Y. S. (2022). Sustainable Food Waste Management: Synthesizing Engineered Biochar for CO2 Capture. *ACS Sustainable Chemistry & Engineering*, *10*(39), 13026–13036. https://doi.org/10.1021/acssuschemeng.2c03029

129. Yuan, Y., Lei, S., Jin, X., Wang, C., Zhai, Z., Zhao, C., & Zhou, C. (2023). Fe(II)/LXQ-10 bifunctional resin materials for boosting synergistic adsorption/oxidation of benzene in industrial waste gas. *Environmental Science and Pollution Research*, *30*(39), 90772–90786. https://doi.org/10.1007/s11356-023-28759-4

130. Zhang, H., Wang, Z., Wei, L., Hou, Z., Liu, Y., Dai, H., Deng, & J. (2025). *Advances in catalytic purification and resource utilization for VOCs pollution control*. https://doi.org/10.1360/csb-2025-5472

131. Zhang, S., Shen, Y., Zheng, C., Xu, Q., Sun, Y., Huang, M., Li, L., Yang, X., Zhou, H., Ma, H., Li, Z., Zhang, Y., Liu, W., & Gao, X. (2024). Recent advances, challenges, and perspectives on carbon capture. *Frontiers of Environmental Science and Engineering*, *18*(6), 1–30. https://doi.org/10.1007/s11783-024-1835-0

132. Zhao, J., Wang, Y., Chen, Z., Gao, Y., Xue, T., Liu, G., Xin, S., Zhou, C., Xin, Y., Wang, Q., & Yan, Q. (2025). Recent advances in catalytic removal volatile organic compounds: Structure activity correlation, mechanism and application insights. *Separation and Purification Technology*, *378*(P2), 134598. https://doi.org/10.1016/j.seppur.2025.134598

133. Zhou, H., Gao, S., Zhang, W., An, Z., & Chen, D. (2019). Dynamic adsorption of toluene on amino-functionalized SBA-15 type spherical mesoporous silica. *RSC Advances*, *9*(13), 7196–7202. https://doi.org/10.1039/C8RA08605B

PHYTOREMEDIATION: A GREEN CHEMISTRY–FOCUSED TREATMENT TECHNOLOGY

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ABSTRACT

Phytoremediation has emerged as a promising nature-based environmental remediation strategy that utilizes plants and their associated microbial communities to remove, stabilize, transform, or degrade a wide range of environmental contaminants. This book chapter provides a comprehensive overview of the conceptual foundations and mechanistic framework of phytoremediation, with a particular emphasis on its integration within the principles of green chemistry and sustainable environmental management. The major phytoremediation pathways—including phytoextraction, phytostabilization, phytodegradation, rhizodegradation, phytovolatilization, rhizofiltration, and hydraulic control—are systematically examined in terms of their underlying biological, chemical, and ecological processes. Each mechanism is discussed through representative model plant species and relevant case studies, highlighting the roles of plant physiology, root–microbe interactions, and soil geochemistry in contaminant fate and transformation. The chapter further explores phytoremediation as a holobiont-based system in which plants, microorganisms, and environmental factors function as an integrated ecological network. While phytoremediation offers significant advantages such as low energy demand, in situ applicability, and compatibility with circular bioeconomy approaches, its limitations including contaminant bioavailability, temporal constraints, and site-specific variability are also critically addressed. Finally, emerging advances in genomics, microbiome engineering, synthetic biology, and data-driven environmental modeling are discussed as key drivers expected to enhance the efficiency and scalability of phytoremediation technologies. Overall, this chapter positions phytoremediation as a multifunctional ecological engineering platform that bridges environmental biotechnology and green chemistry, offering sustainable solutions for the remediation and restoration of contaminated ecosystems.

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1. INTRODUCTION

Environmental pollution represents one of the most pressing global challenges of the twenty-first century, affecting soil, water, and atmospheric systems across all continents. Rapid industrialization, uncontrolled urbanization, mining activities, intensive agricultural practices, and inadequate waste management have significantly increased the release and dispersion of both inorganic contaminants (e.g., heavy metals, excess nitrogen and phosphorus) and organic pollutants (e.g., pesticides, persistent organic pollutants, and emerging contaminants) into natural environments (Alpizar et al., 2019). These anthropogenic pressures compromise ecosystem integrity, reduce biodiversity, and threaten essential ecosystem services such as nutrient cycling, water purification, and soil fertility (FAO & ITPS, 2015; World Health Organization [WHO], 2017).

The scale and complexity of environmental degradation have intensified with rapid population growth and escalating resource demand. The global population is projected to approach 10 billion by 2050, increasing consumption patterns and material throughput beyond sustainable levels (United Nations, 2022). Simultaneously, research on planetary boundaries indicates that critical Earth system processes—including biogeochemical nitrogen and phosphorus cycles and biodiversity integrity—have already been significantly disrupted by human activities (Rockström et al., 2009; Steffen et al., 2015). These transgressions underscore the need for remediation approaches that not only treat contamination locally but also operate within global biogeochemical limits. Accordingly, environmental pollution cannot be viewed as an isolated technical issue but rather as a systemic manifestation of unsustainable production and consumption paradigms.

Historically, environmental management strategies have been largely reactive, relying on end-of-pipe technologies designed to treat contaminants after their release into the environment. Although such approaches may reduce immediate pollutant concentrations, they often require high energy inputs, complex infrastructure, and chemical reagents, sometimes generating secondary waste streams or shifting environmental burdens from one compartment to another (Anastas & Warner, 1998; Alpizar et al., 2019). Moreover, many conventional remediation technologies are tailored to address single pollutants, whereas real-world contamination scenarios typically involve complex mixtures of organic and inorganic substances interacting within dynamic soil–water–plant systems.

This mismatch between environmental complexity and technological response highlights a fundamental problem: current remediation frameworks are insufficiently aligned with the systemic, interconnected, and resource-constrained nature of contemporary environmental challenges. There is an urgent need for integrated treatment strategies that are not only effective in removing contaminants but also energy-efficient, economically feasible, ecologically compatible, and preventive by design. Addressing pollution within planetary limits requires a shift from corrective intervention toward anticipatory and regenerative environmental management.

At a deeper level, the environmental crisis reflects not merely a technological deficiency but an epistemological paradigm that has historically framed nature as an inexhaustible resource to be exploited and controlled. Linear production models—extraction, production, consumption, disposal—have dominated industrial development, operating under the assumption of infinite assimilative capacity. In contrast, sustainability science calls for a systemic reconfiguration of human–nature relationships, emphasizing circularity, resilience, and ecological integration (Geissdoerfer et al., 2017).

Green Chemistry emerged in the 1990s as a response to this necessity, proposing the intentional design of chemical products and processes that reduce or eliminate hazardous substances at their source (Anastas & Warner, 1998). Rather than treating environmental protection as an external regulatory constraint, green chemistry integrates ecological considerations into molecular and process design.Its principles—such as waste prevention, atom economy, renewable feedstocks, energy efficiency, and design for degradation—reflect a preventive and systems-oriented philosophy consistent with sustainable development (Anastas & Eghbali, 2010). In this sense, green chemistry represents not only a technical framework but also a paradigm shift toward anticipatory and multidisciplinary environmental stewardship.

Within this paradigm, nature-based and biologically driven technologies gain particular relevance. Phytoremediation, which utilizes plants and associated rhizospheric microorganisms to remove, stabilize, transform, or degrade contaminants, exemplifies an approach that operates in harmony with ecological processes. By harnessing solar energy, leveraging natural metabolic pathways, and functioning in situ with minimal chemical input, phytoremediation aligns closely with the preventive, renewable, and regenerative principles of green chemistry (Ali et al., 2013). Therefore, evaluating phytoremediation through the lens of green chemistry is not merely a matter of technical compatibility; it reflects a broader effort to reconcile environmental remediation with ecological integrity and long-term sustainability.

This chapter critically evaluates phytoremediation within the conceptual and operational framework of green chemistry, highlighting its mechanistic foundations, sustainability implications, limitations, and future research directions.

2. PHYTOREMEDIATION: CONCEPTUAL FOUNDATIONS AND MECHANISTIC FRAMEWORK

Phytoremediation is broadly defined as the use of green plants and their associated rhizospheric microorganisms to remove, immobilize, degrade, or transform contaminants present in soil, sediments, surface water, or groundwater (Ali et al., 2013). Unlike conventional remediation technologies, which often rely on excavation, chemical oxidation, thermal treatment, or physical containment, phytoremediation utilizes biological processes driven primarily by solar energy, plant metabolism, and plant–microbe interactions. As a result, it represents one of the most environmentally compatible approaches to restoring contaminated ecosystems.

From a systems perspective, phytoremediation represents a bio-integrative remediation strategy embedded within ecological networks. Rather than isolating contamination as a purely chemical problem, it recognizes polluted environments as complex soil–plant–microbe systems characterized by dynamic physical, chemical, and biological interactions (Pilon-Smits, 2005). The fate of contaminants is therefore influenced not only by their intrinsic chemical properties but also by plant physiology, microbial activity, soil geochemistry, hydrological conditions, and climatic factors. This systems-based approach aligns closely with contemporary sustainability science, ecological engineering and green chemistry principles by emphasizing renewable inputs, waste minimization, ecosystem compatibility, and long-term environmental resilience (Anastas & Eghbali, 2010).

Recent advances in plant and microbial ecology have further expanded the conceptual framework of phytoremediation. Plants are increasingly viewed as holobionts, integrated biological entities consisting of the host plant and its associated microbiome. Within this framework, remediation outcomes emerge from coordinated interactions among plant roots, rhizospheric microorganisms, endophytic bacteria, mycorrhizal fungi, and surrounding soil communities. Root exudates, including sugars, amino acids, organic acids, phenolic compounds, and secondary metabolites, actively shape microbial populations capable of transforming contaminants, mobilizing nutrients, alleviating stress, and enhancing plant tolerance. Consequently, the effectiveness of phytoremediation often depends as much on microbial ecology as on plant physiology (Vandenkoornhuyse et al., 2015; Thijs et al., 2016).

At the physiological level, phytoremediation exploits defense mechanisms that plants originally evolved to survive in stressful environments. Exposure to toxic metals and organic pollutants often induces oxidative stress by generating Reactive Oxygen Species (ROS), which can damage cellular structures and disrupt metabolic processes (Ghori et al., 2019). To maintain cellular homeostasis, plants have evolved sophisticated detoxification systems involving antioxidant enzymes, metal-chelating molecules, compartmentalization mechanisms, and xenobiotic transformation pathways (Pilon-Smits, 2005). Modern phytoremediation harnesses these naturally occurring adaptive responses and redirects them toward environmental restoration.

Phytoremediation is not a single technology but rather a collection of interconnected mechanisms whose relative importance depends on contaminant type, plant species, environmental conditions, and remediation objectives. These mechanisms can be categorized into several primary processes: phytoextraction, phytostabilization, phytodegradation, rhizodegradation, phytovolatilization, rhizofiltration, and hydraulic control (Ali et al., 2013). In practice, these processes rarely operate independently; instead, multiple mechanisms frequently occur simultaneously within the same plant–soil system, generating synergistic remediation effects. Each mechanism reflects a distinct interaction pathway between plants and contaminants, as schematically illustrated in Figure 1.

Importantly, phytoremediation is particularly suitable for large-scale, low-to-moderate contamination scenarios where conventional remediation would be economically or environmentally prohibitive (Pilon-Smits, 2005). However, its applicability must be evaluated within the broader context of contaminant chemistry, site hydrology, ecological constraints and temporal requirements. Nevertheless, phytoremediation is constrained by factors such as relatively long remediation timeframes, biomass management challenges, contaminant bioavailability limitations, and climate-dependent performance, all of which must be carefully considered in practical applications.

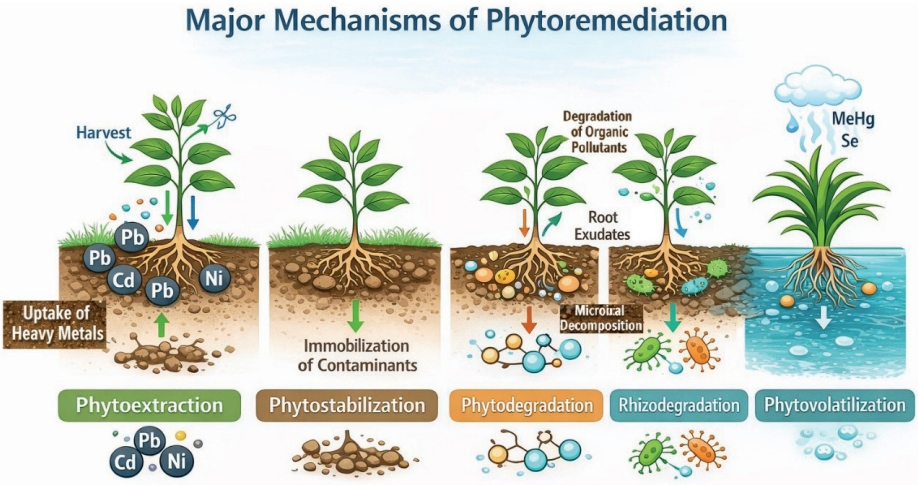

Figure 1. *Schematic representation of the principal phytoremediation mechanisms operating in soil and aquatic environments. Phytoextraction involves the uptake of heavy metals (e.g., Pb, Cd, Ni) by plant roots, their translocation to aboveground tissues, and subsequent removal through harvest. Phytostabilization reduces contaminant mobility and bioavailability via root adsorption, precipitation, and soil stabilization processes. Phytodegradation (phytotransformation) refers to the enzymatic breakdown of organic pollutants within plant tissues. Rhizodegradation occurs in the rhizosphere, where root exudates stimulate microbial communities that enhance the degradation of organic contaminants. Phytovolatilization involves the uptake and transformation of certain elements (e.g., Se, Hg) into volatile forms released into the atmosphere. Together, these mechanisms illustrate the integrated plant–soil–microbe interactions that underpin phytoremediation as a green chemistry–aligned remediation strategy*

3. PHYTOREMEDIATION MECHANISMS: FROM BIOLOGICAL SURVIVAL STRATEGIES TO APPLIED CASE STUDIES

Phytoremediation is not a passive filtration process but rather the ecological reconfiguration of plant survival strategies into environmental remediation tools. Plants have evolved sophisticated biochemical systems to tolerate, compartmentalize, transform, or exclude toxic substances in order to survive in hostile environments. Modern phytoremediation harnesses these intrinsic adaptive mechanisms and directs them toward the restoration of contaminated ecosystems (Pilon-Smits, 2005; Ali et al., 2013). The following sections examine each principal phytoremediation

pathway through mechanistic analysis supported by real-world model species and contaminant case studies.

3.1. Phytoextraction: Biological Mining of Metals

Phytoextraction can be conceptualized as a form of biological mining in which plants actively mobilize, absorb, translocate, and accumulate contaminants from soil into harvestable aboveground tissues. Unlike passive accumulation, phytoextraction is a highly regulated physiological process involving root–soil interactions, membrane transport systems, intracellular chelation mechanisms, and long-term sequestration strategies. The effectiveness of phytoextraction depends on both contaminant bioavailability in the rhizosphere and the ability of plants to tolerate elevated concentrations of potentially toxic elements without suffering severe metabolic damage.

Model Species: *Alyssum bertolonii*, *Thlaspi caerulescens* (now *Noccaea caerulescens*), *Sorghum bicolor, Panicum virgatum* (Baker & Brooks, 1989; Kramer 2010, Testa et al. 2024).

Case Study: Nickel and Cadmium Hyperaccumulation

Hyperaccumulator species possess unique physiological adaptations that enable them to accumulate extraordinarily high concentrations of metals in their shoots, often exceeding toxicity thresholds observed in conventional plants. These adaptations involve multiple coordinated processes operating at molecular, cellular, and whole-plant scales. The initial stage of phytoextraction involves mobilizing metals in the rhizosphere. Root exudates, including low-molecular-weight organic acids, amino acids, and phenolic compounds, can alter local pH conditions and increase metal solubility, thereby enhancing bioavailability for root uptake. Once mobilized, metal ions are transported across root cell membranes through specialized transporter proteins belonging to families such as ZIP (ZRT/IRT-like Proteins), NRAMP (Natural Resistance-Associated Macrophage Proteins), Yellow Stripe-Like (YSL) transporters, and Heavy Metal ATPases (HMAs).

Following cellular entry, metals are rapidly chelated by chelators, including nicotianamine, phytochelatins, organic acids, and metallothioneins. These ligands reduce the concentration of free metal ions within the cytoplasm, thereby minimizing toxicity and facilitating safe intracellular transport. Hyperaccumulator species often exhibit elevated production of these chelators compared with non-accumulator plants.

A critical step in hyperaccumulation is the efficient loading of metal–ligand complexes into the xylem, followed by long-distance translocation to aerial tissues. Enhanced xylem loading, high transpiration rates, and efficient shoot sequestration collectively contribute to the exceptional metal accumulation capacities observed in species such as Noccaea caerulescens. Once transported to leaves and stems, metals are frequently compartmentalized within vacuoles through transporter-mediated sequestration, effectively isolating them from metabolically active cellular compartments.

Exposure to elevated metal concentrations inevitably generates reactive oxygen species (ROS), which can disrupt cellular homeostasis through oxidative damage to proteins, lipids, and nucleic acids. Consequently, hyperaccumulator plants possess highly efficient antioxidant defense systems involving enzymes such as superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX), and glutathione reductase (GR). These antioxidant networks enable plants to maintain redox balance while sustaining metal uptake and accumulation under extreme environmental conditions.

Following harvest, contaminated biomass may be processed through controlled combustion or thermochemical conversion to produce a metal-enriched ash known as bio-ore. Valuable metals can subsequently be recovered through hydrometallurgical or pyrometallurgical techniques in a process referred to as phytomining. By coupling environmental remediation with resource recovery, phytomining transforms contaminated biomass into a secondary source of economically valuable metals. This approach exemplifies several principles of green chemistry and circular bioeconomy, including waste valorization, resource recovery, and the utilization of renewable biological systems.

3.2 Phytostabilization: Immobilization and Geochemical Sealing

When contaminant removal is technically impractical, economically prohibitive, or environmentally risky, phytostabilization provides an alternative remediation strategy by reducing contaminant mobility and bioavailability in situ. Rather than extracting pollutants from the environment, phytostabilization seeks to immobilize them within the soil–root system, thereby minimizing their migration into groundwater, atmospheric dust, surface runoff, and food webs. Consequently, the primary objective of phytostabilization is risk reduction rather than contaminant removal.

Model Species: *Festuca ovina, Agrostis capillaris, Zea mays* (Smith & Bradshaw, 1979; Tasleem et al., 2026).

Case Study: Lead Contamination in Mine Tailings

Abandoned mining sites frequently contain elevated concentrations of lead (Pb), zinc (Zn), copper (Cu), and other potentially toxic elements. These contaminants may become dispersed through wind erosion, water runoff, or dust generation, posing significant ecological and human health risks. Establishing tolerant vegetation cover is one of the most effective strategies for stabilizing such sites and preventing contaminant redistribution.

Phytostabilization operates through a combination of physical, chemical, and biological mechanisms occurring within the rhizosphere. One of the primary mechanisms involves the adsorption of metal ions onto root surfaces and cell wall components. Carboxyl, hydroxyl, and pectic functional groups present in root cell walls possess a high affinity for cationic metals, enabling the formation of relatively stable metal–cell wall complexes. This process reduces metal mobility while limiting translocation to aboveground tissues.

A second mechanism involves the activity of rhizospheric microorganisms. Root-associated bacteria and fungi produce extracellular polymeric substances (EPS), complex matrices rich in polysaccharides, proteins, and humic-like compounds capable of binding substantial quantities of metal ions. These EPS matrices function as biological sorbents, effectively trapping contaminants within the rhizosphere and reducing their bioavailability.

Plants also influence metal behavior by altering rhizosphere chemistry. Root exudates can alter pH conditions, redox potential, and ion composition, thereby promoting the precipitation of metals into poorly soluble mineral phases. For example, phosphate ions released directly by roots or generated through microbial activity may react with dissolved lead to form highly insoluble lead-phosphate minerals. Similar precipitation reactions can occur with carbonates, sulfides, and iron oxides, further decreasing contaminant mobility.

Mycorrhizal fungi frequently contribute to phytostabilization by expanding the effective root surface area and enhancing contaminant immobilization. Arbuscular mycorrhizal fungi (AMF) can bind metals within fungal structures, alter rhizosphere geochemistry, and improve plant tolerance to contaminated conditions. As a result, plant–fungal symbioses often increase the long-term stability of phytostabilized systems.

Beyond geochemical processes, vegetation cover provides a critical physical barrier against contaminant dispersal. Dense root networks stabilize soil structure, reduce erosion, limit sediment transport, and suppress the generation of contaminated dust particles. This function is particularly important in mine tailings, where airborne particulate matter frequently represents a major exposure pathway for surrounding communities.

Unlike phytoextraction, contaminants remain largely confined to the soil–root interface, minimizing trophic transfer and reducing ecological exposure. Phytostabilization, therefore, represents a form of geochemical–biological engineering in which plants actively modify contaminant speciation, mobility, and environmental accessibility rather than removing contaminants from the site. From a sustainability perspective, this approach embodies the green chemistry principle of pollution prevention by reducing contaminant transport and exposure without intensive energy inputs or large-scale soil disturbance.

3.3. Phytodegradation: Enzymatic Green Detoxification

Phytodegradation, also known as phytotransformation, uses plant metabolic pathways to transform organic contaminants into less toxic, less mobile, or biologically inactive forms. Unlike rhizodegradation, where contaminant breakdown is primarily mediated by microorganisms in the rhizosphere, phytodegradation occurs predominantly within plant tissues through enzyme-catalyzed biochemical reactions. The process is frequently compared to xenobiotic detoxification systems in animals and is often described using the "Green Liver Model," which highlights the functional similarities between plant and mammalian detoxification pathways.

Model Species: *Populus deltoides, Salix spp., grasses, Heliconea spp (Zingiberales) and Cyperus haspan* (Dietz and Schnoor, 2001; Delgado et al., 2020).

Case Study: Trichloroethylene (TCE), Explosive Residues, and Pharmaceuticals and Personal Care Products (PPCPs)

Numerous terrestrial and aquatic plant species have demonstrated the ability to transform contaminants such as trichloroethylene (TCE), nitroaromatic explosive residues, pesticides, pharmaceuticals, and personal care products (PPCPs). These compounds are often characterized by high mobility, environmental persistence, and potential toxicity, making them suitable targets for phytodegradation-based remediation strategies.

Mechanistically, phytodegradation proceeds through a multistep detoxification system analogous to that observed in higher animals.

Phase I: Transformation (Activation)

The initial stage involves oxidation, reduction, or hydrolysis reactions that introduce or expose reactive functional groups within contaminant molecules. These reactions are catalyzed by enzymes such as cytochrome P450 monooxygenases, peroxidases, laccases, nitroreductases, and dehalogenases. Although Phase I reactions often reduce contaminant toxicity, they may also generate reactive intermediates that require further detoxification.

Phase II: Conjugation

Following transformation, reactive metabolites are conjugated with endogenous molecules such as glutathione, glucose, amino acids, malonate, or other organic ligands. Enzymes, including glutathione S-transferases (GSTs), glycosyltransferases, and acyltransferases, facilitate these reactions. Conjugation generally increases water solubility while reducing chemical reactivity and toxicity.

Phase III: Compartmentation and Sequestration

The resulting conjugates are actively transported into vacuoles or incorporated into cell wall components through ATP-dependent transport systems. This compartmentalization isolates contaminants from metabolically active cellular regions and represents a critical detoxification mechanism that enables plants to tolerate xenobiotic exposure.

Phase IV: Formation of Bound Residues

In the final stage, conjugated compounds may undergo additional biochemical modifications and become covalently associated with structural components such as lignin, hemicellulose, or cell wall polymers. These products are commonly referred to as "bound residues" because they are resistant to conventional chemical extraction methods. Their incorporation into stable plant tissues substantially reduces environmental mobility and biological availability.

Through this sequential detoxification process, contaminants that were once mobile and potentially hazardous can be transformed into chemically stabilized forms integrated within plant biomass. For example, hybrid poplars have demonstrated the ability to metabolize trichloroethylene (TCE), while numerous aquatic macrophytes can transform pharmaceutical residues frequently detected in wastewater systems. Similar pathways have been reported for nitroaromatic explosives, herbicides, and chlorinated organic compounds.

From a green chemistry perspective, phytodegradation exemplifies the principle of design for degradation by promoting the biological transformation of contaminants into less harmful products through renewable, solar-powered metabolic processes. Rather than transferring pollution from one environmental compartment to another, phytodegradation seeks to reduce contaminant persistence through intrinsic biochemical pathways operating within living plants.

3.4. Rhizodegradation: Microbial Synergy and Rhizosphere Engineering

Unlike phytodegradation, which relies primarily on enzymatic processes occurring within plant tissues, rhizodegradation is driven predominantly by microorganisms inhabiting the rhizosphere. In this mechanism, plants function less as direct degraders and more as ecological engineers that create favorable conditions for microbial contaminant transformation. Through the release of root exudates and the modification of rhizosphere chemistry, plants stimulate microbial communities capable of degrading a wide range of organic pollutants.

Model Species: *Morus alba, Oryza sativa, Trifolium pratense*, *Sorghum* × *drummondii* (sudangrass)(Anderson et al., 1993; Dominguez et al., 2019, Medić & Karadźić, 2022; Guo et al., 2024).

Case Study: Petroleum Hydrocarbons and Polycyclic Aromatic Hydrocarbons (PAHs)

Petroleum-contaminated soils frequently contain complex mixtures of aliphatic hydrocarbons, aromatic compounds, and polycyclic aromatic hydrocarbons (PAHs), many of which exhibit low bioavailability and high environmental persistence. Natural attenuation of these contaminants is often slow because microbial populations are limited by carbon, nutrient, or oxygen availability, or by environmental stress. The establishment of vegetation can substantially accelerate degradation by transforming the rhizosphere into a biologically active hotspot.

A defining characteristic of rhizodegradation is the rhizosphere effect, in which microbial populations in the vicinity of plant roots become significantly more abundant and metabolically active than those in the surrounding bulk soil. Root exudates, including sugars, amino acids, organic acids, phenolic compounds, flavonoids, and secondary metabolites, serve as carbon sources, signaling molecules, and growth substrates for rhizospheric microorganisms. As a consequence, microbial densities in the rhizosphere may be 1 to 2 orders of magnitude higher than those observed in non-vegetated soils.

The enhanced microbial activity supports the proliferation of hydrocarbon-degrading bacteria and fungi possessing specialized catabolic pathways. Key enzymes involved in petroleum degradation include monooxygenases, dioxygenases, dehydrogenases, and other oxygen-dependent oxidoreductases that initiate the breakdown of complex hydrocarbon structures. These enzymes catalyze the incorporation of oxygen into otherwise stable aromatic rings, representing a critical first step in contaminant mineralization.

Plants also contribute indirectly to degradation by modifying the physical and chemical properties of the rhizosphere. Root growth increases soil porosity, improves water infiltration, and enhances the accessibility of contaminants. In wetland species and certain terrestrial plants, radial oxygen loss from roots creates localized aerobic microenvironments that support oxygen-dependent microbial degradation processes. Simultaneously, plant growth-promoting rhizobacteria (PGPR), endophytic microorganisms, and mycorrhizal fungi may further enhance contaminant breakdown while improving plant health under polluted conditions.

The interaction between plants and microorganisms, therefore, represents a highly coordinated biological partnership. Rather than functioning independently, plant roots continuously provide carbon resources, habitat structure, signaling molecules, and oxygen, while microorganisms supply the enzymatic machinery necessary for contaminant degradation. This plant–microbe consortium often accelerates hydrocarbon degradation rates by an order of magnitude compared with natural attenuation alone.

From a systems perspective, rhizodegradation exemplifies the holobiont concept introduced earlier in this chapter, where remediation emerges from the collective metabolic activities of plants and their associated microbiota. The process can be viewed as ecological niche engineering, in which plants construct and maintain a biologically active environment that supports microbial biocatalysis. Consequently, rhizodegradation embodies several principles of green chemistry, including catalysis, the use of renewable biological systems, and the promotion of environmentally compatible degradation pathways.

3.5. Phytovolatilization: Biochemical Conversion to Volatile Forms

Phytovolatilization involves the uptake of contaminants from soil, sediment, or water, followed by their enzymatic transformation into volatile forms that are subsequently released into the atmosphere through plant stomata. Unlike phytoextraction, which retains contaminants within harvestable biomass, phytovolatilization relies on biochemical conversion processes that alter contaminant speciation and facilitate their atmospheric release. Consequently, the mechanism reduces contaminant concentrations in the treated environment but may also redistribute pollutants to other environmental compartments.

Model Species: *Astragalus bisulcatus*, genetically engineered *Arabidopsis thaliana* (Meagher, 2000; Terry et al. 2000).

Case Study: Selenium (Se) and Mercury (Hg)

Selenium-contaminated soils provide one of the best-known examples of natural phytovolatilization. Selenium is chemically analogous to sulfur and is therefore absorbed by plants through sulfate transport systems. Following uptake, selenate (SeO_4^{2-}) is incorporated into sulfur assimilation pathways and subsequently transformed through a series of reduction and methylation reactions. Enzymes utilizing S-adenosylmethionine (SAM) as a methyl donor catalyze the formation of volatile organoselenium compounds such as dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe), which are released through stomatal transpiration.

Mercury phytovolatilization has been studied extensively in genetically engineered plants. In these systems, bacterial merA genes encode mercuric reductase enzymes that convert ionic mercury (Hg^{2+}) into elemental mercury (Hg^0), a volatile form that can diffuse into the atmosphere. Some transgenic plants also express the merB gene, which encodes organomercurial lyase and enables the degradation of organic mercury compounds before they are reduced by MerA. These genetic modifications significantly enhance mercury detoxification and volatilization capacity compared with non-transgenic plants.

The phytovolatilization process generally involves four sequential stages: contaminant uptake, intracellular transport, biochemical transformation, and atmospheric release through stomata. The efficiency of each stage depends on plant genotype, contaminant speciation, environmental conditions, and metabolic activity. Because volatilization is linked to transpiration, climatic factors such as temperature, humidity, and solar radiation may strongly influence remediation performance.

Although phytovolatilization can effectively reduce contaminant concentrations in soils and aquatic systems, it remains one of the most debated mechanisms of phytoremediation. In contrast to degradation processes that destroy contaminants or immobilization processes that reduce their mobility, phytovolatilization may transfer contaminants from terrestrial or aquatic environments into the atmosphere. Consequently, the environmental fate, atmospheric transport, and potential redeposition of volatilized compounds require careful risk assessment and long-term monitoring.

From a broader perspective, phytovolatilization illustrates both the transformative potential and the inherent trade-offs of biological remediation. By altering contaminant speciation through naturally occurring metabolic pathways, plants can significantly reduce local environmental burdens. However, the ultimate sustainability of this approach depends on whether volatilization results in genuine detoxification or merely redistributes contaminants within the broader ecosystem. As such, phytovolatilization highlights the importance of evaluating remediation success at the ecosystem scale rather than within a single environmental compartment.

3.6. Rhizofiltration: Root-Mediated Removal of Aquatic Contaminants

Rhizofiltration is a phytoremediation strategy that utilizes plant root systems to remove, concentrate, or immobilize contaminants from aqueous environments.

Unlike phytoextraction, which targets pollutants in soils, rhizofiltration is primarily applied to contaminated surface waters, groundwater, industrial effluents, and wastewater systems. The process relies on the extensive surface area and sorptive properties of plant roots, which function as dynamic biological filters that capture dissolved contaminants from water.

Model Species: *Helianthus annuus*, *Brassica juncea*, *Lemna minor*, *Eichhornia crassipes*, *Pistia stratiotes* (Dushenkov et al., 1995; Salt et al., 1995).

Case Study: Heavy Metals and Radionuclides in Aquatic Systems

Aquatic environments contaminated with lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), uranium (U), and radionuclides pose significant environmental and public health concerns due to their high mobility in water. Rhizofiltration offers an effective means of reducing contaminant concentrations before they disperse through larger aquatic systems. The remediation process involves several sequential mechanisms:

Adsorption

The initial interaction occurs at the root surface, where metal ions bind to negatively charged functional groups such as carboxyl, hydroxyl, and phosphate groups present in root cell walls and mucilage. This passive sorption process often accounts for a substantial proportion of contaminant removal.

Absorption and Uptake

Following adsorption, certain contaminants may be absorbed into root tissues through membrane transport systems. In many rhizofiltration systems, however, contaminants remain predominantly associated with root structures rather than being translocated to shoots.

Complexation and Immobilization

Within root tissues, contaminants may be complexed by organic ligands such as phytochelatins, metallothioneins, and organic acids. These complexes reduce contaminant toxicity and facilitate sequestration within root cells.

Rhizospheric Interactions

Root-associated microorganisms further enhance contaminant removal through biosorption, bioaccumulation, and changes in rhizosphere chemistry. Alterations in pH, redox conditions, and ion availability can promote contaminant precipitation and immobilization near root surfaces. Because contaminants are concentrated primarily within root biomass, harvested roots can be removed and managed as contaminated waste or processed for resource recovery. This characteristic distinguishes rhizofiltration from many other phytoremediation mechanisms and allows direct removal of contaminants from aquatic systems. From a sustainability perspective, rhizofiltration represents a low-energy, solar-powered treatment technology that

can complement conventional water treatment processes. Constructed wetlands and floating treatment wetlands increasingly employ rhizofiltration principles to improve water quality while simultaneously supporting ecosystem functions.

3.7. Hydraulic Control (Phytohydraulics): Vegetative Management of Contaminant Plumes

Hydraulic control, also known as phytohydraulics, utilizes deep-rooted, high-transpiration plant species to influence groundwater movement and limit the migration of contaminant plumes. Rather than directly transforming or removing contaminants, this approach manipulates site hydrology through plant water uptake, thereby reducing the spread of polluted groundwater and protecting surrounding ecosystems.

Model Species: *Populus deltoides, Populus nigra*, *Salix* spp., *Eucalyptus* spp. (McCutcheon & Schnoor, 2003; Rockwood et al., 2004).

Case Study: Chlorinated Solvents in Groundwater

Groundwater contamination by chlorinated solvents such as trichloroethylene (TCE), perchloroethylene (PCE), and related compounds remains a major environmental challenge worldwide. Conventional pump-and-treat technologies are often expensive and may require decades of operation to achieve remediation goals. In contrast, strategically established tree plantations can function as biological hydraulic barriers that intercept contaminated groundwater before it migrates beyond the source area.

The effectiveness of hydraulic control derives from several interconnected processes:

Groundwater Uptake

Deep root systems access groundwater directly, extracting large volumes of water during transpiration. Mature poplar plantations, for example, may transpire hundreds of liters of water per tree per day under favorable conditions.

Capture of Contaminant Plumes

Continuous water uptake generates localized hydraulic gradients that alter groundwater flow patterns and reduce plume expansion. In some cases, vegetation can effectively contain contaminated groundwater within a defined treatment zone.

Reduction of Leachate Generation

By intercepting infiltrating precipitation and enhancing evapotranspiration, vegetation reduces downward water movement through contaminated soils, thereby limiting contaminant transport toward groundwater.

Coupling with Other Phytoremediation Processes

Hydraulic control frequently operates simultaneously with phytoextraction, phytodegradation, rhizodegradation, and phytovolatilization. Contaminants captured through groundwater uptake may subsequently undergo biological transformation or sequestration within plant–soil systems.

Unlike engineered hydraulic containment systems that require continuous energy inputs, phytohydraulic systems are powered primarily by solar energy and natural transpiration processes. Their effectiveness, however, depends strongly on climatic conditions, rooting depth, groundwater availability, and long-term vegetation health.

From an ecological engineering perspective, hydraulic control illustrates how plant physiological processes can be harnessed to manage contaminant transport at the landscape scale. By integrating hydrological regulation with biological remediation, phytohydraulics extends the scope of phytoremediation beyond contaminant transformation to encompass the active management of environmental flow systems.

4. INTEGRATION WITH GREEN CHEMISTRY PRINCIPLES (12 PRINCIPLES MAPPING)

The mapping presented in Table 1 demonstrates that phytoremediation exhibits a remarkable degree of alignment with the Twelve Principles of Green Chemistry. Unlike many conventional remediation technologies that rely on energy-intensive operations, chemical reagents, or contaminant transfer between environmental compartments, phytoremediation utilizes naturally occurring biological processes to achieve contaminant removal, transformation, or stabilization. As a result, several green chemistry principles are simultaneously addressed within a single remediation framework.

Particularly strong alignment can be observed with the principles of waste prevention, energy efficiency, renewable feedstocks, catalysis, and design for degradation. Because phytoremediation is typically implemented in situ, it minimizes excavation activities, transportation requirements, and secondary waste generation. Furthermore, the process is largely powered by solar energy through photosynthesis, substantially reducing external energy demands compared with conventional remediation approaches. The use of living plants as renewable biological resources further reflects the principle of renewable feedstocks.

The catalytic role of rhizosphere microorganisms represents another important point of convergence between phytoremediation and green chemistry. In rhizodegradation and phytodegradation systems, plant-associated microbial communities function as natural biocatalysts, accelerating contaminant transformation without the continuous consumption of chemical reagents. Similarly, enzymatic detoxification pathways operating within plant tissues contribute to the degradation or transformation of pollutants into less harmful forms, supporting the principle of design for degradation.

Nevertheless, the relationship between phytoremediation and green chemistry should not be interpreted as absolute. Certain principles, particularly atom economy and real-time analysis for pollution prevention, are only partially fulfilled because phytoremediation often focuses on contaminant removal or transformation rather than chemical synthesis. Moreover, challenges associated with contaminated biomass management and long remediation timeframes indicate that trade-offs may still occur under specific environmental conditions. Consequently, phytoremediation should be viewed not as a perfect embodiment of all green chemistry principles but as one of the remediation technologies most closely aligned with the preventive, resource-efficient, and sustainability-oriented philosophy of green chemistry.

Overall, the strong conceptual convergence between phytoremediation and green chemistry reinforces the view that environmental remediation can be integrated with ecological processes rather than relying solely on external technological interventions. This perspective positions phytoremediation as a key example of how green chemistry principles can be translated into practical strategies for sustainable environmental management.

Table 1. *Alignment of the Twelve Principles of Green Chemistry with Phytoremediation Mechanisms*

Green Chemistry Principle	Core Concept	Corresponding Phytoremediation Mechanism(s)	Conceptual Alignment Explanation
Prevention	Waste prevention rather than treatment	All phytoremediation mechanisms	Operates in situ, reducing secondary waste generation and avoiding excavation, transport, or chemical-intensive post-treatment processes.
Atom Economy	Maximizing incorporation of materials into final products	Phytodegradation, Rhizodegradation	Organic pollutants are enzymatically transformed into less toxic metabolites rather than transferred to another compartment.
Less Hazardous Chemical Syntheses	Minimizing toxicity in chemical processes	Phytodegradation	Detoxification occurs via plant enzymatic systems (e.g., peroxidases, dehalogenases) without synthetic oxidants or hazardous reagents.
Designing Safer Chemicals	Design of inherently safer molecules	Phytodegradation (biotransformation pathways)	Plants metabolically transform contaminants into less toxic or bound forms, mimicking safer chemical design principles.
Safer Solvents and Auxiliaries	Avoiding auxiliary chemicals	All mechanisms	Solar-driven, soil-based remediation minimizes reliance on external solvents, surfactants, or extraction agents.
Energy Efficiency	Minimizing energy requirements	All mechanisms	Phytoremediation is powered primarily by solar energy through photosynthesis, reducing fossil-fuel-dependent remediation infrastructure.

Green Chemistry Principle	Core Concept	Corresponding Phytoremediation Mechanism(s)	Conceptual Alignment Explanation
Use of Renewable Feedstocks	Preference for renewable raw materials	All mechanisms	Plants themselves are renewable biological resources that can be cultivated sustainably.
Reduce Derivatives	Avoid unnecessary derivatization steps	Phytostabilization, Phytoextraction	Direct uptake, adsorption, or stabilization of contaminants occurs without complex chemical modification steps.
Catalysis	Prefer catalytic over stoichiometric processes	Rhizodegradation, Phytodegradation	Root-associated microbial communities function as biocatalysts, accelerating contaminant breakdown without stoichiometric reagent consumption.
Design for Degradation	Products degrade into harmless substances	Phytodegradation	Enzymatic pathways transform pollutants into biodegradable or mineralized products compatible with natural cycles.
Real-time Analysis for Pollution Prevention	Monitoring and control to prevent formation of hazardous substances	Phytoextraction (harvest monitoring)	Biomass contaminant accumulation allows measurable, trackable contaminant removal and site progress monitoring.
Inherently Safer Chemistry for Accident Prevention	Minimizing risk of accidents	All mechanisms	Avoids high-pressure, high-temperature, or hazardous chemical operations common in conventional remediation technologies.

5. LIFE CYCLE AND SUSTAINABILITY ASSESSMENT OF PHYTOREMEDIATION

While phytoremediation is frequently described as an environmentally friendly remediation technology, its sustainability performance must be evaluated beyond contaminant removal efficiency alone. Life Cycle Assessment (LCA) provides a systematic framework for quantifying the environmental impacts associated with a remediation process throughout its entire life cycle (ISO 14040, 2006). In phytoremediation systems, LCA has increasingly been applied to evaluate environmental burdens and sustainability trade-offs associated with plant cultivation, harvesting, biomass management, and post-treatment processes(Vigil et al., 2015; O'Connor et al., 2019). However, conventional LCA frameworks may not fully capture the ecological functions and ecosystem services generated by living remediation systems.

Beyond direct contaminant removal, phytoremediation provides additional sustainability benefits through rhizosphere-mediated ecosystem processes. Root exudates, microbial communities, and plant-derived signaling compounds contribute

to nutrient cycling, soil health restoration, and ecological resilience. These ecosystem services are generally absent from conventional remediation technologies and represent an additional sustainability advantage that is often overlooked in life-cycle assessments. Consequently, future sustainability evaluations should incorporate ecosystem service indicators alongside conventional environmental impact metrics.

Conventional remediation technologies such as excavation, soil washing, thermal desorption, and chemical oxidation are often characterized by high energy consumption, intensive material use, and substantial greenhouse gas emissions. In contrast, phytoremediation relies primarily on solar energy and biological processes, resulting in significantly lower energy requirements and reduced carbon footprints compared with many conventional remediation approaches (Amponsah et al., 2018; Espada et al., 2022). Comparative LCA studies have demonstrated that phytoremediation may reduce overall environmental impacts by decreasing fossil fuel consumption, minimizing transportation needs, and limiting the use of chemical reagents.

From a sustainability perspective, phytoremediation contributes simultaneously to environmental, economic, and social dimensions of sustainable development. Environmentally, it improves soil quality, supports biodiversity, and enhances ecosystem services. Economically, it is often more cost-effective than conventional remediation methods, particularly for large contaminated areas with low to moderate pollutant concentrations. Socially, vegetated remediation sites may improve landscape aesthetics, reduce dust generation, and provide recreational or ecological value to local communities (Pilon-Smits, 2005).

However, sustainability assessments must also consider potential trade-offs. Biomass contaminated with accumulated pollutants may require safe disposal, controlled combustion, or resource recovery processes. Furthermore, prolonged remediation periods may increase land occupation and delay site redevelopment. Consequently, the sustainability performance of phytoremediation depends not only on pollutant removal efficiency but also on biomass management strategies, ecosystem responses, and long-term environmental outcomes.

Recent developments increasingly integrate Life Cycle Sustainability Assessment (LCSA), which combines environmental LCA, Life Cycle Costing (LCC), and Social Life Cycle Assessment (S-LCA). Such integrated approaches provide a more comprehensive evaluation of phytoremediation systems and support decision-making aligned with green chemistry, circular economy, and regenerative environmental management objectives (Klöpffer, 2008; Zamagni et al., 2013). By accounting for environmental, economic, and social dimensions simultaneously, LCSA offers a holistic framework for assessing the long-term sustainability of phytoremediation technologies.

6. LIMITATIONS AND RISK CONSIDERATIONS

Despite its numerous environmental advantages, phytoremediation is not universally applicable and should not be regarded as a standalone solution for all contami-

nation scenarios. Its effectiveness is influenced by contaminant characteristics, plant physiology, climatic conditions, soil properties, and site-specific ecological factors.

One of the primary limitations is the relatively slow remediation rate. Because contaminant removal depends on plant growth and metabolic activity, remediation may require several growing seasons or even decades to achieve regulatory targets, particularly for heavily contaminated sites (Ali et al., 2013). This temporal constraint can limit applicability where rapid risk reduction is required.

Another significant challenge is contaminant bioavailability. Many pollutants, particularly heavy metals, may be strongly bound to soil minerals or organic matter, reducing their accessibility for plant uptake. Although amendments such as chelating agents can increase bioavailability, they may also enhance contaminant mobility and increase the risk of groundwater contamination.

Biomass management represents an additional concern. Harvested plant material containing accumulated contaminants may become secondary hazardous waste if not properly treated. For metal-contaminated biomass, thermal treatment, phytomining, or controlled disposal may be necessary. In the case of organic contaminants, incomplete degradation products may sometimes persist within plant tissues, requiring further assessment.

Ecological risks must also be considered. Contaminants accumulated in plant tissues may enter food webs through herbivory, potentially leading to trophic transfer and biomagnification. The introduction of non-native hyperaccumulator species may also alter local biodiversity and ecosystem dynamics. Furthermore, phytovolatilization, while reducing contaminant concentrations in soil or water, may redistribute pollutants into the atmosphere, raising concerns regarding cross-media contamination.

Climate dependency constitutes another important limitation. Plant growth, microbial activity, and contaminant uptake are strongly influenced by temperature, precipitation, soil moisture, and seasonal variation. Consequently, remediation performance may vary substantially among geographic regions and under future climate change scenarios. Rising temperatures, altered precipitation patterns, and elevated atmospheric CO_2 concentrations may influence root exudation, microbial community structure, contaminant bioavailability, and overall remediation efficiency. Consequently, climate resilience is becoming an increasingly important consideration in phytoremediation design and assessment.

These limitations emphasize that phytoremediation should be viewed as a context-dependent remediation strategy whose implementation requires comprehensive risk assessment, site characterization, and long-term monitoring.

A persistent challenge in phytoremediation research is the discrepancy between laboratory-scale performance and field-scale implementation. Rhizosphere interactions identified under controlled conditions may not be reproducible in heterogeneous field environments where contaminant distributions, hydrological conditions, microbial communities, and climatic factors vary substantially. Consequently, field

validation remains essential before large-scale deployment. Moreover, mixed-contaminant scenarios frequently encountered in real-world environments may alter contaminant bioavailability and microbial responses in ways that are difficult to predict from single-pollutant laboratory studies. Such complexity further emphasizes the necessity of long-term field trials and site-specific remediation designs.

7. FUTURE PERSPECTIVES: GENETIC ENGINEERING, OMICS TECHNOLOGIES AND THE CIRCULAR BIOECONOMY

Advances in plant biotechnology, systems biology, and sustainability science are expanding the potential applications of phytoremediation beyond conventional contaminant removal. Emerging research increasingly focuses on enhancing remediation efficiency while integrating resource recovery and circular economy principles.

Genetic engineering offers opportunities to improve plant tolerance, contaminant uptake, translocation, and degradation capacity. Transgenic plants expressing bacterial genes such as merA and merB have demonstrated enhanced mercury detoxification, while modifications targeting metal transporter proteins and antioxidant pathways have improved heavy metal accumulation and stress tolerance (Meagher, 2000). More recently, genome-editing technologies such as CRISPR/Cas systems have enabled precise modification of genes associated with contaminant transport and metabolism, opening new possibilities for next-generation phytoremediation systems.

Simultaneously, omics technologies—including genomics, transcriptomics, proteomics, metabolomics, and microbiomics—are providing unprecedented insight into plant–microbe–contaminant interactions. These approaches facilitate the identification of key metabolic pathways, stress-response mechanisms, and microbial communities involved in remediation processes. Integration of multi-omics datasets with artificial intelligence (AI) and machine learning (ML) is expected to accelerate the selection and optimization of remediation species and microbial consortia. By combining molecular data with environmental variables such as soil chemistry, contaminant speciation, hydrological conditions, and climatic factors, predictive models may enable site-specific phytoremediation design and improve the scalability of remediation strategies.

Another emerging direction is the incorporation of phytoremediation into circular bioeconomy frameworks. Rather than treating contaminated biomass solely as waste, researchers increasingly explore opportunities for biomass valorization. Depending on contaminant type and concentration, harvested biomass may be converted into bioenergy, biochar, industrial feedstocks, or sources of valuable metals through phytomining processes (Robinson et al., 2009; Sheoran et al., 2016). Such approaches transform remediation activities into resource recovery systems, consistent with green chemistry principles of waste prevention and material circularity.

Future phytoremediation systems are therefore likely to evolve from passive remediation technologies into multifunctional ecological infrastructures capable

of contaminant removal, carbon sequestration, biomass production, biodiversity enhancement, and resource recovery. This transition reflects a broader shift toward regenerative environmental management in which remediation contributes not only to pollution control but also to ecosystem restoration and sustainable development.

At the same time, future phytoremediation systems must be designed to remain effective under changing climatic conditions. Elevated atmospheric CO_2 concentrations, increasing temperatures, and altered precipitation regimes may influence root exudation patterns, microbial community assembly, contaminant bioavailability, and remediation efficiency. Consequently, the development of climate-resilient phytoremediation strategies will represent a major research priority, requiring the integration of plant biotechnology, rhizosphere ecology, systems biology, and predictive modeling approaches.

Collectively, these developments reinforce the role of phytoremediation as a green chemistry–aligned technology that integrates renewable biological processes, resource circularity, and ecosystem-based remediation within a sustainability framework.

CONCLUSION

Environmental contamination remains one of the most significant challenges to sustainable development, requiring remediation strategies that are not only effective but also environmentally compatible, resource-efficient, and socially acceptable. Within this context, phytoremediation has emerged as a promising nature-based technology that harnesses the adaptive capacities of plants and their associated microbiota to remove, stabilize, transform, degrade, or contain a wide range of contaminants through naturally occurring biological processes.

As discussed throughout this chapter, phytoremediation encompasses multiple and often interconnected mechanisms, including phytoextraction, phytostabilization, phytodegradation, rhizodegradation, phytovolatilization, rhizofiltration, and hydraulic control. Collectively, these pathways demonstrate the remarkable ability of plant–soil–microbe systems to influence contaminant mobility, bioavailability, transformation, and environmental fate. Rather than relying on intensive mechanical or chemical interventions, phytoremediation primarily uses solar-driven biological processes and ecological interactions, making it inherently compatible with the preventive, sustainability-oriented philosophy of green chemistry.

An evaluation of phytoremediation within the Twelve Principles of Green Chemistry reveals strong conceptual alignment. Phytoremediation minimizes waste generation, reduces external energy requirements, utilizes renewable biological resources, promotes catalytic transformation pathways, and supports the conversion of contaminants into less hazardous forms. Beyond pollution control, phytoremediation contributes to broader sustainability objectives by enhancing ecosystem services, improving soil health, supporting biodiversity, reducing environmental disturbance, and creating opportunities for resource recovery within circular bioeconomy frameworks such as phytomining and biomass valorization.

At the same time, phytoremediation should not be viewed solely as a plant-based technology. Contemporary research increasingly recognizes remediation systems as holobionts in which plants, rhizospheric microorganisms, endophytes, mycorrhizal fungi, and environmental factors function as integrated components of a dynamic ecological network. Consequently, remediation outcomes often emerge from coordinated biological interactions rather than from plant metabolism alone. This systems perspective highlights the importance of considering microbial ecology, soil geochemistry, hydrology, and climatic conditions alongside plant physiology when designing and evaluating phytoremediation strategies.

Despite its numerous advantages, phytoremediation is not without limitations. Challenges related to contaminant bioavailability, remediation time requirements, biomass management, ecological risks, atmospheric redistribution of certain contaminants, climate dependency, and field-scale implementation continue to constrain broader application. These limitations underscore the importance of site-specific design, comprehensive risk assessment, and long-term monitoring to ensure both remediation effectiveness and environmental safety.

Looking forward, advances in microbiome engineering, genome editing technologies, synthetic biology, multi-omics approaches, artificial intelligence, and systems biology are expected to substantially enhance the efficiency, predictability, and scalability of phytoremediation systems. These developments are gradually transforming phytoremediation from an empirical remediation practice into a predictive and optimized environmental biotechnology. Simultaneously, growing interest in climate-resilient remediation strategies and circular bioeconomy models is expanding the role of phytoremediation beyond pollution control toward ecosystem restoration, resource recovery, carbon management, and regenerative environmental stewardship.

Ultimately, phytoremediation represents far more than a collection of contaminant removal techniques. It is a solar-powered ecological engineering platform that integrates plant physiology, microbial metabolism, soil biogeochemistry, and environmental processes into a unified remediation framework. Viewed through the lens of green chemistry and sustainability science, phytoremediation exemplifies the transition from reactive pollution treatment toward preventive, regenerative, and systems-oriented environmental management. As environmental challenges become increasingly complex in the twenty-first century, phytoremediation offers a compelling model for harnessing biological systems to restore contaminated ecosystems while advancing broader sustainability and resilience goals.

SONUÇ

Çevresel kontaminasyon (kirlenme), sürdürülebilir kalkınmanın önündeki en önemli zorluklardan biri olmaya devam etmekte; yalnızca etkili değil, aynı zamanda çevresel olarak uyumlu, kaynak açısından verimli ve toplumsal olarak kabul edilebilir remediasyon (iyileştirme) stratejilerini gerektirmektedir. Bu bağlamda fitoremediasyon; geniş bir kirletici yelpazesini uzaklaştırmak, stabilize etmek, dönüştürmek, parçalamak veya hapsetmek amacıyla, doğal olarak meydana gelen biyolojik süreçler aracılığıyla bitkilerin ve onlarla ilişkili mikrobiyotanın adaptasyon kapasitelerinden yararlanan, gelecek vaat eden, doğa tabanlı bir teknoloji olarak ortaya çıkmıştır.

Bu bölüm boyunca tartışıldığı üzere fitoremediasyon; fitoekstraksiyon, fitostabilizasyon, fitodegradasyon, rizodegradasyon, fitovolatilizasyon, rizofiltrasyon ve hidrolik kontrol dahil olmak üzere çoklu ve genellikle birbiriyle bağlantılı mekanizmaları kapsamaktadır. Bu yollar toplu olarak, bitki-toprak-mikrop sistemlerinin kirletici mobilitesi (hareketliliği), biyoyararlanımı, dönüşümü ve çevresel akıbeti üzerindeki dikkate değer etkileme yeteneğini göstermektedir. Fitoremediasyon, yoğun mekanik veya kimyasal müdahalelere güvenmek yerine, öncelikle güneş enerjisiyle çalışan biyolojik süreçleri ve ekolojik etkileşimleri kullanır; bu da onu yeşil kimyanın önleyici, sürdürülebilirlik odaklı felsefesiyle doğası gereği uyumlu hale getirir.

Fitoremediasyonun Yeşil Kimyanın On İki İlkesi çerçevesinde değerlendirilmesi, güçlü bir kavramsal uyumu ortaya koymaktadır. Fitoremediasyon atık oluşumunu en aza indirir, dış enerji gereksinimlerini azaltır, yenilenebilir biyolojik kaynakları kullanır, katalitik dönüşüm yollarını teşvik eder ve kirleticilerin daha az tehlikeli formlara dönüştürülmesini destekler. Kirlilik kontrolünün ötesinde fitoremediasyon; ekosistem hizmetlerini geliştirerek, toprak sağlığını iyileştirerek, biyoçeşitliliği destekleyerek, çevresel bozulmayı azaltarak ve fitomadencilik (phytomining) ile biyokütle değerlemesi (biomass valorization) gibi döngüsel biyoekonomi çerçeveleri içinde kaynak geri kazanımı için fırsatlar yaratarak daha geniş sürdürülebilirlik hedeflerine katkıda bulunur.

Aynı zamanda fitoremediasyon, yalnızca bitki tabanlı bir teknoloji olarak görülmemelidir. Çağdaş araştırmalar, remediasyon sistemlerini; bitkilerin, rizosferik mikroorganizmaların, endofitlerin, mikorizal mantarların ve çevresel faktörlerin dinamik bir ekolojik ağın entegre bileşenleri olarak işlev gördüğü holobiontlar olarak giderek daha fazla tanımaktadır. Sonuç olarak, remediasyon çıktıları genellikle sadece bitki metabolizmasından ziyade, koordineli biyolojik etkileşimlerden ortaya çıkar. Bu sistem perspektifi, fitoremediasyon stratejileri tasarlanırken ve değerlendirilirken bitki fizyolojisinin yanı sıra mikrobiyal ekoloji, toprak jeokimyası, hidroloji ve iklim koşullarının dikkate alınmasının önemini vurgulamaktadır.

Sayılamayacak kadar çok avantajına rağmen fitoremediasyon sınırlamalardan yoksun değildir. Kirletici biyoyararlanımı, remediasyon süresi gereksinimleri, biyokütle yönetimi, ekolojik riskler, belirli kirleticilerin atmosferik olarak yeniden dağılımı, iklim bağımlılığı ve saha ölçeğinde uygulama ile ilgili zorluklar, daha geniş çaplı uygulamaları kısıtlamaya devam etmektedir. Bu sınırlamalar, hem remediasyon

etkinliğini hem de çevresel güvenliği sağlamak için sahaya özgü tasarımın, kapsamlı risk değerlendirmesinin ve uzun vadeli izlemenin öneminin altını çizmektedir.

İleriye bakıldığında; mikrobiyom mühendisliği, genom düzenleme teknolojileri, sentetik biyoloji, multi-omiks yaklaşımları, yapay zeka ve sistem biyolojisindeki gelişmelerin, fitoremediasyon sistemlerinin verimliliğini, öngörülebilirliğini ve ölçeklenebilirliğini önemli ölçüde artırması beklenmektedir. Bu gelişmeler fitoremediasyonu, ampirik bir remediasyon uygulamasından kademeli olarak öngörülebilir ve optimize edilmiş bir çevresel biyoteknolojiye dönüştürmektedir. Eş zamanlı olarak, iklim dirençli remediasyon stratejilerine ve döngüsel biyoeconomi modellerine duyulan büyüyen ilgi, fitoremediasyonun rolünü kirlilik kontrolünün ötesine; ekosistem restorasyonu, kaynak geri kazanımı, karbon yönetimi ve rejeneratif (yenileyici) çevresel sorumluluğa doğru genişletmektedir.

Nihayetinde fitoremediasyon, kirletici uzaklaştırma tekniklerinin bir araya gelmesinden çok daha fazlasını temsil eder. Bitki fizyolojisini, mikrobiyal metabolizmayı, toprak biyojeokimyasını ve çevresel süreçleri birleşik bir remediasyon çerçevesinde bütünleştiren, güneş enerjisiyle çalışan bir ekolojik mühendislik platformudur. Yeşil kimya ve Sürdürülebilirlik bilimi merceğinden bakıldığında fitoremediasyon; tepkisel kirlilik arıtımından önleyici, rejeneratif ve sistem odaklı çevre yönetimine geçişi örneklemektedir. Çevresel zorluklar yirmi birinci yüzyılda giderek daha karmaşık hale gelirken fitoremediasyon, daha geniş sürdürülebilirlik ve dirençlilik hedeflerini ilerletirken, kontamine olmuş (kirletilmiş) ekosistemleri restore etmek için biyolojik sistemlerden yararlanma konusunda zorlayıcı bir model sunmaktadır.

REFERENCES

1. Ali, H., Khan, E., & Sajad, M. A. (2013). Phytoremediation of heavy metals—Concepts and applications. Chemosphere, 91(7), 869–881. https://doi.org/10.1016/j.chemosphere.2013.01.075
2. Alpizar, F., Backhaus, T., Decker, N., Eilks, I., Escobar-Pemberthy, N., Fantke, P., Geiser, K., Ivanova, M., Jolliet, O., Kim, H.-S., Khisa, K., Gundimeda, H., Slunge, D., Stec, S., Tickner, J., Tyrer, D., Urho, N., Visser, R., Yarto, M., & Suzuki, N. (2019). UN Environment Global Chemicals Outlook II - From Legacies to Innovative Solutions: Implementing the 2030 Agenda for Sustainable Development. https://backend.orbit.dtu.dk/ws/portalfiles/portal/170843838/GCOII_synth.pdf
3. Amponsah, N. Y., Wang, J., & Zhao, L. (2018). A review of life cycle greenhouse gas (GHG) emissions of commonly used ex-situ soil treatment technologies. Journal of Cleaner Production, 186, 514–525.
4. Anastas, P. T., & Eghbali, N. (2010). Green chemistry: Principles and practice. Chemical Society Reviews, 39, 301–312. https://doi.org/10.1039/B918763B
5. Anastas, P. T., & Warner, J. C. (1998). Green chemistry: Theory and practice. 148 p. Oxford University Press.
6. Anderson, T.A., Guthrie, E.A. & Walton, B.T. (1993) Bioremediation in the Rhizosphere. Environmental Science & Technology, 27, 2630-2636. https://doi.org/10.1021/es00049a001
7. Baker, A.J.M. & Brooks, R.R. (1989) Terrestrial Higher Plants which Hyperaccumulate Metallic Elements. A Review of Their Distribution, Ecology and Phytochemistry. Biorecovery, 1, 81-126. https://doi.org/10.1080/01904168109362867
8. Delgado, N., Bermeo, L., Hoyos, D.A., Peñuela, G.A., Capparelli, A., Marino, D., Navarro, A. & Casas-Zapata, J.C. (2020). Occurrence and removal of pharmaceutical and personal care products using subsurface horizontal flow constructed wetlands. Water Res.,187:116448. https://doi.org/10.1016/j.watres.2020.116448.
9. Dietz, A.C. & Schnoor, J.L. (2001). Advances in phytoremediation. Environ Health Perspect. 109 Suppl 1(Suppl 1):163-8. https://doi.org/10.1289/ehp.01109s1163.
10. Dominguez, J.J.A., Bacosa, H.P., Chien, M.-F. & Inoue C. (2019). Enhanced degradation of polycyclic aromatic hydrocarbons [PAHs) in the rhizosphere of sudangrass (Sorghum × drummondii]. Chemosphere, 234,789-795. https://doi.org/10.1016/j.chemosphere.2019.05.290
11. Dushenkov, V., Kumar, P. B. A. N., Motto, H., & Raskin, I. (1995). Rhizofiltration: The use of plants to remove heavy metals from aqueous streams. Environmental Science & Technology, 29(5), 1239–1245. https://doi.org/10.1021/es00005a015
12. Espada, J. J., Rodríguez, R., Gari, V., Salcedo-Abraira, P., & Bautista, L. F. (2022). Coupling phytoremediation of Pb-contaminated soil and biomass energy production: A comparative Life Cycle Assessment. Science of the Total Environment, 840, 156675.
13. FAO & ITPS. (2015). Status of the world's soil resources. FAO. Technical Summary 94 p.
14. Geissdoerfer, M., et al. (2017). The circular economy—A new sustainability paradigm? Journal of Cleaner Production, 143, 757–768. https://doi.org/10.1016/j.jclepro.2016.12.048

15. Ghori, N. H., Ghori, T., Hayat, M. Q., Imadi, S. R., Gul, A., Altay, V., & Ahmad, P. (2019). Heavy metal stress and responses in plants. International Journal of Environmental Science and Technology, 16, 1807-1828.
16. Guo, L., Ouyang, X., Wang, W., Qiu, X., Zhao, Y.L., Xu, P. & Tang H. (2024). Fine-tuning an aromatic ring-hydroxylating oxygenase to degrade high-molecular-weight PAHs. J. Biol. Chem., 300 (6), 107343. https://doi.org/10.1016/j.jbc.2024.107343.
17. ISO. (2006). Environmental management—Life cycle assessment: Principles and framework (ISO 14040:2006). Geneva, Switzerland: International Organization for Standardization.
18. Klöpffer, W. (2008). Life cycle sustainability assessment of products. The International Journal of Life Cycle Assessment, 13(2), 89–95. https://doi.org/10.1065/lca2008.02.376
19. Krämer U. (2010). Metal hyperaccumulation in plants. Annu Rev Plant Biol. 61:517-34. https://doi.org/10.1146/annurev-arplant-042809-112156.
20. Meagher, R.B. (2000). Phytoremediation of Toxic Elemental and Organic Pollutants. Current Opinion in Plant Biology, 3, 153-162. http://dx.doi.org/10.1016/S1369-5266(99)00054-0
21. Medić, A.B. & Karadžić I.M. (2022). Pseudomonas in environmental bioremediation of hydrocarbons World J. Microbiol. Biotechnol., 38 (10), 165. https://doi.org/10.1007/s11274-022-03349-7
22. McCutcheon, S.C. & Schnoor, J.L. (2003). Overview of Phytotransformation and Control of Wastes. In Phytoremediation (eds J.L. Schnoor, A. Zehnder, S.C. McCutcheon and J.L. Schnoor). https://doi.org/10.1002/047127304X.ch1
23. O'Connor, D., Zheng, X., Hou, D., Shen, Z., Li, G., Miao, G., O'Connell, S., & Guo, M. (2019). Phytoremediation: Climate change resilience and sustainability assessment at a coastal brownfield redevelopment. Environment International, 130, 104945. https://doi.org/10.1016/j.envint.2019.104945
24. Pilon-Smits, E. (2005). Phytoremediation. Annual Review of Plant Biology, 56, 15–39. https://doi.org/10.1146/annurev.arplant.56.032604.144214
25. Robinson, B., Bañuelos, G., Conesa, H. M., Evangelou, M. W. H., & Schulin, R. (2009). The phytomanagement of trace elements in soil. Critical Reviews in Plant Sciences, 28(4), 240–266. https://doi.org/10.1080/07352680903035424
26. Rockström, J., Steffen, W., Noone, K., Persson, Å., Chapin, F.S., Lambin, E.F., Lenton, T.M., Scheffer, M., Folke, C., Schellnhuber, H.J., Nykvist, B., de Wit, C.A., Hughes, T., van der Leeuw, S., Rodhe, H., Sörlin, S., Snyder, P.K., Costanza, R., Svedin, U., Falkenmark, M., Karlberg, L., Corell, R.W., Fabry, V.J., Hansen, J., Walker, B., Liverman, D., Richardson, K., Crutzen, P. & Foley, J.A. (2009). A safe operating space for humanity. Nature, 461, 472-475, https://doi.org/10.1038/461472a.
27. Rockwood, D. L., Naidu, C. V., Carter, D. R., Rahmani, M., Spriggs, T. A., Lin, C., Alker, G. R., Isebrands, J. G., & Segrest, S. A. (2004). Short-Rotation Woody Crops and Phytoremediation: Opportunities for Agroforestry? Agroforestry Systems, 61–62, 51–63. https://doi.org/10.1023/B:AGFO.0000028989.72186.e6
28. Salt, D. E., Blaylock, M., Kumar, N. P. B. A., Dushenkov, V., Ensley, B. D., Chet, I., & Raskin, I. (1995). Phytoremediation: A novel strategy for the removal of toxic metals from the environment using plants. Nature Biotechnology, 13(5), 468–474. https://doi.org/10.1038/nbt0595-468

29. Sheoran, V., Sheoran, A. S., & Poonia, P. (2016). Phytomining: A review. Mineral Processing and Extractive Metallurgy Review, 37(5), 336–347. https://doi.org/10.1080/08827508.2015.1115998

30. Smith, R. A. H., & Bradshaw, A. D. (1979). The Use of Metal Tolerant Plant Populations for the Reclamation of Metalliferous Wastes. Journal of Applied Ecology, 16(2), 595–612. https://doi.org/10.2307/2402534

31. Steffen, W., et al. (2015). Planetary boundaries: Guiding human development on a changing planet. Science, 347. https://www.giss.nasa.gov/pubs/docs/2009/2009_Rockstrom_ro02010z.pdf

32. Tasleem, H., Anwar, S., Kausar, A., & Kausar, A. (2026). Phytostabilization of cadmium and lead in maize using biochar and nanobiochar: effects on soil properties and metal dynamics. International Journal of Phytoremediation, 1–15. https://doi.org/10.1080/15226514.2026.2617949

33. Terry N, Zayed AM, De Souza MP, Tarun AS. (2000). Selenium in Higher Plants. Annu Rev Plant Physiol Plant Mol Biol. 51:401-432. https://doi.org/10.1146/annurev.arplant.51.1.401.

34. Testa, G., Ciaramella, B. R., Fernando, A. L., Kotoula, D., Scordia, D., Gomes, L. A., Cosentino, S. L., Alexopoulou, E., & Papazoglou, E. G. (2024). Harnessing Lignocellulosic Crops for Phytomanagement of Contaminated Soils: A Multi-Country Study. Plants, 13(19), 2671. https://doi.org/10.3390/plants13192671

35. Thijs, S., Sillen, W., Rineau, F., Weyens, N., & Vangronsveld, J. (2016). Towards an enhanced understanding of plant–microbiome interactions to improve phytoremediation: engineering the metaorganism. Frontiers in Microbiology, 7, 341.

36. United Nations. (2022). World population prospects 2022. https://www.un.org/development/desa/pd/sites/www.un.org.development.desa.pd/files/wpp2022_summary_of_results.pdf

37. WHO. (2017). Guidelines for drinking-water quality. https://iris.who.int/server/api/core/bitstreams/1b7a285e-3635-45dd-a1a9-6068c8fbe173/content

38. Vandenkoornhuyse, P., Quaiser, A., Duhamel, M., Le Van, A., & Dufresne, A. (2015). The importance of the microbiome of the plant holobiont. New Phytologist, 206(4), 1196-1206

39. Vigil, M., Marey-Pérez, M. F., Martínez Huerta, G., & Álvarez Cabal, J. V. (2015). Is phytoremediation without biomass valorization sustainable? Comparative life-cycle assessment of landfilling versus anaerobic co-digestion. Science of the Total Environment, 505, 844–850. https://doi.org/10.1016/j.scitotenv.2014.10.047

40. Zamagni, A., Pesonen, H. L., & Swarr, T. (2013). From LCA to life cycle sustainability assessment: Concept, practice and future directions. The International Journal of Life Cycle Assessment, 18, 1637–1641.

GREEN CHEMISTRY TECHNOLOGIES FOR SUSTAINABLE PLANT PRODUCTION

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ABSTRACT

Demand for food has increased exponentially in recent years. In addition, technological advancements and the aim of making plant production faster, more efficient, and more economical have led to the use of various new applications and materials. In this context, all these innovations have created significant potential for environmental pollution from pre-planting preparation through harvesting in plant production. The increase in environmental pollution, which disrupts the balance of the ecosystem every passing day, the destruction of living spaces, and the serious problems caused by the negative effects of climate change have led humanity towards more environmentally friendly and sustainable approaches. Green chemistry is one of the techniques adopted due to its beneficial effects on health as well as ecological balance. In this study, the methods and applications developed to prevent environmental pollution in plant production at the design and process levels, from a technological and engineering perspective within the green chemistry approach, have been emphasized. In plant production, in addition to fertilizers, pesticides, and nanotechnology applications using green chemistry approaches, engineering solutions for conserving natural resources and managing waste in covered production have been introduced, with details provided. For all applications, the environmental and economic contributions to be obtained by reviewing the literature have been emphasized.

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1. INTRODUCTION

In the world, 40% of the primary production resulting from photosynthesis is directly consumed by humans and human-related activities. The continued population growth has also contributed to this situation, leading to an even greater rise in consumption (Haktanır, 2009). In this context, the use of chemical-intensive inputs and advanced technologies has started to become widespread in parallel with the need for plant production and food. The irresponsible and incorrect use of these innovations, while providing benefits in terms of production speed and economic profitability, has caused significant damage to the environment, such as the pollution of underground waters, the formation of harmful toxicities in foods for human health, damage to the ecosystem, salinity, and erosion. In particular, the growing impact of environmental issues has made the subject's importance recognized worldwide (Karaer and Gürlük, 2003; Aydın Eryılmaz and Kılıç, 2018). Therefore, the transition to smarter, more sustainable methods has been facilitated. Sustainable plant production practices that adopt green chemistry (GC) approaches stand out in this context.

The increased use of newly developed technologies with a GC approach, compared to traditional plant production methods, represents a significant advancement in minimizing environmental pollution and achieving sustainable plant production. In this context, there are various applications for every stage of plant production. The replacement of chemical products with biological fertilizers and pesticides, the implementation of soil pollution prevention practices, the proper management of irrigation water, and the use of plant waste for energy recovery are all examples of GC approaches in plant production (Valavanidis, 2016). All these practices have direct and significant impacts on ensuring food security, a major issue in plant production.

This study aims to examine practices aimed at reducing environmental pollution from plant production at the design and process levels within the framework of GC principles. In this context, the detailing of macro and micro applications with engineering and technological dimensions and the summarization of studies in the literature that include these applications have been carried out.

2. AGRICULTURAL POLLUTION IN PLANT PRODUCTION: SOURCES AND EFFECTS

Plant production is a fundamental resource in meeting people's nutritional needs. Additionally, today, plant production offers many benefits, including serving as a food source for people, contributing to the national economy and national income, providing raw materials for industry, and impacting ecological balance. Especially the lack of any alternative to this sector has made plant production indispensable throughout human history (Doğan et al., 2015). However, plant production has reached its present state through certain stages and transformations from the very first day. In ancient times, simple tools and equipment were used, animals were

utilized, and natural animal manure and plant residues were utilized. Since the 1950s, due to population growth, technological advancements, and the expansion of the economic market, all these parameters have been replaced by heavy machinery and modern tools, chemical fertilizers, and pesticides. However, in addition to the negative effects of these developments, the introduction of incorrect and unconscious practices has led to environmental pollution issues in plant production (Sönmez et al., 2008; Tapkı et al., 2021; Akkeçeci, 2025). Agricultural pollution sources that arise during plant production are shown in Figure 1.

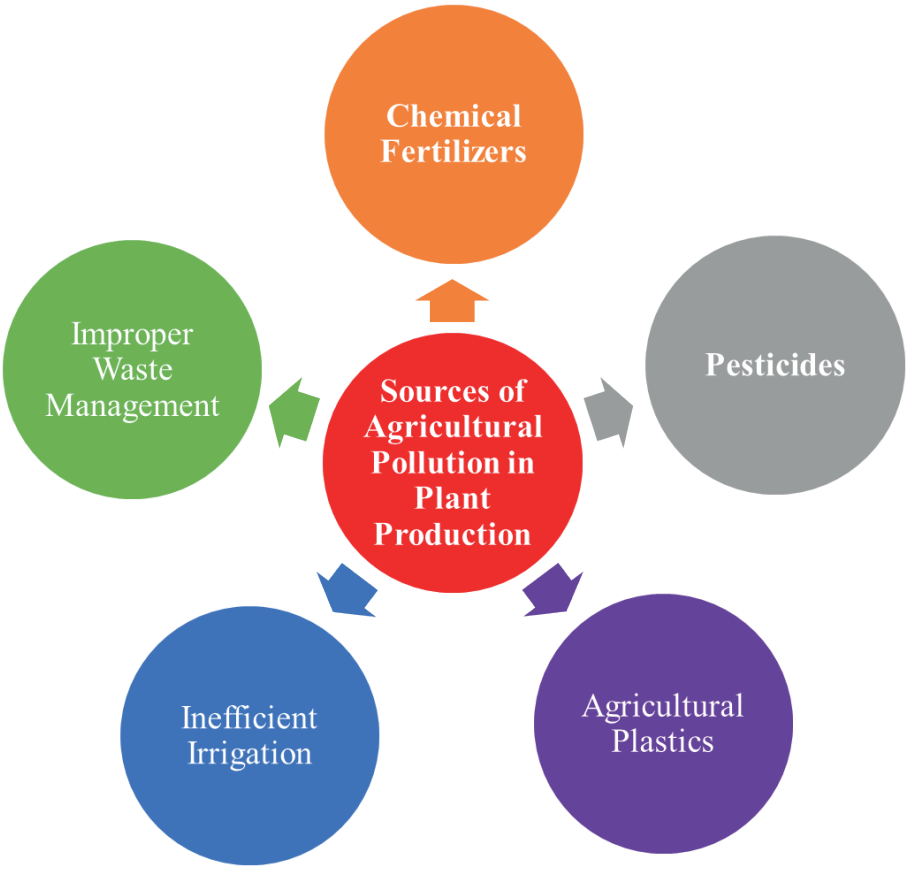

Figure 1. *Sources of agricultural pollution arising during plant production*

2.1. Chemical Fertilizer-Induced Pollution

Chemical fertilizers have positive effects on plant quality and growth in plant production. Additionally, it has advantages such as being a cost-effective food source, requiring no specific fermentation period compared to organic fertilizers, and being suitable for immediate use (Finez and Talimbay, 2023; Jote, 2023). For this reason, its use has become extremely widespread in today's world. However, the use of chemical fertilizers also brings along several environmental issues. Chemical fer-

tilizers have various adverse impacts on all components of nature (Cüre, 2022). The negative effects arising from these environmental components also pose a danger to soil-dwelling organisms and to humans and animals that drink the water and breathe the air. Types of pollution and their possible effects resulting from chemical fertilizers are presented in Table 1 (Sönmez, 2008; Cüre, 2022).

Table 1. *Types of pollution and their possible effects resulting from chemical fertilizers (Sönmez, 2008; Cüre, 2022)*

Environmental Component	Type of Pollution	Possible Effects
Soil	Heavy Metal Accumulation	Changes in plant metabolic activity can lead to reductions in quality and yield.
	Salinity	Losses in product quality and efficiency can occur.
	pH Decrease	It can lead to decreased productivity and increased levels of hazardous chemicals in the soil.
Water	Eutrophication	It can degrade water quality and harm aquatic life.
	Nitrate Accumulation	A decrease in vitality and water consumption by living beings can lead to health problems.
Air	Gas Emission	It can deplete the ozone layer and increase the greenhouse effect.

2.2. Pesticide-Induced Pollution

The absence of pesticide use during plant production can lead to product losses reaching up to 60%. To minimize product losses, the use of pesticides has become quite widespread worldwide (Tiryaki et al., 2010). The immoderate and unnecessary use of these chemicals is harming ecosystems and human health. Pesticides can be ingested, inhaled, or absorbed through contact by living organisms. Therefore, while the formation of food contamination in plant production due to pesticide effects poses a danger, their spread into the environment through air and water also poses various dangers to all living beings. The possible adverse consequences of pesticide use can be expressed as follows (Maksymıv, 2015; Mahmood et al., 2016);

- Pesticides pose a health risk to aquatic ecosystems and organisms that use water.
- It can mix with groundwater, causing pollution.
- In agricultural production, it can negatively affect not only harmful weeds but also harmless trees and plants in the region.
- It can cause reproductive and immune system problems, as well as diseases like cancer, in people exposed to the area.

2.3. Improper Waste Management-Induced Pollution

In plant production, in addition to chemical fertilizers, natural fertilizers obtained from livestock animal farms can also be used. These fertilizers need to be properly stored from their collection from livestock farms to their application on

agricultural land. In this process, improper storage or mismanagement of fertilizers can lead to nutrient loss before they are used for plant production, while also causing environmental pollution. Failure to use stored animal manure under appropriate weather conditions during plant production can pollute water sources around agricultural land and kill living organisms. Additionally, improper application of natural fertilizer to agricultural land can lead to odor problems, soil compaction, and disruption of soil nutrient balance (Olgun, 2011).

2.4. Inefficient Irrigation-Induced Pollution

One of the most important practices in plant production, improper and unconscious irrigation, has many negative effects on environmental health and the economy. Uncontrolled irrigation of agricultural lands leads to soil salinization and deterioration in groundwater quality (Emekli and Topakçı, 2009). Additionally, mismanagement and excessive water consumption during unconscious irrigation lead to drought, decreased yields, and, consequently, the inability to carry out agricultural production in some areas (Çakmak and Gökalp, 2013). Incorrect irrigation practices, along with the application of chemical fertilizers and pesticides to the land, can lead to the emergence of diseases among people and animals living in and consuming water from rivers and reservoirs, as well as among those swimming in them (Kendal and Sayar, 2013).

2.5. Agricultural Plastics-Induced Pollution

Environmental pollution arises from the plastic packaging of equipment and materials used at various stages of plant production, or from their transformation into plastic waste over time. In this context, fertilizers, seeds, pesticide packaging, irrigation pipes and equipment, greenhouse covers, pots, and crates are sources of plastic waste in plant production (Doru and Atış, 2025). Plastic waste is a significant contributor to ecosystem pollution. It negatively affects plant development, significantly degrading soil physical properties and polluting underground waters. Additionally, the accumulation of these plastic wastes in plant products and their consumption by humans also has negative effects on human health (Lakhiar et al., 2024).

3. PRINCIPLES OF GREEN CHEMISTRY AND INTEGRATION INTO PLANT PRODUCTION

Green chemistry can be defined as an approach that encompasses many principles aimed at eliminating or minimizing the consumption and formation of materials that threaten the environment and the health of living beings at every stage, from the design of chemicals to their application for various purposes (Anastas and Warner, 1998; Çakmak et al., 2012; Sogut and Çelebi, 2020). GC practices have a significant impact on creating a more sustainable production process and enhancing animal welfare. In this context, the use of GC in production processes and industries has started to become widespread due to its environmentally friendly,

safe, and economical nature (Gerçek, 2012). Pharmaceuticals, textiles, household products, automotive, plant production, and many other sectors are examples of industries where GC applications are widely used. Examples of sectors and applications where GC practices are used are provided in Table 2 (Karagölge and Gür, 2016; Idoko et al., 2024).

Table 2. *Sectors and areas of application for GC practices (Karagölge and Gür, 2016; Idoko et al., 2024)*

Sector	Application Area
Pharmaceuticals	Solvent reduction and catalysis in pharmaceuticals
Household Products	Cleaning products and paints with lower toxic substances
Automotive	Lightweighting materials and eco-friendly coatings
Agriculture	Applications for the protection of biodiversity regarding pesticides and fertilizers.
Textiles	Development of eco-friendly paint and sustainable fibers

The plant production process is inherently in a holistic relationship with the environment. Therefore, incorrect practices in traditional plant production pose significant pollution risks and negative environmental impacts on all living beings (Sönmez et al., 2008). The use of GC practices in plant production for various purposes minimizes risks for all stakeholders while also supporting farmers' economic sustainability. In the application of fertilizers and pesticides, which are indispensable inputs in plant production, nanotechnology-supported GC applications are utilized in various practices to prevent soil and water pollution and in other stages of plant production.

The GC approach fundamentally relies on twelve principles that focus on eliminating or minimizing the utilization of hazardous chemicals. These GC principles are provided in Figure 2. Here, the 7th principle defines the first material that enters the system, and the other principles must be designed accordingly. Principles 1, 2, and 11 of GC focus on waste reduction, while principles 4 and 10 ensure that the resulting products are environmentally friendly, and principles 3, 5, 6, 8, 9, and 12 encompass safe production requiring minimal energy (Fenibo et al., 2022).

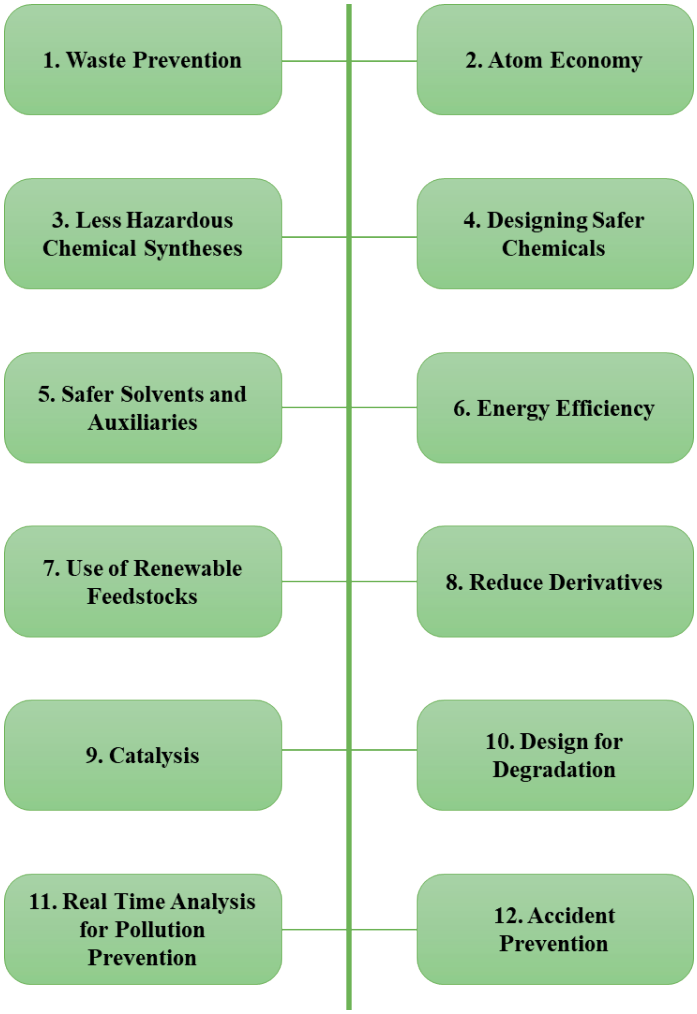

Figure 2. *Principles of GC (Çakmak et al., 2012)*

4. FERTILIZER TECHNOLOGIES BASED ON GREEN CHEMISTRY IN PLANT PRODUCTION

Due to population growth, demand for food has been rising, creating a need for more, higher-quality, and more economical products. Therefore, as the need for plant production increases, so do the negative environmental impacts in direct proportion. To reduce the negative environmental impacts of fertilizers, which are a basic input in plant production, and to ensure sustainable production, it has become imperative to transition from traditional methods to GC-based fertilizer technologies. The principles of GC, such as the use of renewable feedstocks, less hazardous chemical syntheses, energy efficiency, and atom economy, are highlighted for both maintaining product quality and for producing or applying fertilizers in ways that

minimize environmental harm. GC-based fertilizer development strategies can be grouped into four main classes: minimizing environmental losses, utilizing nanotechnology, using renewable raw materials, and eco-friendly synthesis (Munjal et al., 2026). Among these strategies, the controlled release of chemical fertilizers and innovative GC-based technologies such as nanofertilizers and biofertilizers stand out as approaches to reduce these negative impacts.

4.1. Controlled Release of Chemical Fertilizers

Controlled-release application is the controlled delivery of nutrients to soil and plants by coating chemical fertilizers with various materials. These practices have benefits such as efficient and adequate nutrient use and storage, improvements in product quality and yield, ensuring food safety and environmental sustainability, and achieving economic gains (Govil et al., 2024). As a result of controlled applications, similar yield rates can be achieved compared to traditional practices, with a 10%-40% reduction in fertilizer use and a 75% reduction in labor costs. Due to differences in coating and nutrient-release times among fertilizers, fertilization periods can range from 6 weeks to 18 months. The proper selection of coatings is a fundamental factor in the proper release of nutrients (Srivastava, 2023). The basic classification of controlled-release fertilizers is provided in Figure 3.

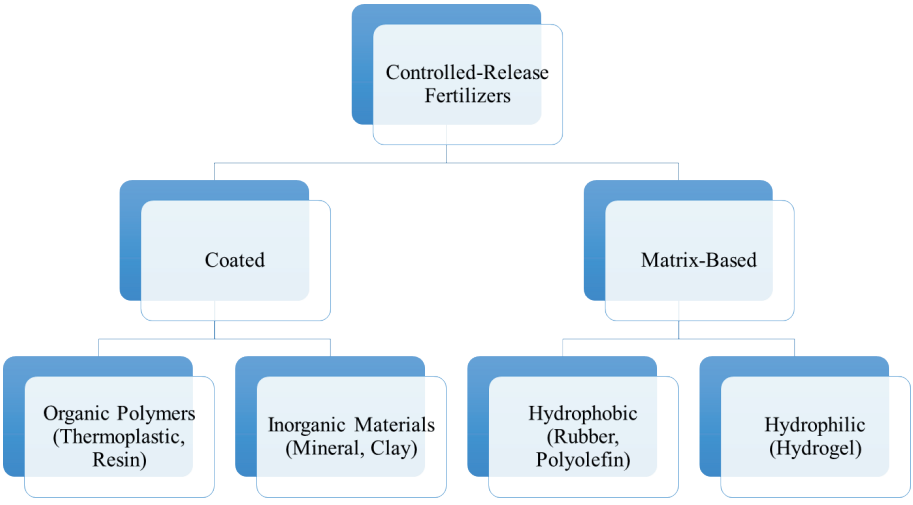

Figure 3. *Basic classification of controlled-release fertilizers (Lawrencia et al., 2021)*

Incrocci et al. (2020) conducted a study in which they produced tomatoes in a greenhouse by controlling the release of coated urea, nitrogen, and ammonium fertilizers in three different seasons. In their studies, they aimed to achieve the best results by comparing the balance of water and nitrogen and the yield and quality conditions of the products. As a result of their studies, they found that yields between the traditional and controlled-release groups were similar, and the amount of fertilizer in the controlled-release group could be reduced by 25%. Mao et al. (2024) conducted a study in which they produced tomatoes in open fields in Chi-

na using no-fertilizer production, traditional fertilization, and controlled-release methods, and compared environmental pollution parameters with tomato yield. The study results showed that the controlled-release application reduced leaching of total, nitrate, and ammonia nitrogen between 24.89% and 65% compared to other methods. Additionally, they concluded that the controlled-release application provided 60.25% more yield than no fertilizer application and 15.03% more than the traditional N375 fertilizer application.

4.2. Application of Nanofertilizers

Nanofertilizers are more environmentally friendly alternatives that can quickly penetrate plants because of their nanoscale size. They prevent nutrient loss due to leaching by releasing nutrients in a controlled manner and ensuring their targeted, long-term use (Öztürk, 2026). Methods for delivering nutrients to plants using nanofertilizers are shown in Figure 4. The transition from traditional fertilizers to nanofertilizers brings many advantages. Examples include achieving higher yields with lower fertilizer use and economic costs, improving product quality, reducing environmental pollution, and saving labor and reducing the number of pesticide applications (Dağhan, 2017).

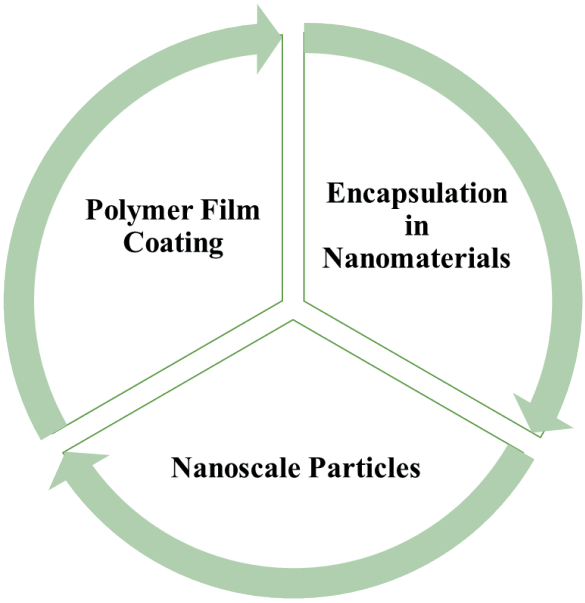

Figure 4. *Pathways of nutrient element delivery to plants by nanofertilizers (Dağhan, 2017)*

Helal et al. (2023) applied a controlled-release nanofertilizer at five doses for tomato production in their study and compared the results with those of commercial fertilizers. As a result of their studies, they achieved better plant development at all doses than with commercial fertilizers. While they found the nitrogen uptake efficiency of the plants in the commercial fertilizer group to be 33%, they found the

nitrogen uptake efficiency in the 5 groups where the controlled release of the nano fertilizer was performed to vary between 47% and 88%. In this context, they have concluded that nanofertilizers increase plant productivity and quality compared to commercial fertilizers. Nofal et al. (2021) aimed to determine the changes in yield and quality in lettuce production when using traditional NPK fertilizer at 12.5%, 25%, and 50% ratios as nanofertilizer. As a result of their studies, they determined that using nanofertilizer at a 50% lower rate than traditionally used NPK fertilizer significantly increased quality and efficiency. Additionally, they have concluded that the nitrate content has also significantly decreased compared to the use of traditional fertilizers.

4.3. Application of Biofertilizers

Biofertilizers are eco-friendly fertilizers that contain specific microorganisms and help plant growth by supplying nutrients to crops when used in agricultural production (Yolci and Tunçtürk, 2022). In other words, they are fertilizers containing beneficial microorganisms in active or inactive forms that can settle in the plant's roots and internal tissues (Santos et al., 2024). The advantages of using biofertilizers in plant production include the following (Daniel et al., 2022).

- They are economical alternatives to chemical fertilizers.
- They have positive effects on soil fertility while reducing environmental pollution.
- They can reduce the negative effects brought by chemicals.
- They have the potential to increase product yield by 10-40%.
- They have a positive effect on plant growth through the microorganisms they harbor.

Hadwan et al. (2019) conducted a study to evaluate the impact of biofertilizer use on soil nutrient levels and yield during wheat production in Iraq. In their studies, they used biofertilizer and commercial fertilizer in wheat production and compared the results. They have determined that using biofertilizer increases wheat yield and reduces environmental pollution. Additionally, they have stated that the results of biofertilizer applications can be obtained at a lower cost. Adesemoye et al. (2009) aimed to achieve the former yield and determine the minimum fertilizer level by reducing chemical fertilizer use and supplementing it with biofertilizer. As a result of their studies, they determined that if 25% of the fertilizer mixture used is biogas, the same efficiency and nutrient content can be achieved as with the full dose of chemical fertilizer. They have concluded that when the amount of chemical fertilizer falls below 70%, yield losses will occur.

5. APPLICATIONS OF GREEN PESTICIDES AND BIOPESTICIDES IN PLANT PRODUCTION

Pesticides are the most commonly used method in plant production to protect crops from diseases and pests, accounting for over 95%. However, despite their

widespread use, pesticides also pose risks and negative effects on the environment and living beings, alongside their benefits (Tiryaki et al., 2010). Therefore, both to benefit from the advantages of pesticides and to minimize their negative effects, green pesticides and biopesticide applications are utilized. Biopesticides are eco-friendly products derived from plant residues, natural minerals, bacteria, and animal organisms, and delivered to plants (Balcı and Durmuşoğlu, 2020). Biopesticides are fundamentally divided into three main classes. This classification is shown in Figure 5.

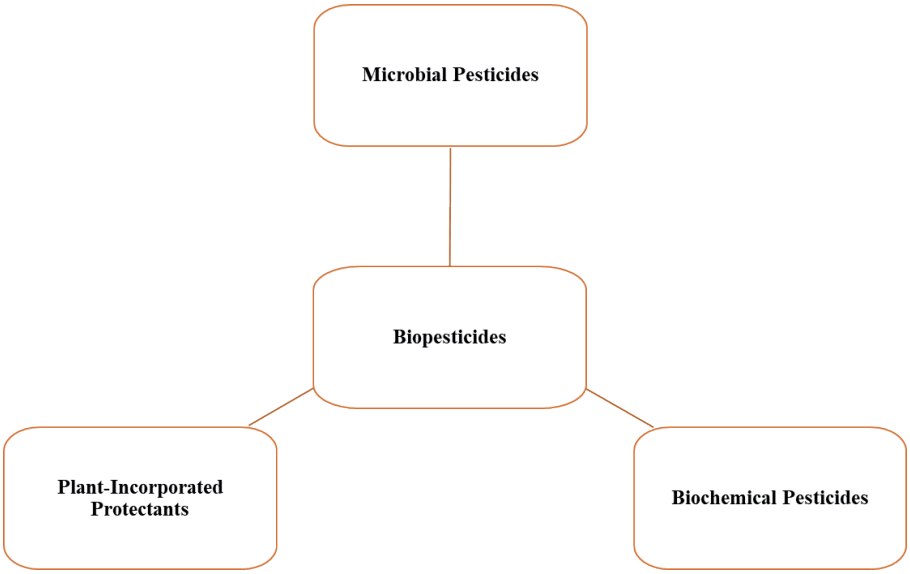

Figure 5. *Biopesticide groups (EPA, 2025)*

5.1. Microbial Pesticides

Microbial pesticides are plant protection products that contain microorganisms as the active ingredient to protect plants from pests and diseases. By bringing together microorganisms normally found in nature with the target pests in mind, successful plant protection is achieved through microbial pesticides. Their main advantages include being lower cost than chemicals, targeting only the intended pests, not causing environmental pollution, and achieving more effective, long-term results in plant protection (Balcı and Durmuşoğlu, 2020; Işık and Çınar, 2022).

In the literature, numerous studies aim to prevent pests and diseases in plant production by using microbial pesticides. Aktepe (2021) used a microbial pesticide (biological formulation) in his study to prevent bacterial spot disease in tomato production. In this study, it was demonstrated that applying microbial pesticides could reduce disease severity on leaves by 15.79%-20% and on stems by 25%-35%. Karabüyük et al. (2012) used three bacterial and three fungal isolates (microbial pesticides) in their study to determine their effects on *Tuta absoluta* larvae. As a result of their studies, they concluded that three bacterial isolates were affected by 30.55%-33.33% and three fungal isolates by 61.11%-63.88%.

5.2. Biochemical Pesticides

Biochemical pesticides are pesticides that lack toxic structures, are of natural origin, and are used to control pests in plant production. These products are used to control pests rather than eliminate them, compared to chemical pesticides (EPA, 2025). Biochemical pesticides are separated into three primary groups depending on their purposes and compositions: pheromones, plant extracts, and insect growth regulators (Table 3).

Table 3. *The purposes and compositions of biochemical pesticides (Kumar et al., 2021)*

Compositions	Purpose of Use
Plant extracts	They are extracts obtained from plants. They are used to keep insects away from products, reduce their reproduction, and decrease their respiration.
Pheromones	They are chemicals produced by insects. It is used to prevent mating, thereby stopping pest reproduction and controlling their population.
Insect Growth Regulators	It is used to prevent and control targeted pests.

Özkan et al. (2017) deployed pheromone traps to combat the Tuta absoluta moth in two different greenhouses in Konya province. As a result of the study, they captured 640 and 626 adult moths per week in greenhouses one and two, respectively. They concluded that the population could be reduced by decreasing the number of adult moths using pheromone traps. Karabüyük et al. (2012) used a commercial preparation, KingBo (biochemical pesticide), to determine its effect on plant damaging larvae production. In this study, they demonstrated that the use of the KingBo preparation had an efficacy of 75%-100% on the larvae.

5.3. Plant-Incorporated Protectants

Plant-incorporated protectants are plant-produced pesticides resulting from genetic modification (Yarsan and Çevik, 2007). The transfer of the gene producing a natural pesticide protein to the plant can also be described as the plant producing its own protective substance against the target pests affected by the relevant gene (EPA, 2025). Changes to the genetics of the products will reduce the need for insecticides during the production of those plants. For example, the production of Bt corn resistant to insects in the Eastern Mediterranean will reduce insecticide use, providing economic benefits and reducing environmental pollution (İnce et al., 2013).

Klümper and Qaim (2014) conducted a study evaluating real data from 147 scientific studies on environmental pollution, pesticide use, and the economic profitability of genetically modified plant products. In their studies, they stated that product efficiency and economic profit increased by 22% and 68%, respectively. In addition to the profits obtained, they concluded that there was a 37% reduction in pesticide consumption. They stated that the increases in efficiency and reductions in pesticide use observed as a result of the study were more pronounced with insect-resistant products (those with plant-incorporated protectants) than with her-

bicide-tolerant products. Brookes and Barfoot (2020) determined rates of change in pesticide use and greenhouse gas emissions resulting from the widespread adoption of genetically modified crops during 1996-2018. As a result of their studies, they stated that pesticide use decreased by 8.3% compared to previous periods. The use of these technologies in plant production has reduced field processing traffic and increased soil carbon storage, equivalent to the carbon dioxide produced by 15.27 million vehicles in 2018.

6. NANOTECHNOLOGY-SUPPORTED GREEN CHEMISTRY APPLICATIONS

Nanotechnology can be defined as the creation and implementation of new systems, components, and methods at the atomic and molecular level, with nanoscale dimensions. The nanoscale corresponds to an average of 100,000ths of a human hair thickness (Ramsden, 2005; Erkoç, 2007). The aim is to obtain products with higher strength and lighter weight by using less material and energy through nanotechnology. This situation also provides additional economic benefits by preventing production costs from exceeding raw material costs (Turgut et al., 2011). All these purposes and benefits of nanotechnology are related to the principles of GC, such as energy efficiency, atom economy, and the design of safer chemicals. Nanotechnology in plant production can be used for various purposes, such as real-time monitoring of production conditions and plants, smart biosensors, and controlled release systems (Erol Demirbilek, 2015). In this context, examples of nanotechnology use in plant production include nano-seed enhancement applications, biodegradable nanohydrogels for water optimization, and nanosensors for stress management.

6.1. Nanopriming Applications

Nanopriming is a method that mitigates the negative effects of stress during germination and the seedling stage, thereby increasing yield and quality. In this method, nano-sized particles containing elements such as gold, iron, silver, and zinc are applied to seeds and used in plant production (Özmen and Mavi, 2023). The use of the nanopriming method offers benefits such as facilitating germination, increasing plant growth, and suppressing factors that could cause plant stress. Currently, it has regarded as a successful alternative among sustainable agricultural practices (Özmen et al., 2022).

Kumar et al. (2025) studied the effects of ZnO nanoparticle treatment through nanopriming on germination and seedling height in three tomato varieties. As a result of their studies, they found an increase of 25.2% in germination, 18.2% in average seedling length, and 15.9% in average root length compared to the control group. In this context, they concluded that applying nanopriming significantly improved seed quality and seedling height parameters in their studies. Sembada and Lenggoro (2024) monitored tomato plant growth by applying nanopriming to their seeds. They determined that the presence of copper and barium heavy metals in the production environment delayed germination by 28.38% and 26.9%,

respectively, but that the application of nanopriming reduced these delays by 10.45% and 11.54%, respectively. In their study, they demonstrated that the nanopriming method reduces heavy metal stress.

6.2. Biodegradable Nanohydrogel Applications

Hydrogels are polymers with a high water-retention capacity. Due to their low cost, generally non-toxic effects, and high water retention capacities, they have various uses in plant production, primarily controlled release (Kemeç, 2023). Hydrogels can be divided into two groups: synthetic and bio-based hydrogels (Hernandez-Echave et al., 2025). Although hydrogels make up only a small portion, some synthetic types can leave toxic residues in the soil. Biohydrogels, on the other hand, do not cause toxic effects but have the disadvantage of low strength (Palanivelu et al., 2022). In this context, nanohydrogels have combined the positive properties of hydrogels with the ability of nanoparticles to be applied more controllably to the desired area, allowing for the emergence of much more sustainable and environmentally friendly applications (Trombino et al., 2023).

Jumpapaeng et al. (2023) used a biodegradable nanocomposite hydrogel as a conrolled release fertilizer. In their studies, they found that ın contrast to a control, the swelling ratio of nanocomposite hydrogels was 70 times higher, the strength was 2.6 times higher, and the nitrogen release efficiency was 39.1% higher. In conclusion, they stated that, further to these advantages, nanocomposite hydrogels have a lower cost, 4 times lower. Cholavardan et al. (2023) examined the impact of nanohydrogel use on wheat yield and water-use efficiency. By applying 20 kg of nanohydrogel per hectare for plant production, they achieved a 33.6% increase in maximum grain yield and a 22.9% increase in straw yield compared to the control group. Consequently, they concluded that water-use efficiency enhanced significantly with the use of nanohydrogel.

6.3. Stress Management with Nanosensors

In plant production, stress is an important factor at all stages from sowing to harvesting. Changes in climate, toxic substances, pests, and disease agents are among the sources of stress in plants. Stress in plants negatively affects yield and quality (İmriz et al., 2023). At this point, nanosensors are used to detect all these factors that will stress the plants early on. Nanosensors are systems that detect changes in physical and chemical parameters in plants quickly and with high precision (Altındal and Altındal, 2022). In plant production, nanosensors are used to determine nutrient requirements, identify diseases, and evaluate the effects of humidity and other environmental factors. Nanosensors can transform traditional agriculture into sustainable smart systems based on GC principles that are environmentally friendly and energy-efficient (Yenilmez, 2024).

Zhan et al. (2018) aimed to identify Phytophthora infestans, which poses a threat to potato and tomato production, using a nanoparticle-assisted biosensor. In their studies, they found that the sensors sensed genomic DNA at 0.1 pg mL^{-1}

and accurately identified three *Phytophthora* species and two harmful fungal species. As a result of the study, they concluded that nanoparticle-based biosensors have high potential for early disease diagnosis and outbreak prevention. Li et al. (2022) developed nanosensors capable of measuring water management and irrigation in plant production without harming the plants. In their studies, they monitored plant transpiration and water transport using nanosensors and detected changes in plant moisture over a period of 20.3 seconds. In summary, they revealed that nanosensors could be a pioneering method for determining product stress in plant production.

7. GREEN CHEMISTRY APPROACHES IN PREVENTING SOIL AND WATER POLLUTION

In addition to the technological application of the GC approach in plant production, there are many engineering applications where it is preferred at the scale of managing facilities and systems. In this context, applications in the management of facilities and systems where the principles of GC, such as the use of renewable feedstocks, energy efficiency, and waste prevention, are prominent; waste management and biogas technologies, rainwater harvesting systems in greenhouses for water conservation and recovery, and the phytoremediation method for reducing pollutants in soil and water can be given as examples.

7.1. Waste Management and Biogas Technologies

Greenhouses are structures that provide the necessary conditions for year-round plant production, protecting plants from external weather events (Öz, 2012). Large amounts of plant waste are generated during greenhouse production periods. The majority of this waste is managed by burning or by being thrown into nearby water sources. The disposal of waste in this manner causes environmental pollution (Görgülü, 2019). When considering GC approaches, the proper management of these plant wastes is completely intertwined with the principles of energy efficiency and waste prevention. The biogas method is one of the methods that can be used within the scope of waste management to meet these principles and also achieve economic gains. Biogas is a source of energy produced from the fermentation of organic waste. In biogas production, residues from plant-based production, such as stalks, straw, corn, and grass; waste mushroom compost; and greenhouse vegetable waste can be widely used (Gülen and Çeşmeli, 2012; Sönmez et al., 2016).

Atılgan et al. (2020) assessed the biogas potential of the annual waste generated during greenhouse production in the province of Antalya. As a result of the study, it was found that a total of 488,597.20 kg of waste was generated annually from the greenhouses they researched, and the amount of biogas energy to be produced from this waste was calculated at 8,035,073.43 MJ. Görgülü (2019) determined the biogas potential of certain annual plant wastes in Burdur province in 2018. In Conclusion, the biogas potential from plant waste sources in 2018 was estimated at 10,296,237. It has been concluded that it is 93 GJ. All these studies in the literature show that when waste is managed within the framework of GC, environmental

pollution from plant waste can be prevented, and a high level of renewable energy production can be achieved.

7.2. Rainwater Harvesting Method

Rainwater harvesting is an environmentally friendly approach that involves collecting, storing, and reusing rainfall without waste (Çakar, 2022). The rainwater harvesting method has advantages such as reducing the need for groundwater, preventing erosion, preventing water pollution, and preventing floods (Yeniçeri, 2018). In this context, it is one of the important practices that can be used to recover water and prevent water pollution.

In this context, numerous studies examine the use of rainwater-harvesting methods on greenhouse roofs. Boyacı and Sezer (2025) determined the potential to meet the required plant water demand in greenhouses through rainwater harvesting in three cities in their study. They have determined that the necessary plant water consumption in the greenhouses of Antalya, İzmir, and Samsun can be met at 55.4%, 33.8%, and 37.9%, respectively. Kılıç et al. (2024) aimed to determine the rainwater harvesting potential of 4 greenhouses with a total roof area of 2278 m^2 in Bursa province. In their studies, they determined that the entire 1066 m^3 of water required annually for lettuce production in greenhouses could be met through rainwater harvesting. All these results from scientific studies show that the rainwater harvesting method can meet the water requirements for plant production to a high degree, making it a strong alternative for reducing environmental pollution and mitigating drought.

7.3. Phytoremediation Method

Phytoremediation is the use of plants to clean soils contaminated with heavy metals. In this method, the aim is to prevent pollution by utilizing the microorganisms found in plants. The phytoremediation method has advantages such as being cost-effective, easy to apply, non-polluting, and applicable directly to the desired area without requiring much energy (Hamutoğlu et al. 2012).

Özkan et al. (2016) applied phytoremediation using different plants and amounts to remove cadmium from soil. As a result of the study, it was concluded that the phytoremediation process using canola could remove 93.5% of the cadmium. Dağhan (2016) examined the phytoremediation potential of *Tagetes patula L.* for treating cadmium-contaminated environments. The study concluded that, as a result of the application, the cadmium hyperaccumulation threshold in *Tagetes patula L.* increased eightfold, achieving successful remediation.

CONCLUSIONS

In this study, various input methods and management strategies for greenhouse production facilities that incorporate the GC approach to reduce pollution from plant production sources were examined; scientific studies summarizing the benefits of these applications in the literature were reviewed. The use of fertilizers and pesticides, which are indispensable inputs in plant production, by utilizing biological and technological methods within the framework of GC principles, has led to significant reductions in various pollutant parameters, achieving similar yields with lower input usage, and noticeable declines in plant diseases. Additionally, GC approaches yield effective results by enhancing product quality and efficiency while minimizing pollution in applications such as plant stress management, water optimization, and seed improvement, with a significant impact across various stages of plant production. The GC approach has been adopted not only in the production stages of plant-based production but also in efforts to improve facility and waste management processes. The practices carried out within this framework show positive effects, such as protecting water resources, improving energy efficiency, and increasing the efficiency of natural resource use. The adoption of GC approaches in all these practices greatly contributes to establishing a more environmentally friendly, efficient, economical, and sustainable production process. In conclusion, the adoption of GC principles in plant production practices provides significant support in minimizing negative environmental impacts, meeting the increasing food demand, ensuring food security, and preserving the ecosystem, especially considering the current effects of global warming. In this context, it is evident that the transition from traditional methods to smart agriculture, including GC approaches, is inevitable.

SONUÇ

Bu çalışmada, bitkisel üretim kaynaklı kirliliğin azaltılması amacıyla yeşil kimya yaklaşımını içeren çeşitli girdi yöntemleri ve örtü altı üretim tesislerinin yönetim stratejileri incelenmiş; literatürdeki bu uygulamaların sağladığı faydalara ilişkin bilimsel çalışmalar özetlenmiştir. Bitkisel üretimde vazgeçilmez girdilerden olan gübre ve pestisitlerin, yeşil kimya ilkeleri çerçevesinde biyolojik ve teknolojik yöntemlerden faydalanılarak kullanılması; çeşitli kirletici parametrelerde önemli azalmalar yaşanmasına, daha düşük girdi kullanımıyla benzer verimlerin yakalanmasına ve bitki hastalıklarında belirgin gerilemelerin görülmesini sağlamıştır. Ek olarak, yeşil kimya yaklaşımları; bitkisel üretimin farklı aşamalarında büyük etkiye sahip bitki stres yönetimi, su optimizasyonu ve tohum iyileştirilmesi gibi uygulamalarda minimum kirlilik oluşturarak ürün kalitesi ve verimliliğin artması üzerinde etkili sonuçlar ortaya koymaktadır. Yeşil kimya yaklaşımı, bitkisel üretimde yalnızca üretim aşamalarında değil, aynı zamanda tesis ve atıkların yönetimi süreçlerindeki iyileştirme çalışmalarında da benimsenmiştir. Bu kapsamda gerçekleştirilen uygulamalar su kaynaklarının korunması, enerji verimliliğinin sağlanması ve doğal kaynak kullanım verimliliğinin artırılması gibi olumlu etkiler göstermektedir. Tüm bu uygulamalarda yeşil kimya yaklaşımlarının benimsenmesi, daha doğa dostu, verimli, ekonomik ve sürdürülebilir bir üretim sürecinin kurulmasında büyük katkılarda bulunmaktadır. Sonuç olarak, yeşil kimya ilkelerinin bitkisel üretim uygulamalarında benimsenmesi, günümüzdeki küresel ısınma etkisi de göz önüne alındığında, olumsuz çevresel etkilerin minimuma inmesine, artan gıda talebinin karşılanabilmesine, gıda güvenliğinin sağlanabilmesine ve ekosistemin korunabilmesine büyük bir destek sağlamaktadır. Bu kapsamda, mevcut geleneksel yöntemlerden yeşil kimya yaklaşımlarını içeren akıllı tarıma doğru geçişin kaçınılmaz olduğu görülmektedir.

REFERENCES

1. Adesemoye, A. O., Torbert, H. A., & Kloepper, J. W. (2009). Plant growth-promoting rhizobacteria allow reduced application rates of chemical fertilizers. *Microbial Ecology, 58(4)*, 921-929. https://doi.org/10.1007/s00248-009-9531-y
2. Akkeçeci, Ş. The historical process of fertilizer application in agriculture: an evaluation from the perspective of field crops. *Agro-Science Journal of Iğdır University, 3(2)*, 72-84.
3. Aktepe, B. P. (2021). Domateste bakteriyel benek hastalığının biyolojik mücadelesinde farklı bitki aktivatörleri ve biyolojik preparatların etkisi. *Mustafa Kemal Üniversitesi Tarım Bilimleri Dergisi, 26 (2)*, 355-364. https://doi.org/10.37908/mkutbd.908921
4. Altındal, D., & Altındal, N. (2022). Sürdürülebilir Tarımda Nanosensör Kullanımı. A. Atik (Ed.), Ziraat, orman ve su ürünleri alanında güncel tartışmalar. Duvar Yayınları.
5. Anastas, P. T., & Warner, J. C. (1998). Green chemistry: Theory and practice. Oxford University Press.
6. Atılgan, A., Saltuk, B., Ertop, H., & Aksoy, E. (2020). Sera atıklarından biyogaz enerji potansiyelinin belirlenerek sayısal haritalarının oluşturulması: Antalya ili örneği. *Euroasia Matematik, Mühendislik, Doğa ve Tıp Bilimleri Dergisi Medical Sciences, 7(12)*, 19–30. https://doi.org/10.38065/euroasiaorg.270
7. Aydın Eryılmaz, G., & Kılıç, O. (2018). Türkiye'de sürdürülebilir tarım ve iyi tarım uygulamaları. *Kahramanmaraş Sütçü İmam Üniversitesi Tarım ve Doğa Dergisi, 21(4)*, 624-631. https://doi.org/10.18016/ksudobil.345137
8. Balcı, H., & Durmuşoğlu, E. (2020). Bitki koruma ürünü olarak biyopestisitler: tanımları, sınıflandırılmaları, mevzuat ve pazarları üzerine bir değerlendirme. *Türkiye Biyolojik Mücadele Dergisi, 11(2)*, 261-274. https://doi.org/10.31019/tbmd.807300
9. Boyacı, S., & Sezer, M. (2025). Türkiye'de farklı iklim koşullarına sahip bölgelerde sera çatısından yağmur suyu hasadı potansiyelinin belirlenmesi. *Alatarım, 24(2)*, 131-141.
10. Brookes, G., & Barfoot, P. (2020). Environmental impacts of genetically modified (GM) crop use 1996–2018: Impacts on pesticide use and carbon emissions. *GM Crops & Food, 11(4)*, 215–241. https://doi.org/10.1080/21645698.2020.1773198
11. Cholavardan, D., Krishna, V. V. S. J., & Sushant. (2023). Assessing the effect of irrigation levels and hydrogel on growth and yield of wheat (Triticum aestivum L.). *International Journal of Environment and Climate Change, 13(10)*, 2644–2649. https://doi.org/10.9734/ijecc/2023/v13i102929
12. Cüre, B. (2022). Kimyasal ve organik gübrelerin çevre üzerine etkisi. *Biyosistem Mühendisliği Dergisi, 3(2)*, 98-107.
13. Çakar, H. (2022). İzmir ili koşullarında bahçeli bir sitenin yağmur suyu hasadı potansiyelinin değerlendirilmesi. *Turkish Journal of Agricultural and Natural Sciences, 9(2)*, 446-452. https://doi.org/10.30910/turkjans.1084095
14. Çakmak, R., Topal, G., & Çakmak, M. (2012). Kimya öğretiminde yeşil bir kavram: Yeşil kimya. *The Journal of Academic Social Science Studies, 5(8)*, 359-371.
15. Çakmak, B., & Gökalp, Z. (2013). Kuraklık ve tarımsal su yönetimi. *Gaziosmanpaşa Bilimsel Araştırma Dergisi, 4*, 1-11.
16. Dağhan, H. (2016). Tagetes patula L. bitkisinin fitoremediasyon amaçlı kullanım potansiyelinin su kültürü koşullarında araştırılması. *Toprak Su Dergisi, 5(2)*, 25-31. https://doi.org/10.21657/topraksu.269118
17. Dağhan, H. (2017). Nano gübreler. *Türkiye Tarımsal Araştırmalar Dergisi, 4(2)*, 197-203. https://doi.org/10.19159/tutad.294991

18. Daniel, A. I., Fadaka, A. O., Gokul, A., Bakare, O. O., Aina, O., Fisher, S., Burt, A. F., Mavumengwana, V., Keyster, M., & Klein, A. (2022). Biofertilizer: The future of food security and food safety. *Microorganisms, 10(6)*, 1220. https://doi.org/10.3390/microorganisms10061220

19. Doğan, Z., Arslan, S., & Berkman, A. N. (2015). Türkiye'de tarım sektörünün iktisadi gelişimi ve sorunları: Tarihsel bir bakış. *Niğde Üniversitesi İktisadi ve İdari Bilimler Fakültesi Dergisi, 8(1)*, 29-41.

20. Doru, S., & Atış, E. (2025). Çiftçilerin tarımsal plastik atıklara yönelik tutumlarının çevresel sürdürülebilirlik açısından incelenmesi. *Ege Üniversitesi Ziraat Fakültesi Dergisi, 62(1)*, 87-100

21. Emekli, N. Y., & Topakçı, M. (2009). Hassas uygulamalı tarım teknolojilerinin sulama alanında kullanımı. *Gaziosmanpaşa Üniversitesi Ziraat Fakültesi Dergisi, 26(2)*, 9-17.

22. EPA (2025, October 8). What are Biopesticides? https://www.epa.gov/ingredients-used-pesticide-products/what-are-biopesticides

23. Erkoç, Ş. (2007). Nanobilim ve nanoteknoloji. ODTÜ Yayıncılık.

24. Erol Demirbilek, M. (2015). Tarımda ve gıdada nanoteknoloji. *Gıda ve Yem Bilimi Teknolojisi Dergisi, 15, 46-53*. https://izlik.org/JA65AA88SY

25. Fenibo, E. O., Ijoma, G. N., Nurmahomed, W., & Matambo, T. (2022). The potential and green chemistry attributes of biopesticides for sustainable agriculture. *Sustainability, 14,* 14417. https://doi.org/10.3390/su142114417

26. Finez, D. D. E., & Talimbay, J. E. (2023). Advantages and disadvantages of using ınorganic fertilizers for agriculture. *International Journal of Transdisciplinary Research and Innovations, 1(1)*, 1-7.

27. Gerçek, Z. (2012). Kimya'nın yeni rengi: yeşil kimya. *Yükseköğretim ve Bilim Dergisi, 2(1)*, 50-53.

28. Govil, S., Long, N. V. D., Escrib'a-Gelonch, M., & Hessel, V. (2024). Controlled-release fertilizer: recent developments and perspectives. *Industrial Crops & Products, 219,* 119160. https://doi.org/10.1016/j.indcrop.2024.119160

29. Görgülü, S. (2019). Burdur ilinin hayvansal ve bazı tarımsal atık kaynaklı biyogaz potansiyelinin belirlenmesi. *El-Cezeri Fen ve Mühendislik Dergisi, 6(3)*, 543-557. https://doi.org/10.31202/ecjse.556915

30. Gülen, J., & Çeşmeli, Ç. (2012). Biyogaz hakkında genel bilgi ve yan ürünlerinin kullanım alanları. *Erzincan Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 5(1)*, 65-84. https://izlik.org/JA43GR68SS

31. Hadwan, H. A., Francis, A. J., Rafal, E. M., & Muntaser, M. M. (2019). Effect of biofertilizers on yield and yield components of wheat (Triticum aestivum L.) under Iraqi conditions. *International Journal of Applied Agricultural Sciences, 5(2)*, 45–49. https://doi.org/10.11648/j.ijaas.20190502.13

32. Haktanır, K. (2009). Çevresel değisimlerde tarımın etkileri ve yönetim arayısları. *Ankara Üniversitesi Çevrebilimleri Dergisi, 1(1)*. https://doi.org/10.1501/Csaum_0000000001

33. Hamutoğlu, R., Dinçsoy, A. B., Cansaran-duman, D., & Aras, S. (2012). Biyosorpsiyon, adsorpsiyon, fitoremediasyon yöntemleri ve uygulamaları. *Türk Hijyen ve Deneysel Biyoloji Dergisi, 69(4)*, 235-253. https://izlik.org/JA25DS53ZZ

34. Helal, M. I. D., El-Mogy, M. M., Khater, H. A., Fathy, M. A., Ibrahim, F. E., Li, Y. C., Tong, Z., & Abdelgawad, K. F. (2023). A controlled-release nanofertilizer ımproves tomato growth and minimizes nitrogen consumption. *Plants, 12(10)*, 1978. https://doi.org/10.3390/plants12101978

35. Hernández-Echave, D. G., Casillas-Moreno, G., Romo-Galindo, A. I., Gutiérrez-Gómez, T. A., Velázquez-Juárez, G., Rodríguez-Ortega, M. A., Muñoz-García, R. O., & Lomelí-Rosales, D. A. (2025). Advances in the application of nanocomposite hydrogels in crops. *Gels, 11(12)*, 957. https://doi.org/10.3390/gels11120957

36. Idoko, F. A., Ezeamii, G. C., Ojochogwu, O. J. (2024). Green chemistry in manufacturing: Innovations in reducing environmental impact. *World Journal of Advanced Research and Reviews, 23(3)*, 2826-2841. https://doi.org/10.30574/wjarr.2024.23.3.2938

37. Incrocci, L., Maggini, R., Cei, T., Carmassi, G., Botrini, L., Filippi, F., Clemens, R., Terrones, C., & Pardossi, A. (2020). Innovative controlled-release polyurethane-coated urea could reduce N leaching in tomato crop in comparison to conventional and stabilized fertilizers. *Agronomy, 10(11)*, 1827. https://doi.org/10.3390/agronomy10111827

38. Işık, Ç., & Çınar, A. (2022). Bitki korumada mikrobiyal pestisitlerin kullanım olanakları ve etki mekanizmaları. *Avrupa Bilim Ve Teknoloji Dergisi, 36*, 214-221. https://doi.org/10.31590/ejosat.1113033

39. İmriz, G., Keleş, R., & İnal, N. (2023). Tohumlarda biyo-priming uygulaması: tarımsal üretimde sürdürülebilir stres yönetimi için doğa dostu bir yaklaşım. *ANADOLU Journal of Aegean Agricultural Research Institute, 33(2)*, 310–320. https://doi.org/10.18615/anadolu.1398603

40. İnce, H. Ö., Bahadıroğlu, C., Toroğlu, S., & Bozdoğan, H. (2013). Genetiği değiştirilmiş mısır bitkisinin bazı böcek türlerine karşı direnci üzerine değerlendirmeler. *Nevşehir Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 2(1)*, 78-89.

41. Jote, C. A. (2023). The ımpacts of using ınorganic chemical fertilizers on the environment and human health. *Organic and Medicinal Chemistry, 13(3)*. https://doi.org/10.19080/OMCIJ.2023.13.555864

42. Jumpapaeng, P., Suwanakood, P., Nanan, S., & Saengsuwan, S. (2023). Novel biodegradable nanocomposite hydrogels based on biopolymers and various montmorillonite contents as high-strength coating membranes for efficient slow-release fertilizers. *Journal of Industrial and Engineering Chemistry, 127*, 191–209. https://doi.org/10.1016/j.jiec.2023.07.005

43. Karabüyük, F., Horuz, S., Aysan, Y., & Ulusoy, M. R. (2012). Domates yaprak galeri güvesi Tuta absoluta (Meyrick) (Lepidoptera: Gelechiidae)'nın biyolojik mücadelesine yönelik çalışmalar. *Türkiye Biyolojik Mücadele Dergisi, 3(2)*, 133-144. https://izlik.org/JA24GZ33DU

44. Karaer, F., & Gürlük, S. (2003). Gelişmekte olan ülkelerde tarım-çevre-ekonomi etkileşimi. *Doğuş Üniversitesi Dergisi, 4(2)*, 197-206. https://izlik.org/JA99UW94UP

45. Karagölge, Z., & Gür, B. (2016). Sustainable chemistry: Green chemistry. *Journal of the Institute of Science and Technology, 6(2)*, 89-96. https://izlik.org/JA92TL93UE

46. Kemeç, S. (2023). Tarımda su kıtlığına yenilikçi çözüm:'Hidrojeller'. *Agro Science Journal of Igdir University, 1(1)*, 1–5. https://izlik.org/JA47TM88HA

47. Kendal, E., & Sayar, M. S. (2013). Dicle ve Fırat havzalarında bilinçsiz sulamanın ekolojik denge üzerinde oluşturduğu riskler. *Türk Bilimleri Derlemeler Dergisi, 6(1)*, 89-91.

48. Kılıç, U., Yaylı, B., & Kılıç, İ. (2024). Bursa Uludağ Üniversitesi ziraat fakültesi bünyesinde bulunan seralarda yağmur suyu hasadı potansiyelinin belirlenmesi ve ekonomik analizi. *Bursa Uludağ Üniversitesi Ziraat Fakültesi Dergisi, 38(2)*, 313-324. https://doi.org/10.20479/bursauludagziraat.1476500

49. Klümper, W., & Qaim, M. (2014). A meta-analysis of the ımpacts of genetically modified crops. *PLoS ONE 9(11)*, Article e111629. https://doi.org/10.1371/journal.pone.0111629

50. Kumar, J., Ramlal, A., Mallick, D., & Mishra, V. (2021). An overview of some biopesticides and their ımportance in plant protection for commercial acceptance. *Plants, 10(6)*, 1185. https://doi.org/10.3390/plants10061185

51. Kumar, S. M., Yadav, S., Choudhary, R., Anumantharaj, A., Yadav, A., Hussain, Z., Singh, P. K., Singh, S. P., Mandal, A., Singh, N., Sushkova, S., Ercisli, S., Sarker, U., & Yadav, S. K. (2025). Nanopriming with zinc oxide nanoparticle boosts seed vigour, photosynthesis, osmolytes accumulation and antioxidant activity in tomato. *Scientific Reports, 15*, 37375. https://doi.org/10.1038/s41598-025-09269-4

52. Lakhiar, I. A., Yan, H. Zhang, J., Wang, G., Deng, S., Bao, R., Zhang, C., Syed, T. N., Wang, B., Zhou, R., & Wang, X. (2024). Plastic pollution in agriculture as a threat to food security, the ecosystem, and the environment: An overview. *Agronomy, 14,* 548. https://doi.org/10.339/ agronomy14030548

53. Lawrencia, D., Wong, S. K., Low, D. Y. S., Goh, B. H., Goh, J. K., Ruktanonchai, U. R., Soottitantawat, A., Lee, L. H., & Tang, S. Y. (2021). Controlled release fertilizers: A review on coating materials and mechanism of release. *Plants, 10,* 238. https://doi.org/10.3390/plants10020238

54. Li, D., Li, G., Li, J., & Xu, S. (2022). Wearable crop sensor based on nano-graphene oxide for noninvasive real-time monitoring of plant water. *Membranes, 12(4)*, 358. https://doi.org/10.3390/membranes12040358

55. Mahmood, I., Imadi, S. R., Shazadi, K., Gul, A., & Hakeem, K. R. (2016). Effects of Pesticides on Environment. K. R. Hakeem, M. S. Akhtar, S. N. A. Abdullah (Eds.), Plant, soil and microbes volume 1: Implıcations in crop science. Springer.

56. Maksymıv, I. (2015). Pesticides: Benefits and hazards. *Journal of Vasyl Stefanyk Precarpathian National University, 2(1)*, 70-76.

57. Mao, X., Gu, J., Wang, F., Wang, K., Liu, R., Hong, Y., Wang, Y., & Han, F. (2024). Yield, quality, and nitrogen leaching of open-field tomato in response to different nitrogen application measures in northwestern China. *Plants, 13(7)*, 924. https://doi.org/10.3390/plants13070924

58. Munjal, R., Bhatia, Y., & Rana, V. (2026). Green chemistry strategies in the development of sustainable multi-nutrient fertilizers for enhanced soil and crop health. *Agrochemicals, 5(2)*, 21. https://doi.org/10.3390/agrochemicals5020021

59. Nofal, A. S., Ashmawi, A. E., Mohammed, A. A., El- Abd, M. T., & Helaly, A. A. (2021). Effect of soil application of nano NPK fertilizers on growth, productivity, and quality of Lettuce (Lactuca sativa). *Al-Azhar Journal of Agricultural Research, 46(1)*, 91–100.

60. Olgun, M. (2011). Tarımsal yapılar. Ankara Üniversitesi Yayınları.

61. Öz, Ü. (2012). Su ürünleri yetiştiriciliğinde sera sisteminin kullanımı. *Yunus Araştırma Bülteni, 2012(3)*, 24-30. https://doi.org/10.17693/yunusae.v2012i21908.235435

62. Özkan, A., Banar, M., Günkaya, Z., Kulaç, A., Yalçın, G., Taşpınar, K., & Altay, A. (2016). Fitoremediasyon ve piroliz işlemlerinin ardışık uygulamasıyla kadmiyum stabilizasyonu. *Pamukkale Üniversitesi Mühendislik Bilimleri Dergisi, 22(6)*, 497-502. https://izlik.org/JA36JD29SU

63. Özkan, Z., Ünlü, L., & Öğür, E. (2017). Örtü altı domates yetiştiriciliğinde domates güvesi (tuta absoluta meyrick)'ne karşı kullanılan feromon ve ferolite tuzaklarının etkinliğinin karşılaştırılması. *Harran Tarım ve Gıda Bilimleri Dergisi, 21(4)*, 394-403. https://doi.org/10.29050/harranziraat.290747

64. Özmen, K., Toprak, S., Coşkun, Ö. F., Şahin, B., & Mavi, K. (2022). Nanopriming uygulamalarının kavun (Cucumis melo L.) tohumlarında çıkış ve fide kalitesine etkisi. *Bahçe, 51(Özel Sayı 1),* 117-122. https://izlik.org/JA55JS25SM

65. Özmen, K., & Mavi, K. (2023, November 28-29). Sürdürülebilir tarımda yenilikçi bir yaklaşım olarak nanomateryallerin sebze tohum uygulamalarında kullanımı. 13th International Conference on Agriculture, Animal Science and Rural Development, Uşak, Türkiye.

66. Öztürk, H. (2026). Nano gübrelerin toprak mikrobiyal aktiviteleri üzerindeki etkileri. *Euroasia Matematik, Mühendislik, Doğa ve Tıp Bilimleri Dergisi Medical Sciences, 13(1)*, 41–48. https://doi.org/10.5281/zenodo.19218267

67. Palanivelu, S. D., Armir, N. A. Z., Zulkifli, A., Hair, A. H. A., Salleh, K. M., Lindsey, K., Che-Othman, M. H., & Zakaria, S. (2022). Hydrogel application in urban farming: Potentials and limitations—A review. *Polymers, 14(13)*, 2590. https://doi.org/10.3390/polym14132590

68. Ramsden, J. J. (2005). What is nanotechnology? *Nanotechnology perceptions, 1(1)*, 3–17.

69. Santos, F., Melkani, S., Oliveira-Paiva, C., Bini, D., Pavuluri, K., Gatboni, L., Mahmud, A., Torres, M., McLamore, E., & Bladha, J. H. (2024). Biofertilizer use in the United States: Definition, regulation, and prospects. *Applied Microbiology and Biotechnology, 108*. https://doi.org/10.1007/s00253-024-13347-4

70. Sembada, A. A., & Lenggoro, I. W. (2024). Nanopriming of tomato (Solanum lycopersicum) seeds against heavy metal stress during germination and seedling formation. *BIO Web of Conferences 91*, 01005. https://doi.org/10.1051/bioconf/20249101005

71. Sogut, O., & Çelebi, B. (2020). Daha temiz analizler: Yeşil kimya. *Duzce University Journal of Science and Technology, 8(1)*, 160-175. https://izlik.org/JA84UY86FD

72. Sönmez, İ., Kaplan, M., & Sönmez, S. (2008). Kimyasal gübrelerin çevre kirliliği üzerine etkileri ve çözüm önerileri. *Batı Karadeniz Tarımsal Araştırma Enstitüsü Derim Dergisi, 25(2)*, 24-34.

73. Sönmez, İ., Kalkan, H., Demir, H., Külcü, R., Kaplan, M., & Yaldız, O. (2016). Sera bitki atıkları, kullanılmış kokopit ve atık mantar kompostundan elde edilen kompostların toprakların besin içerikleri üzerine etkileri. Çukurova Tarım ve Gıda Bilimleri Dergisi, 31(3), 21-28. https://izlik.org/JA62TG79ZZ

74. Srivastava, A. (2023). Green chemistry: A promising route to sustainable agriculture. *Internatıonal Journal of Innovative Research In Technology, 9(8)*, 631–640.

75. Tapkı, N., Öztornacı, B., & Kantar Davran, M. (2021). Tarımsal çevre kirliliği açısından üreticilerin bilinç düzeyi: Doğu Akdeniz bölgesi örneği. *ISPEC Tarım Bilimleri Dergisi, 5(3)*, 641-651. https://doi.org/10.46291/ISPECJASvol5iss3pp641-651

76. Tiryaki, O., Canhilal, R., & Horuz, S. (2010). Tarım ilaçları kullanımı ve riskleri. *Erciyes Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 26(2)*, 154-169.

77. Trombino, S., Sole, R., Di Gioia, M. L., Procopio, D., Curcio, F., & Cassano, R. (2023). Green chemistry principles for nano- and micro-sized hydrogel synthesis. *Molecules, 28(5)*, 2107. https://doi.org/10.3390/molecules28052107

78. Turgut, O., Keskin, H. L., & Avşar, A. F. (2011). Nanoteknoloji nedir? *Turkish Medical Journal, 5(1)*, 45-49. https://izlik.org/JA87JN57FP

79. Valavanidis, A. (2016). Green chemistry and new technological developments. *New Avenues for the Green Economy and Sustainable Future of Science and Technology,* 1-33.

80. Yarsan, E., & Çevik, A. (2007). Vektör mücadelesinde biyopestisitler. *Türk Hijyen ve Deneysel Biyoloji Dergisi, 64(1)*, 61-70.

81. Yeniçeri, M. (2018). Yağmur sularının hasadı ve aktif olarak tarımsal sulamada kullanılması. *Afet ve Risk Dergisi, 1(2)*, 126-136. https://doi.org/10.35341/afet.447687

82. Yenilmez, A. (2024). Sürdürülebilir tarım için nanoteknoloji ve uygulamaları. A. Çakır (Ed.), Bahçe bitkilerinde inovasyon ve sürdürülebilirlik yaklaşımları. İksad Yayın Evi.

83. Yolci, M. S., & Tunçtürk, R. (2022). Biyogübre uygulamaları ve inorganik gübrelemenin aspir (carthamus tinctorius l.) bitkisinin bazı agronomik özellikleri üzerine etkisi. *Yüzüncü Yıl Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 27(3)*, 683-694. https://doi.org/10.53433/yyufbed.1134728

84. Zhan, F., Wang, T., Iradukunda, L., & Zhan, J. (2018). A gold nanoparticle-based lateral flow biosensor for sensitive visual detection of the potato late blight pathogen, Phytophthora infestans. *Analytica Chimica Acta, 1036*, 153-161. https://doi.org/10.1016/j.aca.2018.06.083

FROM POLLUTION TO SUSTAINABILITY IN ANIMAL PRODUCTION: GREEN CHEMICAL TECHNOLOGIES

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ABSTRACT

Animal production plays an important role in fulfilling the nutritional demands of the increasing population. However, it also causes various environmental issues such as gaseous pollutants, ecological disruption, and waste production. Therefore, animal production should change production processes with more sustainable, environmentally friendly production processes. Green chemistry is important approach that aims to prevent the formation of pollutants at their source, use natural resources more efficiently, and recycle waste.

This study discusses green chemistry applications aimed at reducing environmental pollution from animal production. Biochemical approaches to reducing greenhouse gas emissions, naturally derived additives, and innovative feed strategies are evaluated. The roles of biochar, natural adsorbents, and biological treatment applications in reducing water and soil pollution are also examined. In addition, applications for converting animal waste into valuable agricultural outputs, including biogas and biofertilizer, are included. In conclusion, it is determined that green chemistry technologies can mitigate the environmental burden of animal farming systems, improving their environmental performance, reducing emissions, and achieving sustainable production goals.

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1. INTRODUCTION: GREEN TRANSFORMATION FROM FARM TO THE FUTURE

Although livestock production is one of the most fundamental sectors of humanity's food supply, it has come under increasing scrutiny in recent years for its environmental impacts. Rapid population growth, increased urbanization, and shifts in consumption patterns (particularly between plant-based and animal protein) have driven a surge in food demand. Therefore, production techniques have shifted towards more intensive, faster, and higher-efficiency systems. However, as production grows and efficiency increases, it also brings serious environmental problems. Today, livestock activities are considered a major driver of numerous ecological issues, such as gaseous pollutants, soil deterioration, water quality issues, antibiotic residues, heavy metal trace elements, and uncontrolled waste. More importantly, the large waste load generated by such mass-production models poses threats to public health, ecological balance, and levels of natural resource contamination.

The ecophysiological characterization of animal production has, for years, been carried out with an approach that prioritizes increasing productivity to fulfill the nutritional needs of an expanding population. Despite resources often claimed to be limitless, productivity has been prioritized over environmental impact. However, today it is clear that this is unsustainable, as the current production method is consuming natural resources at alarming rates, and signs of environmental degradation are becoming more visible. Producing more is no longer enough. It is also crucial to minimize environmental damage caused by production and to maximize resource-use efficiency, ensuring that future generations can enjoy the right to life. Therefore, cattle breeding systems in such agricultural systems need to shift towards more environmentally friendly and sustainable livestock farming.

Green chemistry (GC) technologies are among the most important avenues for this transformation. GC differs from traditional environmental thinking because, instead of focusing on cleaning up existing pollution, it aims to prevent pollution from occurring in the first place. Consequently, it is an evidence-based way of thinking that focuses on developing processes to prevent environmental impact, rather than seeking solutions only after damage has been done. In this sense, GC is not limited to technologies developed in the laboratory; it also involves a holistic transformation perspective that requires rethinking the processes involved in production. The primary objectives of GC include reducing the consumption of toxic chemicals, increasing energy efficiency, using renewable resources, and minimizing waste.

GC for animal production encompasses a wide range of applications. Examples include replacing chemicals in feed with less harmful alternatives, developing environmentally friendly disinfectants, applying bio-based additives, and recycling waste generated during production. In particular, converting animal manure into energy, organic fertilizer, or other bio-based products has significant potential for both environmental benefits and economic returns. In numerous regions worldwide, the use of livestock waste for biogas production is already a key component

of sustainable energy policies. With appropriate technologies, waste (considered an environmental nuisance) can be transformed into economic value.

The fundamental principle of GC is also strongly related to the idea of a circular economy. Unlike traditional production systems based on a "use-and-throw" mentality, the circular economy aims to keep resources within the system for as long as possible. According to this understanding, materials considered as waste are recovered and reintroduced into the production cycle, reducing material loss. The key components of this transition are recycling organic waste generated by animal production, improving water use, and developing energy-efficient systems. This approach not only reduces environmental impacts but also lowers production costs.

Sustainability has evolved from a purely environmental concern to one of the three fundamental pillars that must be considered alongside economic and social dimensions in recent years. With increasing consumer pressure for more sustainable production methods, stricter regulations, and a global wave of policies aimed at securing ecosystem services, the livestock sector faces growing challenges and incentives to develop new solutions. In this context, green chemical technologies are among the key tools for limiting environmental impacts without compromising production efficiency. This enables cleaner production processes, low-toxicity substitutes, and energy-optimized systems; it also facilitates the utilization of renewable materials to help minimize the ecosystem stresses created by animal production.

This book chapter will address critical aspects of some key factors responsible for environmental pollution in animal production within the framework of GC principles. It will also examine in detail how the fundamental core concepts of GC can be applied within animal production systems, which technologies are at the forefront of developing sustainable production models, and which innovative approaches exist for waste management. Furthermore, value-added waste management practices, energy-efficient systems, and next-generation technologies with lower environmental impact will be discussed.

Today, pollution control alone is insufficient. The real challenge is preventing environmentally harmful practices from taking root. Environmentally friendly production models and efficient resource utilization, prioritizing human Health, are essential for a sustainable future in livestock farming. GC technologies, in turn, provide the necessary scientific foundation for this transformation, making it possible and representing one of the most critical strategies in shaping the future of the livestock sector.

2. POLLUTION SOURCES AND ENVIRONMENTAL IMPACTS IN ANIMAL PRODUCTION

Environmental pollution is defined as the degradation of ecological compartments including primary environmental matrices by waste materials and energy resulting from human activities. Today, various studies are being conducted at local and global levels across many scientific disciplines to prevent environmental pollu-

tion. The different types of this environmental pollution are being examined, and solutions are being developed (Karaman, 2006). In order to fulfill the increasing need for livestock-derived protein, livestock farming is carried out using intensive production systems. However, the environment created near large settlements leads to serious environmental problems (Mutlu, 1999). Technological advancements in livestock production have increased production, but management practices have also contributed to environmental pollution. While the effects of the resulting degradation can be reduced, they cannot be eliminated (Karaman, 2006). Factors causing disruptions in operational activities include improper storage of manure, failure to properly control dead animals in accordance with hygiene rules, and inadequate planning of slaughterhouses and feed storage facilities.

Furthermore, this situation leads to conditions such as bad odor, visual pollution, and pest infestation. It is important to consider the necessary technical standards and storage criteria to prevent harm to the animals living in the livestock area (Mutlu, 1999). In modern livestock farming, careless use or open-air storage of manure can cause nitrogen- and phosphorus-rich leachate to mix with groundwater and surface water. This leachate causes eutrophication in the water supply, reducing dissolved oxygen levels and threatening aquatic life. Greenhouse gases including nitrous oxide (N_2O) and methane from livestock activities lead to atmospheric pollution and global warming. The transfer of heavy metals, like copper as well as zinc utilized as dietary additives, from manure to soil can pollute the soil. Unlike industrial pollution, pollution from animal production is a diffuse source spread over wide areas. Therefore, animal waste mixes with groundwater and surface water through surface runoff, degrading water quality and affecting storage structures (Karaman, 2006; Ongley, 1996).

2.1. Animal Waste (Manure and Liquid Waste)

Animal waste includes solid manure, urine, bedding materials (straw, sawdust, etc.), spilled feed, milking parlor washing water, and production water generated in cattle, sheep, and poultry facilities. When properly managed, it is an efficient source of organic fertilizer and biogas. However, when left uncontrolled, it leads to air, water, and soil pollution. When solid and liquid wastes are applied together, within certain limits, manure and urine are no longer considered waste; instead, they gain value for plant yield. Maintaining the organic matter balance in the soil is possible through this type of use. However, excessive use harms both product quality and soil structure. Deterioration is observed in groundwater and surface water. The healing of disease-causing agents leads to the spread of a foul odor throughout the environment, living organisms, and the entire ecosystem. Contamination of animal shelters with manure leads to the proliferation of bacteria, making the foul odor even more pervasive (Karaman, 2006).

2.2. Gas Emissions and Atmospheric Pollution

In animal barns, the livestock farming structure, along with haphazard waste management and ruminant animals' digestive processes (enteric fermentation), sig-

nificantly contributes to global atmospheric pollution and greenhouse gas emissions. Different types of gases are produced in shelters during the breakdown of feed, animal respiration, and the biological decomposition of manure. These gases are generally released into the environment through ventilation systems. Gases such as carbon dioxide (CO_2), methane (CH_4), nitrogen oxides (NOx), sulfur compounds (H_2S, SO_2, etc.), and ammonia (NH_3) released into the atmosphere both affect air quality and exacerbate climate change (Kılıç & Şimşek, 2009).

Carbon dioxide (CO_2) is a gas that is produced and accumulates in enclosed animal shelters, particularly in closed-type housing. This gas is produced due to animal respiration and biological activity in manure. Carbon dioxide is odorless, colorless, and 1.5 times heavier than air. CO_2 production by animals inside the shelter is directly related to heat production. Therefore, CO_2 production is a function of animal weight, feeding level, and the thermal environment. The CO_2 level in the external environment the permitted level in shelters, and the level of harmful effects all affect CO_2 levels inside the shelter. It is closely related to the harmful effects of its concentration (Iserman, 1994; Kılıç & Şimşek, 2009).

Methane (CH_4) is an invisible, scentless gas having a lower density than air. A methane-air blend at concentrations of 5-15% by volume can be flammable. In a confined space and under the same conditions, the volume of methane gas is approximately 7-9% of carbon dioxide production. Methane gas production in animals decreases with reduced food intake; animals with poor appetite do not produce any methane gas (Iserman, 1994; Kılıç & Şimşek, 2009).

Nitrogen oxides (NOx) are generated as a result of the microbial breakdown of nitrogen substances that are organically present in livestock waste. NOx emission depends on the occurrence of denitrification following nitrification. Nitrification is the biologically driven oxidative breakdown of NH_3 to nitrates (NO_3^-) and nitrites (NO_2^-) and needs aerobic conditions. In this process, NH_3 is converted to NO_3^- in primary phase and NO_2^- in the second phase by biological oxidation by a group of bacteria called Nitrosomonas. Denitrification is a microbial-driven reaction in which NO_2^- and NO_3^- are converted into nitrogen gas (N_2, N_2O, and NO) under conditions devoid of oxygen. N_2 is the primary yield of the denitrification process. Thus, for nitrogen to be emitted from animal farms, the manure must initially be processed oxygenated environment (dry) and then oxygen depleted environment (wet). The main nitrogen oxides originating from animal farms are N_2O, nitrogen monoxide (NO), and nitrogen dioxide (NO_2) (Anonymous, 2001).

Ammonia (NH_3) is a transparent gas with an acrid odor, has a lower density than air, and dissolves in water. In barns, NH_3 is generated as a consequence of the accumulation of waste in the bedding and its decomposition under anaerobic conditions. In other words, the origin of ammonia gas is biological activity in the feces and in the bedding material (straw, hay) used for the animals. This activity, which occurs in the bedding, is affected by the length of time the bedding remains in the shelter, the ventilation rate, temperature, humidity, and the frequency with which the animals are placed in the shelter (Kılıç & Şimşek, 2009).

Sulfur compounds are one of the most prevalent pollutants produced in animal barns, with hydrogen sulfide (H_2S) being discharged into the air through mechanical ventilation systems. Reduced sulfur compounds follow H_2S. Some of the volatile organic sulfur compounds released are methyl mercaptan, diethyl sulfide, dimethyl sulfide, dimethyl disulfide, and carbonyl sulfide (Sweeten et al., 1998). Other reduced sulfur compounds are released in small amounts (Anonymous, 2001). H_2S emissions from animal barns are minimal in comparison to different natural sulfur forms (volcanoes, swamps) on a global and national scale. This emission amount indicates that H_2S from animal barns affects the minimally to the ecological system. Nevertheless, within a regional context, areas with high concentrations of animal shelters and a few other sources contribute significantly to the atmospheric sulfur load (Schnoor et al., 2002; NAPAP, 1991). H_2S is produced anaerobically by the microbial transformation of sulfates in the environment and the microbial breakdown of sulfur-based organic compounds in waste. H_2S, which is known by its characteristic sulfurous odor, is generated by living organisms in an atmosphere without oxygen where sulfate is converted to sulfide. Anaerobic conditions are usually found in animal manure storage areas (Xue et al., 1998). There are two primary origins of sulfur in animal waste. One is sulfur-containing amino acids found in the dietary formulation, and the other is mineral-based sulfur substances introduced to the dietary formulation to promote healthy development. Although sulfates are used across all branches of animal husbandry, they are more common in the poultry industry. In some regions, the third source of sulfur is trace minerals in drinking water (Anonymous, 2001).

In terms of the impact of these gases on atmospheric pollution, non-toxic carbon dioxide, which functions as an essential part in the air composition, increases after the use of fossil fuels and becomes the main factor in global warming. This gas deepens the greenhouse effect, disrupting environmental systems. Its impact is not limited to this; the process in the atmosphere is a long-term growth. Fossil fuel energy production also releases sulfur dioxide and nitrous oxide. When these substances interact with water vapor, they contribute to the formation of acid rain. High pollutant emissions undergo chemical transformation under sunlight. The resulting new structures appear as smog, reducing visibility and clouding the air. Methane, on the other hand, is a much more efficient heat sink due to its binding structure. As a result, it accelerates climate change faster than carbon dioxide. In the atmosphere, it reacts with nitrous oxides, increasing the production of ozone (O_3) at the surface. This situation leads to both lung problems in humans and a decline in plant life.

Sulfur-containing products, especially sulfur dioxide, are produced because use of fossil fuels and directly disrupt the composition of the air. When these gases come into contact with moisture, they form acidic precipitates. Acidic precipitates damage natural habitats, endanger human Health, and exacerbate climate change. Sulfur dioxide released into the environment reacts with water vapor and oxygen to form sulfuric acid (H_2SO_4). As a result the pH of lakes and rivers decreases, po-

tentially leading to the extinction of aquatic organisms. Ammonia, when combined with other sources of atmospheric pollution, can form new chemical structures. Among these products, ammonium sulfate and similar compounds produced by certain chemical processes can form dust particles. These substances, which reduce visibility, negatively affect human Health.

2.3. Veterinary Drugs and Antibiotic Residues

In general, antibiotics and veterinary drugs are indispensable tools in intensive animal production systems worldwide, including in our country. These drugs are generally used to treat animal diseases, to increase product yield, and to improve health control. The fact is that almost three-quarters of animals used for food production and that have reached adulthood receive at least one drug treatment in their lifetime (Yıbar & Soyutemiz, 2013). "The most frequently used antibiotics in veterinary medicine are: β-lactam (penicillins and cephalosporins), tetracycline group, chloramphenicol, macrolides, spectinomycin, lincomycin, sulfonamide, nitrofuran, nitroimidazole, trimethoprim, polymyxin, quinolone, and macrocyclic (Ansamycin, glycopeptides, and aminoglycosides) groups" (Chafer et al., 2010, p.1038). These antibiotics found in animal bodies can leave permanent marks not only in muscles but also when they accumulate in tissues such as the kidneys and liver. From a product perspective, transmission can occur from milk to eggs. Overdosing and waste products resulting from treatment methods mixed into feed can manifest themselves in food. Unauthorized drug treatment of some animals, or failure to wait until slaughter after treatment, may contribute to various health issues for humans. Products like as milk, eggs, and honey produced through such erroneous practices carry risks.

Insufficient monitoring at every stage of animal production maintains the potential for problems in food production and consumption. Therefore, strict controls are necessary from production to feeding.

3. GREEN CHEMISTRY PRINCIPLES AND THEIR APPLICABILITY TO ANIMAL PRODUCTION

GC is an approach focused on preventing waste at its source and reducing or eliminating substances that could harm human, environmental, and animal health. This enables increased feed efficiency in animal production, reduced greenhouse gas emissions, the adoption of green approaches in medicine, and the transformation of farm waste into valuable resources. Developed by Paul Anastas and John Warner, the twelve principles can be applied to animal production processes (livestock, milk, and egg production) in the following ways:

3.1. Waste Prevention

***Application*:** To prevent animal manure from barns and stables from harming the environment (water resources), it is processed in biogas plants, where it is converted into energy and organic fertilizer.

3.2. Atomic Economy

***Application*: Balanced and precise feeding to optimize the digestive system of animals (focus). Implementation of feeding programs. This ensures that the feed is converted into meat and milk at the highest rate, and that nutrient losses through feces are minimized.

3.3. Less Hazardous Chemical Syntheses

***Application*: In animal health,** phytobiotics containing plant extracts and natural ingredients (e.g., thyme, garlic extracts) should be preferred over chemical drugs.

3.4. Designing Safer Chemicals and Products

Application: Development of biodegradable vaccines and medicines that support animal welfare and do not accumulate in nature.

3.5. Safer Solvents and Auxiliary Substances

***Application*: Using environmentally friendly, organic acid - based or microbial cleaners, compliant with the 12 Principles of GC, instead of synthetic and toxic chemicals for disinfection and cleaning processes on farms.

3.6. Design for Energy Efficiency

***Application*: Reducing energy costs in modern poultry houses and barns through automation, sustainable LED lighting solutions, and the implementation of green power sources like solar and wind energy.

3.7. Use of Renewable Raw Materials

***Application*: Using natural** probiotics and enzymes obtained through the fermentation of agricultural by-products, instead of fossil fuel-derived feed additives or synthetic amino acids.

3.8. Reducing Derivatives (Derivative Products)

***Application*: In feed production,** ensiling high-quality forage crops in their natural form avoids the need for additional chemical treatments (and associated waste) to preserve nutritional value.

3.9. Catalysts (Instead of Stoichiometric Reagents)

***Application*: Utilizing natural biocatalysts (enzymes) such as** phytase and carbohydrate to facilitate feed digestion.

3.10. Design for Degradation (Disintegration)

***Application*: Selecting** bioplastics for plastic equipment (baler twine, covers, etc.) used on farms, which can decompose without leaving toxic microplastics in nature.

3.11. Real-Time Monitoring of Pollution

***Application*: Using** precision livestock technologies and sensors, real-time monitoring of animal condition and ammonia levels inside barns enables immediate prevention of contamination and disease.

3.12. Safe Chemistry That Prevents Accidents

***Application*:** Preventing leaks in the storage of pharmaceuticals, fertilizers, and feed additives, "One Health. " The concept of 'Health' aims to reduce the risk of poisoning in veterinary practice to zero.



Figure 1. *The 12 Fundamental Principles of GC (Source: https://medium.com/@eberber 9811/kimyay%C4%B1-ye%C5%9Fertmek-5f46ea3da96b)*

4. GREEN CHEMISTRY TECHNOLOGIES IN ANIMAL WASTE MANAGEMENT

Animal waste, which has lost its nutritional value, cannot produce the desired effect when applied to fields without proper care. Substances that cannot be retained in the soil are carried away by rainfall and mix with water. Inappropriate storage methods increase the environmental damage caused by this waste. Applications

carried out without a project create problems for both producers and the ecology. Long-term regulations are needed instead of temporary solutions. If agricultural waste is not distributed in a measured and planned manner, the results can be negative. In soils where chemical balances are disrupted, the product's reliability decreases over time. Waste from livestock activities can be beneficial for control purposes. In cases of uncontrolled management, it generally causes damage that is difficult to reverse. The application of all existing regulations is important, especially in water supply. Biogas is generated through oxygen-free natural breakdown of organic matter such as animal remains; it is a clean form of energy. However, it offers the possibility of use in various areas such as transportation, electricity, or savings. The remaining waste is functional in agriculture as fermented fertilizer. This situation puts it at the forefront of certain changes. Its accessibility increases as it is produced through technological systems, and it can also be obtained through simple village production lines. Given Turkey's significant livestock potential, effective management of waste and its conversion into biogas is important. Waste is thus not only disposed of but also becomes part of a beneficial cycle: both energy is generated and the amount of natural nutrients provided increases. (Dindar, 2018)

4.1. Biogas and Bioenergy Production

Biogas is an energy source derived from many types of biomass. In other words, it is an energy source derived from various organic materials or waste. When biogas is produced, the resulting gas is not completely pure. It contains approximately 55-75% CH_4 (methane), 25-45% CO_2 (carbon dioxide), 1-10% hydrogen (H_2), 0-0.3% nitrogen (N_2), and 0-3% H_2S. Biogas and bioenergy are produced from animal waste by the decomposition of animal manure and other organic waste by microorganisms in an anaerobic environment. This method allows for waste control while yielding valuable resources, such as electricity and heat, as well as high-quality organic fertilizer. The residues left over after biogas production can also be used as organic fertilizer. Fertilizer generated from the oxygen-free breakdown of organic matter, particularly animal manure, increases soil fertility and growth rate by approximately 10%. Therefore, biogas production for organic fertilizer is quite advantageous for both energy generation and organic fertilizer production (Şenol et al., 2017).

Methane production from animal manure occurs in three stages: Hydrolysis, Acid Production, and Methane Production. In the first stage, high-molecular-weight, solid or dissolved organic substances such as cellulose, starch, hemicellulose, fat, and protein are hydrolyzed by the cells' extracellular enzymes. That is, they are transformed into lower-molecular-weight organic compounds. The following phase involves acid formation. Here, acid bacteria convert small organic molecules into fatty acids of varying densities, which are then converted into acetic acid. In the final stage, the resulting acetic acid is broken down or synthesized into CO_2 and H_2, producing CH_4 (Deviren et al., 2017).

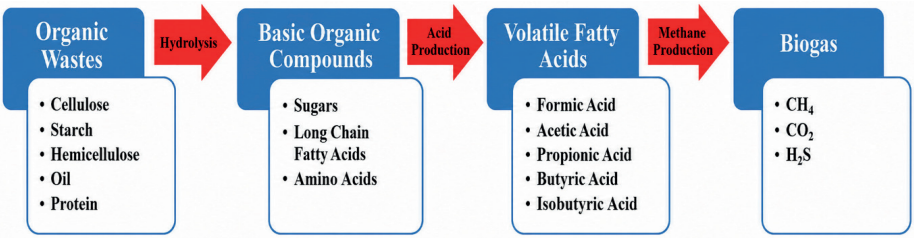

Figure 2. *General Representation of the Steps of Anaerobic Decomposition. (Source: https://dergipark.org.tr/en/download/article-file/390296)*

4.2. Composting and Chemical Stabilization

"Compost: Fertilizers obtained by the decomposition of waste from plant and animal production activities by microorganisms. Compost fertilizers are used in agricultural activities to increase the nutrient content, water retention capacity, and soil fertility. Composted Animal Manure: Organic fertilizers formed as a result of the controlled decomposition of animal waste by microorganisms under suitable conditions." (Ektiren et al., 2026, p. 798).

When biochemically produced animal-derived waste is processed, odor is reduced, and microbes are eliminated. This transformation process, beneficial to the soil, alleviates environmental pressures. The product obtained from combined solids is rich in organic matter. When natural parameters are prioritized over chemicals, the final use of the waste becomes safer. Maintaining long-term balance in agriculture is crucial. When considering factors affecting composting to maintain balance, the type of organic waste to be processed is one such factor. Moisture level is very important because it directly affects microbial systems. A certain ratio of carbon and nitrogen is required. As temperatures increase, biological transformation can be disrupted. Information regarding the quantity and type of pathogens, etc., is presented in Table 1 (Şahin et al., 2020).

Table 1. *Optimal Values Required for an Ideal Composting Process*

Parameter	Desired Values
C: N Ratio	25–30
Particle Size	10 mm in aerated systems
Moisture Content	50–60%
Air Flow	Oxygen content should be maintained between 10–18%
Temperature	55–60°C
pH	5.5–9.0
Pile Height	If natural aeration is used, the pile should be 1.5 m high, 2.5 m wide, and of the desired length.
Microbial Activity	Cellulolytic fungi and biofertilizers

The management or neglect of these environmental and biological factors directly affects the practical advantages and disadvantages of composting. Maintaining these variables under ideal conditions ensures that the numerous environmental and economic benefits of composting are fully realized. For example, compost is a powerful soil conditioner and also has commercial value. It also provides fertilizer additives and expands the scope of agricultural practices. It eliminates disease microbes and prevents weed germination. It also stops the transmission of viruses from the soil to plants. However, ignoring or mismanaging the factors that need to be considered in this process can lead to practical difficulties and disadvantages in composting. Sometimes the natural composting process can take several months. Poor air circulation can lead to unpleasant odors, creating an undesirable impression on the environment. Among external conditions, wind speed and air humidity can jeopardize the balance in the material pile. An imbalance in the carbon-to-nitrogen (C/N) ratio can affect both plant growth and soil stability. Compost products with low maturity levels have limited sales unless they are commercially accepted. Production losses due to problems in livestock farming should also be considered. Chemical stabilization of waste involves reducing the irritancy of animal manure using specific chemicals. Chemicals such as lime or chlorine help prevent bad odors. This method also eliminates dangerous microorganisms. The acid-base balance of the waste can also change during this process. The fundamental difference from composting is the methods used to dispose of organic waste.

4.3. Approaches to Transforming Waste into Value

Some animal waste, like plant waste, plays a role in the economy. Among the tissue samples from products leaving slaughterhouses daily are gallbladders. These gallbladders are often discarded without being processed. The substances they contain – sodium chloride, potassium chloride, sodium bicarbonate, phosphates, as well as bile salts and pigments – can be specifically separated. These systems, isolated in laboratory settings, can be adapted for various applications. Gallbladders should be seen not as waste, but as a resource containing valuable compounds. Separating and utilizing the parts within them can help protect the economy. The resulting products have the potential to gain functionality in new areas. This approach both reduces resource waste and ensures efficient transformation (Kök, 2021).

5. GREEN CHEMISTRY APPLICATIONS FOR EMISSION REDUCTION IN ANIMAL PRODUCTION

Animal husbandry industry serves as a key part in ensuring worldwide food security and supporting rural economies, but it is also central to sustainability discussions due to its environmental impacts. In particular, atmospheric pollutants, water use, soil contamination, nutrient losses, and waste management are critical variables impacting the ecological performance of livestock production processes. The livestock production sector is responsible for approximately 14.5% of worldwide

human-induced greenhouse gas emissions, with a significant portion originating from biological and operational processes (Gerber et al., 2013; FAO, 2017).

International policies focused on minimizing the ecological impact of the agricultural industry, as part of the fight against climate change, have made the development of more sustainable technologies for animal production systems imperative. In this context, the GC methodology provides a holistic approach that aims to reduce the ecological effects of chemical processes, prevent waste generation, utilize renewable feedstocks, maximize energy conservation, and design ecologically friendly compounds. The twelve fundamental principles of GC, put forward by Anastas and Warner (1998), include sustainable production goals such as preventing waste, using safer chemicals, reducing energy use, and utilizing renewable raw materials.

In animal production systems, GC applications, unlike traditional environmental protection approaches, focus not on removing pollutants after they have appeared, but on preventing their formation at the source. In this context, feed additives that reduce enteric methane formation, biochar and natural adsorbent applications, biological fertilizer processing technologies, circular biomass utilization, bio-based additives from renewable resources, and processes aimed at converting waste into value-added products stand out. Thus, it is possible to minimize greenhouse gas emissions and utilize bio-based resources with enhanced efficiency (Grossi et al., 2019).

In recent years, biochemical approaches to reducing methane emissions, particularly from ruminant animals, emission-reducing technologies in manure management, and applications for the utilization of animal waste within the framework of the circular economy have become significant research areas. These technologies support environmental conservation, enhance feed utilization, minimize nutrient losses, and provide economic advantages at the farm level. Therefore, GC applications are considered a fundamental tool for developing sustainable animal production systems today.

This section discusses emissions in animal production. GC practices aimed at reducing methane; biochemical strategies for methane reduction; innovative technologies used in fertilizer management; natural adsorbents and biochar applications; biological treatment systems; and circular biomass-based approaches will be examined and evaluated from environmental and sustainability perspectives.

5.1. Biochemical Approaches to Methane Reduction

Methane emissions from animal production systems constitute a major proportion of worldwide greenhouse gas emissions. Methane generated by gastrointestinal processes, particularly in ruminant species, is a major problem for both environmental sustainability and feed energy loss. Methane synthesis by methanogenic archaea in the rumen helps remove hydrogen produced during fermentation, but it also leads to a reduction of approximately 2–12% of the energy ingested (Johnson & Johnson, 1995). Therefore, in recent years, studies aimed at developing biochemical strategies that directly or indirectly suppress methane formation have

accelerated. Biochemical approaches generally involve inhibiting methanogens, modifying hydrogen-utilization pathways, and reshaping the rumen microbiota (Hristov et al., 2013).

3-Nitrooxypropanol (3-NOP)

3-NOP is now regarded as one of the most successful methane-reducing dietary additives. This compound is methanogenic. It blocks the last stage of methane production by inhibiting the methyl-coenzyme M reductase enzyme found in archaea. Studies have reported that it may lower methane outputs by 20–40% in cattle production systems (Hristov et al., 2013; Kebreab et al., 2023). It has high commercial potential due to its minimal negative effects on animal performance.

Nitrate and Nitrite- Based Approaches

Nitrates function as another hydrogen acceptor in the forestomach, allowing hydrogen to be used in the conversion of ammonia instead of methane. This mechanism can reduce methane production (Ungerfeld, 2020). When used at appropriate doses, nitrites can reduce methane production by 10–20%. The risk of toxicity must be carefully managed.

Use of Sulfate and Fumarate

Additional electron acceptors including sulfate and fumarate might limit methane formation by removing hydrogen from methanogens. Fumarate, in particular, increases hydrogen consumption by promoting propionate formation. However, its applications have been limited due to economic costs and variable efficiency levels (Ungerfeld, 2020).

Red Seaweed (Asparagopsis) spp.)

Asparagopsis species are methanogenic due to the bromoform they contain. It suppresses the enzyme systems of archaea. Studies have reported decreases in methane emissions of between 60–90% (Kinley et al., 2020; Roque et al., 2021). However, factors such as large-scale production, bromoform residues, and cost limit the widespread adoption of this application.

Tannins

Tannins, methanogens, and the rumen. They can reduce methane formation by exerting suppressive effects on protozoa. Studies using condensed tannins, in particular, have reported reductions in methane of 5–20% (Patra & Saxena, 2011). However, excessive use can negatively affect feed digestibility.

Saponins

Saponins weaken the symbiotic relationship with methanogens by reducing the rumen protozoa population. This indirectly suppresses methane formation. However, varying results have been reported regarding the sustained effectiveness of their effects. (Jayanegara et al., 2011).

Essential Oils

Essential oils of plant origin have antimicrobial properties that protect the rumen. microbiota. They can modify it. In particular, oils containing thymol, carvacrol, eugenol, and cinnamaldehyde are reported to suppress methanogenic activity. However, the effects vary depending on the compound used and the dose (Cobellis et al., 2016).

Flavonoids and Other Phenolic Compounds

Flavonoids, polyphenols, and other secondary plant metabolites. Romanian They can reduce methane formation by altering microbial activity. Due to their antioxidant and antimicrobial properties, these compounds have been evaluated as alternative feed additives in recent years (Patra & Saxena, 2011).

Fat and Lipid Supplements

Unsaturated lipids may exert an unmediated suppressive impact on methanogens and enhance hydrogen-consuming biohydrogenation processes. Reductions in methane emissions ranging from 10–25% have been reported with the addition of fats (Beauchemin et al., 2008).

Probiotics and Directly Feeding Microorganisms

Some types of bacteria and yeast in the rumen can alter fermentation, redirecting hydrogen toward different metabolic pathways. This is especially true for Saccharomyces. Extensive research is being conducted on cerevisiae and some propionate- producing bacteria. However, the results obtained are not yet consistent (Newbold & Rode, 2006).

Vaccination Practices

The development of vaccines targeting methanogenic archaea has emerged as an important field of research over the past few years. The aim is to neutralize methanogens. The goal is to achieve long-term methane reduction by suppressing the rumen population. However, due to the complexity of its microbiota, commercial success has not yet been achieved (Wedlock et al., 2013).

Romanian Microbiome Engineering

Thanks to new-generation sequencing technologies, the structure of the microbiota has been elucidated in more detail. Microbiome engineering approaches involve supporting alternative microorganisms that utilize hydrogen or methanogens. It is based on the principle of population reduction. This area is considered one of the most promising future research topics (Hook et al., 2010).

CRISPR and Genetic Approaches

Advances in molecular biology are enabling the genetic regulation of microbial communities responsible for methane production. While CRISPR-based applica-

tions are still in the experimental stage, they are considered among the technologies that could be used in methanogen control in the future.

Biochar

Biochar, rumen, can alter electron transfer processes by affecting fermentation and, in some studies, reduce methane emissions. However, the results obtained are inconsistent, additional study is necessary to determine the level of effectiveness (Leng et al., 2012).

Biochemical approaches to methane reduction contribute to environmental sustainability and also enable more efficient use of feed energy. However, factors such as economic costs, potential impacts on animal performance, ease of application, consumer acceptance, and regulatory compliance determine the widespread use of these technologies. Currently, 3-NOP and Asparagopsis-based applications stand out as technologies with the highest reduction potential.

Biochemical approaches developed to lower enteric methane emissions in animal production are among the important instruments in the struggle against global warming. 3-NOP, nitrates, seaweeds, plant secondary metabolites, probiotics, and microbiome-based technologies can suppress methane formation through different mechanisms of action. It is predicted that integrated strategies using these approaches together will achieve greater success in the future.

5.2. Ammonia and Odor Control

Barn ventilation, animal waste storage units, and land-applied manure are the primary origins of odor and gas emissions in the livestock industry. Ammonia, a colorless, toxic gas with a strong odor, is one of the most critical emissions from this sector. Ammonia gas is discharged as a consequence of the breakdown of urea in animal feces by microorganisms that secrete the urease enzyme (Avşar et al., 2018).

In enclosed livestock farming, strong odors originating from ammonia, sulfur, and hydrocarbons, caused by animal feces and metabolic waste, are a serious problem. Ammonia levels exceeding 20–30 ppm cause mucosal damage, respiratory diseases, and restricted movement in animals. Since this directly reduces animal welfare and production efficiency, odor control is of great importance (Uyar, 2007).

6. PREVENTING WATER AND SOIL POLLUTION IN ANIMAL PRODUCTION

Water and soil pollution in animal production results from uncontrolled manure runoff, overgrazing, and veterinary drug residues. To prevent pollution, leak-proof manure pits should be constructed, manure should be applied to the soil at the correct time, pasture rotation should be implemented, and wastewater should be treated and reused in agriculture.

Fertilization is a frequently used method for providing the nutrients necessary for plant growth. However, excessive or inappropriate use can lead to environmental

pollution. The improper application of chemicals to the land reduces agricultural productivity and damages water resources. Looking at alternative approaches, the use of organic compounds, such as compost, can help achieve chemical changes (Yeşilyurt, 2025). Fertilizers derived from waste materials offer more environmentally friendly solutions. These options may be stored and maintained for a many years. Biogas or compost derived from animal manure helps collect waste and control waste streams, creating opportunities for reuse without harming the environment. Organic fertilizers that play a role in soil conservation – for example, compost or worm castings – can help reduce pollution as an alternative to chemical fertilizers.

Waste from livestock farms and leachate from the storage of certain agricultural products, such as silage, generally pollute water. Animal wastewater can carry disease-causing agents and add other substances, such as nitrogen and phosphorus, to the water. Smaller livestock farms have fewer problems with this waste. In these places, the manure produced is considered beneficial for the soil, as it nourishes it.

Livestock farms generally choose the simplest method for wastewater storage. They collect wastewater and sewage in a simple pond or small pool. With this method, waste is not spread outside and is easier to manage. Waste collection is not difficult; in most places, these simple ponds are sufficient. Thus, both the environment and the farm are protected (Karaman, 2006).

6.1. Biological and Chemical Treatment Systems

Biological treatment systems are green systems in which microorganisms biodegrade natural pollution loads in their natural environments. In biological treatment, highly effective treatment efficiencies are achieved using trickling filtration and activated sludge systems, which are preferred methods for treating wastewater from livestock slaughterhouses. Furthermore, it has been stated that trickling filtration systems achieve 81-90% BOD (Biochemical Oxygen Demand) removal; two-stage trickling filtration reaches 95%; and in biological treatment, activated sludge systems (90-95% BOD removal) or oxidation ditches are used. (Bozkurt, 2013).

Chemical treatment systems are used when biological treatment alone is insufficient, or for phosphorus removal and/or suspended-solid precipitation. The EC (Electrocoagulation) process has been applied as an innovative wastewater treatment technology for treating slaughterhouse wastewater. The EC process is an environmentally friendly technology for removing organic matter, nutrients, heavy metals, and even pathogens from slaughterhouse wastewater using electric current without the use of chemicals. Several electrode types are used in the EC process, including Al, Fe, Pt, $SnO_{2,}$ and $TiO_{2;}$ however, Fe and Al are the most commonly used (Yılmaz & Karagözoğlu, 2019).

Applications of Natural Adsorbents and Biochar

High volumes of wastewater and animal manure runoff generated from animal production activities contain high concentrations of nitrogen (N), phosphorus (P), heavy metals (especially copper and zinc from feed additives), and antibiotic resi-

dues. Treating these pollutants with conventional methods is both costly and risks generating secondary waste. Within the framework of GC principles, agro-waste-based natural adsorbents and biochar (a pyrolytic product) applications stand out as sustainable, closed-loop-economy alternatives for solving this problem.

Natural Adsorbents: Valorization of Agricultural By-Products

Agricultural and animal by-products, used without the need for chemical modification processes or with minimal green activation (e.g., via weak organic acids), can bind pollutants in wastewater with high efficiency thanks to their porous structures and functional surface groups. Hydroxyl and carboxyl groups on the surfaces of lignocellulosic materials such as hazelnut shells, rice husks, wheat straw, and tea wastes act as chelating agents, retaining cationic heavy metals (Cu2+, Zn2+) in animal wastewater (Anastas & Eghbali, 2010).

In the literature, it is known that the adsorption capacities of these unmodified natural polymers exhibit phase-dependent variability in terms of metal selectivity. However, the biggest limitation of these materials is their limited regeneration capacity and the potential for final disposal problems once they reach saturation. From a GC perspective, saturated natural adsorbents are currently under consideration. It is suggested that these be reintroduced into the economy as soil conditioners by being included in composting processes.

Biochar Technology and Pollutant Immobilization

Biochar is a stable, carbon-rich, highly porous solid material obtained through the thermochemical transformation (pyrolysis) of biomass in anaerobic or oxygen-limited environments. As a GC technology in animal production, biochar has a dual function: it both treats pollution in animal wastewater at the source. It stabilizes soil structure, preventing leaching into groundwater.

Pyrolysis temperature is the most critical parameter determining the surface chemistry and pore size distribution of biochar. Biochars produced at high temperatures (500°C) retain micropollutants (e.g., veterinary drugs and antibiotics) through physical adsorption (pore-filling) due to their large surface area. In comparison, those produced at low temperatures (400°C) bind heavy metals via electrostatic attraction and ion-exchange mechanisms, facilitated by the oxygen-containing functional groups on their surfaces (Ahmad et al., 2014).

Recent research has centered on recovery of the phosphorus and ammonium (NH_4^+) ions, which trigger eutrophication—one of the biggest environmental problems in animal production—using biochar. Specifically, green modified biochars enriched with magnesium or calcium can precipitate phosphate from wastewater onto their surfaces via a mechanism similar to struvite ($MgNH_4PO_4 \cdot 6H_2O$) crystallization (Yao et al., 2012). Biochar that reaches this saturation level transforms into a "slow-release organo -mineral fertilizer" that can be applied directly to agricultural soils, thus preventing soil pollution and minimizing the use of synthetic fertilizers (Sohi et al., 2010).

In conclusion, natural adsorbents and biochar technologies have the potential to transform the linear "waste generation" model created by animal production into a circular resource in line with the "waste prevention" and "atomic economy" principles of GC.

7. REDUCING THE USE OF ANTIBIOTICS AND CHEMICALS IN ANIMAL PRODUCTION

In today's intensive and industrial livestock systems, epidemic diseases can cause significant economic losses. To treat infectious diseases in herds, antibiotic administration under veterinary supervision for a specific period is necessary, similar to human medicine. However, antibiotics administered during treatment can be transferred to animal source foods. This prevents these products from being offered to consumers until the withdrawal period (elimination period) of the pharmacologically active substances has passed; it necessitates the collection and destruction of products obtained during the treatment period (Şentürk Demirel & Demirel, 2020). In addition to the direct economic losses incurred during these disposal processes, failure to comply with drug withdrawal deadlines or continued lack of oversight will lead to an increased risk of antibiotic residues in animal-derived foods. These residues enter the ecosystem through food products and animal waste, causing antimicrobial resistance (AMR), leading to the most significant worldwide crises threatening societal well-being, and creating the risk that even simple infections may become untreatable in the future (WHO, 2014).

At the academic level, global policies and regulations to minimize the use of antibiotics and chemicals in animal production worldwide are well accepted to avoid these risks and economic losses. In order to break the chain of transmission of resistant bacterial strains (Van Boeckel et al., 2015), it has become necessary to limit the uncontrolled consumption of antimicrobials in the agricultural and livestock sectors. This has led to the emergence of the "One Health" approach, often emphasized in the international literature, and which is based on the idea that human, animal and environmental health are inextricably linked, and that drug management in livestock farming should be integrated into global health policies (Ong et al., 2026). This holistic vision aims to legally framework the restriction of routine chemical inputs for growth factors or preservatives, and the rational use of antibiotics only in cases of absolute cure.

The most critical aspect of this transformation is the integration of sustainable alternatives and preventive management strategies into production that will fundamentally reduce the need for treatment. The use of natural feed additives such as probiotics, prebiotics, organic acids, and herbal extracts to support the immune system and intestinal health of animals is rapidly becoming widespread (Allen et al., 2013). However, minimizing chemical interventions is possible not only with alternative additives but also by tightening biosecurity measures at the farm level, optimizing vaccination programs, and implementing rational housing designs that consider animal welfare (Mallioris et al., 2025). Consequently, the most lasting way to prevent disposal losses and residue risks due to withdrawal periods is through a holistic management strategy that protects herd health.

CONCLUSION

Animal production systems play an essential part in fulfilling the protein needs of the world's increasing population. Nevertheless, they are also a major contributor various ecological problems, including carbon emissions, nutrient losses, and aquatic and soil contamination (Gerber et al., 2013). In recent years, amid attempts to fight global warming, the reduction of environmental impacts from the agricultural and livestock sectors has accelerated. Within this framework, GC has been recognized as an important tool for developing sustainable animal production systems (Anastas & Warner, 1998).

The applications discussed in this section aim to prevent the formation of environmental pollutants at their source and to use natural resources more efficiently, according to the basic fundamentals of GC. This condition especially holds true for enteric diseases. Biochemical strategies for reducing methane emissions from fermentation offer significant potential for reducing the environmental footprint of ruminant animals. 3-nitrous oxypropanol (3-NOP), seaweed, and plant secondary metabolites. metabolites, and alternative hydrogen acceptors have been reported to limit methane formation through different mechanisms and, in certain instances, yield substantial emission reductions (Hristov et al., 2013; Kinley et al., 2020).

Furthermore, the ecological effects of animal husbandry extend beyond greenhouse gas emissions. Manure management, wastewater generation, and nutrient losses are also important for environmental sustainability. In this context, applications such as biochar, natural adsorbents, and biological treatment technologies offer significant advantages for reducing nitrogen and phosphorus losses, immobilizing heavy metals, and conserving water resources (Lehmann & Joseph, 2015; Wang & Peng, 2010). Furthermore, converting animal waste into biogas, biofertilizer, or other value-added products enables its use within the circular economy, removing it as an environmental burden (FAO, 2017).

The application of GC technologies in animal production extends beyond ecological advantages, offering significant opportunities to increase resource efficiency, recover energy, recycle nutrients, and support long-term agricultural viability (Grossi et al., 2019). However, for these technologies to be widely adopted, their economic viability needs to be increased, solutions tailored to regional conditions need to be developed, and producers' access to the technology needs to be facilitated.

In conclusion, approaches to reducing environmental problems in animal production should focus not only on controlling pollutants but also on preventing their formation. Technologies based on GC principles have a substantial capacity to enhance the ecological footprint of livestock farming and contribute to sustainable development goals. It is anticipated that future research in biotechnology, microbiome engineering, circular biomass use, and innovative bio-based materials will further accelerate the transformation of animal production from "pollution to sustainability".

SONUÇ

Hayvansal üretim sistemleri, artan dünya nüfusunun protein ihtiyacının karşılanmasında kritik bir rol üstlenmekle birlikte, sera gazı emisyonları, besin maddesi kayıpları, su ve toprak kirliliği gibi çeşitli çevresel sorunların da önemli kaynaklarından biridir (Gerber et al., 2013). Son yıllarda iklim değişikliği ile mücadele kapsamında, tarım ve hayvancılık sektörlerinden kaynaklanan çevresel etkilerin azaltılmasına yönelik çalışmalar hız kazanmış ve bu süreçte yeşil kimya yaklaşımı, sürdürülebilir hayvansal üretim sistemlerinin geliştirilmesinde önemli bir araç olarak öne çıkmıştır (Anastas & Warner, 1998).

Bu bölümde ele alınan uygulamalar, yeşil kimyanın temel ilkeleri doğrultusunda çevresel kirleticilerin oluşumunu kaynağında önlemeyi ve doğal kaynakların daha verimli kullanılmasını hedeflemektedir. Özellikle enterik fermantasyondan kaynaklanan metan emisyonlarının azaltılmasına yönelik biyokimyasal stratejiler, geviş getiren hayvanların çevresel ayak izinin azaltılmasında önemli bir potansiyel sunmaktadır. 3-nitrooksipropanol (3-NOP), deniz yosunları, bitkisel sekonder metabolitler ve alternatif hidrojen alıcıları gibi uygulamaların metan oluşumunu farklı mekanizmalarla sınırlandırabildiği ve bazı durumlarda önemli düzeylerde emisyon azaltımı sağlayabildiği bildirilmektedir (Hristov et al., 2013; Kinley et al., 2020).

Diğer taraftan, hayvansal üretimden kaynaklanan çevresel etkiler yalnızca sera gazı emisyonlarıyla sınırlı değildir. Gübre yönetimi, atık su oluşumu ve besin maddesi kayıpları da çevresel sürdürülebilirlik açısından önemli konular arasında yer almaktadır. Bu kapsamda biyokömür, doğal adsorbanlar ve biyolojik arıtım teknolojileri gibi uygulamalar; azot ve fosfor kayıplarının azaltılması, ağır metallerin immobilizasyonu ve su kaynaklarının korunması bakımından önemli avantajlar sağlamaktadır (Lehmann & Joseph, 2015; Wang & Peng, 2010). Ayrıca hayvansal atıkların biyogaz, biyogübre veya diğer katma değerli ürünlere dönüştürülmesi, atıkların çevresel yük olmaktan çıkarılarak döngüsel ekonomi içinde değerlendirilmesine olanak tanımaktadır (FAO, 2017).

Yeşil kimya teknolojilerinin hayvansal üretimde uygulanması yalnızca çevresel faydalar sağlamakla kalmamakta, aynı zamanda kaynak kullanım etkinliğinin artırılması, enerji geri kazanımı, besin maddelerinin yeniden değerlendirilmesi ve üretim sistemlerinin uzun dönemli sürdürülebilirliğinin desteklenmesi açısından da önemli fırsatlar sunmaktadır (Grossi et al., 2019). Bununla birlikte, bu teknolojilerin yaygın olarak benimsenebilmesi için ekonomik uygulanabilirliklerinin artırılması, bölgesel koşullara uygun çözümlerin geliştirilmesi ve üreticilerin teknolojiye erişiminin kolaylaştırılması gerekmektedir.

Sonuç olarak, hayvansal üretimde çevresel sorunların azaltılmasına yönelik yaklaşımlar yalnızca kirleticilerin kontrol edilmesine değil, kirleticilerin oluşumunun önlenmesine de odaklanmalıdır. Yeşil kimya ilkelerine dayalı teknolojiler, hayvansal üretim sistemlerinin çevresel performansını iyileştirme ve sürdürülebilir kalkınma hedeflerine katkı sağlama açısından önemli bir potansiyel taşımaktadır. Gelecekte biyoteknoloji, mikrobiyom mühendisliği, döngüsel biyokütle kullanımı ve yenilikçi biyobazlı materyaller alanlarında gerçekleştirilecek çalışmaların, hayvansal üretimin "kirlilikten sürdürülebilirliğe" dönüşüm sürecini daha da hızlandıracağı değerlendirilmektedir.

REFERENCES

1. Ahmad, M., Rajapaksha, A., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S., & Ok, Y.S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere, 99*, 19–33. https://doi.org/10.1016/j.chemosphere.2013.10.071
2. Allen, H. K., Levine, U. Y., Looft, T., Bandrick, M., & Casey, T. A. (2013). Treatment, promotion, commotion: Antibiotic alternatives in food-producing animals. *Trends in Microbiology*, *21*(3), 114–119. https://doi.org/10.1016/j.tim.2012.11.001
3. Anastas, P. T., & Warner, J. C. (1998). Green chemistry: Theory and practice. Oxford University Press. Online ISBN: 9780197704059
4. Anastas, P., & Eghbali, N. (2010). Green Chemistry: Principles and Practice. *Chemical Society Reviews, 39* (1), 301–312. https://doi.org/10.1039/B918763B
5. Anonymous. (2001). *Emissions from animal feeding operations*. US Environmental Protection Agency.
6. Avşar, E., Uyar, Ö., Alp, K., & Hanedar, A. (2018). Investigation of the effectiveness of biofilters in the treatment of odorous gases originating from animal husbandry. *Sakarya University Journal of Science Institute, 22* (2), 459–467. https://doi.org/10.16984/saufenbilder.340048
7. Beauchemin, K.A., Kreuzer, M., O'Mara, F., & McAllister, T. A. (2008). Nutritional management for enteric methane abatement: A review. *Australia Journal of Experimental Agriculture, 48* (2), 21–27. https://doi.org/10.1071/EA07199
8. Bozkurt, H. (2013). *Treatability of slaughterhouse and leachate water in an anaerobic upflow reactor* (Doctoral dissertation).
9. Chafer-Pericás, C., Maquieira, Á., & Puchades, R. (2010). Fast screening methods to detect antibiotic residues in food samples. *Trends in Analytical Chemistry, 29* (9), 1038–1049. https://doi.org/10.1016/j.trac.2010.06.004
10. Cobellis, G., Trabalza-Marinucci, M., Marcotullio, M.C., Face., (2016). Evaluation of different essential oils in modulating methane and ammonia production, rumen fermentation, and Romanian bacteria in vitro. *Animal Feed Science and Technology, 215*, 25–36. https://doi.org/10.1016/j.anifeedsci.2016.02.008
11. Demirel, D. Ş., & Demirel, R. (2020). Feed-derived toxic substances in animal products. *Osmaniye Korkut Ata University Journal of Science Institute, 3* (2), 185–192. https://doi.org/10.47495/okufbed.764116
12. Deviren, H., İlkılıç, C., & Aydın, S. (2017). Materials usable in biogas production and application areas of biogas. *Batman University Journal of Life Sciences, 7* (2/2), 79–89. https://izlik.org/JA72GF46HA
13. Dindar, E. (2018). Environmental impacts, alternative uses, and management of animal waste. *Workshop Proceedings*, 97. 97-108.
14. Ektiren, M. N., Boydak, E., & Dumanoğlu, Z. (2026). Effects of plant, animal, and microbial fertilizers on the sustainability of agriculture. 794-803.
15. FAO. (2017). Livestock solutions for climate change. Food and Agriculture Organization of the United Nations. https://openknowledge.fao.org/handle/20.500.14283/i8098en

16. Gerber, P. J., Steinfeld, H., Henderson, B., Mottet, A., Opio, C., Dijkman, J., Falcucci, A., & Tempio, G. (2013). Tackling climate change through Livestock: A global assessment of emissions and mitigation Opportunities. Food and Agriculture Organization of the United Nations. ISBN: 9789251079201

17. Grossi, G., Goglio, P., Vitali, A., & Williams, A. G. (2019). Livestock and climate change: Impact of livestock on climate and mitigation strategies. Animal Frontiers, 9(1), 69–76. https://doi.org/10.1093/af/vfy034

18. Hook, S. E., Wright, A. D. G., & McBride, B. W. (2010). Methanogens: Methane producers of the Romanian and mitigation strategies. *Archaea, 2010(1)*, 945785. https://doi.org/10.1155/2010/945785

19. Hristov, A. N., Oh, J., Firkins, J. L., Dijkstra, J., Kebreab, E., Waghorn, G., et al. (2013). Special topics — Mitigation of methane and nitrous oxide emissions from animal operations: I. A review of enteric methane mitigation options. *Journal of Animal Science, 91* (11), 5045–5069. https://doi.org/10.2527/jas.2013-6583

20. Isermann, K. (1994). Agriculture's share in the emission of trace gases affecting the climate, and some cause-oriented proposals for sufficiently reducing this share. *Environmental Pollution, 83* (1–2), 95–111. https://doi.org/10.1016/0269-7491(94)90027-2

21. Jayanegara, A. Leiber, F., & Kreuzer, M. (2011). Meta- analysis of the relationship between diet tannin level and methane formation in ruminants *Journal of Animals Physiology and Animal Nutrition, 96* (3), 365–375. https://doi.org/10.1111/j.1439-0396.2011.01172.x

22. Johnson, K. A., & Johnson, D. E. (1995). methane emissions from Cattle. *Journal of Animal Science, 73* (8), 2483–2492. https://doi.org/10.2527/1995.7382483x

23. Karaman, S. (2006). Environmental problems arising from animal production and possible solutions. *KSÜ Journal of Science and Engineering, 9* (2), 133–139.

24. Kebreab, E., Bannink, A., Pressman, E.M., Walker, N., Karagiannis, A., van Gastelen, S., & Dijkstra, J. (2023). A meta-analysis of effects of 3-nitrooxypropanol on methane production, yield, and intensity in dairy Cattle. *Journal of Dairy Science, 106* (2), 927–936. https://doi.org/10.3168/jds.2022-22211

25. Kılıç, İ., & Şimşek, E. (2009). Gas emissions from animal shelters and their environmental impacts. *Uludağ University Faculty of Engineering Journal, 14* (2). 151-160. https://izlik.org/JA76FG97HE

26. Kinley, R. D., Martinez-Fernandez, G., Matthews, M.K., de Nys, R., Magnusson, M., & Tomkins, N.W. (2020). Mitigating the carbon footprint and improving the productivity of ruminant livestock agriculture using red Seaweed. *Journal of Cleaner Production, 259*, 120836. https://doi.org/10.1016/j.jclepro.2020.120836

27. Kök, F. (2021). Management, recycling, and applications of organic waste. *National Environmental Sciences Research Journal, 4* (2), 99–108. https://izlik.org/JA57TZ32KK

28. Lehmann, J., & Joseph, S. (Eds.). (2015). Biochar for Environmental Management: Science, Technology, and Implementation (2nd ed.). Routledge. ISBN: 978-1-84407-658-1

29. Leng, R. A., Inthapanya, S., & Preston, T. R. (2012). Biochar lowers net methane production from Romanian fluid in vitro. *Livestock Research for Rural Development, 24* (6).

30. Mallioris, P., Dhaka, P., Makovska, I., Van Sabben, N., Wagenaar, J. A., Stegeman, A., Mughini-Gras, L., & Dewulf, J. (2025). Improved animal husbandry, biosecurity and vaccination as a strategy to reduce antimicrobial use. *Scientific and Technical Review*, *44*(1), 32–45. https://doi.org/10.20506/rst.44.3682

31. Mutlu, A. (1999). *A study on environmental pollution caused by waste generated in livestock facilities around Adana province* (Master's thesis, Çukurova University).

32. National Acid Precipitation Assessment Program. (1991). *acidic deposition: State -of- science and state -of- technology* (Vols. I–IV).

33. Newbold, C. J., & Rode, L. M. (2006). Dietary additives to control methanogenesis in the rumen. *International Congress Series, 1293*, 138–147. https://doi.org/10.1016/j.ics.2006.03.047

34. Ong, C. J. N., Ogaya, J. B., Nazari, R., Ahmed, M. M., & Lucero-Prisno III, D. E. (2026). Reframing the one health approach to antimicrobial resistance: The epidemiologic significance of environmental water quality. *Journal of Taibah University Medical Sciences*, *21*(1), 114–121. https://doi.org/10.1016/j.jtumed.2026.01.001

35. Ongley, E. D. (1996). *Control of water pollution from agriculture* (FAO Irrigation and Drainage Paper No. 55). Food and Agriculture Organization.

36. Patra, A. K., & Saxena, J. (2011). Exploitation of diet tannins to improve Romanian metabolism and ruminant nutrition. *Journal of the Science of Food and Agriculture, 91* (1), 24–37. https://doi.org/10.1002/jsfa.4152

37. Roque, B.M., Venegas, M., Kinley, R.D., de Nys, R., Duarte, T.L., Yang, X., & Kebreab, E. (2021). Rejection seaweed (Asparagopsis taxiformis) supplementation reduces enteric methane by over 80% in beef steers. PLOS ONE, 16 (3), e0247820. https://doi.org/10.1371/journal.pone.0247820

38. Şahin, ST Ö., Turan, MA, & Akça, H. (2020). Environmental and waste management in agricultural production. *Proceedings of the IX. Technical Congress of Turkish Agricultural Engineering* (Vol. 1), 141-154.

39. Schnoor, J. L., Thorne, P. S., & Powers, W. (2002). Fate and transport of air pollutants from CAFOs. In *Iowa Concentrated Animal Feeding Operation Air Quality Study* (pp. 86–100). Environmental Health Sciences Research Center, University of Iowa. https://ehsrc.public-health.uiowa.edu/wp-content/uploads/2019/08/CAFO_final2-14.pdf

40. Şenol, H., Elibol, EA, Açıkel, Ü., & Şenol, M. (2017). Main biomass sources for biogas production in Turkey. *Bitlis Eren University Journal of Science, 6* (2), 81–92. https://doi.org/10.17798/bitlisfen.315118

41. Sohi, S.P., Krull, E., Lopez- Capel, E., & Bol, R. (2010). A review of biochar and its use and function in soil. *Advances in Agronomy, 105*, 47–82. https://doi.org/10.1016/S0065-2113(10)05002-9

42. Sweeten, J.M., Parnell, C.B., Shaw, B.W., & Auvermann, B.W. (1998). Particle size distribution of cattle feedlot dust emission. *Transactions of the ASAE, 41* (5), 1477–1481. https://doi.org/10.13031/2013.17297

43. Ungerfeld, E. M. (2020). Metabolic hydrogen flows in rumen Fermentation: Principles and Possibilities of interventions. *Frontiers in Microbiology, 11*, 589. https://doi.org/10.3389/fmicb.2020.00589

44. Uyar, Ö. (2007). *Control of ammonia emissions with biofilters*. http://hdl.handle.net/11527/8963

45. Van Boeckel, T. P., Brower, C., Gilbert, M., Grenfell, B. T., Levin, S. A., Robinson, T. P., Teillant, A., & Laxminarayan, R. (2015). Global trends in antimicrobial use in food animals. *Proceedings of the National Academy of Sciences*, *112*(18), 5649–5654. https://doi.org/10.1073/pnas.1503141112

46. Wang, S., & Peng, Y. (2010). Natural zeolites as effective adsorbents for water and wastewater treatment. Chemical Engineering Journal, 156(1), 11–24. https://doi.org/10.1016/j.cej.2009.10.029

47. Wedlock, D. N., Janssen, PH, Leahy, SC, Shu, D., Buddle, BM (2013). Progress in the development of vaccines against Romanian methanogens. *Animal, 7* (S2), 244–252. https://doi.org/10.1017/S1751731113000682

48. World Health Organization. (2014). *Antimicrobial resistance: Global report on surveillance*. World Health Organization. ISBN:9789241564748

49. Xue, S.K., Chen, S., & Hermanson, R. E. (1998). Measuring ammonia and hydrogen sulfide emitted from manure storage facilities *Transactions of the ASAE, 41* (4), 1125–1130. https://doi.org/10.13031/2013.17259

50. Yao, Y., Gao, B., Zhang, M., Inyang, M., & Zimmerman, A. R. (2012). Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil . *Chemosphere, 89* (11),1467–1471. https://doi.org/10.1016/j.chemosphere.2012.06.002

51. Yeşilyurt, S. (2025). *Soil pollution*. 209-238. https://doi.org/10.37609/akya.3810.c821

52. Yıbar, A., & Soyutemiz, E. (2013). Antibiotic use and potential residue risk in food-grade animals. *Atatürk University Journal of Veterinary Sciences, 8* (1), 97–104. https://izlik.org/JA46PH83ZG

53. Yılmaz, Z., & Karagözoğlu, MB (2019). Electrocoagulation applications in wastewater treatment. *Bitlis Eren University Journal of Science, 8* (1), 319–334. https://doi.org/10.17798/bitlisfen.466114

GREEN EXTRACTION METHODS: PRINCIPLES, ADVANCES, AND APPLICATIONS

ÖNDER AYBASTIER*

ABSTRACT

To counter the environmental, economic, and operational disadvantages inherent in conventional extraction techniques, green extraction methods have emerged as a next-generation approach that is sustainable, safeguards human health, and enhances product quality. Based on the "Six Principles of Green Extraction" of Farid Chemat was newly proposed to the field, this book chapter reviews the modern solvent systems and emerging extraction techniques for natural compounds in terms of the risks associated with the traditional toxic VOCs, and the working principle and merits of various environment-friendlier alternatives including subcritical water, scCO, ionic liquids (ILs), deep eutectic solvents (DES), and bio-solvents (agro-solvents). The emerging technologies enhancing mass transfer kinetics while reducing thermal damage including ultrasound-assisted (UAE), microwave-assisted (MAE), pressurized liquid (PLE), enzyme-assisted (EAE), electric field-assisted (EFAE) and mechanochemical extraction (MCE), are also introduced with principle of working. Finally, the industrial applications of green extraction technologies on the field of food, nutraceutical, cosmetic, pharmaceuticals, waste valorization, and biomaterials/polymers are discussed. In conclusion, besides producing high-purity and safe food products, medicine, the green extraction is proved to be an innovation tool with the principle of sustainability to translate the industrial processes to the circular economy.

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1. INTRODUCTION

1.1. Definition and Importance of Green Extraction

Traditional extraction methods, such as Soxhlet extraction and maceration, have been traditionally recognized as the workhorse analytical and industrial techniques for extracting bioactive molecules from plant matrices. However, given the recent trend focused at sustainability and ensuring they are green products, these traditional methods are technologically unsound due to environmental, economic and operational shortcomings. The most alarming feature of these traditional extraction methods, including Soxhlet extraction and maceration, is the utilization of large amounts of toxic volatile organic solvents (VOCs; for instance; hexane, methanol, ethanol, chloroform). This aspect mitigates the health of the human extraction workers and the environment, but it also affects negatively the reliability of food and pharmaceutical extracts due to the increase of residual VOCs (Ameer et al. 2017). The massive energy consumption, time waste and thermal stresses imposed on the molecules of interest by Soxhlet extraction machine also constitutes the major disadvantages of the all traditional methods. For thermally-labile molecules, the bioactivity might be lost due to the heat stress involved for several hours (Azmir et al., 2013).

In the context here, green extraction is defined as a sustainable future oriented approach environmental friendly and cost effective fo over the regular techniques that would bring human health and product quality at higher standards. The main purpose of green extraction will be to extract target compound at the highest yield and purity with a sustainable energy input from renewable resources by means of non-toxic alternative solvents as well as using minimized consumption of energy. In comparison to classic techniques, green extraction also increased extraction kinetics and prevents the active biomedical contents such as drug, drug delivery system, bioactive material to be degradation at biomolecular level. The existing of this kind of transformation is not only an environmentally obligation but also will be a strategic need for extracting low cost and high quality product sales at the industrial level (Picot-Allain et al., 2021).

1.2. The Six Principles of Green Extraction (Chemat Principles)

"The Six Principles of Green Extraction," introduced to the literature by Farid Chemat and his colleagues, serves as a universal guideline for all stages of a sustainable extraction process, from its design to industrial application (Chemat et al., 2012). Inspired by Paul Anastas and John Warner's foundational 12 guidelines of green chemistry, Farid Chemat redefined these principles for specific laboratory and industrial applications, such as the isolation of natural compounds from biomass (Anastas&Warner, 1998). These principles aim to minimize the environmental footprint while increasing efficiency in chemical operations and extraction processes.

These principles represent a specific adaptation of green engineering and green chemistry philosophies to extraction processes:

Use of renewable resources:

The first step of a sustainable process is to transition from depleting petrochemical-based resources to renewable biomass sources. This principle emphasizes the preservation of biodiversity and the optimized use of agricultural resources without harming the ecosystem. It also advocates for the integration of agricultural innovations that enhance the synthesis of targeted compounds. Cultivating the plant matrices (e.g., fruit peels, plant leaves, or seeds) from which the target molecules will be obtained through sustainable agricultural practices falls within this scope.

Use of alternative solvents:

This involves replacing toxic and volatile petrochemical solvents with water, supercritical fluids (especially CO_2), agricultural-based bio-solvents (ethanol, glycerol), and Deep Eutectic Solvents (DES/NADES), which have shown great potential in recent years. These alternative solvents stand out for offering high solvation capacity while being eco-friendly and reducing volatile organic compound (VOC) emissions to zero (Dai et al., 2013).

Reduction of energy consumption:

This involves utilizing innovative technologies to lower the high energy costs associated with conventional heating methods. Utilizing the cavitation effect in Ultrasound-Assisted Extraction (UAE) or providing heating by directly increasing molecular mobility via Microwave-Assisted Extraction (MAE) reduces processes that typically take hours down to a matter of minutes. In this way, energy consumption is significantly reduced, and the preservation of thermolabile compounds is ensured (Chemat et al., 2020).

Valorization of by-products (biorefinery approach):

This is the principle of evaluating process outputs as secondary raw materials rather than generating direct waste. For instance, after extracting phenolic compounds from a plant matrix, isolating lignin from the remaining lignocellulosic pomace for use in the polymer industry or directing it toward biofuel production, instead of disposing of it as waste, serves as an excellent example of the circular economy model (Dai et al., 2013).

Reduction of unit operations (process intensification):

This entails integrating multiple sequential and time-consuming steps—such as extraction, filtration, purification, and concentration—and reducing them to a single step or fewer steps. Process intensification shrinks equipment sizes, prevents material losses during intermediate stages, and improves overall efficiency, thereby allowing for the establishment of more compact and safer industrial facilities (Chemat et al., 2020).

Production of biodegradable, non-denatured, and safe products:

This is the ultimate goal, which considers the environmental and biological fate of the final extract. The obtained product should be easily biodegradable in nature after use, contain no toxic residues, and preserve its natural form as in the original matrix. This principle guarantees the safety of the extract, especially for the nutraceutical, cosmetic, and food industries aimed at human consumption (Cvjetko Bubalo et al., 2019).

2. GREEN SOLVENTS

The solvent utilized constitutes the primary selectivity mechanism in extraction processes. Petrochemical-based volatile organic solvents used in conventional extraction methods represent the most significant obstacle to the green chemistry philosophy due to their high environmental burdens, toxicity risks, and the high energy costs associated with their recovery processes. This situation has driven chemists to search for "Green Solvents" that are eco-friendly, renewable, exhibit low toxicity, and offer high selectivity. For a solvent to be classified as "green," it is not sufficient for it to merely possess a low vapor pressure or high biodegradability; it must also generate a minimal carbon footprint throughout its Life Cycle Assessment (LCA) and exhibit high mass transfer kinetics in the separation of target bioactive compounds from the matrix (Capello et al., 2007).

2.1. Water

As the most abundant, non-toxic, non-flammable, and non-explosive substance in nature, water is undoubtedly the most ideal green solvent candidate. However, under room temperature and atmospheric pressure, water is effective primarily in the extraction of hydrophilic compounds due to its high polarity ($\varepsilon = 80$). It remains insufficient for dissolving medium-polar and non-polar secondary metabolites (e.g., phenolic acids, flavonoids, essential oils) that are abundantly found in plant matrices. This limitation is overcome by adjusting the pressure and temperature of the water and utilizing it in the subcritical phase (Somat et al. 2026).

Subcritical water is obtained at temperatures between the boiling point (100 °C) and the critical point of water (374 °C, 22.1 MPa), under sufficient pressure to keep the system in the liquid phase. With an increase in temperature, the hydrogen bonds between water molecules weaken, and molecular mobility increases. This situation leads to a decrease in the dielectric constant of water (Figure 1). For example, when water reaches a temperature of 250 °C, its dielectric constant drops to levels around 25–30. This value is equivalent to the polarity of ethanol or acetone at room temperature. Thus, by dynamically altering its polarity, subcritical water gains the ability to sequentially extract both hydrophilic and hydrophobic compounds using a single solvent system simply through temperature adjustment. Furthermore, the high temperature lowers the surface tension and viscosity of water, facilitating its penetration into the pores of the plant matrix and accelerating mass transfer. In

the supercritical water phase (>374 °C, >22.1 MPa), however, water transforms into an extremely corrosive and reactive state, despite being capable of completely dissolving organic compounds. For this reason, rather than for extraction, it is generally preferred in waste disposal and gasification processes (Teo et al. 2010).

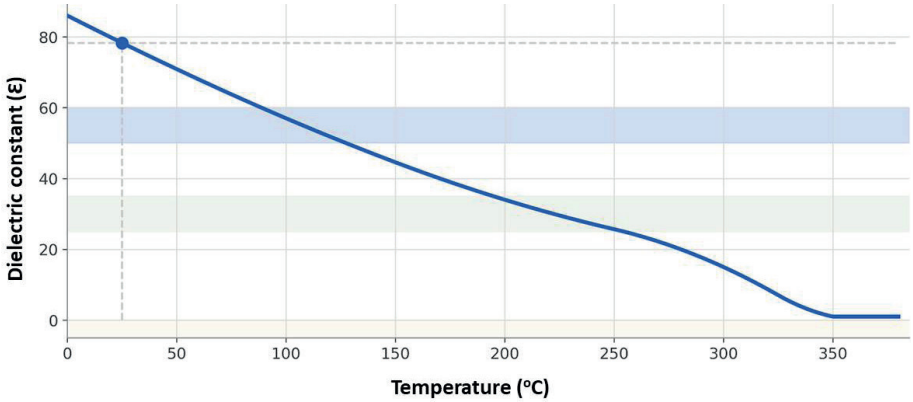


Figure 1. *The variation of the dielectric constant of water with temperature*

2.2. Supercritical Fluids

Supercritical Fluid Extraction (SFE) functions by employing a substance as an extraction solvent, once it has been heated and pressurized above its critical point (Figure 2). Supercritical fluids exhibit the high diffusion coefficient and low viscosity of gases, together with the high density and solvating power of liquids, en masse into a single phase. The application of supercritical carbon dioxide ($scCO_2$) in green extraction is the world the most common.

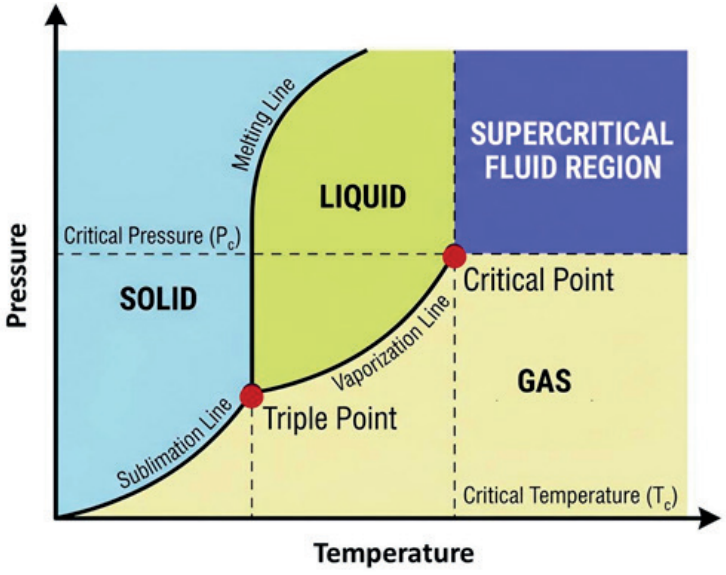


Figure 2. *General representation of a phase diagram*

The main advantages of CO_2 are that the critical temperature (31.1 °C) and pressure (7.38 Mpa) are readily achievable at both laboratory and industrial scales. The low critical temperature also means that temperature sensitive compounds can be recovered without degradation and due to the scope to alter the parameters such as temperature and pressure, one of the biggest benefits of supercritical CO_2 is that by varying the conditions we have the ability to directly influence the density and hence selectivity of the fluid. Following depressurisation the fluid is entirely in the gaseous state and the resultant extract is pure, of the solvent and therefore requires no further solvent removal (Herrero et al., 2010).

$scCO_2$ has a non-polar structure, and its dielectric constant is close to that of hexane. While this characteristic makes it an excellent solvent for triglycerides, essential oils, and carotenoids, it renders it insufficient for the extraction of polar bioactive compounds. To overcome this limitation and broaden the solvent selectivity to encompass polar compounds, a co-solvent or modifier is added to the system in low proportions (1%–10%). To adhere to the principles of green extraction, agricultural-based ethanol or water is generally preferred as the co-solvent. The use of a co-solvent increases the polarity of the $scCO_2$ phase, enabling the formation of hydrogen bonds or dipole-dipole interactions between the target molecules and the solvent, thereby enhancing the extraction yield of polar matrices (Da Silva et al. 2010).

2.3. Ionic Liquids (ILs)

In recent years, the analytical concept of "designer solvents" has made a strong entry into the literature through ionic liquids (ILs). Defined by melting temperatures below 100 °C (mostly at room temperature), ionic liquids are purely ionic salts consisting of an organic cation paired with an organic or inorganic anion. Unlike conventional molecular solvents, their physicochemical properties—such as polarity, viscosity, density, and hydrophobicity—can be precisely tuned by altering their anion-cation combinations to maximize the extraction yield of a specific target molecule. One of the primary goals of green extraction is to achieve maximum mass transfer while expending minimum solvent and energy. Due to the interchangeability of their anion-cation combinations, ionic liquids can be optimized for a specific molecule. Furthermore, they possess an extraordinary solvating capacity owing to the multiple intermolecular interactions (hydrogen bonds, π-π interactions, dipole-dipole, and electrostatic forces) they establish with target molecules (Passos et al., 2014).

The main reason for the ionic liquids being known as green solvents and transforming extraction methods is their capability of replacement of traditional volatile organic compounds. Conventional extraction solvents are volatile into the atmosphere because of their high vapor pressures, loaded with problems of environmental pollution and occupational health and safety (fire and explosion risks). Ionic liquids have negligible vapor pressures which translated to zero emission into the atmosphere during extraction process, clearly meeting with 'Designing Safer Chemicals'

and 'Safer Solvents and Auxiliaries' principles of Green Chemistry. Ionic liquids green chemistry attribute to current debate in the literature about their full green status. While they make the extraction undoubtedly green because of zero emission into the atmosphere and high efficiency, there is argument over how green the chemical itself is. Their synthesis processes are very complex, purification steps are difficult and high cost of conventional imidazolium- or pyridinium-based ionic liquids make them disadvantage on industrial scale. Most importantly, the persistent toxicity of these compounds on aquatic ecosystems and their poor biodegradability profiles have raised concerns regarding the environmental devastation they would cause if released into nature. In other words, while the problem of atmospheric emissions is resolved, the potential risk of water and soil pollution has emerged. This situation, despite the indisputable superiority of ionic liquids in extraction performance, has necessitated the search for truly sustainable and fully biocompatible next-generation solvents (Petkovic et al., 2011).

2.4. Deep Eutectic Solvents (DES)

Following the observation of a drastic reduction in the melting point of a choline chloride and urea mixture, Abbott and his team coined the term deep eutectic solvent (DES) in 2003 (Abbott et al. 2003). Following this initial DES, it was succeeded by choline chloride-glycerol and choline chloride-ethylene glycol. A deep eutectic solvent is defined as a substance prepared by homogeneously mixing two or more components in specific proportions, characterized by a melting point lower than that of its individual constituent substances (Figure 3) (Smith et al. 2014).

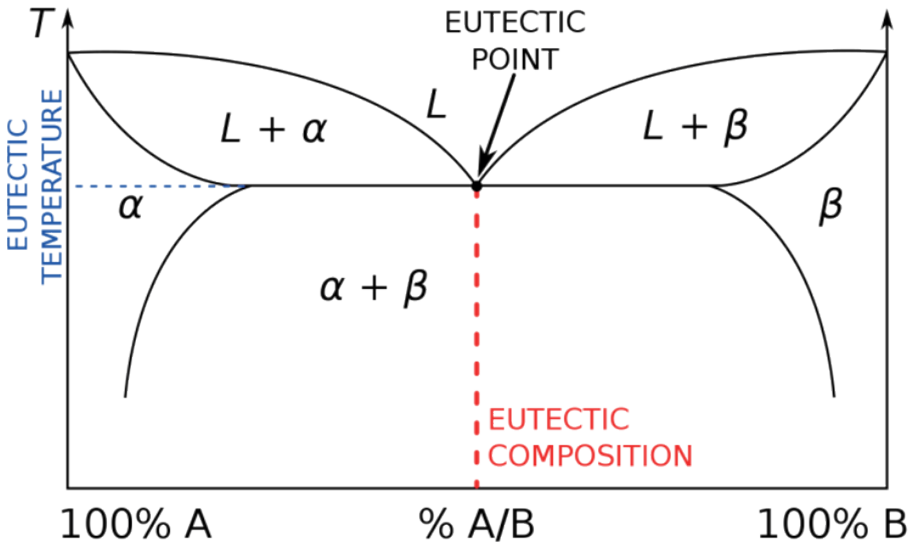


Figure 3. *General eutectic phase diagram of a binary system*

Developed to overcome the toxicity and cost handicaps of ionic liquids, DES are considered a revolutionary step in the field of green extraction. DESs are eutectic systems obtained by mixing a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) at a specific molar ratio. The dense hydrogen bond network between these two components alters the thermodynamics of the system, causing the melting point of the mixture to be dramatically lower than the melting points of both individual components in their pure states. Their synthesis does not require complex reactions; they are obtained simply by heating and mixing the components, and they do not generate by-products.

Deep eutectic solvents are classified into four categories based on the compounds that constitute their structures:

- Type 1: A quaternary ammonium salt (QAS) and a metal chloride
- Type 2: A QAS and a metal chloride hydrate
- Type 3: A QAS and a HBD
- Type 4: A HBD and a metal chloride

Due to its fast and easy preparation and lack of reactivity with water, Type 3 is the most frequently used category when formulating a deep eutectic solvent (Smith et al. 2014).

Natural Deep Eutectic Solvents (NADES), which are completely natural versions of deep eutectic solvents derived from primary cellular metabolites (amino acids, organic acids, sugars), have entirely eliminated toxicity debates. Because of their biological origin, they offer a truly green extraction medium with high biodegradability, zero volatility, and a minimal cytotoxicity profile.

At the core of NADES's success in plant extraction lies its unique solvation mechanism. However, due to the dense hydrogen bond network they contain, their viscosities are considerably higher compared to conventional solvents. This high viscosity can decrease the diffusion coefficient, thereby slowing down mass transfer. To overcome this limitation, NADES systems are generally diluted with a limited amount of water (10%–30%). While the addition of water in this proportion optimizes viscosity without disrupting the eutectic structure, extraction processes are frequently combined with assistive technologies that generate cavitation and thermal effects, such as ultrasound (UAE) or microwave (MAE), to maximize process efficiency (Dai et al. 2015).

2.5. Bio-based Solvents (Agro-solvents)

Bio-based solvents (agro-solvents) are renewable solvents obtained through the fermentation, distillation, or chemical transformation of agricultural raw materials, by-products, or biomass. They are designed as direct substitutes for petrochemical solvents.

- **d-Limonene:** It is a by-product obtained from the processing of citrus peels. Thanks to its strong non-polar character, it is the most important

green alternative to hexane, which is a carcinogenic and toxic petrochemical. It demonstrates excellent performance in the extraction of vegetable oils, carotenoids, and aromatic compounds (Chemat et al. 2019).

- **α-Pinene:** It is a natural bicyclic terpene obtained by processing pine tree resins and forestry waste. Due to its strong non-polar structure, it is a highly effective green alternative that can be used in place of toxic petrochemical solvents. It exhibits a high solvating capacity in the extraction of oils, waxes, and lipophilic bioactive compounds (Sicaire et al., 2015).
- **Ethanol:** Bioethanol is produced through the fermentation of biomass sources such as starch or sugarcane. Its amphiphilic structure, which can exhibit both hydrophilic and lipophilic characteristics, renders it a universal, safe, and GRAS (Generally Recognized as Safe) status solvent for many compounds (Chemat et al. 2019).
- **Glycerol:** As the main by-product of biodiesel production, glycerol is a non-flammable, odorless, non-toxic triol with a high boiling point. Thanks to its excellent miscibility with water and stable structure, it is a highly reliable green alternative to conventional volatile and toxic polar solvents such as methanol. Especially in the preparation of hydrophilic plant extracts for the cosmetic and food industries, it can be used directly as a formulation ingredient, as it does not need to be removed from the final product (Gu&-Jerome, 2010).
- **Ethyl lactate:** Formed via the esterification reaction between ethanol and lactic acid, it is a solvent that can be completely biodegraded into carbon dioxide and water in nature. With its ability to mix with both water and organic solvents, it is one of the most important alternatives to toxic petrochemical solvents like ethyl acetate and acetone. It demonstrates high performance, particularly in the simultaneous, single-step extraction of both hydrophilic and lipophilic bioactive compounds. (Pereira et al. 2011).

3. ADVANCED GREEN EXTRACTION TECHNOLOGIES

The disadvantages inherent in conventional extraction methods, such as mass and heat transfer limitations, long processing times, and high solvent consumption, have necessitated the development of advanced technologies. These technologies overcome thermodynamic barriers by utilizing physical energies such as cavitation, electromagnetic radiation, electrical permeabilization, or mechanical forces. While the transition of target compounds into the solvent phase is accelerated, the risk of thermal degradation is minimized, and the process is brought into alignment with environmental sustainability principles (Chemat et al. 2020).

3.1. Microwave-assisted Extraction (MAE)

Microwave application: microwave radiations are high frequency electromagnetic waves (between 300 MHz and 300 GHz) and transfer energy directly into the system in a totally different way than conventional ways. In MAE system, volumetric heating is achieved mainly by two mechanisms: dipole rotation and ionic conduction. The rapidly changing electromagnetic energy (billions of times per second) causes the polar molecules in the system to repeatedly change orientation (dipole rotation) so as to become aligned with the oscillating electromagnetic field. Simultaneously, the electric component of the field impels the free ions in the medium to drift in the same directions, consequently inducing frequent molecular collisions (ionic conduction). Very intense molecular friction results in a very rapid and homogeneous local heating from the inside of the matrix to the outside (called as "inside-out"). In case of plant material extraction, the vapor pressure of the internal heated intracellular fluids increase, then cell wall will burst and transfered intracellular compounds into solution is maximized (Chan et al. 2011).

In recent years, one of the most innovative applications of MAE is Solvent-Free Microwave Extraction (SFME) technology. In this method, no external solvent is added to the system. It essentially utilizes the *in situ* water inherently present within the structure of the fresh plant material. The water molecules inside the cells are rapidly heated via dipole rotation and ionic conduction. The intracellular water abruptly evaporates, creating high internal pressure. This pressure causes the cell walls to crack. The compounds released upon the rupture of the cell wall are entrained with the cell's own water vapor, condensed in a condenser system, and collected (Li et al. 2013).

Although SFME is mostly standardized for aromatic plants and agricultural wastes at the industrial and academic levels, it is not limited solely to plants. The fundamental prerequisites for the system to operate are that the biological matrix to be extracted must possess a cellular structure, contain water within its cells (or be capable of being moistened immediately prior to processing), and the target compounds must have volatile, semi-volatile, or lipid characteristics enabling them to be carried out via microwave-induced vapor entrainment. Therefore, this method can be utilized for the extraction of various compounds from macro- and microalgae, fungi, insects, and seafood residues (Li et al. 2013).

3.2. Ultrasound-assisted Extraction (UAE)

Based on the principle of applying sound waves above the upper limit of human hearing (>20 kHz) to a liquid medium, ultrasound-assisted extraction (UAE) is one of the most popular green approaches in analytical and industrial extraction. The method relies on the formation of acoustic cavitation resulting from the consecutive compression and rarefaction cycles generated by sound waves in the liquid phase (Figure 4) (Chemat et al. 2017).

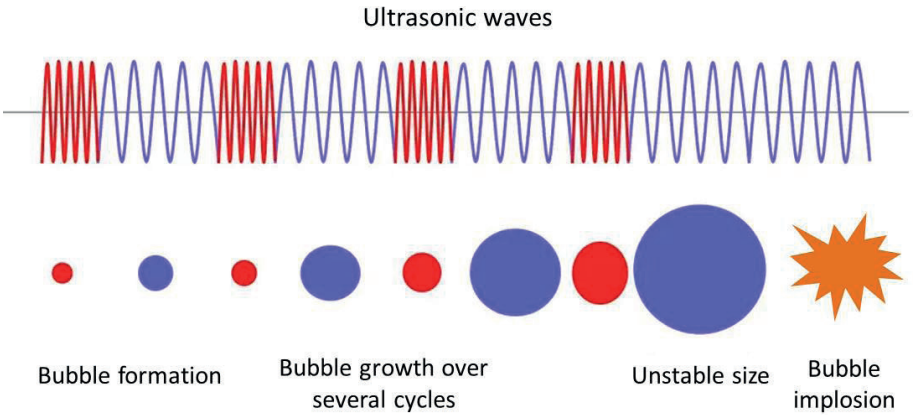


Figure 4. *The phenomenon of ultrasonic cavitation in ultrasound-assisted extraction (UAE) processes*

Cavitation produces numerous tiny bubbles in the liquid medium and causes the mechanical agitation of solids, leading to the detachment of particles. Cavitation bubbles form and grow during the rarefaction phases, where the ambient pressure drops below the vapor pressure of the liquid. Upon reaching a critical size, these bubbles violently collapse inward (implosion) during the high-pressure compression phase. At the moment of this collapse, micro-jets reaching very high velocities are generated, accompanied by localized extreme temperatures and pressures. Striking the surface of the extraction material, these violent micro-jets cause mechanical disruption, leading to erosion and pore formation (sonoporation) in the cell wall. Reducing mass transfer resistance acoustically in this manner enables the extraction of particularly thermolabile compounds in a very short time at low temperatures (Shirsath et al., 2012).

Depending on the strategy for transmitting acoustic energy to the matrix, UAE equipment is fundamentally divided into two main configurations: ultrasonic baths and ultrasonic probes. Ultrasonic baths, which are the most common and low-cost option in the literature, are frequently preferred in routine procedures as they allow for the simultaneous processing of a large number of samples. However, the inhomogeneous energy distribution within the tank may limit the extraction kinetics. In contrast, probe systems, in which a cylindrical titanium probe is directly immersed into the solvent-sample mixture, shorten the extraction time by focusing the cavitation energy in a localized and high-intensity manner. Although the wear of probe tips over time, their higher cost, and the restriction of processing a limited number of samples are disadvantages, the high cellular disruption power they offer makes this equipment more efficient, especially in solid-liquid extractions where strong physical barriers must be overcome. Depending on the objectives, both types of equipment can be used statically; alternatively, they can be successfully integrated into dynamic extraction modes where fresh solvent is continuously pumped into the extraction cell. The dynamic configuration continuously drives the mass transfer equilibrium in the forward direction by ensuring the analyte is removed from the

medium as soon as it transitions into the solvent, while also strongly supporting the principles of green analytical chemistry by enabling the on-line connection of the process to instrumental analysis systems (Luque de Castro&Priego-Capote, 2007).

3.3. Pressurized Liquid Extraction (PLE)

Pressurized Liquid Extraction (PLE), also known as Accelerated Solvent Extraction (ASE), is based on the principle of using liquid solvents at temperatures well above their atmospheric boiling points, but under high-pressure conditions that prevent the system from transitioning into the vapor phase. As the increasing temperature reduces the viscosity and surface tension of the solvent to minimum levels, the applied high pressure ensures that the solvent remains in the liquid phase and penetrates deeply into the solid matrix. This synergistic effect maximizes mass transfer kinetics by increasing the solubility of the analytes and their diffusion from the matrix into the solvent.

From an operational point of view, PLE is totally in accordance with the primary goals of green chemistry. Thanks to the use of PLE techniques, procedures which normally require several hours or even days of extraction, with a classic procedure, are now accomplished within a few minutes (5 to 20 min). Its operation in a completely sealed and inert system, free of oxygen and light, prevent thermal and oxidative degradation of the target molecules even at really high temperature and provide protection for very sensitive bioactive compounds. In addition, the reduction in the volume of organic solvent required and the possibility to fully automate the procedure make this technology a really efficient, reproducible and friendly process (Mustafa&Turner, 2011).

One of the most striking and green applications of the PLE system is the use of pure water as the solvent. Heating water below its critical point but above its normal boiling point (in the range of 100–374°C), and under sufficient pressure to maintain it in the liquid region, causes a very sharp decrease in its dielectric constant. Water, which has a high dielectric constant ($\varepsilon \approx 80$) at room temperature, regresses to the dielectric constant values of organic solvents like methanol or ethanol ($\varepsilon \approx$ 25–30) as the temperature approaches the 200–250°C bands. This unique phase change weakens the hydrogen bond network of water, thereby lowering its polarity. Thus, while enabling the dissolution of semi-polar or non-polar compounds that are normally insoluble in water, the extraction of high-value-added molecules can be performed in a single step and without the use of organic solvents. By reducing solvent costs and generating no toxic waste, the use of subcritical water is elevated to a unique position for green extraction processes (Plaza&Turner, 2015).

3.4. Enzyme-assisted Extraction (EAE)

Enzyme-Assisted Extraction (EAE), a biocatalytic approach, utilizes enzymes instead of physical or chemical disruption. It is an eco-friendly, sustainable, and highly selective innovative technique. The fundamental mechanism of the method is based on the specific hydrolysis of the cell wall components that constitute the

structural integrity of the plant material via enzymes. When the complex polysaccharide networks of the cell wall, such as hemicellulose, cellulose, and pectin, are disrupted, the mass transfer of bioactive substances trapped within the matrix into the solvent medium is significantly accelerated. Thanks to the biocatalytic properties of enzymes that lower the activation energy of the reaction, high reaction rates are achieved under milder conditions. Success in the EAE process depends on the selection of specific enzymes or enzyme mixtures suitable for the chemical composition of the raw material matrix. Due to the biological nature of enzymes, parameters such as pH, temperature, enzyme-to-substrate ratio, liquid-to-solid ratio, and extraction time must be precisely optimized to maximize the reaction yield (Puri et al., 2012).

From a green chemistry of view, this system opens the possibility for water- or water-ethanol based systems, abating the need for toxic solvents on an industrial scale. In addition, it is possible to carry out the process at quite low temperature, thus preserving thermolabile compounds. The high selectivity of enzymatic reactions accounts for the lower formation of by-products and the following possibility for the recovery of higher pure extracts. The main drawbacks of the present method are the high costs of commercially available purified enzymes as well as their sensitivity to external factors such as pH or heat. As a residual free enzyme in the medium at the end of the extraction can lead to further unwanted reactions in the end product, it must either be inactivated by thermal treatment or separated from the system at the end of the process. Nowadays, in order to reduce this problem, shorten the process time, and moreover improve the mass transfer, ENE is combined with other green processes, including ultrasound (UAEE) or microwave (MAEE), so that hybrid systems are developed. Furthermore, in order to decrease the industrial costs, immobilization technologies would be the most promising fields of research, as they enable enzyme reuse and no further enzyme inactivation (Nadar et al., 2018).

3.5. Electric Field-assisted Extraction (EFAE)

Electric field-assisted extraction technologies, which fall under the category of non-thermal green technologies, are fundamentally based on the principle of accelerating mass transfer by increasing the electrical permeability of cell membranes. The fundamental mechanism lying at the core of the method is the phenomenon of electroporation. When a biological tissue is exposed to an external electric field, a transmembrane potential that exceeds a critical threshold value accumulates across the cell membrane. This electrical stress causes the formation of microscopic pores within the lipid bilayer of the cell membrane. Depending on the intensity of the applied electric field, these pores become irreversible, completely disrupting the semi-permeable structure of the cell membrane and allowing the rapid release of bioactive compounds trapped within the matrix into the solvent medium. Occurring in very short durations, such as seconds or milliseconds, this phenomenon maximizes the outward transfer of intracellular fluids without requiring chemical or intense thermal intervention (Barba et al. 2015).

Electric field technologies are divided into different categories based on the intensity and waveform of the applied voltage, namely Pulsed Electric Field (PEF), High Voltage Electrical Discharges (HVED), and Moderate Electric Field (MEF). For a successful process, parameters such as electric field strength (kV/cm), pulse duration, frequency, and the liquid-to-solid ratio must be meticulously optimized in accordance with the tissue characteristics of the target material.

In the PEF method, electric field pulses of 10–50 kV/cm intensity are applied on a microsecond scale. The resulting electroporation allows the intracellular contents to freely diffuse into the solvent phase without causing a temperature increase within the matrix. In the HVED method, much more intense electrical arcs are generated between two electrodes within the solvent. This situation generates shock waves, UV radiation, and localized cavitation bubbles, physically disrupting the cell wall. HVED, which is a more aggressive mechanism than electroporation, extraordinarily increases mass transfer, especially in extractions performed from resistant matrices such as solid wastes or hard seeds (Boussetta&Vorobiev, 2014).

From a green chemistry perspective, these technologies prevent the oxidation or degradation of heat-sensitive chemicals by enabling the process to occur at room temperature or very low temperatures. By operating in perfect harmony with eco-friendly solvents such as water or water-ethanol, they limit the use of toxic chemicals. Nevertheless, there are certain aspects that restrict the widespread use of the method on an industrial scale. The high initial investment costs of the systems, which require high-voltage generators and electrode designs, is the most prominent disadvantage. Furthermore, since the efficiency of the process is directly dependent on the electrical conductivity of the solvent in the medium, solvent selection and homogeneity require additional precision (Golberg et al. 2016).

3.6. Mechanochemical Extraction (MCE)

One of the closest mechanistic approaches to the "solvent-free" green chemistry ideal are the principles of mechanochemistry. Where the limiting step of mass transfer in traditional extracitive approaches is the stiff cellular matrix of the plant materials, mechanochemical extraction (MCE) is able to utilize direct energy input in the form of mechanical processes (friction, shearing, crushing, collision, etc.) rather than heat or liquid solvents to initiate chemical reactions or physical separations. In the case of solid biomass the application of this devastating level of physical stress via a ball mill, planetary mill, extruder, or other means, can irreversibly rupture resistant polymeric networks of the plant cell wall (cellulose, hemicellulose, lignin) at the nanometer or micrometer level bringing structural integrity into disarray and transforming the crystalline matrix to amorphous states and a tremendous explosion in surface area that break the cell membranes at the macroscopic level allowing bioactive compound liberation (Wu et al., 2017).

MCE processes can be carried out in a completely solvent-free environment, or they can be subjected to a co-grinding process where solid auxiliary reagents (e.g., salts like sodium carbonate), copolymers, or a hydrogen bond donor/acceptor

(urea, citric acid, etc.) are added to the medium to improve friction and reaction kinetics. By triggering solid-solid interactions under intense mechanical forces, the targeted bioactive molecules are transformed into soluble supramolecular complexes. To further optimize the process, the Liquid-Assisted Grinding (LAG) concept, in which deep eutectic solvents or trace amounts of green solvents are incorporated into the system, is also frequently utilized. After grinding, by adding a minimal amount of water or a green co-solvent, the active components in complex form are obtained in a pure state within seconds via leaching. For a successful and efficient recovery, parameters such as grinding time, rotational frequency/speed, ball-to-powder mass ratio, and the type of auxiliary reagents added must be meticulously optimized according to the target compound (Lomovsky et al., 2016).

From a green chemistry perspective, MCE is a highly sustainable alternative as it reduces toxic organic solvent consumption to almost zero, decreases extraction time from hours to minutes, and requires no external heating source. The rich component profiles of the obtained extracts confirm the industrial potential of the method. However, the most significant limitation of the method in practice is the localized heat (hot-spot) increases generated at the microscopic level during intense mechanical collisions. This uncontrolled localized heating can degrade the structure of highly sensitive thermolabile compounds. Additionally, engineering challenges in the integration of ball mills into continuous flow systems at an industrial scale (scale-up) and the high mechanical wear rates of the equipment are considered the primary obstacles to the large-scale commercial applications of the method (James et al. 2012).

4. APPLICATIONS

Green extraction technologies are no longer merely a laboratory-scale preparatory step; they are transforming into standard operating procedures (SOPs) across a broad industrial spectrum, including food, cosmetics, pharmaceuticals, and materials science. The primary driving force behind this transformation is the restrictions imposed by regulatory authorities such as the Food and Drug Administration (FDA) and the European Medicines Agency (EMA) on toxic solvent residues, coupled with the increasing consumer demand for completely natural and sustainable products. In this context, the industrial applications of green extraction intersect at the dual objectives of achieving high product quality and minimizing environmental harm.

4.1. Food and Nutraceuticals

The isolation of bioactive molecules intended for use in food supplements, nutraceuticals, and functional food formulations represents one of the most extensive application areas of green chemistry principles on an industrial scale. In this product group, which is presented for direct human consumption, even the slightest risk of residue that conventional organic solvents (petroleum derivatives, aromatic hydrocarbons, etc.) might generate at the end of the process is strictly unacceptable in terms of both consumer health and legal regulations. International regulatory bodies such as the Food and Drug Administration (FDA) and the European Food

Safety Authority (EFSA) pursue a zero-tolerance policy regarding solvent residues that may be present in food matrices, directing manufacturers toward solvents with a Generally Recognized as Safe (GRAS) status (Carocho et al., 2015).

The prolonged high temperatures applied in conventional extraction methods disrupt the structural integrity of bioactive compounds sensitive to thermal degradation in food and nutraceutical formulations, consequently causing a severe decline in the functional capacity of the product. Green extraction technologies reduce process times to a matter of minutes and allow for operations at lower temperatures, thereby isolating these valuable compounds without degradation (Picot-Allain et al., 2021).

Furthermore, extracts obtained using green solvents can, in most cases, be directly integrated into food matrices without the need for any additional processing. This situation triggers the industrial use of bioactive compounds not only as food supplements but also as natural additives replacing artificial food colorings, synthetic preservatives, or synthetic antioxidants. Consequently, green extraction is crucial for the production of functional ingredients in the food industry that are sustainable, safe, and fully compliant with the clean-label philosophy (Ruesgas-Ramón et al. 2017).

4.2. Pharmaceuticals and Cosmetics

In the pharmaceutical and high-quality cosmetics industries, the purity and toxicological profile of the final product are parameters just as critical as the bioactivity of the active ingredients obtained from natural sources. Organic solvents frequently used in conventional extraction methods, such as hexane, chloroform, dichloromethane, or methanol, carry the risk of leaving trace amounts of residue within the matrix, even if they are removed at the end of the process (Prat et al., 2012).

The ICH Q3C guideline, published by the International Council for Harmonisation (ICH)—the highest-level international authority determining the technical and scientific standards required for the licensing of human medicines—classifies residual solvents that may be present in pharmaceutical products based on their toxicity potentials and subjects them to extremely strict limits. According to this guideline, many conventional solvents widely used in the industry fall into the Class 1 (solvents to be avoided) or Class 2 (solvents to be limited) categories due to the risks they pose to human health, and they are routinely monitored using sensitive analytical methods. Similarly, modern cosmetic regulations exhibit a similar sensitivity regarding the purity of formulations and trace element/solvent residues to prevent the risk of systemic toxicity in topical applications (Born et al., 2019).

At this precise point, green extraction technologies offer both a regulatory and an operational turning point for the pharmaceutical and cosmetic industries. Extractions performed using green solvents, such as supercritical CO_2 or NADES, reduce the risk of exceeding the strict residue limits imposed by international guidelines to zero. This situation not only reduces the operational burden during the analytical validation and licensing processes for pharmaceutical and cosmetic

manufacturers but also inherently brings along clean-label and high consumer safety standards (Zainal-Abidin et al. 2017).

4.3. Waste Valorization

The green extraction is closely related to the concept of zero waste towards the transformation of wastes of the agricultural and food sectors into added-value commodities. As opposed to a waste of ecology and economy, conventionally seen as a line of cost of production, the organic residues issued from bioprocessing should rather be considered as a valuable and sustainable secondary raw material source of the circular economy. In this field green extraction is the crucial step of this integrated biorefinery concept, to add back biomass to economy at the highest efficiency rate (Matharu et al., 2016).

In the recovery of agro-industrial wastes, specialized green strategies tailored to the structure of the matrix are implemented. For instance, pectin, d-limonene, and resveratrol can be obtained from citrus peels and apple/grape pomace generated during industrial fruit juice production (Putnik et al., 2017). The recovery of bioactive molecules such as hydroxytyrosol and oleuropein from olive mill wastewater—a waste product of olive oil production characterized by a high chemical oxygen demand (COD) value—is made possible through green extraction techniques. While mitigating the burden of environmental pollution, these processes simultaneously provide raw material inputs derived from waste for the pharmaceutical and nutraceutical industries (Dermeche et al., 2013). Ultimately, the integration of green extraction techniques into waste valorization processes optimizes environmental sustainability alongside industrial profitability, thereby constituting one of the fundamental pillars of the bioeconomy vision of the future.

4.4. Biomaterials and Polymer Industry

The quest for sustainability, situated at the intersection of conventional chemistry and materials science, is fundamentally transforming industrial production processes. One of the most powerful catalysts for this transformation is the green extraction methods utilized in obtaining bioactive compounds and natural building blocks. These approaches, which enable the acquisition of eco-friendly, energy-efficient, and high-purity products, have become not merely a pre-treatment step in the biomaterials and polymer industries but a strategic mechanism that directly determines the performance and biocompatibility of the final material.

The toxic volatile organic solvents and long processing times used in conventional extraction techniques create a significant disadvantage, particularly in the design of biomaterials intended for medical, pharmaceutical, or food-contact applications. Thanks to green extraction methods, the risk of solvent residue is minimized, yielding high-purity materials suitable for direct use in sensitive applications such as tissue engineering and drug delivery systems. When integrated into polymeric networks, bioactive compounds obtained from natural materials act as natural additives that extend the shelf life of the material or endow it with a biological function (Mbous et al. 2017).

To reduce its dependence on fossil-based raw materials, the polymer industry is turning to biomass-derived polymers with increasing momentum. Green extraction acts as a bridge in the conversion of this biomass into value-added polymers. Natural phenolics or other secondary metabolites extracted via green methods can directly be incorporated into polymeric films, replacing synthetic antioxidants or UV stabilizers. This situation ensures that the material both preserves its mechanical properties and assumes a functional role, especially in smart packaging technologies (Gomez-Estaca et al., 2014).

Next-generation green solvents can serve not only as an extraction medium but also as a non-toxic, reactive environment for subsequent polymerization or cross-linking reactions. This approach reduces the overall energy cost of the process by decreasing purification steps. Macromolecular building blocks obtained from industrial or agricultural by-products via green techniques find practical application in the production of high-performance industrial polymers by being utilized in the manufacturing of biodegradable polymer composites. By optimizing extraction kinetics and thermodynamics, adjustments can be made to the mechanical, thermal, and biological properties of the final polymer (Zdanowicz et al., 2018). Ultimately, green extraction methods are not merely an environmental obligation for the biomaterial and polymer industries, but also a fundamental innovation tool in the design of innovative, safe, and high-performance materials. The synergy between these two disciplines will continue to steer the production of the functional and fully sustainable materials of the future.

CONCLUSION

Today, the green extraction is no more only common sense for ecological conscience in chemistry and process engineering; it is made become a real need for efficiency, safety in products and economic sustainability. Conventional extraction processes based on predominantly toxic volatile organic solvents and energy consuming methods are quickly replaced by hi-tech processes built around Chemat Six Principles. The combined application of promising green solvents and modern technologies mark this revolution.

Through solvent innovation, supercritical fluids, subcritical water, deep eutectic solvents (DES), and bio-based solvents eliminate the toxicity and environmental footprint problems generated by conventional solvents. Technologies such as ultrasound (UAE), microwave (MAE), pressurized liquid (PLE), enzyme (EAE), and mechanochemical (MCE) extractions overcome thermodynamic and kinetic barriers via physical forces, extraordinarily increasing mass transfer. Consequently, valuable bioactive compounds sensitive to thermal degradation can be isolated in short periods while preserving their structural integrity.

From an industrial scale perspective, the increasingly stringent residual solvent regulations enforced by international regulatory authorities in the food, nutraceutical, cosmetic, and pharmaceutical sectors are shifting green extraction from being an optional preference to the position of an industrial standard. Simultaneously, the integration of waste valorization directly serves the circular economy model by converting agricultural by-products into high-value-added molecules. The utilization of these extracts as natural functional agents in the biomaterials and polymer industries proves how vastly the interdisciplinary boundaries of green chemistry have expanded.

Green extraction methods are the most powerful scientific tool for making the rich bioactive potential offered by nature available for industrial use without harming nature itself. Focusing future research on overcoming the engineering challenges of these methods during the industrial scale-up phase and on the optimization of thermodynamic models through artificial intelligence integration will propel the global bioeconomy vision much further forward.

SONUÇ

Günümüzde yeşil ekstraksiyon, kimya ve proses mühendisliğinde yalnızca çevresel duyarlılığın bir yansıması olmaktan çıkmış; verimlilik, ürün güvenliği ve ekonomik sürdürülebilirlik açısından gerçek bir ihtiyaç hâline gelmiştir. Ağırlıklı olarak toksik uçucu organik çözücülere ve yüksek enerji tüketen yöntemlere dayanan geleneksel ekstraksiyon prosesleri, yerini hızla Chemat'ın Altı Temel İlkesi üzerine inşa edilen ileri teknoloji proseslere bırakmaktadır. Yenilikçi yeşil çözücülerin ve modern ekstraksiyon teknolojilerinin birlikte kullanımı, bu dönüşümün temel itici gücünü oluşturmaktadır. Çözücü teknolojilerindeki gelişmeler sayesinde süperkritik akışkanlar, subkritik su, derin ötektik çözücüler (DES) ve biyo-temelli çözücüler, geleneksel çözücülerin neden olduğu toksisite ve çevresel ayak izi sorunlarını büyük ölçüde ortadan kaldırmaktadır. Ultrasonik destekli ekstraksiyon (UAE), mikrodalga destekli ekstraksiyon (MAE), basınçlı sıvı ekstraksiyonu (PLE), enzim destekli ekstraksiyon (EAE) ve mekanokimyasal ekstraksiyon (MCE) gibi teknolojiler ise fiziksel kuvvetler aracılığıyla termodinamik ve kinetik sınırlamaları aşarak kütle transferini önemli ölçüde artırmaktadır. Bu sayede, termal bozunmaya duyarlı değerli biyoaktif bileşikler yapısal bütünlükleri korunarak çok daha kısa sürelerde izole edilebilmektedir.

Endüstriyel ölçekte değerlendirildiğinde, gıda, nutrasötik, kozmetik ve ilaç sektörlerinde uluslararası düzenleyici kuruluşlar tarafından giderek daha sıkı şekilde uygulanan kalıntı çözücü düzenlemeleri, yeşil ekstraksiyonu isteğe bağlı bir tercih olmaktan çıkarıp endüstriyel bir standart hâline getirmektedir. Bununla birlikte, atıkların değerlendirilmesine yönelik yaklaşımların ekstraksiyon süreçlerine entegre edilmesi, tarımsal yan ürünlerin yüksek katma değerli moleküllere dönüştürülmesini sağlayarak döngüsel ekonomi modeline doğrudan katkı sunmaktadır. Elde edilen ekstraktların biyomalzeme ve polimer endüstrilerinde doğal fonksiyonel ajanlar olarak kullanılabilmesi, yeşil kimyanın disiplinler arası etki alanının ne kadar genişlediğini açıkça göstermektedir. Yeşil ekstraksiyon yöntemleri, doğanın sunduğu zengin biyoaktif potansiyelin, doğaya zarar vermeden endüstriyel kullanıma kazandırılmasını sağlayan en güçlü bilimsel araçlardan biridir. Gelecekteki araştırmaların, bu yöntemlerin endüstriyel ölçek büyütme aşamasında karşılaşılan mühendislik zorluklarının aşılmasına ve yapay zekâ entegrasyonu ile termodinamik modellerin optimize edilmesine odaklanması, küresel biyoekonomi vizyonunun daha da ileri taşınmasına önemli katkılar sağlayacaktır.

REFERENCES

1. Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). Novel solvent properties of choline chloride/urea mixtures. Chemical Communications, (1), 70–71. https://doi.org/10.1039/B210714G
2. Ameer, K., Shahbaz, H. M., & Kwon, J. H. (2017). Green extraction methods for polyphenols from plant matrices and their byproducts: A review. Comprehensive Reviews in Food Science and Food Safety, 16(2), 295–315. https://doi.org/10.1111/1541-4337.12253
3. Anastas, P. T., & Warner, J. C. (1998). Green chemistry: Theory and practice. Oxford University Press.
4. Azmir, J., Zaidul, I. S. M., Rahman, M. M., Sharif, K. M., Mohamed, A., Sahena, F., Jahurul, M. H. A., Ghafoor, K., Norulaini, N. A. N., & Omar, A. K. M. (2013). Techniques for extraction of bioactive compounds from plant materials: A review. Journal of Food Engineering, 117(4), 426–436. https://doi.org/10.1016/j.jfoodeng.2013.01.014
5. Barba, F. J., Parniakov, O., Pereira, S. A., Wiktor, A., Grimi, N., Boussetta, N., Saraiva, J. A., Raso, J., Belloso, O. M., Rajchert, D. W., Lebovka, N., & Vorobiev, E. (2015). Current applications and new opportunities for the use of pulsed electric fields in food science and industry. Food Research International, 77, 773–798. https://doi.org/10.1016/j.foodres.2015.09.015
6. Bom, S., Jorge, J., Ribeiro, H. M., & Marto, J. (2019). A step forward on sustainability in the cosmetics industry: A review. Journal of Cleaner Production, 225, 270-290. https://doi.org/10.1016/j.jclepro.2019.03.255
7. Boussetta, N., & Vorobiev, E. (2014). Extraction of valuable biocompounds assisted by high voltage electrical discharges: A review. Comptes Rendus Chimie, 17(3), 197-203. https://doi.org/10.1016/j.crci.2013.11.011
8. Capello, C., Fischer, U., & Hungerbühler, K. (2007). What is a green solvent? A comprehensive framework for the environmental assessment of solvents. Green Chemistry, 9(9), 927-934. https://doi.org/10.1039/B617536H
9. Carocho, M., Morales, P., & Ferreira, I. C. F. R. (2015). Natural food additives: Quo vadis?. Trends in Food Science & Technology, 45(2), 284-295. https://doi.org/10.1016/j.tifs.2015.06.007
10. Chan, C. H., Yusoff, R., Ngoh, G. C., & Kung, F. W. L. (2011). Microwave-assisted extractions of active ingredients from plants. Journal of Chromatography A, 1218(37), 6213-6225. https://doi.org/10.1016/j.chroma.2011.07.040
11. Chemat, F., Rombaut, N., Sicaire, A. G., Meullemiestre, A., Fabiano-Tixier, A. S., & Abert-Vian, M. (2017). Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review. Ultrasonics Sonochemistry, 34, 540-560. https://doi.org/10.1016/j.ultsonch.2016.06.035
12. Chemat, F., Vian, M. A., & Cravotto, G. (2012). Green Extraction of Natural Products: Concept and Principles. International Journal of Molecular Sciences, 13(7), 8615-8627. https://doi.org/10.3390/ijms13078615
13. Chemat, F., Vian, M. A., Fabiano-Tixier, A.-S., Nutrizio, M., Režek Jambrak, A., Munekata, P. E., Lorenzo, J. M., Barba, F. J., Binello, A., Cravotto, G. (2020). A review of sustainable and intensified techniques for extraction of food and natural products. Green Chemistry, 22(8), 2325-2353. https://doi.org/10.1039/C9GC03878G

14. Chemat, F., Vian, M. A., Ravi, H. K., Khadhraoui, B., Hilali, S., Perino, S., & Fabiano-Tixier, A. S. (2019). Review of alternative solvents for green extraction of food and natural products: Panorama, principles, applications and prospects. Molecules, 24(16), 3007. https://doi.org/10.3390/molecules24163007

15. Cvjetko Bubalo, M., Vidović, S., Radojčić Redovniković, I., & Jokić, S. (2018). New perspective in extraction of plant biologically active compounds by green solvents. Food and Bioproducts Processing, 109, 52-73. https://doi.org/10.1016/j.fbp.2018.03.001

16. Da Silva, R. P. F. F., Rocha-Santos, T. A. P., & Duarte, A. C. (2016). Supercritical fluid extraction of bioactive compounds. TrAC Trends in Analytical Chemistry, 76, 40-51. https://doi.org/10.1016/j.trac.2015.11.013

17. Dai, Y., van Spronsen, J., Witkamp, G. J., Verpoorte, R., & Choi, Y. H. (2013). Natural deep eutectic solvents as new potential media for green technology. Analytica Chimica Acta, 766, 61-68. https://doi.org/10.1016/j.aca.2012.12.019

18. Dai, Y., Witkamp, G. J., Verpoorte, R., & Choi, Y. H. (2015). Tailoring properties of natural deep eutectic solvents with water to facilitate their applications. Food Chemistry, 187, 14-19. https://doi.org/10.1016/j.foodchem.2015.03.123

19. Dermeche, S., Nadour, M., Larroche, C., Moulti-Mati, F., & Michaud, P. (2013). Olive mill wastes: Biochemical characterizations and valorization strategies. Process Biochemistry, 48(10), 1532-1552. https://doi.org/10.1016/j.procbio.2013.07.010

20. Golberg, A., Sack, M., Teissie, J., Pataro, G., Pliquett, U., Saulis, G., Stefan, T., Miklavcic, D., Vorobiev, E., Frey, W. (2016). Energy-efficient biomass processing with pulsed electric fields for bioeconomy and sustainable development. Biotechnology for Biofuels, 9, 94. https://doi.org/10.1186/s13068-016-0508-z

21. Gómez-Estaca, J., López-de-Dicastillo, C., Hernández-Muñoz, P., Catalá, R., & Gavara, R. (2014). Advances in antioxidant active food packaging. Trends in Food Science & Technology, 35(1), 42-51. https://doi.org/10.1016/j.tifs.2013.10.008

22. Gu, Y., & Jérôme, F. (2010). Glycerol as a sustainable solvent for green chemistry. Green Chemistry, 12(7), 1127-1138. https://doi.org/10.1039/C001628D

23. Herrero, M., Mendiola, J. A., Cifuentes, A., & Ibáñez, E. (2010). Supercritical fluid extraction: Recent advances and future trends. Journal of Chromatography A, 1217(16), 2495-2511. https://doi.org/10.1016/j.chroma.2009.12.019

24. James, S. L., Adams, C. J., Bolm, C., Braga, D., Collier, P., Friščić, T., Grepioni, F., Harris, K. D. M., Hyett, G., Jones, W., Krebs, A., Mack, J., Maini, L., Orpen, A. G., Parkin, I. P., Shearouse W. C., Steed, J. W., Waddell, D. C. (2012). Mechanochemistry: opportunities for new and cleaner synthesis. Chemical Society Reviews, 41(12), 4131-4147. https://doi.org/10.1039/c1cs15171a

25. Li, Y., Fabiano-Tixier, A. S., Vian, M. A., & Chemat, F. (2013). Solvent-free microwave extraction of bioactive compounds provides a tool for green analytical chemistry. TrAC Trends in Analytical Chemistry, 47, 1-11. https://doi.org/10.1016/j.trac.2013.02.007

26. Lomovsky, O. I., Lomovskiy, I. O., Orlov, D. V. (2017). Mechanochemical solid acid/base reactions for obtaining biologically active preparations and extracting plant materials. Green Chemistry Letters and Reviews, 10(4), 171-185. https://doi.org/10.1080/17518253.2017.1339832

27. Luque de Castro, M. D., & Priego-Capote, F. (2007). Ultrasound-assisted preparation of liquid samples. Talanta, 72(2), 321-334. https://doi.org/10.1016/j.talanta.2006.11.013

28. Matharu, A. S., de Melo, E. M., & Houghton, J. A. (2016). Opportunity for high value-added chemicals from food supply chain wastes. Bioresource Technology, 215, 123-130. https://doi.org/10.1016/j.biortech.2016.03.039

29. Mbous, Y. P., Hayyan, M., Hayyan, A., Wong, W. F., Hashim, M. A., & Looi, C. Y. (2017). Applications of deep eutectic solvents in biotechnology and bioengineering. Biotechnology Advances, 35(2), 105-134. https://doi.org/10.1016/j.biotechadv.2016.11.006

30. Mustafa, A., & Turner, C. (2011). Pressurized liquid extraction as a green approach in food and herbal plants extraction: A review. Analytica Chimica Acta, 703(1), 8-18. https://doi.org/10.1016/j.aca.2011.07.018

31. Nadar, S. S., Rao, P., & Rathod, V. K. (2018). Enzyme assisted extraction of biomolecules as an approach to novel extraction technology: A review. Food Research International, 108, 309-330. https://doi.org/10.1016/j.foodres.2018.03.006

32. Passos, H., Freire, M. G., & Coutinho, J. A. P. (2014). Ionic liquid solutions as extractive solvents for value-added compounds from biomass. Green Chemistry, 16(12), 4786-4815. https://doi.org/10.1039/C4GC00236A

33. Pereira, C. S. M., Silva, V. M. T. M., & Rodrigues, A. E. (2011). Ethyl lactate as a solvent: Properties, applications and production processes–a review. Green Chemistry, 13(10), 2658-2671. https://doi.org/10.1039/C1GC15523G

34. Petkovic, M., Seddon, K. R., Rebelo, L. P. N., & Pereira, C. S. (2011). Ionic liquids: a pathway to environmental acceptability. Chemical Society Reviews, 40(3), 1383-1403. https://doi.org/10.1039/c004968a

35. Picot-Allain, C., Mahomoodally, M. F., Ak, G., & Zengin, G. (2021). Conventional versus green extraction techniques—a comparative perspective. Current Opinion in Food Science, 40, 144-156. https://doi.org/10.1016/j.cofs.2021.02.009

36. Plaza, M., & Turner, C. (2015). Pressurized hot water extraction of bioactives. TrAC Trends in Analytical Chemistry, 71, 39-54. https://doi.org/10.1016/j.trac.2015.02.022

37. Prat, D., Wells, A., Hayler, J., Sneddon, H., McElroy, C. R., Abou-Shehada, S., & Dunn, P. J. (2016). CHEM21 selection guide of classical-and less classical-solvents. Green Chemistry, 18(1), 288-296. https://doi.org/10.1039/C5GC01008J

38. Puri, M., Sharma, D., & Barrow, C. J. (2012). Enzyme-assisted extraction of bioactives from plants. Trends in Biotechnology, 30(1), 37-44. https://doi.org/ 10.1016/j.tibtech.2011.06.014

39. Putnik, P., Kovačević, D. B., Jambrak, A. R., Barba, F. J., Cravotto, G., Binello, A., Lorenzo, J. M., Shpigelman, A. (2017). Innovative "green" and novel strategies for the extraction of bioactive added value compounds from citrus wastes—A review. Molecules, 22(5), 680. https://doi.org/10.3390/molecules22050680

40. Ruesgas-Ramón, M., Figueroa-Espinoza, M. C., & Durand, E. (2017). Application of deep eutectic solvents (DES) for phenolic compounds extraction: overview, challenges, and opportunities. Journal of Agricultural and Food Chemistry, 65(18), 3591-3601. https://doi.org/10.1021/acs.jafc.7b01054

41. Shirsath, S. R., Sonawane, S. H., & Gogate, P. R. (2012). Intensification of extraction of natural products using ultrasonic irradiations—A review of current status. Chemical Engineering and Processing: Process Intensification, 53, 10-23. https://doi.org/10.1016/j.cep.2012.01.003

42. Sicaire, A. G., Vian, M. A., Fine, F., Joffre, F., Carré, P., Tostain, S., & Chemat, F. (2015). Alternative bio-based solvents for extraction of fat and oils: Solubility prediction, global yield, extraction kinetics, chemical composition and cost of manufacturing. International Journal of Molecular Sciences, 16(4), 8430-8453. https://doi.org/10.3390/ijms16048430

43. Smith, E. L., Abbott, A. P., & Ryder, K. S. (2014). Deep Eutectic Solvents (DESs) and their applications. Chemical Reviews, 114(21), 11060-11082. https://doi.org/10.1021/cr300162p

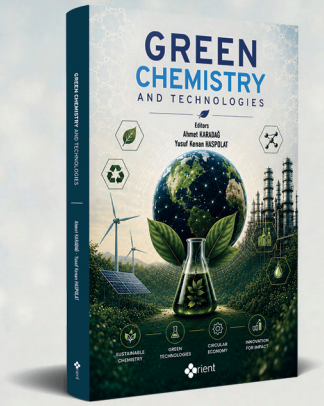
44. Somat, H. A., Thani, N. M., Mustapha, W. A. W., Lim, S. J., Seng, N. S. S., Rahman, H. A., Razali, N. S. M., Ali, M. M., & Kamal, S. M. M. (2026). Subcritical water extraction of bioactive compounds from plant materials: recent advances. Journal of Future Foods, 6(5), 753-764. https://doi.org/10.1016/j.jfutfo.2024.10.005

45. Teo, C. C., Tan, S. N., Yong, J. W. H., Hew, C. S., & Ong, E. S. (2010). Pressurized hot water extraction (PHWE). Journal of Chromatography A, 1217(16), 2484-2494. https://doi.org/10.1016/j.chroma.2009.12.050

46. Wu, K., Ju, T., Deng, Y. & Xi, J. (2017). Mechanochemical assisted extraction: A novel, efficient, eco-friendly technology. Trends in Food Science & Technology, 66, 166-173. https://doi.org/10.1016/j.tifs.2017.06.011

47. Zainal-Abidin, M. H., Hayyan, M., Hayyan, A., & Jayakumar, N. S. (2017). New horizons in the extraction of bioactive compounds using deep eutectic solvents: A review. Analytica Chimica Acta, 979, 1-23. https://doi.org/10.1016/j.aca.2017.05.012

48. Zdanowicz, M., Spychaj, T., & Makowska, K. (2018). Deep eutectic solvents for polysaccharides processing. A review. Carbohydrate Polymers, 200, 361-380. https://doi.org/10.1016/j.carbpol.2018.07.078



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