Development of a Renewable Fuel Nanotechnology

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ABSTRACT

The authors have developed a technology to blend biomass-derived oxygenates – alcohols and free fatty acids together with water to form a renewable blend stock. When blended into diesel, the resulting low-carbon intensity microemulsion fuel has been shown to have a nano-structure, and has been used to power unmodified diesel engines, and has exhibited reductions in emissions of particulate matter (PM) and nitrogen oxides (NOx). This paper describes the optimization of the chemical formulation for performance properties, as well as characterization of the fuel's molecular nano-structure using dynamic light scattering (DLS) and small angle neutron scattering (SANS).

Keywords: microemulsion, renewable fuel, critical micelle concentration, micelle, nanoscale chemistry

1 BACKGROUND

Ethanol, water, and polar hydrophilic compounds have limited solubility with diesel and nonpolar long-chain hydrocarbons, and are therefore prone to phase separation. Sylvatex has developed a technology that uses high concentrations of combustible, renewable fatty acids that act as a surfactant form inverse micelles that solubilize the oxygenates within the diesel, resulting in a microemulsion system that is thermodynamically stable. The benefit to a nanostructured fuel is that the ethanol and oxygenates have a "cooling effect" on the combustion temperature of the fuel, thereby reducing unwanted side products of particulate matter (PM) and nitrogen oxides (NOx). Commercialization of this technology will have the following impacts: availability of an affordable cleaner burning renewable alternative diesel fuel that will meet the Low Carbon Fuel Standard and does not compete with food crops, reduced emissions of nitrogen oxides and particulate matter, and reduced dependence on petroleum.

2 PERFORMANCE OPTIMIZATION

To identify the most promising formulations of microemulsion fuel, a series of emissions tests were performed to identify the concentrations of water and cetane improver that would give the best emission reductions, while keeping the concentrations of ethanol and surfactant constant at levels previously identified as satisfactory in keeping the water-diesel mixture as clear and monophasic. Emissions were measured while using each of the test fuels in a 100 kW portable generating set. All of the emission tests were conducted over the same operating cycle, which was an adaptation of the ISO 8178 D2 tet cycle for constant speed engines. The test engine was a Volvo TAD720GE diesel engine, certified to California Tier II emission standards. The engine was rated at 190 mechanical horsepower (142 kWm) at full load, while the generating set was rated at 100 kW (electric) power output, with a 10% overload capacity [1, 2].

For Tier 2 non-road engine and generator test cycle used, the best emission reductions were obtained with a formulation containing 6%. Compared to the baseline fuel, ultra-low sulfur diesel (ULSD), this formulation could reduce PM emissions by 36%, NOx emissions by 3%.

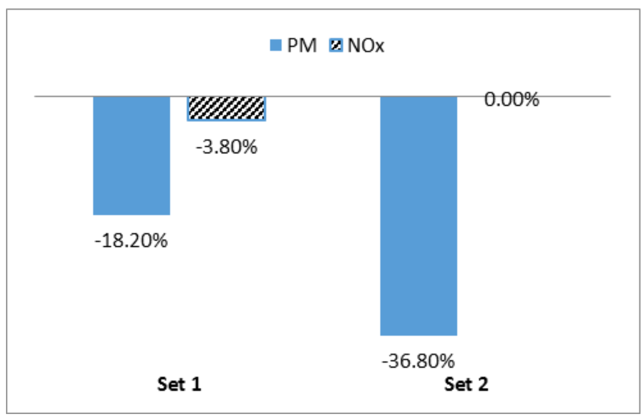

Figure 1: Emission datas of 6% formulations.

Because of the oxygenated that it contains, the microemulsion fuel has lower energy density than does conventional diesel fuel. Table 2 shows the average mass of fuel consumed per test for the baseline diesel fuel and for the best microemulsion blend. The energy produced was constant for all tests, thus the average volume of microemulsion fuel burned to produce 1 kWh of electrical energy from the generator was 14% greater than for conventional diesel. Conventional diesel fuel contains 15% more energy per unit volume, however, so that the fuel energy consumed per kWh was about 1.2% less than for the baseline fuel.

Fuel	Energy Density (LHV) kJ/kg	Fuel Mass Consumed kg/test	Fuel Vol liters	Fuel Energy kJ/test
Baseline ULSD	42,744	4.321	5.13	184,705
Best Fuel Blend	36,926	5.948	5.84	184,721
Ratio: Fuel Blend/ ULSD	86%	114.5%	113.8%	98.9%

Table 1: Average Fuel and Energy Consumed per test.

3 STRUCTURE CHARACTERIZATION

The performance benefits that we observed are assumed to be a result of the micellar size, shape, and nano-scale structure with the microemulsion.

Sylvatex developed a preliminary model of the microemulstion using dynamic light scattering (DLS). By assuming a simple reverse-micelle spherical structure with a shell that is roughly 2.25 nm thick (the length of the surfactant), the DLS results of Sylvatex microemulsions in low-sulfur diesel indicate structures ranging from ~4.5 to 45 nm, with variations based on the blend stock. As water is added, the nanopool interior core grows proportionally until it reaches a maximum size, at which point the system becomes turbid and the emulsion breaks, presumably because the surfactant lower critical micelle concentration has been reached.

Multi-component reverse micelles in hydrocarbons have been studied extensively by Small Angle Neutron Scattering (SANS) by, for example, Kaler et al. [3], Simmons et al. [4] and Compere et al. [5] , where in multiple studies the best-fit shapes were not necessarily polydisperse spheres, but, rather, prolate ellipsoids or vesicles. A variety of microemulsions were made with both industrial (Ultra Low Sulfur Diesel) and model (hexadecane) mixtures with a blend stock of water, ethanol, neutralizer, and surfactant added. Industrial mixtures used hydrolyzed corn oil waste as a surfactant, whereas model mixtures used reagent grade oleic acid. These systems were then studied using SANS, assuming ellipsoid models. Table 2 shows a comparison of the results obtained from DLS and SANS measurements, for mixtures containing 10% (vol) of renewable blend stock in base solvent. To simplify the model, it was assumed that spherical micelles are formed, and that 100% of the water and ethanol goes into the interior of the nanopool. It should also be noted that DLS measurements are based on the full hydrodynamic radius including the surfactant shell whereas SANS only detects the nanopool interior which was deuterium labeled. Concequently, the DLS measurements are expected to be roughly 2 to 3 nm higher than those for SANS.

Relative H_2O %	Semi major Axis, a (nm)	Semi minor axis, b (nm)	Semi minor axis, c (nm)	Axis Average	DLS (nm)
0	6.17	2.63	1.91	3.57	5.82
0.25	7.19	2.38	2.38	3.98	8.25
0.5	19.03	2.77	2.77	8.19	9.85
0.75	24.91	5.47	2.14	10.84	11.2
1	21.15	4.25	2.28	9.23	12.5

Table 2: DLS and SANS cross sectional micelle diameter size dimensions for selected formulations.

As predicted, the results obtained from both DLS and SANS measurements indicate that both model and industrial mixtures have micelles that increase in size as the concentration of water increases. At above a relative water concentration of 1.0, the DLS data becomes noisy as the systems presumably become saturated. This would indicate that either the micelles burst or that their structure changes.

Since the contrast from the micelle's surfactant shell nearly matches the hydrocarbon phase, we assumed a two-phase system and calculated the volume fraction (ϕ) of the micelles from the invariant (Q_I).). Data was then fit to the triaxial ellipsoid model provided by NIST to obtain the radii [6] of the ellipsoids.

Another variable that was investigated was the concentration of the renewable blend stock component in the ULSD or hexadecane. Previous work using DLS was not able to elucidate how the ethanol in the system was partitioning thus convoluting proper volume fraction-size calculations. DLS measurements have indicated that the micelle size remains relatively constant for 5% and 10% (vol.) blends, so it is to be expected that the micelle populations become more sparse as the blend stock concentration is diluted. Table 3 shows that as blend stock volume increases (represented by relative water %), the volume fraction of the micelles, as calculated from the invariant also increases.

Nanopool Vol. Fraction (Calculated)	Nanopool Vol. Fraction from Invariant	Relative Water %
4.38%	1.43%	0
4.48%	2.00%	0.25
4.58%	2.17%	0.5
4.67%	2.06%	0.75
4.77%	2.84%	1

Table 3: Calculated volume fractions compared to SANS invariant based observations for select samples.

A general trend of increasing volume fractions can be seen as the relative water increases. However, there is a large discrepency in the calculated values with the SANS based values. This discrepency is attributed to the partitioning of the deuterium labeled ethanol in both the nanopool and dispersant phases. Subsequent experiments have been done more recently that will elucidate this partitioning behavior further.

4 FUTURE WORK

To date, Sylvatex has completed performance evaluation on emissions and fuel consumption, accumulated over 10,000 miles in on-road vehicle demonstrations, characterized the physical, chemical and structural properties of the microemulsion system, and assessed the compatibility of the resulting fuel product with elastomers and metals. We are currently developing processing methods to economically derive the renewable surfactant from waste products, and are working on methods to effectively scale the production of the renewable fuel nanotechnology.

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