

Media for Water Separation from Biodiesel-Ultra Low Sulfur Diesel Blends

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ABSTRACT

Emergence of fatty acid methyl esters (biodiesel) as a diesel fuel blend component, as well as fuel additization for management of mandated fuel sulfur reductions, have resulted in dramatic increases in fuel surfactant levels. This step change in fuel surfactancy has given rise to consistent failures of conventional separation and coalescence media used for separation of water from diesel fuel. Reported here are results of coalescing media development efforts that focused on treating fuel-water separation as an adsorption based or liquid-solid separation problem. Stationary phase surface area invariably promotes separation in adsorption based regimes. Media were developed with 60 and 160 fold increases in surface area relative commercial separation media currently used for this application. Media were tested in 7 (B7), 20 (B20), and 40 (B40) percent biodiesel in ultra low sulfur diesel blends. Developed media 09-17 yielded unadjusted time weighted average water removal efficiency in flat sheet SAE J1488 fuel-water separation tests of 96% (B7), 88, 91% (B20), and 84% (B40). Adjusted for dissolved water content, B40 performance for 09-17 was 90%. Under the same test conditions, unadjusted time weighted average water removal efficiency of conventional coalescence media was 74% (B7) and 68% (B20), and traditional barrier media was 70, 83% (B7) and 50% (B40). Results support the role for high surface area media in successful removal of water from Biodiesel-Ultra Low Sulfur Diesel blends.

INTRODUCTION

The United States Environmental Protection Agency (EPA) initially established emission standards for new heavy duty diesel engines targeting the 1974 model year. Over the subsequent twenty five years, emission targets have declined incrementally^{i,ii}. Mandated reductions of particulate (PM_{2.5}) and nitrogen oxide (NO_x) emissions in the EPA 2007 Heavy Duty Highway Diesel Rule represent 90% and 92% respective reductions relative to prior limitsⁱⁱⁱ. As sulfur sensitive exhaust after treatment was considered necessary to meet 2007 particulate and NO_x requirements, the 2007 Highway Rule also requires sulfur levels in diesel fuel to drop 97% to 15 ppm.

With tightening requirements, emission reduction strategies revolve increasingly around the high pressure common rail (HPCR) fuel injection equipment (FIE). Combustion temperature and completeness, fundamental drivers of NO_x and particulate emissions, are manipulated through combustion event control and fuel atomization. In the HPCR, injection volumes are on microliter levels, injection time is controlled at millisecond intervals and injection pressures operate in the vicinity of 30,000 psi. Injector spray holes have dropped to 150 μm , with operating clearances within the injector itself below 5 μm ⁴.

High operating pressure and micron level tolerances make FIE vulnerable to contaminants and dependent on a minimal level of lubricity. Lubricity requirements have been dictated to date from a linear correlation between

ISO 12156-1 High Frequency Reciprocating Rig (HFRR) mean wear scar diameter (WS 1.4) and assessed fuel pump wear rating. A maximum wear scar diameter of 460 μm was established as the upper limit for adequate durability and performance in the fuel injection system^{4,5}.

Water is a fuel contaminant of concern for corrosion of steel components and promotion of microbiological growth. Both factors clearly interfere with durability and performance of diesel injectors. For this reason, European Union diesel specification, EN 590 (2005) limits maximum dissolved water content to 200 ppm, with zero tolerance for free water.

Separation of emulsified water from diesel fuel is a long standing requirement for diesel engine operation. Water removal has been historically met through the use of hydrophobic barrier filtration media, such as silicone treated cellulose found in fuel-water separators, or hydrophilic depth coalescing media, such as glass micro-fiber. Effective water removal from fuel is considered fundamental to the preservation of fuel injection systems, and as a result, attaining emission targets.

Control of fuel lubricity and water content became inextricably entwined with the advent of post 2007 Highway Rule hydrodesulfurized, ultra low sulfur diesel (ULSD) fuels and Biodiesel in the market. Hydrodesulfurization involves hydrotreatment, a refining step that removes sulfur as well as other heteroatoms and conjugated aromatic systems from the petroleum fraction. As a result of this refining step, diesel fuel loses its inherent lubricity. In initial ULSD field trials, HFRR wear scar diameters jumped to 600-650 μm and fuel injector pumps and rails failed due to excessive wear⁵. To improve ULSD lubricity, rust inhibitors, lubricity enhancers and anti-wear fuel additives were added to ULSD blends. Moving on an independent course is Biodiesel, a blend of fatty acid methyl esters derived from methanol esterification of plant and animal triglycerides. Escalating oil prices as well as pressure for domestic fuel supply development and minimization of fossilized carbon emission create conducive conditions for biodiesel incorporation in fuel blends. Biodiesel was also found to improve ULSD lubricity, and as a result generated additional impetus for its use as a blend component for ULSD fuel. Although additives and biodiesel salvaged ULSD lubricity needs, such blends created conditions where systems designed in the past for water removal from fuel fail and allow 50-100% of entrained water into the injection manifold, opening another concern for injector integrity.

The root cause of fuel-water separator / coalescer failure in ULSD and ULSD-Biodiesel blends is increased fuel surfactancy. Although given separate titles, rust

inhibitors, lubricity enhancers, anti-wear additives, and biodiesel can all be grouped into a single molecular family: surface active agents, or surfactants. Surfactant molecules contain both hydrophilic and hydrophobic moieties and display unique activity in systems containing immiscible water-like and oil-like phases. The term immiscible denotes the presence of an energetic barrier to creation of an interface. The energetic barrier is manifest as interfacial tension, γ , between the two liquids. The Gibbs Free Energy, G , of such a system increases with interface formation as expressed in Equation 1 below,

$$\delta G = -S\delta T + V\delta p + \gamma \delta \sigma \quad (1)$$

where σ represents interface surface area, and S , T , V , p are entropy, temperature, volume and pressure, respectively.

In systems containing immiscible phases, surfactants align at interfaces with the hydrophilic head group associated with the water-like phase, and the hydrophobic tail extended into the oil-like phase. This is the lowest energy conformation of the surfactant. When functioning in rust inhibition or lubricity roles, surfactant hydrophilic head groups align with metal surfaces with hydrophobic tails extended into the surrounding hydrocarbon.

Alignment of a surfactant at the interface lowers the interfacial tension between the phases. At constant temperature and pressure, γ is the slope of a linear relationship between input energy and interface surface area, σ . As such, a given increment of input energy will result in a higher interface surface area in the presence of a surfactant. The smallest contact surface area occurs with two separate bulk phases separated by a single interface. Increased interface surface area occurs with formation of an emulsion, when one of the phases exists in the form of suspended droplets in a continuous phase of the other component. By lowering interfacial tension, surfactants promote drop rupture and the formation of emulsions. For this reason, surfactants are also classified as emulsifiers.

Lowering the energy barrier to drop rupture is not the only manner in which surfactants impact emulsions. From Equation 1, emulsions are high energy states, requiring energy input for formation and persistence. Higher input energy and/or lower interfacial tension result in increased surface area of emulsified drops. Higher surface area of emulsified drops corresponds to lower drop size distribution. An emulsion will relax to the lowest surface area configuration of two separate bulk phases separated by a single interface without continuous energy input. An emulsion that is considered "stable" is one where phase separation occurs very

slowly. For an emulsion to relax, drops must encounter one another, collide, and coalesce to a larger drop. This process is kinetic and its speed is subject to factors that alter the energy barrier to coalescence. The presence of a surfactant adsorbed to a drop surface creates steric and/or electrostatic barriers to coalescence with other drops. Such energy barriers to coalescence lead to dramatic differences in emulsion lifetime and persistence of a smaller drop size distribution^{6,7,8}.

Past diesel fuels were prone to formation of water-in-fuel emulsions. This warranted the initial development of fuel-water separators. The emulsions formed in these systems, however, were relatively weak and the result of the molecular content of the blend. The difference with ULSD and ULSD-biodiesel blends lies in the fact that the surfactants added in the form of anti-rust, lubricity, and anti-wear agents have been specifically designed to adsorb at an interface. As a result, diesel fuel additives can be extremely efficient stabilizers against coalescence, creating highly stable emulsions of small water drops in the fuel. In addition, the presence of adsorbed species on water droplet surfaces can interfere with the interaction between the droplet and filtration media that is necessary for successful water separation. Biodiesel happens to mimic emulsifier behavior of fuel additives because of similarity in molecular structure. Both of these factors, stabilized water particles and interfered interactions with media surfaces, create the failures of phase separation by traditional coalescers and separators in ULSD and ULSD-Biodiesel blends. They are dependent on the nature of the surfactant, though, and as a result vary with fuel additive packages.

It is important to highlight the dependence of emulsion drop size, persistence, and resistance to separation on resistance to coalescence, not interfacial tension depression. Lobo and Svereika⁹ describe emulsion creation as involving two processes, *drop rupture*, driven by interfacial tension, and *drop coalescence*, driven by resistance to coalescence of surfactant stabilized drops. In high-pressure homogenized systems, such as found in diesel transfer, the roles of drop rupture and resistance to coalescence are not equal. Lobo and Svereika found that drop sizes in emulsions were driven not by the degree to which a surfactant depressed interfacial tension, a property they described as insignificant in the role of creating small drops. Rather, they found that drop size and persistence were nearly exclusively a property of the surfactant's ability to stabilize drops from coalescence.

The role of surfactants in mediating droplet coalescence and separation of emulsions is well understood outside the filtration industry. Emulsion creation and destruction is of considerable interest to the petrochemical, pharmaceutical, cosmetic, metal working, and food

industries. A survey of the literature from these disciplines demonstrates routine investment of time and resources in surfactant design to achieve target resistance to coalescence performance in specific emulsions^{10,11,12,13,14,15}. With regard to filtration, irrespective of the method selected for water separation from a hydrocarbon – barrier separation or coalescence – the separation is dependent on coalescence of small droplets into drops sufficiently large in size to separate gravimetrically against a counter flow of dry hydrocarbon. Successful separation requires coalescence. As such, the resistance of water drops to coalescence in surfactant containing fuels would appear to be an important variable to characterize for those interested in successful fuel-water separation. Results reported for ULSD systems support this concept. Fuels with the same interfacial tension displayed quite different emulsion separation profiles as measured by turbidity decay. It was the emulsion decay, an indicator of resistance to coalescence that correlated with ease of separation in diesel filtration systems, not interfacial tension depression¹⁶.

In the United States, fuel-water separation is measured using the SAE J1488 Emulsified Water/Fuel Separation Test Procedure. The SAE J1488 specifies only an interfacial tension range for the fuel, and the specified range no longer represents interfacial tensions found in surfactant-containing fuels. A proposal to adapt the interfacial tension to one more representative of current fuels was recently accepted¹⁷; however, resistance to coalescence remains unspecified and uncontrolled in the procedure. This leads to fuel dependence of SAE J1488 results which negatively impacts efforts to develop fuel-water separation solutions for current Biodiesel / ULSD fuels. Several methods exist for measurement of resistance to coalescence^{16,18}, and two have been proposed for addition to the SAE J1488^{16,19}. This fuel dependence, however, highlights the need for rigorous separation media capable of water separation irrespective of the fuel interfacial tension and resistance to coalescence.

The alarming failure consistency of current fuel dewatering systems has catalyzed wide ranging development efforts for fuel independent water separators. However, innovation in the coalescence and separation arena often involves complete separation systems. The systems involve multiple media types, multiple media elements, and multiple layers of media. The innovation often concerns packaging the media and flowing the emulsion in novel ways. The drawback of this approach is complexity, which translates directly to manufacturing and raw material costs. The same factors that give rise to complexity and increased cost, also limit universal applicability of the solution. New solutions invariably concern a single or extremely limited set of coalescing filter designs. Missing from the

development effort is a media capable of water separation from high surfactant content fuel that is universally compatible with the range of separation systems already in use in the field and the range of converting technologies used by filter manufacturers.

Reported here are development efforts targeting a fuel independent, system independent, universally applicable coalescing media. The approach treated fuel-water separation as a solid-liquid separation problem, where reliable separation can be effected through increased surface area of the separation media. The focus of this study was water separation in ULSD/Biodiesel blends through media design using enhanced surface area materials.

THEORY

Separation of a fuel-water emulsion via contact with a solid coalescing media can be best understood as a liquid-solid or adsorption based separation. Separation occurs as a result of unique associations formed between the solid media and the fuel, fuel additives, and water comprising the emulsion. In a flowing system, these unique associations translate to differing elution times from the media. As a result, when emulsion components spread through the media based on differing affinities for the solid, areas of elevated concentration of each component are created. When these conditions are brought about for water, the result is coalescence from exceedingly small drops of 3.5 or 10.0 μm diameter¹⁷, to drops sufficiently massive to gravimetrically settle out of fuel flow. Invariably, it is the gravimetric settling that dehydrates the fuel.

Partitioning of emulsion components between the solid media surface and the fuel is driven by free energy minimization (Eqn.1). An emulsion component will associate with the solid media if that interaction lowers the overall energy of the system. At constant temperature and pressure, energy minimization will be driven by the $\gamma\delta\sigma$ term. Components with a low solid-liquid interfacial tension (high affinity for solid) will exhibit a higher surface of interaction compared to components with high solid-liquid interfacial tension (low affinity for solid). Surface of interaction or surface area, translates to path length available for that component's journey through the stationary phase. Path length drives elution time from the media. In difficult to resolve mixtures, where only minimal differences exist between phases to be separated, elution time differences are exaggerated by increasing the available path length. As a result, in adsorption-based separation, surface area of the stationary phase, is the single most critical parameter for successful separation²⁰.

Water emulsions in surfactant-stabilized ULSD and Biodiesel-ULSD qualify as difficult to resolve mixtures. In these systems, partitioning and separation become a markedly more complicated task than confronted with historically encountered fuel-water emulsions. Media surfaces must compete for water that is energetically stabilized in the fuel by surfactants. The probability of water partitioning between the fuel and the solid media is therefore reduced. Due to their molecular nature, surfactants will readily partition between the liquid and solid phases, altering the surface energy of the solid presented for adsorption by the water and hydrocarbon fractions. The result is a mass homogenization of system energetics that requires extended path length for successful resolution in an adsorption-based separation regime. Stationary phase surface area must increase for successful resolution of emulsion components in surfactant-stabilized ULSD and Biodiesel-ULSD systems.

The work presented here focused on increasing separation media surface area to effect water separation from surfactant containing fuel. The implicit challenge of high surface area coalescence media development is its relationship with caliper increase and/or permeability decrease. These are in direct conflict with product face velocity and pressure differential targets. To place this task in technological context, enantiomers – molecules that differ only in the direction of polarized light rotation – are separable via exposure to current chromatographic media, as are sugar isomers and other chemically similar species. These are truly difficult separations. Advances in chromatographic separation, however, depend less on novel media, where silica-based stationary phases continue to dominate. Rather, advances came with precisely controlled stationary phase particle size reductions that provided required uniformity and surface area, as well as associated hardware developments (valve, injection system, and pump) needed to manage skyrocketing pressure differentials. It is not accidental that HPLC, the acronym for High Performance Liquid Chromatography is equally defined as High Pressure Liquid Chromatography. Operating pressures required to deliver manageable flow rates for needed surface area fall in the 350-500 bar (5000-7000 psi) range²¹.

For a given media caliper, permeability loss with increased surface area is a legitimate concern. Generally, permeability suffers less when surface area is brought to the sheet through a fibrous structure, thus preserving media porosity. The most successful separation and coalescence media in the current market rely on this strategy using fine diameter meltblown polyester or glass micro-fiber. Table 1 compares surface areas achieved with these media to that available from a traditional cellulose filtration media. Meltblown and micro-glass surface area of