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Evaluation of Superhydrophobic Surfaces for Improving Corrosion Resistance of Nozzle Shafts in Diesel Injection Systems

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Abstract

Recent emission regulations have significantly altered the operating conditions of modern diesel engines, leading to increased low-load operation, frequent start–stop events, and aggressive cooling and exhaust gas recirculation strategies. These conditions promote water condensation and the formation of acidic vapors in fuel injector environments, accelerating corrosion mechanisms on nozzle shaft components and posing new durability challenges for diesel injection systems.

This study investigates superhydrophobic surface concepts for diesel injector nozzle shafts with a focus on application-relevant corrosion mechanisms. Due to the cylindrical geometry and strict dimensional tolerances of nozzle shafts, experimental investigations were conducted on flat test specimens manufactured from the same material to enable controlled surface modification and systematic characterization. Surface structuring was performed using laser-based texturing techniques to generate micro- and nano-scale surface features. In addition, controlled surface modification steps were applied to further tailor surface morphology. Selected surfaces were subsequently treated with a low-surface-energy modification to stabilize hydrophobic behavior.

Wettability characterization demonstrated that laser-textured surfaces exhibit a pronounced increase in water contact angle compared to untreated references, approaching the superhydrophobic regime. Further enhancement of water repellency was achieved through the combined application of surface structuring and surface modification. Preliminary corrosion screening was conducted using short-term salt spray exposure, while ongoing work focuses on more application-representative testing involving acidic vapor environments. The results provide an application-driven framework for improving the corrosion resistance of injector nozzle shaft surfaces under increasingly aggressive diesel engine operating conditions.

Keywords

Superhydrophobic surface; Lotus effect; Diesel injection system; Nozzle shaft; Wettability; Corrosion resistance; Laser texturing

1.Introduction

The continuous tightening of global emission regulations has significantly altered the operating conditions of modern diesel engines. Strategies such as downsizing, extended low-load operation, frequent start–stop cycles, and aggressive cooling and exhaust gas recirculation (EGR) are increasingly applied to reduce emissions and improve efficiency. While effective from a combustion and emission perspective, these strategies unintentionally promote water condensation and the development of chemically aggressive environments within fuel injection systems, particularly during cold-start and low-temperature operation (Fig. 1).

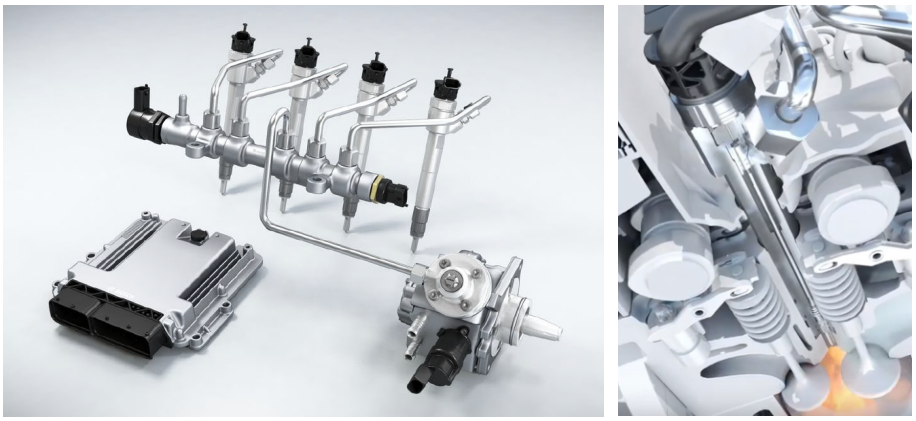


Fig.1: Fuel injection systems & Combustion environments

In parallel, the rapid growth of diesel-powered vehicles in emerging markets introduces additional challenges related to fuel quality and operating environment. Variations in fuel composition, insufficient refining, and fuel contamination contribute to the formation of corrosive species during combustion. In addition, environmental factors such as coastal or marine exposure may introduce chloride-containing species into the operating atmosphere, further increasing the corrosive potential.

Under transient and low-temperature operating conditions, these corrosive species may exist in the gas phase and subsequently condense together with water vapor on metallic surfaces. Injector nozzle shafts are among the most critical components exposed to such combined chemical and environmental effects. Cyclic condensation of water and acidic species can promote the formation of localized electrochemical corrosion cells on nozzle shaft surfaces. The corrosion initiation mechanism, including vapor condensation, liquid film formation, and subsequent surface degradation, is schematically illustrated in **Fig. 2**.

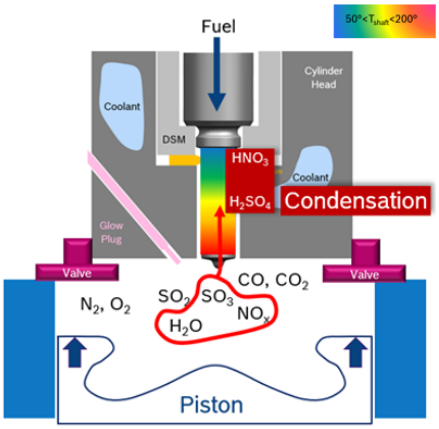


Fig. 2 Schematically illustrates the corrosion formation mechanism

The consequences of these mechanisms are not limited to superficial surface degradation. **Fig. 3** presents a representative example of corrosion-related damage observed on a nozzle shaft, where localized material loss and surface irregularities are associated with crack initiation. Such damage can adversely affect mechanical integrity, facilitate crack propagation under cyclic loading conditions, and ultimately reduce injector durability and functional reliability over extended service life.

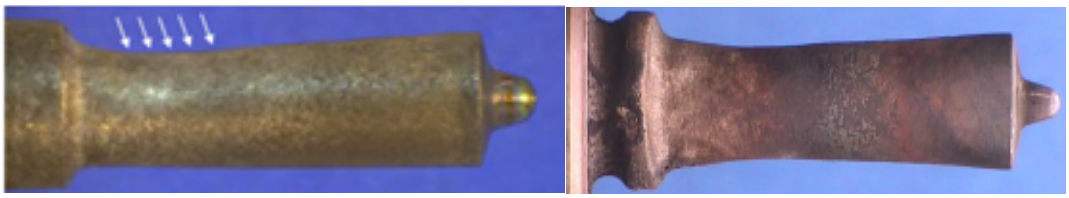


Fig. 3 Corrosion-induced damages on nozzle shaft

It should be noted that the surface modification concept investigated in this study is part of ongoing industrial research and development activities. Intellectual property related to this approach has been secured by **Robert Bosch**, and further investigations are currently in progress to assess long-term durability, scalability, and applicability under representative operating conditions. The present study focuses on the experimental evaluation of wettability control and corrosion-related behaviour, providing scientific insight that supports and complements these continuing industrial development activities.

2.Experimental Methodology

2.1 Test Specimens and Material Selection

Due to the cylindrical geometry, limited accessible surface area, and strict dimensional tolerances of diesel injector nozzle shafts, direct wettability characterization on real components is not feasible. Reliable water contact angle measurements on curved nozzle shaft surfaces are impractical and subject to significant measurement uncertainty, as illustrated in Fig. 4. Fig. 5 further presents representative laser-textured nozzle shaft surfaces in comparison with flat test specimens, highlighting the geometric constraints associated with real components.

To enable accurate wettability measurements and detailed surface characterization, flat test specimens with planar surfaces were employed. These specimens were manufactured from the same material as the nozzle shafts and processed using comparable surface texturing conditions to ensure representative surface characteristics. As shown in Fig. 4, the use of flat specimens allows reproducible water contact angle measurements, high-resolution surface imaging, and consistent comparison between different surface modification routes. This approach ensures that the observed wettability and surface morphology trends are representative of nozzle shaft materials while providing reliable and repeatable experimental data.

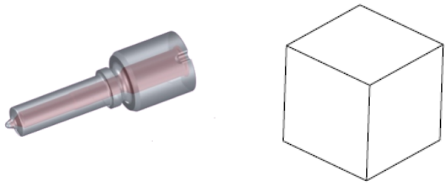


Fig.4: Cylindrical geometry of Nozzle shaft and Flat test specimen

2.2 Laser Surface Texturing

Surface structuring was performed using both nanosecond (ns, **Fig. 5 left**) and femtosecond (fs, **Fig. 5 right**) laser systems to generate hierarchical micro- and nano-scale surface features, as shown in **Fig. 5**. Nanosecond laser texturing was selected as the primary approach due to its industrial relevance and scalability, whereas femtosecond laser processing was applied in selected cases to evaluate the influence of finer surface structures on wettability behavior.

For nanosecond laser processing, four different surface design patterns were implemented to investigate the effect of surface geometry on wettability. Linear scan strategies with a fixed low line were employed, while the pitch-to-diameter (P/D) ratio was systematically varied to obtain different surface morphologies. The corresponding nanosecond laser design parameters and surface configurations are summarized in **Table 2**.

Laser parameters such as pulse energy, scanning speed, and hatch spacing were varied to control surface morphology. The resulting surface textures were designed to promote air entrapment and reduce liquid–solid contact in accordance with classical wetting theories [1,2].

For femtosecond laser processing, a blackmarking strategy was applied to generate finer surface features and modify surface topography at the micro- and nanoscale. This approach enabled the evaluation of femtosecond-induced surface structures as a comparative reference to nanosecond-textured surfaces in terms of wettability performance. Representative laser-texturing conditions and corresponding surface characteristics are summarized in **Table 1**.

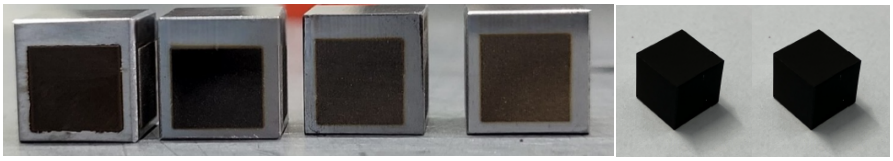
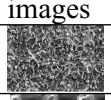
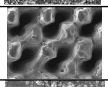
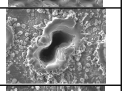
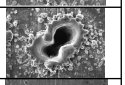
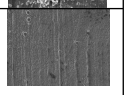


Fig.5: Nanosecond & femtosecond laser texturing

Table 1: Sample table

Sample	Nanosecond Laser (Ns)	Femtosecond Laser (Fs)	Chemical Etching	Organic Coating
Sample 1	X		X	X
Sample 2	X			X
Sample 3	X		X	
Sample 4	X			
Sample 5		X		X
Sample 6		X		

Table 2: Nanosecond & Femtosecond laser design parameters table

Face	Design	P/D	SEM images
Face 1	Line	-	
Face 2	Circle	Low	
Face 3	Circle	Medium	
Face 4	Circle	High	
Femto second All surfaces	Black Marking	-	

2.3 Chemical Surface Modification

To further modify surface topography and enhance hierarchical roughness, selected specimens were subjected to short-duration acidic etching using acidic process, as shown in **Fig. 6**. The chemical modification was limited to a controlled exposure time to avoid excessive material removal while promoting the formation of nano-scale surface features.

It was observed that acidic etching did not result in a fully linear or consistent increase in water contact angle. While an increase in wettability performance was obtained in several cases, a reduction in contact angle was also observed for certain surface conditions. This behavior indicates that the etching process is sensitive to the initial surface morphology and does not act as a standalone or uniformly predictable method for wettability enhancement. Nevertheless, when applied after laser surface texturing, the etching process contributed to the development of hierarchical micro–nano surface structures, which is beneficial for stabilizing hydrophobic behavior.

Following laser surface structuring and chemical modification, organic-based surface modification was applied to selected specimens in order to reduce surface energy and stabilize hydrophobic behavior. This approach is widely

employed to enhance water repellency on textured metallic surfaces by introducing low-surface-energy functional groups [3–5].

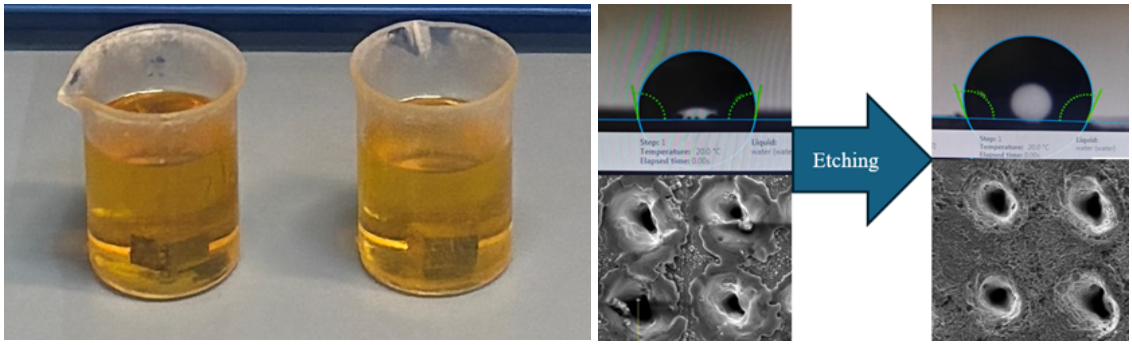


Fig.6: Using acidic chemical for surface hierarchical roughness

2.4 Wettability Characterization

Surface wettability was evaluated through static water contact angle measurements using the sessile drop method under ambient conditions. A fixed droplet volume was used for all measurements to ensure consistency and comparability. For each surface condition, contact angles were measured at multiple locations, and average values were reported to account for surface heterogeneity.

Representative images of the water droplet profile during WCA measurements and the droplet resting behavior on textured surfaces are presented in **Fig.7** respectively. In addition to static WCA measurements, droplet mobility was qualitatively assessed by monitoring the sliding behavior of the water droplet during tilting of the specimen surface. Sliding angle observations were used to evaluate droplet adhesion and the stability of hydrophobic behavior.

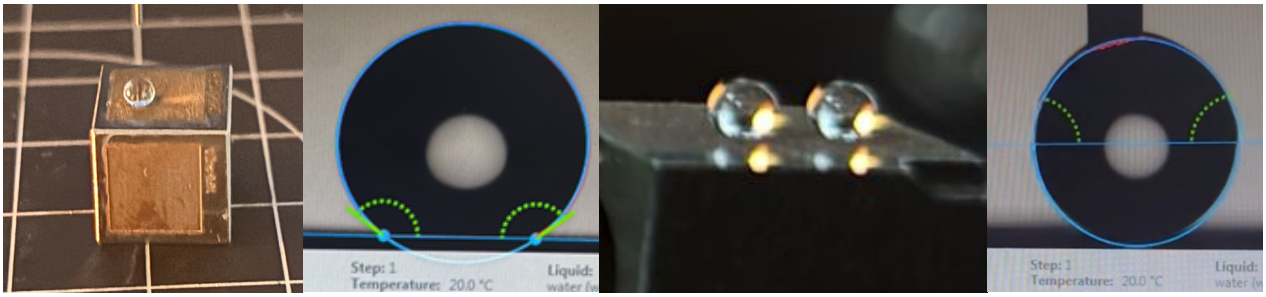


Fig.7: WCA (Wetting Contact Angle) measurement

2.5 Short-Term Corrosion Testing

It should be noted that the results of short-term salt spray testing (**Fig.8**) may be influenced by specimen positioning, orientation, and local exposure conditions within the test chamber. Therefore, while the salt spray test provides useful comparative information, a more representative assessment of corrosion behaviour should ultimately be conducted directly on nozzle shaft components under application-relevant conditions. In addition to salt spray exposure, the development of a dedicated test setup incorporating acidic vapours is considered more realistic for simulating field conditions in diesel injection systems. Such an approach would better reflect condensation-driven corrosion mechanisms involving water vapor and acidic species acting on nozzle shaft surfaces.



Fig.8: Salt Spray test

2.6 Data Evaluation and Analysis

Experimental results were evaluated by correlating the applied surface modification routes with measured wettability characteristics and observed corrosion-related surface changes. Comparative analysis was performed to assess the individual and combined effects of laser surface texturing, surface modification, and organic coating application. This experimental framework enables the identification of surface modification strategies that provide enhanced water repellence and potential corrosion mitigation while preserving the bulk material properties.

3.Results & Discussions

3.1 Theoretical Framework for Pattern Design

Based on classical wetting theories [1,2], a lower pitch-to-diameter (P/D) ratio increases the density of surface features, generating sufficient capillary pressure to support the water droplet in a stable Cassie–Baxter or mixed Cassie–Wenzel wetting regime. This behavior explains why *Face 2* exhibited the highest wettability performance, achieving a water contact angle of up to 160°.

In contrast, higher P/D ratios, as applied in *Face 3* and *Face 4*, theoretically reduce the solid–liquid area fraction (f_s). However, the increased spacing between surface features may facilitate partial droplet penetration into the textured structures. This effect can promote a transition toward a Wenzel-like wetting state (Fig. 9), resulting in higher droplet adhesion and reduced effective hydrophobic performance.

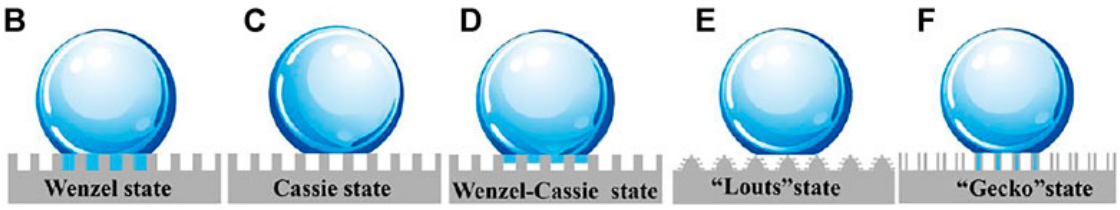


Fig.9: Wetting definitions

3.2 Influence of Surface Modification Routes on Wettability

The experimental results demonstrate that the combined application of laser surface texturing, surface modification, and organic coating plays a key role in achieving highly water-repellent behavior. The wettability characteristics of the six investigated samples conditions are summarized and discussed below.

- Sample 1 (Full Treatment) Specimens subjected to nanosecond laser texturing followed by chemical etching and organic coating exhibited the highest hydrophobic performance. Among these, *Face 2* achieved a water contact angle of up to 160° with a sliding angle below 10°. These results indicate a stable Cassie–Baxter or mixed Cassie–Wenzel wetting regime with low droplet adhesion.
- Sample 2 (No Etching): Surfaces processed without chemical etching lacked pronounced hierarchical roughness. While organic coating modifications significantly enhanced water repellence, the surfaces approached but did not fully reach the superhydrophobic threshold. The presence of laser-induced molten layers and metallic residues increased the effective solid–liquid contact area, resulting in higher droplet adhesion compared to *Sample 1*.

- Sample 3 & 4 (No Coating): Specimens without organic coating modification remained hydrophilic or only slightly hydrophobic. This behavior confirms that the inherently high surface energy of steel must be compensated by low-surface-energy functional layers in order to achieve significant water repellency.
- Sample 5 & 6 (Femtosecond Laser): Femtosecond laser texturing produced relatively uniform surface morphologies and resulted in consistent water contact angles. However, these values did not reach the superhydrophobic threshold (>150°) achieved by the optimized nanosecond laser–based full treatment route.

3.3 Effect of Organic Coating and Hierarchical Surface Morphology

Surface morphology observations indicate that nanosecond laser ablation generates the primary micro-scale roughness, while subsequent chemical etching using acidic process effectively removes laser-induced molten residues and introduces additional nano-scale surface features. However, the stabilization of the highly water-repellent state is strongly dependent on the application of organic-based surface modification. The combination of hierarchical surface topography and low-surface-energy chemistry is essential for achieving and maintaining superhydrophobic behavior.

The resulting dual-scale hierarchical structure, when combined with organic coating:

- promotes stable air entrapment within the surface textures, supporting a Cassie–Baxter-type wetting regime,
- significantly reduces the effective solid–liquid contact area by lowering surface energy and amplifying surface tension–dominated forces,
- leads to extremely low droplet–surface adhesion, as evidenced by droplet detachment behavior during contact angle measurements, where the adhesion between the water droplet and the dispensing needle exceeds the interaction with the textured and organic-modified surface.

4. Conclusions

This study successfully developed a superhydrophobic surface treatment for diesel injector nozzle shafts using a multi-step surface modification route. The main conclusions can be summarized as follows:

- Optimized strategy: The combined application of nanosecond laser surface structuring, short-duration acidic etching, and organic-based surface modification (Sample 1) was identified as the most effective approach for achieving superhydrophobic behavior.
- Wettability performance: A maximum water contact angle of 160° and a sliding angle below 10° were achieved using a circular surface pattern with a low pitch-to-diameter ratio, indicating a stable low-adhesion wetting regime.
- Underlying mechanism: Chemical etching plays a critical role in establishing hierarchical surface morphology by removing laser-induced molten residues and enabling nano-scale roughness, which supports the stabilization of a Cassie–Baxter or mixed Cassie–Wenzel wetting state.
- Engineering relevance: The developed surfaces provide a promising framework for mitigating corrosion caused by acidic vapor exposure and water condensation on injector nozzle shafts in modern diesel engines, with potential benefits for component durability and long-term injection system reliability.

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