Development of a Novel Biofuel Blend Using Ethanol−Biodiesel−Diesel Microemulsions: EB-Diesel

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Development of a Novel Biofuel Blend Using Ethanol−Biodiesel−Diesel Microemulsions: EB-Diesel

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Oxygenated diesel fuel blends have advantages over regular diesel. Oxygenation significantly reduces particulate matter (PM) and reduces toxic gases such as CO, sulfur oxides (SO_x), and, at times, nitrogen oxides (NO_x) from tailpipe emissions. Ethanol, which is the oxygenate in E-diesel, is a renewable fuel that reduces the dependency of non-oil-producing countries on foreign petroleum. However, a major drawback with E-diesel is that ethanol is immiscible in diesel over a wide range of temperatures. Studies have revealed that biodiesel, which is another renewable fuel, can be used successfully as an amphiphile (a surface-active agent) to stabilize ethanol and diesel. Research also has revealed that ethanol−biodiesel−diesel (EB-diesel) fuel blend microemulsions are stable well below sub-zero temperatures and have shown equal or superior fuel properties to regular diesel fuel. Microemulsions of certain component concentrations have shown substantially increased lubricity without compromising the cetane numbers and energy values. Despite ethanol having a considerably lower energy value, cetane number, and lubricity value than biodiesel or diesel fuel alone, the heat of combustion and cetane numbers of the EB-diesel blends remained steady, without significant reduction. The minimal change of the heat of combustion suggested that microemulsions may be contributing to the overall combustion process in a positive way. This work has paved the way to formulate a new form of biofuel blend from renewable material—a blend that has energy values comparable to those of fossil fuels but also has superior lubricity and environmentally friendly characteristics.

Introduction

The global energy crisis in the 1970s prompted many countries to search for alternative energy sources, after being vulnerable to crude oil embargoes and shortages. The use of vegetable oil ester-based biodiesel and ethanol-based E-diesel occurred primarily as a direct result of that fuel crisis. Both biodiesel and E-diesel (blends of ethanol in diesel) are currently being used in fleet vehicles in the European Union and the United States.

The use of biofuels that are based on renewable resources has several advantages.[1] Biofuels are an ideal alternative to dwindling fossil resources. The increasing dependence on imported crude oil also has led to a major interest by non-fossil-fuel-producing countries, in regard to expanding the use of bioenergy. In preparation for a future petroleum fuel crisis, the United States recently made a commitment to triple bioenergy usage within 10 years. The European Union also has made a similar proposal to ensure that biofuels account for at least 2% of the petroleum-based fuels market by the end of 2005 and a minimum of 5.75% of the market by the end of 2010.[2,3]

Biofuels have a major advantage over conventional fossil fuels: biofuels are environmentally friendly.[4,5] Studies on the fuel-cycle energy and emissions impacts of 13 combinations of fuels and propulsion systems that were potential candidates for light-duty vehicles with tripled fuel economy (3X vehicles) at Argonne National Laboratories[6] have revealed that compression−ignition engines that were operating on biodiesel yielded substantial reductions in urban emissions of carbon monoxide (CO) and greenhouse gases (primarily carbon dioxide, CO_2). On the other hand, studies on E-diesel yielded significant reductions of particulate matter

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(PM).[6,7] Recent studies conducted on E-diesel confirm substantial reductions in PM, sometimes up to 40%, depending on the test methods and operating conditions.[8–12] It was also reported that the CO and nitrogen oxide (NO_x) emissions were significantly lower when a 20% blend of E-diesel was used in a constant-speed stationary diesel engine, as opposed to diesel fuel.[13] A separate study reported that a 20% E-diesel blend resulted in reductions of 55%, 36%, and 51% in CO, hydrocarbons (HC), and PM emissions, respectively.[13] This study also reported that the optimum percentage for ethanol in E-diesel fuel blends was 15%, which produced reductions of 43.3%, 34%, and 32% in CO, HC, and PM emissions, respectively. The addition of ethanol to diesel may result in a volumetric reduction in sulfur, by as much as 20%, thus significantly reducing SO_2 emissions.[13]

The major drawback in E-diesel is that ethanol is immiscible in diesel over a wide range of temperatures. Our preliminary studies have indicated that, at a temperature of 25°C, ethanol and diesel mixtures separate rapidly into two distinct phases. Because all automotive fuels are required to be a clear, single-phase liquid,[16] various commercial surfactants are used as emulsifiers to form ethanol−diesel emulsions. Typically, these surfactants are added at a concentration of ≤5%. The literature suggests that the various commercially available surfactants include alkanols, decaglycerol mono-oleate (MO750), and alkanolamides.[17–19] However, the performance of such surfactants, in terms of phase behavior or phase stability, has not been reported.[20–27] Also, to prevent engine and fuel system damage, the phase behavior of alternative fuels and regular fossil fuel blends should be investigated extensively under differing conditions.[26] In this study, we investigated the use of biodiesel (soybean oil methyl esters) as an amphiphile in stabilizing ethanol in diesel emulsions, the phase stability of ethanol−biodiesel−diesel (EB-diesel) three-component systems, and their properties at different temperatures and different component concentrations.

Objectives

The overall objective of this study was to determine the relative compatibilities of ethanol, biodiesel, and diesel fuel. The specific objectives were as follows:

(1) To develop phase diagrams and determine the phase behavior of an EB-diesel three-component fuel system for low-sulfur and super-low-sulfur diesel fuels blended with ethanol and biodiesel fuels;

(2) To determine the effects of ethanol denaturants, diesel fuel types, temperature, and water on such blends; and

(3) To measure selected blends, within the single-phase region (clear microemulsion region) for lubricity, flashpoint temperature, sulfur content, cetane number, and energy value.

Materials and Methods

The phase behavior of the ethanol−biodiesel−diesel (EB-diesel) three-component fuel system was studied with the following reference fuel components: (i) No. 2 low-sulfur (0.05%) diesel certification (reference) fuel (from Chevron Phillips, The Woodlands, TX), (ii) fuel ethanol (reference) denatured with natural gasoline (from Nebraska Energy LLC, Aurora, NE), and (iii) biodiesel (from AGP, Omaha, NE). The initial phase behaviors were determined at a temperature of 22 °C under isobaric (1 atm) conditions. The temperature was maintained by a thermostat in the laboratory where the experiments were conducted.

Ternary phase diagrams are widely used to depict the phase behavior of three-component systems.[28,29] In this study, phase boundaries were determined using the titration method.[30] Initially, a mixture of 5% ethanol and 95% diesel (5% E-diesel) was titrated with biodiesel to get a clear endpoint. Similarly, mixtures of E-diesel concentrations ranging from 5% to 95% in 5% increments were titrated with biodiesel to develop the phase diagram. The experiment was designed as a completely randomized design with three replicates.

To study the effect of temperature on the reference No. 2 low sulfur (LS) diesel−fuel ethanol−biodiesel three-component system, the following treatments were used: (i) No. 2 low-sulfur (0.5%) (reference) diesel fuel, (ii) fuel ethanol (reference)

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Table 1. Experimental Design Used To Test the Effect of Temperature on the Phase Behavior of No. 2 Low-Sulfur Reference Diesel−Denatured (Fuel) Ethanol−Biodiesel System

ethanol (%)	diesel (%)	biodiesel (% of 5:95 mix)									
		0	10	20	30	40	50	60	70	80	90
5	95	100	90	80	70	60	50	40	30	20	10
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
95	5	100	90	80	70	60	50	40	30	20	10

(purchased from the Nebraska Energy LLC ethanol plant), and (iii) biodiesel (purchased from AGP).

To detect the phase behavior of the three-component system at different temperatures effectively, it was necessary to design an experiment to cover the entire spectrum of concentrations of the components. To accomplish this goal, the most effective way was to change the concentrations of two components from a lower concentration to a higher concentration (and vice versa) and add the third component from a lower concentration to a higher concentration to each of the mixtures of the initial two components. It was decided to select ethanol and diesel as the two initial mixtures. This decision was further justified because our objective was to identify an amphiphile for E-diesel. Accordingly, arrays of ethanol−diesel blends, ranging from E-5 (5% ethanol in 95% diesel) to E-95 (95% ethanol in 5% diesel) were prepared with low-sulfur reference diesel fuel. From each ethanol diesel mixture, a series of EB-diesel blends then was made, so that the concentration of the E-diesel mixture ranged from 100% to 10% in 10% increments, whereas the respective biodiesel concentration varied from 0% to 90%, in 10% increments (Table 1). Consequently, the sample size was $10 \times 19 \times 3 = 570$ samples. An experimental unit consisted of a glass test tube with a given mixture of ethanol, biodiesel, and diesel. After sample preparation, all the samples were transferred to a −70 °C blast freezer. After solidification, the samples were taken from the freezer and gradually warmed while stirring. When the temperature was increased, the frozen samples thawed initially to a turbid liquid. The temperature at which this turbidity disappeared and a clear liquid appeared was recorded as the 2Φ to 1Φ phase transition temperature (PTT).

The experiment was a split-plot design in which the main-plot factors were the percent of diesel and the percent of ethanol, whereas the split-plot factor was the percent of biodiesel that went into an experimental unit. The data were analyzed as response surfaces/regression models.

The effects of ethanol denaturants (natural gasoline, kerosene, etc.) were determined by comparing the phase diagrams that were developed by changing the respective parameters. The treatments consisted of (i) fuel ethanol (reference) denatured with natural gasoline and purchased from AGP; (ii) 200 proof ethanol purchased from Pharmcoproducts, Inc. (Brookfield, CT); (iii) denatured ethanol SD-1 purchased from Fisher Scientific; (iv) No. 2 diesel fuel; and (v) biodiesel purchased from AGP.

Individual phase diagrams were developed as completely randomized design with treatment setups similar to the three-component system described previously. The phase boundaries were compared by overlaying the ternary phase diagrams.

An experiment was designed to study the effect of diesel type with the following treatments: (i) No. 2 low-sulfur (0.5%) (reference) diesel fuel; (ii) No. 2 ultralow-sulfur (1.2 ppm) (reference) diesel fuel; (iii) fuel ethanol (reference) (purchased from Nebraska Energy LLC); and (iv) biodiesel (purchased from AGP).

Using the results of the analysis of the phase behavior of the No. 2 diesel certification fuel−fuel ethanol−biodiesel system at room temperature, treatments were narrowed down for this experiment according to the following criteria:

(1) The treatments consisted of at least 60% diesel fuel;

(2) The 1Φ to 2Φ PTT was <10 °C; and

(3) Neither the biodiesel concentration nor the ethanol concentration was >30%.

Initially, an array of ethanol−diesel fuel blends ranging from E-5 to E-30 was mixed with low-sulfur reference diesel fuel and ultralow-sulfur diesel fuel. From each ethanol−diesel fuel mixture, a series of EB-diesel fuel blends were made, so that the E-diesel concentrations of the mixtures ranged from 75% to 100%, whereas the biodiesel concentration varied from 25% to 0% at 5% increments. An experimental unit consisted of a glass test tube with a given mixture of ethanol, biodiesel, and diesel fuel.

The experiment was a split-plot design, where the volumes of diesel fuel and ethanol were the main-plot factors and the volume of biodiesel was the split-plot factor. The treatment design was a 6×6 factorial, and the analysis was conducted as a response surface/regression.

After preparation, the samples were transferred to a freezer that was set at −70 °C. After the samples had solidified, the samples were removed from the freezer and gradually warmed, while stirring, until the turbidity disappeared, as described previously. The temperature at which a clear liquid was observed was recorded as the PTT.

The aforementioned sample population was tested for their capacity to hold water. Enough water was added into each of the selected samples such that the final water content was 0.05%. A 0.05% level of water was used because it was the maximum allowable water content in regular diesel fuel. The samples then were transferred to a blast freezer. As done previously, the temperature of each sample was increased after the samples had solidified (for ~24 h) and new PTT was recorded.

From the sample population, four treatments (two from the low-sulfur diesel (LSD) fuel system and two from the ultralow-sulfur diesel (ULSD) fuel system), which had the highest stabilities as single-phase microemulsions (lowest 1Φ to 2Φ PTT), were subjected to standard laboratory testing. The test parameters included cetane number, lubricity (HFRR wear scar test), flash point, energy value, and sulfur content. The samples were tested at the Southwest Research Institute in The Woodlands, TX.

Results and Discussion

Phase Behavior of No. 2 Low-Sulfur (0.5%) Diesel Certification (Reference) Fuel−Ethanol−Biodiesel System at Room Temperature (20 °C). The addition of biodiesel to the fuel system made 200-proof ethanol and diesel miscible in each other at room temperature (20 °C). This miscibility was due to the fact that biodiesel acted as an amphiphile (a surface-active agent) and formed micelles that had nonpolar tails and polar heads. These molecules, called surfactants, were attracted to liquid/liquid interfacial films and each other. In small amounts, the biodiesel molecules were in random order; however, in larger numbers, the molecules bound together in an ordered form. The concentration at which they became ordered is called the critical micelle concentration. At this concentration, in the ordered arrangement, they formed micelles that were bound together by van der Waals forces. These micelles acted as polar or nonpolar solutes, depending on the orientation of the biodiesel molecules. When diesel fuel was in the continuous phase, the polar head in a biodiesel molecule oriented itself with the ethanol and the nonpolar tail was oriented with the diesel. This phenomenon held the micelles in a thermodynamically stable state, depending on the component concentrations and other physical parameters.
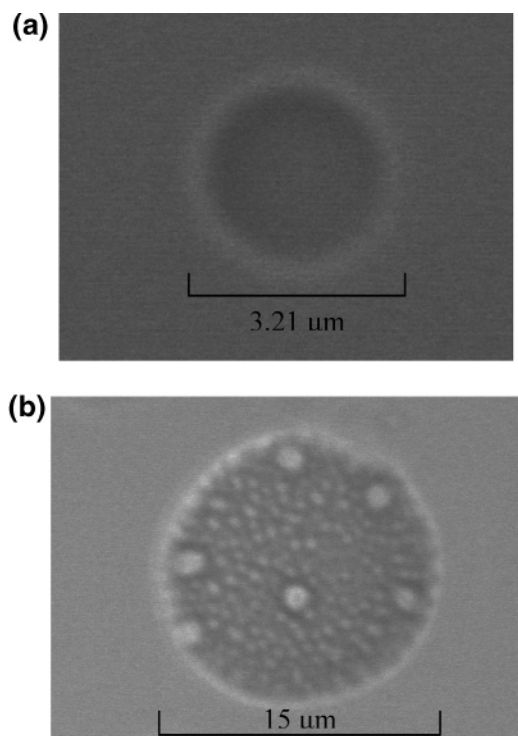
Figure 1. (a) Confocal laser scanning microscopic image of an ethanol−biodiesel−diesel micelle system. (b) Typical process of Oswald ripening, where smaller micelles of the fuel system coalesced together to form a larger thermodynamically stable molecule. (A 50× water immersion lens was used in conjunction with a 10× ocular lens; thus, the total magnification of the original images was 500×.)

Figure 1a denotes a confocal laser scanning microscopic image of an EB-diesel micelle. The mean micelle diameter just after mixing was 3.21 μm. Figure 1b shows the typical process of Oswald ripening, where smaller micelles coalesced together to form a larger, thermodynamically stable molecule. The mean diameter stabilized at ∼15 μm.

The ternary phase diagram of the No. 2 diesel certification (reference) fuel−200-proof ethanol−biodiesel system at room temperature is given in Figure 2. The triangle on the right depicts, from the intensity of the colors, the respective concentrations of the three components at any point inside the triangle. The percentage composition of components at any given point is proportional to the lengths of perpendicular lines from that point to each of the baselines, respectively. The figure on the left depicts how the concentrations of respective components change along the three axes of the triangle. Note that the nonexistence of lines inside the phase triangle indicates that, at any concentration combination, the three-component system was in an identical phase (in this case, a clear single-phase liquid).

Figure 3 represents the phase behavior of the three-component system where the type of ethanol used was fuel ethanol. Fuel ethanol is denatured with natural gasoline, which is a low-grade byproduct of petroleum distillation. Interestingly, note that, as given in Figure 3, at room temperature, No. 2 diesel certification fuel and fuel ethanol were completely miscible when the diesel concentration in the E-diesel mix was <20% or when the diesel concentration was >80%. This means

that whenever one component in the system was in excess of the aforementioned specified concentrations, the two components were completely miscible in each other. Miscibility and solubility, although they sound similar, have significant differences. Miscibility is the formation of a single, homogeneous phase when two or more liquid phases are brought together. Solubility, on the other hand, is the incorporation of material from a second phase to form a single, homogeneous solution in the first liquid phase when two or more phases are brought together. Two miscible liquids will continue to form a single phase, regardless of the ratio of one material to another, whereas two materials that are soluble will have a finite capacity for the amount of material of one phase that can be incorporated into another. Thus, it is possible for an excess of the second dissolved phase to be present.

Solubility can be termed as "partial miscibility" and can be regarded as a spectrum. If two liquid phases are mixed, at one end of the solubility spectrum, the two phases are totally miscible and a single phase is formed. At the other end, they are totally immiscible and remain two distinct separate phases. According to this definition, diesel and ethanol could be regarded as being soluble in each other.

Figure 4 presents the phase behavior of the three-component system when SD-1 denatured ethanol was used. This phase diagram illustrates how significant the effect of ethanol denaturant could be on phase behavior. In this three-component system, three phases appeared. The single-phase region was apparent only at the periphery of the phase diagram, especially when the diesel concentration or ethanol concentrations were low.

The best way to study the effect of ethanol in this situation is to select a mixture combination that is on the right baseline of the triangle and to draw a line to the ethanol apex/vertex. For example, if you start with a mixture of 60% biodiesel and 40% diesel (point A), the addition of ethanol would move the composition of the mixture along line AF. When moving along this line from point A to point B, it can be seen that, from point A to point B, the mixture is a single-phase microemulsion. As you move from point B to point C, the mixture becomes turbid, and allowing the mixture to settle will result in two distinct phases, an ethanol-rich upper phase and diesel-rich lower phase. Moving further along the line to point C, a third phase appears, which again disappears at point D. From point D to point E, the two-phase region reappears. From point E onward, the mixture remains a clear microemulation. Note that, for biofuel development, a mixture should be in the single-phase microemulsion region. Therefore, performing the titrations and creating tie-lines that would give compositions within the two-phase regions was not within the scope of this study.

Phase Behavior of No. 2 Low-Sulfur (0.05%) Diesel Certification Fuel−Denatured (Fuel) Ethanol−Biodiesel System at Different Temperatures. As stated previously, the experiment was designed to capture a wide spectrum of data points in a ternary phase diagram, relative to temperature, in the z-plane. However, the results will be presented in binary phase diagrams, because it will be easier to interpret
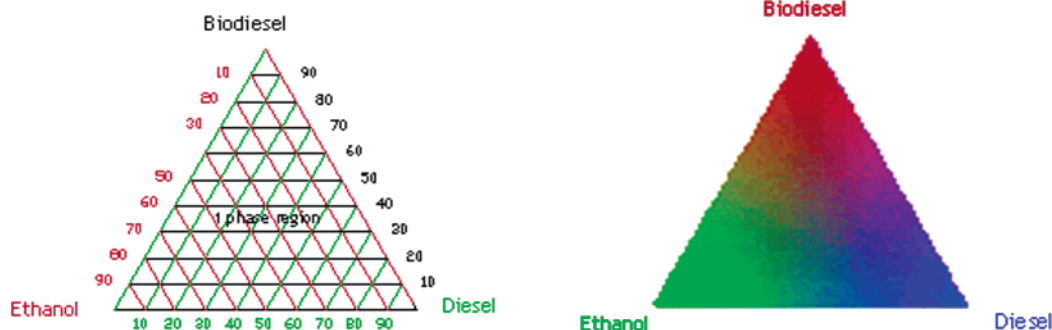
Figure 2. Effect of 200-proof ethanol on the phase behavior of the three-component system.
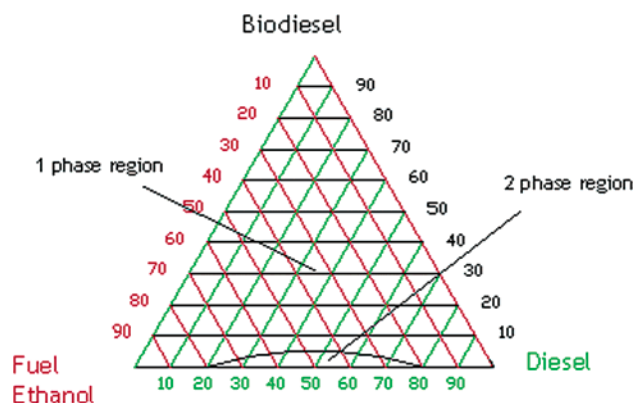

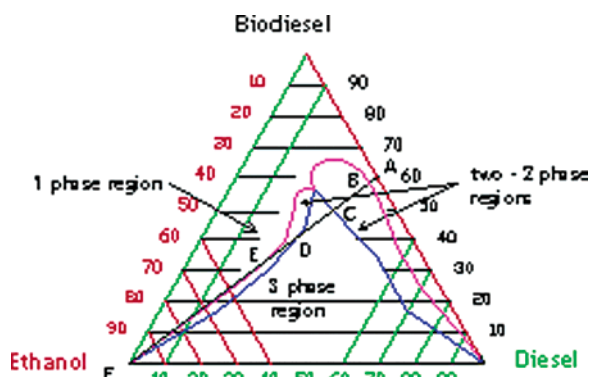**Figure 3.** Effect of fuel ethanol on the phase behavior of the three-component system.

Figure 4. Effect of ethanol SD-1 on the phase behavior of the three-component system.

and more useful to the reader who is interested in biofuel blends to use as a reference tool than when presented as a prismatic ternary phase diagram.

Figure 5 presents the phase behavior of E-diesel blends ranging from E-5 to E-30. Each line represents the phase boundary of a single-phase isotropic region from the anisotropic region. Any point above a line would be a single-phase microemulsion and a point below the line would be in an anisotropic state. The nature of the system below any line would be either two- or three-phase, crystalline, gel, or solid, depending on the amount of biodiesel present or the temperature. The interest of this study was focused solely on single-phase isotropic microemulsion regions; therefore, the physical nature of the system below the lines was not thoroughly investigated. Generally, it was observed that the blends in the anisotropic region were in liquid form from 0% to ~30% biodiesel in the mixture, followed by a gel region at ~50% biodiesel. Above a biodiesel concentra-

tion of 60%, the system had a tendency to solidify a few degrees from the single-phase boundary, followed by a relatively narrow gel phase. At higher biodiesel concentrations (>80%), the system suddenly melted and became a single-phase microemulsion without a gel phase.

The binodal curves of E-5 to E-30 E-diesel blends behaved similarly. At zero amphiphile (biodiesel) concentration, the phase-separation temperatures of all of E-diesel blends were >20 °C. This means that if the temperature fell below 20 °C, the ethanol and diesel would separate into two distinct phases. When biodiesel concentration was increased from 5% to 20%−30%, the phase-separation temperature decreased gradually, following a quadratic pattern. When biodiesel concentration was increased further, the binodal curves had a tendency to converge to a point at ~15−20 °C. The minimum temperature values were in the range of −5 °C to −10 °C. Note that the color variation at the phase transitions (from milky to colorless) in the E-5 to E-30 category were not as prominent as the two categories described below. In this initial phase of the study, the end points were taken after giving ample time for the liquid to clarify. The air bubbles that formed also interfered with visual observations. However, the same points were observed in a subsequent replication with a higher resolution when determining the effect of different diesel types on the phase behavior. At that instance, each data point was verified a second time by cooling the sample and observing the endpoint, in addition to the aforementioned procedure. By doing that, it was possible to collect more-accurate data points for each category of E-diesel blend.

The binodal curves of E-diesel mixtures ranging from E-35 to E-55 behaved in a fashion similar to the E-diesel mixtures described previously. The only difference in these samples was the relatively high phase-separation temperatures of pure E-diesel mixtures. The phase transition when the temperature was increased was quick (within a few drops of the titrant) and easy to detect.

The major difference in E-diesel mixtures ranging from E-65 to E-95 was that the minimum PTTs were in the range of −4 °C to 2 °C. The formulations in this category were not feasible as fuels, because the lowest temperature that a fuel with such a composition could withstand without separation was between −4 °C and 2 °C.

Figure 6 represents the physical state of the component system at a temperature of −13 °C. In the figure, along any row from left to right, the ethanol concentra-
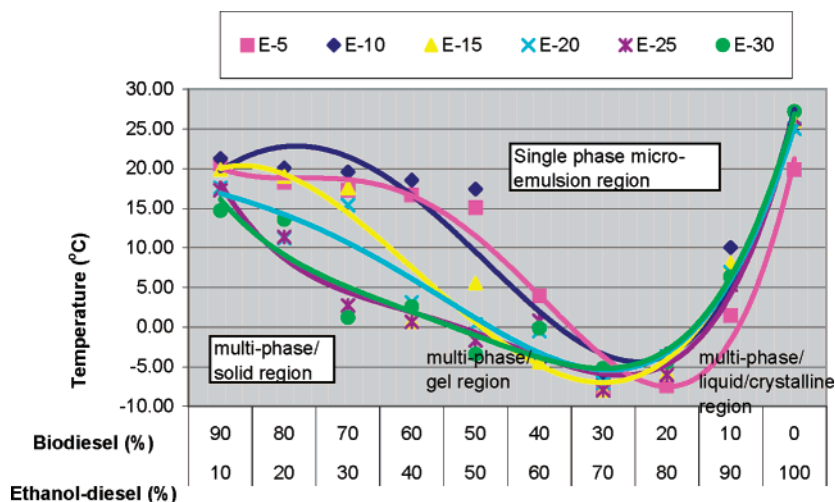
Figure 5. Phase behavior of E-diesel mixtures (E-5 through E-30) for varying concentrations of biodiesel.

Mix (%)	10	20	30	40	50	60	70	80	90	100
Biodiesel (%)	90	80	70	60	50	40	30	20	10	0
E-5	S	S	S	S	S	G 2Φ	LC 1Φ	L 1Φ	LC 3Φ	L 2Φ
E-10	S	S	S	S	S	G 2Φ	LC 1Φ	LC 2Φ	LC 3Φ	L 2Φ
E-15	S	S	S	S	G 1Φ	L 1Φ	L 1Φ	LC 2Φ	L 3Φ	L 2Φ
E-20	S	S	S	S	G 1Φ	LC 1Φ	LC 1Φ	L 2Φ	L 3Φ	L 2Φ
E-25	S	S	S	S	G 1Φ	LC 2Φ	L2Φ	L2Φ	L 3Φ	L 2Φ
E-30	S	S	S	S	G 1Φ	LC 2Φ	L2Φ	L 3Φ	L 3Φ	L 2Φ
E-35	S	S	S	S	S	G 1Φ	L2Φ	L 3Φ	L 3Φ	L 2Φ
E-40	S	S	S	S	G 1Φ	LC 2Φ	L2Φ	L2Φ	L 3Φ	L 2Φ
E-45	S	S	S	S	S	LC 2Φ	L 3Φ	L 3Φ	L 3Φ	L 2Φ
E-50	S	S	S	S	G 1Φ	LC 2Φ	L 2Φ	L 3Φ	L 3Φ	L 2Φ
E-55	S	S	S	S	S	LC 2Φ	L 2Φ	L 2Φ	L 3Φ	L 2Φ
E-60	S	S	S	S	S	LC 2Φ	L 2Φ	L 2Φ	L 3Φ	L 2Φ
E-65	S	S	S	S	S	G 1Φ	LC 2Φ	L 2Φ	L 2Φ	L 2Φ
E-70	S	S	S	S	S	LC 2Φ	LC 2Φ	L 2Φ	L 2Φ	L 2Φ
E-75	S	S	S	S	G 1Φ	LC 2Φ	LC 2Φ	L 2Φ	L 2Φ	L 2Φ
E-80	S	S	S	S	S	S	S	LC 2Φ	L 2Φ	L 2Φ
E-85	S	S	S	S	S	S	S	LC 2Φ	L 2Φ	L 2Φ
E-90	S	S	S	S	S	S	S	LC 2Φ	L 2Φ	L 2Φ
E-95	S	S	S	S	S	S	S	S	L 2Φ	L 2Φ

Figure 6. Physical state of the three-component system at −13 °C. Legend: S, solid; L, liquid; C, crystalline; G, gel; and Φ, phase.

tion increases while the biodiesel concentration in the mixture decreases accordingly. The phase behavior of this three-component system was complex. At a given temperature, it was observed that biodiesel concentration increased (and ethanol concentration decreased) along a row from right to left and the mixture melting point increased. Consequently, the blends on the right were in the liquid phase, whereas samples in the middle were gels, followed by solidification of the samples on the left. At −30 °C, all the samples separated into two distinct phases whenever the biodiesel amphiphile was absent. When biodiesel concentrations were 10%−30% and the diesel concentration was at least 10%, the mixtures remained in the liquid phase. It was observed that high biodiesel concentrations, as well as high ethanol concentrations, in the blend increased the melting points.

The crystallization that occurred at low temperatures was governed by the component that was in excess in the liquid system. When the diesel concentration in the overall blend was >30% and when ethanol concentration was greater than the biodiesel concentration, the system showed resistance to crystallization. However, when the diesel concentration was <30%, semitransparent crystals appeared in the solution. These crystals disappeared relatively quickly when the system temperature was increased. Because these crystals appeared when the ethanol concentration was higher than biodiesel, it could be assumed that the majority of the crystals were alcohol.

Regardless of the amount of diesel present in a blend, higher biodiesel concentrations, in comparison to ethanol, triggered crystallization. These crystals were white in color and slow to dissolve when the system temperature was increased. Because these white crystals formed when the biodiesel concentrations were higher in comparison to ethanol, it seems reasonable to assume that they were soybean fatty acid methyl ester crystals.
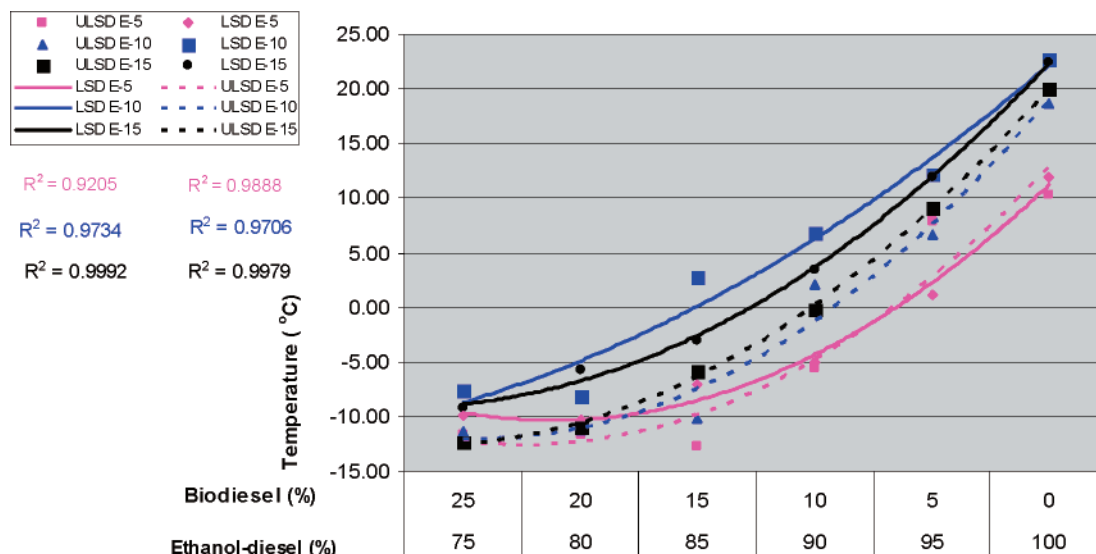
Figure 7. Comparison of E-5, E-10, and E-15 blends with low-sulfur diesel (LSD) and ultralow-sulfur diesel (ULSD).

Table 2. Statistical Analysis of Data Points for Minimum Phase-Separation Temperature

	Treatment					
	1	2	3	4	5	6
amount of e-diesel (%)	75	80	85	90	95	100
amount of biodiesel (%)	25	20	15	10	5	0

	Treatment						difference between treatments[a]		
e-diesel blend	1	2	3	4	5	6	1 and 2	2 and 3	average of 1&2 and 3
LSD E-5	−9.9	−10.3	−7.1	−5.0	1.2	11.9	NSD	NSD	0.04
LSD E-10	−7.6	−8.0	2.7	6.8	12.2	22.7	NSD	(<0.0001)	(<0.0001)
LSD E-15	−9.2	−5.7	−3.0	3.5	12.0	22.5	(0.001)	NSD	(0.002)
LSD E-20	−8.5	−3.9	6.3	4.8	15.0	25.3	NSD	(0.002)	(0.0002)
LSD E-25	−8.5	−7.0	−2.4	4.4	14.2	27.2	NSD	(<0.0001)	(<0.0001)
LSD E-30	−5.0	−4.0	−1.8	7.0	18.3	29.1	NSD	(0.04)	(0.01)
ULSD E-5	−11.6	−11.7	−12.8	−5.6	7.9	10.3	NSD	NSD	NSD
ULSD E-10	−11.4	−11.3	−10.2	2.1	6.7	18.7	NSD	NSD	NSD
ULSD E-15	−12.3	−11.0	−5.8	−0.1	9.1	20.0	NSD	(0.0002)	(<0.0001)
ULSD E-20	−11.6	−9.8	−5.2	1.0	10.0	22.9	NSD	(0.0011)	(<0.0001)
ULSD E-25	−11.1	−9.8	−5.5	1.2	13.9	26.1	NSD	(0.02)	(0.005)
ULSD E-30	−13.6	−10.1	−7.0	0.7	12.8	25.3	0.004	(0.007)	(0.0001)

[a] Legend of abbreviations used in the table: LSD, low-sulfur diesel; ULSD, ultralow-sulfur diesel; and NSD, not significantly different. All analyses done at a 0.05 level of significance. Values in parentheses represent the probability greater than F when parameter differences are significant.

Note that, after formation, the crystals did not disappear instantaneously when the temperature was increased. It was observed that, for both crystal types, the crystal melting temperature was higher than crystal forming temperature.

At −13 °C, experimental units that were within the oval region in Figure 6 were stable, single-phase clear microemulsions. This region was selected for further study with increased resolution and will be discussed in a later section.

Effect of Diesel Type on Phase-Separation Temperatures. Figure 7 depicts the phase behavior of LSD and ULSD at different temperatures. Interestingly, note that the statistical analyses resulted in significant quadratic relationships for all E-diesel blends with LSD and ULSD. The correlation coefficient (R^2) values and regression equations are given in the respective figures. The statistics to the left of the legend pertain to the LSD curve, and those to the right pertain to the ULSD curve.

It was stated previously that the accuracy of these data points were higher dependent on the refined methodology that was adopted in identifying the PTT endpoints. Similar to earlier binary phase diagrams, any point above a binodal curve would be in an isotropic single-phase microemulsion region, whereas a point below a binodal curve would be in an anisotropic state.

Statistical analyses revealed that, in all instances, the quadratic models were significant. Also, in all instances, the phase separation behavior for LSD was significantly different than that of ULSD. ULSD had a tendency to be more stable at low temperatures than LSD.

The objective of this segment of the study was to determine the formulations that were most stable at low temperatures; therefore, a statistical test was performed to identify the treatments that had the lowest mean phase-separation temperatures. The results of the statistical analysis are given in Table 2.

Referring to Table 2, note that, in most instances, the phase-separation temperatures of the 75% E-diesel mix with 25% biodiesel and the 80% E-diesel mix with 20% ethanol were not significantly different. This is verified by referring to Figure 7, where the E-5, E-10, and E-15

Table 3. Fuel Properties of the Reference Diesel Fuels and Selected Ethanol−Biodiesel−Diesel (EB-Diesel) Blends[a]

fuel	heat of combustion [ASTM D240]	sulfur content [ASTM D2622]	HFRR wear scar diameter [ASTM D6079]	cetane number [ASTM D613]	flash point [ASTM D93]
0.05% low-sulfur diesel	18461 BTU/lb (net)	0.033%	0.35 mm	47.1	142.2 °F
LSD Blend, 80% E-5/20% BD, E:BD:LSD = 4:20:76	18787 BTU/lb (gross)	0.0218%	0.15 mm	45.4	140 °F
percentage change	N/A	−34%	−57%	−3.60%	−1.5%
ultralow-sulfur diesel	18555 BTU/lb (net)	1.2 ppm	0.6 mm	44.84	154 °F
ULSD Blend, 80% E-5/20% BD, E:BD:ULSD = 4:20:76	18862 BTU/lb (gross)	18 ppm	0.155 mm	44.3	140 °F
percentage change	N/A	+1400%	−75%	−1.2%	−9%

[a] ASTM method used to measure each property is listed in brackets beneath the property.

blends with LSD and ULSD have been overlaid. In the case of ULSD, with the exception of E-30 with 25% biodiesel blend, all E-diesel types had a tendency to have phase-separation temperatures of ∼11 °C. Also, ULSD blends had better low-temperature stability, in comparison to LSD blends. It was clear that the treatments that had the highest low-temperature stability had biodiesel concentrations in the range of 15%−25%. Because of these results, it was not possible to pick the best two treatments out of the population just by performing a statistical mean separation procedure.

Effect of Water Content on Phase-Separation Temperature. When 0.05% of water was added to the treatments, all but two treatments separated into two distinct phases at room temperature (20 °C). Water droplets percolated to the bottom of the liquid. After the mixture was shaken vigorously for a few seconds, it was set aside and allowed to settle. Note that phase separation occurred almost instantaneously. The two treatments that did not separate with either LSD or ULSD were

(1) A mixture of 75% of E-5 in 25% of biodiesel, ethanol:biodiesel:diesel = 3.75%:25%:71.25%.

(2) A mixture of 80% of E-5 in 20% of biodiesel, ethanol:biodiesel:diesel = 4.00%:20%:76.00%.

The vulnerability of stable fuel blends to phase separation because of water is a significant observation; this is due to practical reasons. The storage tanks in gasoline/diesel filling stations are exposed/open to the atmosphere during filling. The moisture that gets into the storage tanks condenses and settles to the bottom. Fuel stations must remove this water frequently to eliminate water from being pumped into a vehicle. Because of this practical limitation, although one could pick a treatment that has a lower phase-separation temperature, the mixture may not be a practically viable option. Consequently, from the four previously mentioned treatments that showed resistance to separation when water was introduced, two were sent to Southwest Research Institute for further analysis.

Standard Laboratory Tests. The test results of the two samples (test 1, a mixture of 80% of E-5 in 20% of biodiesel (ethanol:biodiesel:LS diesel = 4.00%:20%:76.00%) and test 2, a mixture of 80% of E-5 in 20% of biodiesel (ethanol:biodiesel:ULS diesel = 4.00%:20%:76.00%)) that were sent for standard fuel testing are given in Table 3. The test parameters were compared with standard 0.05% low-sulfur reference diesel fuel and ultralow-sulfur reference diesel fuel. According to the test results, it was interesting to note that the microemulsion fuel blends had the same energy value as their reference diesel counterparts. The reason may have

been due to microemulsions having molecular configurations, chemically and physically, that favored combustion. Theses observations are consistent with finding of Hicks and Song.[31]

The sulfur content of the new biofuel with LSD was reduced by 34%. However, the sulfur content of the blend with ULSD increased from 1.2 ppm to 18 ppm. The reason may have been due to natural gasoline that was used as the denaturant in fuel ethanol. The material safety data sheet (MSDS) for natural gasoline suggests several trace compounds that have sulfur in their chemical structures.

As expected from the preliminary studies, the lubricity of the new biofuel blend was extremely high, in comparison to reference diesel fuels. When LSD was used in the blend, a 2.3-fold increase of lubricity was observed. The increase of lubricity when ULSD was used was 4-fold. The high lubricity of the blend was attributable to the biodiesel. Methyl esters, which are present in biodiesel, have inherently good lubricating characteristics (Fernando and Hanna, 2002).

LSD and ULSD blends had slightly lower cetane numbers than their reference diesel counterparts. The cetane number is an indication of the ignition delay that occurs from the point a fuel molecule exits the injection nozzle until the time it ignites. This is the time period between the start of injection and the start of combustion (ignition) of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. The cetane number (diesel fuel) and octane number (gasoline) both measure the tendency of the fuel to ignite spontaneously. In the cetane number scale, high values represent fuels that ignite readily and, therefore, perform better in a diesel engine. In the octane number scale, high values represent fuels that resist spontaneous ignition and, therefore, have less tendency to knock in a gasoline engine. Because both scales were developed so that higher numbers represent higher quality for the respective use, high cetane number fuels have low octane numbers, and vice versa. Although some researchers support higher cetane numbers, recent studies indicate that having excessively high cetane numbers is not as advantageous to diesel engines as it was thought to be. In fact, Duralt (Los Angeles, CA) suggested that the cetane number requirements are dependent on engine design, size, the nature of speed and load variations, and the starting and atmospheric conditions. Increases in the cetane number over those actually required do not materially

(31) Hicks, R. H.; Song. B. C. U.S. Patent Application, 2002, 16 pp. (Cont.-in-part of U. S. Ser. No. 588,029.)

improve engine performance. Accordingly, the cetane number specified should be as low as possible, to ensure maximum fuel availability. Accordingly, it would be best to have the lowest cetane number within the range specified by the engine manufacturer. Because many engine manufacturers recommend a cetane number of >40, a fuel with a cetane number of ∼40 would be advantageous. However, note that having a cetane number of <40 would create serious problems in an engine, because the mixture would ignite too soon. This will create knocking problems that will be harmful to the engine. Accordingly, the biofuel proposed herein has even more favorable properties, with regard to cetane number, when compared to both reference diesel fuels.

One interesting observation was that the blend flash point was expected to be reduced, because of the presence of ethanol in the blend. One of the main limitations of E-diesel, according to the literature, is the low flash point of the blends due to ethanol. Therefore, E-diesel must be handled as a highly flammable liquid (such as gasoline), rather than as regular diesel. Interestingly, note that, at correct composition, when microemulsions are formed, the flash points of both of the aforementioned EB-diesel fuel blends were reduced only by a few degrees. This ability to increase the flashpoints of the EB-diesel, blends in comparison to pure ethanol, may due to the presence of intermolecular forces within the micelles that keep the ethanol molecules intact in the microemulsion and thereby do not allow the ethanol to evaporate freely.

Conclusions

(1) Binary and ternary phase diagrams were developed for ethanol−biodiesel−diesel (EB-diesel) three-component fuel systems with low-sulfur diesel (LSD) and ultralow-sulfur diesel (ULSD) fuels blended with fuel ethanol and biodiesel. It was observed that the sulfur content of diesel fuels had a significant effect on the phase transition temperature (PTT) of the three-component system. A minimum PTT of 11°C was obtained for several viable fuel formulations with LSD fuel. The phase stability of EB-diesel fuel blends using ULSD had better low-temperature phase stabilities than those with LSD fuel. A minimum PTT range of 11 °C was obtained for several viable fuel formulations that contained ULSD fuel.

(2) The type of ethanol denaturant had a significant effect on the phase behavior of an EB-diesel three-component system. At 20 °C, 200-proof ethanol was completely miscible in regular No. 2 diesel at all concentrations. Fuel ethanol, which was denatured with natural gasoline, was completely miscible in diesel when the diesel concentration in the E-diesel mix was <30% or when the diesel concentration was >85%. A SD-1 denatured ethanol showed much more complex phase behavior, forming single-phase isotropic microemulsions, two-phase regions, and three-phase anisotropic regions. Fuel ethanol behaved in a similar manner when the three-component system was subjected to cooling. Water in an EB-diesel blend proved to separate the phases, with the exception of two blends when LSD and ULSD each were used. The two blends were ethanol:biodiesel:diesel = 3.75%:25%:71.25% and ethanol:biodiesel:diesel = 4.00%:20%:76.00%.

(3) The microemulsion fuel blends had the same energy values as their reference diesel counterparts. The sulfur content of the new biofuel with LSD was reduced by 34%. However, the sulfur content of the blend with ULSD increased from 1.2 ppm to 18 ppm. When LSD was used in the blend, a 2.3-fold increase of lubricity was observed. The increase of lubricity when ULSD was used was 4-fold. LSD and ULSD blends had slightly lower cetane numbers than their reference diesel counterparts. The flash points of both of the aforementioned EB-diesel fuel blends were reduced only by a few degrees, in comparison to low-sulfur and ultralow-sulfur reference diesel fuels.