



# Uncommon wetting on a special coating and its relevance to coalescence separation of emulsified water from diesel fuel



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## ABSTRACT

Emulsified water separation from ultralow sulfur diesel fuel on board a vehicle is critical for modern diesel engine protection. However, such a separation poses great challenges to the commonly used coalescence filter media. These media must be designed to be able to cope with surfactants in the fuel typically by chemical surface modification. In this work, we examined several chemical coatings on glass slide and studied their response to water wetting in both air and diesel fuels containing monoolein, a designated fuel additive for SAE J1488 test standard. It was found that one coating behaved dramatically differently than others. This coating is a fluorochemical (FC) with undisclosed chemistry, which leads to uncommon but favorable water wetting under fuel that further boosts coalescence separation of emulsified water with a commercial stainless steel filter felt. The feature and the chemistry of the coating were then revealed and rationalized with SEM, XPS, FTIR, NMR, GPC-LS and MALDI-TOF MS analyses. Quartz crystal microbalance (QCM) was also used to determine the characteristics of monoolein adsorption on the coatings. The results show that the FC coating chemistry is unique as it provides in one molecule a hard hydrophobic segment and a soft hydrophilic segment, both of which are desired for effective coalescence separation in light of easy capture of small droplets and easy release of grown droplets, even subject to the presence of surfactants in the fuel. Such a chemistry also results in surprisingly intensive adsorption of monoolein. Based on further observation of the relatively faster coalescence of two water droplets under static conditions in fuel on the FC coating surface, it is speculated that the strong adsorption forces the surfactant molecules to be pulled away from the fuel/water interface, thus triggering the subsequent coalescence. It is also postulated that the unique chemistry allows the adsorbed surfactant molecules to redistribute, leading to the very wetting phenomenon first time observed.

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## 1. Introduction

Emulsified water separation from oil in the presence of surfactants by physical means is a difficult problem [1–4]. One example is to remove such water effectively from ultralow sulfur diesel fuel polished with fuel additives such as lubricant, cetane improver and fuel injector detergent. Water and other water-based fuel impurities can cause fuel filter plugging, fuel starvation, damage of engine components, promotion of microbiological growth and so forth. Removing them effectively is therefore of critical importance for advanced engine protection and motor tail pipe emission reduction [5–7].

Coalescence separation of emulsified water with a fibrous filter medium is an economical technique [8–10]. However, the

performance of a coalescer can be seriously challenged by the presence of surfactants in two ways: (1) reduction in oil/water interfacial tension to form more stable water-in-oil emulsions (2) surfactant adsorption on coalescence material to change the surface wettability with regard to water and/or oil [11]. Obviously, more stable emulsion is more difficult to separate, and the change in surface wettability is another cause of deteriorated coalescence separation [12].

A coalescence filter medium is typically made from randomly packed non-woven fibers treated with certain chemicals [8,13]. There are cases where no chemical treatment is applied for some specialty fibers, but a multi-layer structure is often needed to construct the medium with a combination of different materials [14,15]. When this happens, it is difficult to tell why such multi-layer structure is effective, especially when the medium is exposed to surfactant-stabilized emulsions. So the design of a coalescence medium is usually considered an art than science [16–19].

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A coalescer separates water droplets by allowing them to pass into the fibrous material where the small droplets are captured first, then combine to form larger droplets, which subsequently are released on the downstream side of the material [20–22]. In fact, the conventional mechanism of coalescence separation can be described by Hazlett model [23], where four events occur in sequence: (a) approach of a droplet to a fiber, (b) attachment of the droplet to the fiber, (c) coalescence of attached droplets on the fiber, and (d) release of enlarged droplets from the filter medium. Glass microfiber is the most commonly used material for water coalescence from hydrocarbon liquids, but very hydrophilic glass fibers tend to be quickly disabled because of surfactant adsorption [15]. The reason is that the polar head of the surfactant bonds to the polar glass surface, rendering the surface hydrophobic that alters the affinity of water to the fibers, leading to reduced separation efficiency as a result.

It has been recognized that glass fiber treated with certain organic compounds is less prone to surfactant adsorption and provides better coalescence efficiency. However, a precise selection of the organic compounds is not easy to come by as expected. An appropriate treatment is believed to be featured with balanced water adhesion onto the fibers and release from the fibers. This is equivalent to say that the fibers must have both hydrophilic sites to capture in place the small water droplets for them to grow, and hydrophobic sites to easily let go off the coalesced droplets subject to fluid flow. In industrial practice, reactive silicone of low surface energy is often used to impart water repellency to a material [24–26]. Fluorocarbon chemical (FC) can also be applied to treat a material for both water repellency and oil resistance [27]. However, their chemistries are designed dramatically differently, aiming for different applications including water/oil separation. To gain a material's surface water repellency for applications involving air-water-solid interfaces, both chemicals can be used; to gain a material's surface oil repellency, for example, stain resistance, FC is the choice. Conventionally, mixing silicone with FC is prohibited for surface treatment because of their contradictory nature in surface property tailoring, especially for oil repellency. Silicone treated filter media are often used to separate large water droplets from diesel fuel by size exclusion, but such media can be readily disarmed when used to cope with surfactant-stabilized emulsions having smaller water droplet size.

In this work, we came across a unique FC coating that behaves dramatically differently than others in response to water wetting under diesel fuels containing monoolein. The coating was then applied to treat a commercial stainless steel fiber felt to separate water-in-fuel emulsions via coalescence. The fuel was obtained from the market place and was first treated with fuller's earth to remove additives in it. It was then added with monoolein as a fuel lubricity reagent. Monoolein is a natural component from soybean-based biodiesel and a designated non-ionic surfactant in SAE (society of automobile engineering) J1488 test standard [28]. Its use results in the reduction of fuel/water interfacial tension and the disabling of many coalescence materials. The coating was proven effective in fighting against the surfactant and led to higher coalescence separation efficiencies. Detailed studies were then carried out to focus on the coating chemistry and the mechanism of emulsion breakdown subject to this coating. It was discovered for the first time that the coating itself allowed more water wetting in contrast with other coatings. Chemical analysis indicates the coating consists of a long but soft hydrophilic chain of repeated unit of  $-\text{CH}_2\text{CH}_2\text{O}-$ , attaching to a hard segment composing of a fully fluorinated urethane head. The chain adsorbs monoolein competitively and forces monoolein molecules to depart from water/fuel interface, thus triggering the coalescence of water droplets. The head is hydrophobic, allowing easy migration of captured water droplets to go somewhere else. The work provides

counter-intuitive insight of coalescence separation that's never been revealed in prior art, and is expected to guide future research on filtration and separation of surfactant stabilized water-in-oil emulsions.

## 2. Experimental

### 2.1. Materials

Poly(dimethylsiloxane), hydroxy terminated (average  $M_n \sim 550$ , viscosity  $\sim 25$  cSt) was purchased from Aldrich. Nona fluorohexyltriethoxysilane and 3-chloropropyltrimethoxysilane were purchased from Gelest Inc. A urethane type of fluorochemical (FC) emulsion initially designed for oil stain resistance was obtained from a local company. Monoolein was supplied from Dalian Meilun Biotech Co., Ltd. Ultra-low sulfur diesel fuel (0#) was provided by a diesel station in Beijing. The commercial fuel was pretreated with clay (fuller's earth) to remove additives by adsorption. Commercial stainless steel fiber felt purchased from Filter Company (Zhejiang, China) was used as the coalescence filter medium. The felt has a mean flow pore size of  $7.9 \mu\text{m}$  and a thickness of  $500 \mu\text{m}$ . Its pore size distribution is shown in Fig. S1 in the Supplementary Information.

### 2.2. Coating preparation

Glass slides were first cut into squares ( $25 \text{ mm} \times 25 \text{ mm} \times 1 \text{ mm}$ ), then washed with detergent to remove organic residues, rinsed with deionized (DI) water and dried. The dry slides were further cleansed in a piranha solution (a mixture of 70 v.% sulfuric acid and 30 v.%  $\text{H}_2\text{O}_2$ ) for 1 h followed by rinsing with DI water for a few times, and then dried at  $50^\circ\text{C}$ . The different chemicals with controlled amount of concentrations were spin-coated on the cleaned slides, cured at  $100^\circ\text{C}$  under vacuum for 12 h to form uniform thin coatings.

## 3. Characterization

### 3.1. Interfacial tension

Interfacial tension measurement was conducted on a contact angle analyzer (DM-701, Kyowa Interface Science CO., Ltd.). Briefly, a suitable size ( $5\text{--}7 \mu\text{l}$ ) of a pendant drop of water was generated inside a transparent quartz cuvette filled with fuel containing different amounts of monoolein. Immediately after the drop became steady, the CCD camera on the instrument was triggered to take images of the drop continuously for a chosen length of time. The images were later processed to give the instant interfacial tension of fuel and water at different times using the built-in software. Experimental details can be found in the Supporting Information as "Interfacial tension measurement procedure".

### 3.2. Contact angle

Contact angle measurements were carried out by using the same instrument mentioned above. A drop volume of  $4 \mu\text{l}$  liquid probe of either water or fuel was used for contact angle measurement in air unless otherwise indicated. The results reported are the mean value of at least 3 replicates. For under-oil dynamic water contact angle measurements, a transparent cell was used to host the sample (glass slide) mounted on a stainless steel stand first, and the cell was then filled with diesel fuel. The sample was placed on the stand with the coating side facing upward. A fresh pendant drop of water was generated at the tip of the needle immersed in the fuel, and allowed to gently detach from the needle to contact

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