Emulsions of Crude Glycerin from Biodiesel Processing with Fuel Oil for Industrial Heating

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ABSTRACT: There is considerable interest in using crude glycerin from biodiesel production as a heating fuel. In this work crude glycerin was emulsified into fuel oil to address difficulties with ignition and sustained combustion. Emulsions were prepared with several grades of glycerin and two grades of fuel oil using direct and phase inversion emulsification. Our findings reveal unique surfactant requirements for emulsifying glycerin into oil; these depend on the levels of several contaminants, including water, ash, and components in MONG (matter organic non-glycerin). A higher hydrophile−lipophile balance was required for a stable emulsion of crude glycerin in fuel oil compared to water in fuel oil. The high concentration of salts from biodiesel catalysts generally hindered emulsion stability. Geometric close-packing of micelles was carefully balanced to mechanically stabilize emulsions while also enabling low viscosity for pumping and fuel injection. Phase inversion emulsification produced more stable emulsions than direct emulsification. Emulsions were tested successfully as fuel for a waste oil burner.

KEYWORDS: emulsions, fuel oil, glycerin, biodiesel

INTRODUCTION

Biodiesel fuel has become a significant product of interest because it can be produced from renewable resources such as natural triglyceride seed oils and can be used as an alternative to petroleum-sourced diesel fuel. Soybean oil is a major resource in the United States, while rapeseed (canola) oil is of interest in many other countries. Jatropha oil is important in countries with tropical climates because of its high productivity of oil per acre with no value as a food crop. More recently, there has been interest in obtaining triglyceride oil from algae due to its high production in small areas. Straight vegetable oil (SVO) usually consists of triglycerides, which have too high of a viscosity at ambient temperature to be used as a diesel engine fuel. Biodiesel fuel is most commonly produced by transesterification of triglycerides with methanol using a catalyst in the form of sodium or potassium methoxide. This produces a fatty acid methyl ester (FAME) with a liquid viscosity low enough to be used as diesel fuel. Using a typical soybean oil triglyceride mixture as an example, the transesterification reaction stoichiometry predicts that 9.5 kg of glycerin will be produced for each 100 kg of biodiesel produced.[1−3]

The glycerin byproduct formed during transesterification generally forms a second liquid phase called "raw glycerin" that is decanted from raw FAME. The raw glycerin is usually stripped to recover methanol and then acidulated to produce a "crude glycerin" product plus another liquid phase containing free fatty acids.[1] Crude glycerin contains many impurities, including MONG (matter organic non-glycerin), water, and salts. Additional costs for purification are incurred before the glycerin can be used for food, personal care, and pharmaceutical applications. Depending on the market value, purification and resale may not be profitable.[4] Some biodiesel facilities have sent the crude glycerin to a landfill or incinerator. The current EPA Renewable Fuel Standard II (RFS-2) mandates 1.0 billion gallons of biobased biodiesel from 2012 and each year going forward,[5] which by calculation will yield approximately 66 million gallons of crude glycerin annually.

One potential use of byproduct glycerin could be as a liquid fuel in industrial furnaces. At approximately 86 000 Btu per gallon,[6] the potentially available crude glycerin as a result of EPA RFS-2 could provide up to 5.7×10^{12} Btu of energy each year. However, glycerin is difficult to burn due to several factors, including its high autoignition temperature. Furthermore, incomplete combustion can lead to the emission of acrolein, an irritant and carcinogen. Therefore, several investigations have focused on these issues.

Patzer reported test runs to burn a mixture of crude glycerin and yellow grease (used cooking oil) in an industrial fire tube boiler.[6] A problem with maintaining adequate pump mixing of glycerin and yellow grease to keep a uniform mixture to the nozzle of the furnace was reported; this was because glycerin is not miscible with oil. High ash content was also cited as a potential issue.

Bohon et al. reported on a special refractory lined burner capable of burning glycerin which included a general analysis of emissions, including particulates, hydrocarbons, and carbonyls, including acrolein.[7] Additional emissions measurements on the same burner system by Steinmetz et al. indicated that glycerin combustion in their burner was not found to produce significant levels of acrolein.[8] However, they noted significant levels of particulate fly ash from soluble biodiesel catalysts and therefore suggested that glycerin that contains soluble catalysts would not be suitable as a boiler fuel. However, they also stated

that the eventual move toward solid-state catalysts will mitigate this issue.

Furnaces can be equipped for feeding two liquid fuels simultaneously for igniting and maintaining a flame, which is an option for using glycerin for its heating value. An earlier project in our laboratory successfully demonstrated the use of glycerin as a liquid fuel in an industrial waste oil boiler by coinjection with diesel fuel, biodiesel, and soybean oil.[9] The oils ignited easily and provided the heat needed to vaporize glycerin to sustain a flame. Preliminary analysis of stack emissions for acrolein using an adaptation of ASTM 5197-97[10] showed no increase of acrolein over that from burning straight heating oil. This dual fuel test was accomplished by drawing glycerin and fuel oil from separate fuel reservoirs and sending both through the same injector to the burn chamber. Since most furnaces are not capable of handling two separate fuel lines, employing that method would require added cost for modification of existing oil furnaces.

The purpose of the research described in this paper was to generate a stable emulsion of glycerin and heating oil for use as a single fuel in conventional industrial furnaces without major furnace or burner modifications. Wilson made reference to the addition of glycerin to stearic acid in water emulsions using triethanolamine as a saponifying agent to make a cream.[11] While the amount of glycerin was not disclosed, the paper suggests it is a minor component, and the surfactant levels were comparatively high. Peterson and Hamill described emulsions of glycerin in olive oil and of olive oil in glycerin using fatty acids and saponifying amines for surfactants.[12] While their work was with 99+% glycerin and did not address impurities, such as those present in crude glycerin from biodiesel processing, they did note different surfactant requirements of glycerin compared to water-containing polar phases.

Striugas et al. reported the use of fatty acid monoglycerides and fatty acid soaps such as sodium oleate as surfactants to emulsify glycerin, heavy fuel oils, and biofuels for burning in industrial furnaces.[13] The main motivation for their work was to reduce the sulfur content of fuel to meet stringent regulations by substituting the bioderived crude glycerin. The surfactant hydrophile–lipophile balance (HLB) and the identity of dispersed and continuous phases were not described in their work.

Bombos et al. described the emulsification of glycerin in fuel oil primarily as an oxidant for the purpose of reducing emissions.[14] However, their emulsions were only monitored for stability up to 10 h, and they reportedly used pure glycerin rather than crude glycerin. Our work has revealed substantial differences in emulsifying crude glycerin compared to pure or reagent grade glycerin. In a subsequent paper, Bombos et al. described combustion tests of 10% glycerin emulsified in fuel oil, noting favorable combustion.[15] Elsewhere, Biodiesel Experts International, LLC in Texas report that glycerin may need 10–12% biodiesel fuel to burn in an industrial boiler but did not provide technology about emulsifiers and formulations that would provide stable emulsions in that area.[16]

Emulsions generally consist of two immiscible liquids, such as oil and water, where one is dispersed as droplets in the other. This dispersion is usually facilitated by the addition of approximately 2–4 vol % surfactants to reduce or eliminate coalescence of the dispersed droplets. They occupy the interface between the two liquids, lower the interfacial tension, and protect the droplets through the formation of micelle assemblies. Surfactants consist of molecules capable of interacting with both of the immiscible liquids. The lipophilic moiety often consists of a hydrocarbon chain, while the hydrophilic moiety may be ionic (such as carboxylate or sulfonate salts) or nonionic (ethylene oxide and hydroxyl groups).[17]

Emulsions of water and oil can be of the type where oil is dispersed in water (o/w) or water dispersed in oil (w/o). Dispersion of the phases is determined primarily by the HLB of the surfactant blend that is used. The HLB scale was originally defined for nonionic surfactants as the percentage of the molecular weight that is hydrophilic divided by 5.[18,19] Later, the scale was modified to take into account the strength of certain polar groups.[20] Surfactants of different HLB values are often mixed with one another to obtain the optimum HLB that will stabilize an emulsion. High HLB values between 8 and 16 favor the dispersion of oil droplets in water, while low values between 4 and 6 favor the dispersion of water droplets in oil. According to the Bancroft rule, the phase in which the surfactant is most soluble will become the continuous phase.[21] In the research described here, we used crude glycerin as the phase opposite fuel oil.

Emulsions can be made by a direct or phase inversion emulsification method. With direct emulsification, the surfactants are mixed with the intended continuous phase according to the Bancroft rule and then the intended dispersed phase is mixed in, usually by a high shear process.[22] The phase inversion method begins by mixing the surfactants in the intended dispersed phase followed by mixing the intended continuous phase; this method intentionally begins with the phases reversed.[22−25] As portions of intended continuous phase are added, the phase inversion point is reached and the phases reverse, or flip, from their initial conditions. It is generally accepted that phase inversion emulsification can produce more stable emulsions than direct emulsification.[24]

There are limits to the proportions of the dispersed and continuous phases that can be initially defined using a geometric model of micelles as spheres. Using simple geometric calculations, it can be shown that an emulsion consisting of close-packed spheres with uniform diameter would contain 74 vol % dispersed phase and 26 vol % continuous phase. A lower volume percent dispersed phase would not be close packed, and in such cases movement of the micelles can occur more freely, thereby lowering viscosity and enabling settling compared to the close-packed condition. A higher than close-packed volume percent dispersed phase can be possible with nonuniform diameter spheres or with micelles deformed from spherical shapes.

Our experience in burning glycerin shaped the direction of our research in developing emulsions.[9,26] To effectively utilize the emulsions in an oil-fired furnace or boiler, a low viscosity was preferred for ease of pumping and fuel injection. For efficient and complete combustion of glycerin, we found that approximately 50% by volume fuel oil or more is preferred. We developed both fuel oil in glycerin emulsions and glycerin in fuel oil emulsions. This paper will focus on glycerin in fuel oil emulsions because they can be made at more viscous and stable close-packed compositions which can be readily diluted with fuel oil to desired proportions just prior to use. Also, the continuous oil phase makes flushing fuel lines and other parts of the fueling system possible when changing between emulsified fuel and regular fuel oil.

Our initial attempts to prepare glycerin in fuel oil emulsions meeting the above criteria were unsuccessful. The parameters

Table 1. Glycerin Compositions

analysis	units	glycerin–water[a]	glycerin–brine[a]	crude 1	crude 2	crude 3
Karl Fisher moisture	mass %	20	11.7	14.1	19.2	17.1
glycerol	%	80	79.4	72.3	50.1	63.4
methanol	%			0.05	0.37	0.21
ash	%	0	8.9	5.81	9.69	6.92
soap	%	0	0	0.17	0.46	0.04
calcd wt	lb/gal			10.5	10.5	10.5
MONG	%	0.0	0.0	7.81	21.1	12.6
specific gravity	g/mL at 25 °C	1.23	1.24	1.26	1.26	1.26

[a]As mixed; all others by measurement.

governing emulsion stability, phase arrangement, and physical properties were not obvious in the literature for phases consisting of crude glycerin and fuel oil. This work uniquely addresses issues relevant to the practical utilization of crude glycerin as a major component in an emulsified fuel. Accordingly, a practical method was developed to determine surfactant HLB requirements and prepare crude glycerin in fuel oil emulsions.

■ MATERIALS AND METHODS

Materials. USP grade glycerin (Glycerin Skin Protectant by HUMCO) containing 99.5% anhydrous glycerin was obtained locally, while several grades of crude glycerin samples were obtained from Michigan Biodiesel, LLC of Bangor, MI, and Natures Fuel of Ft. Wayne, IN, and Defiance, OH. Sodium chloride was from Fisher Scientific. The surfactants Tween 80 and Span 80 were obtained from Fisher Scientific and Sigma-Aldrich, respectively. Tall oil fatty acid (TOFA) was obtained from Arizona Chemical of Jackonsville, FL. Triethanolamine (TEA) was obtained from The Personal Formulator (www.personalformulator.com). No. 2 diesel fuel oil (equivalent to no. 2 fuel oil) was from a local filling station. Bunker C fuel (no. 6 fuel oil) was obtained from the Waterfront Petroleum Co., Dearborn, MI. The waste oil boiler was purchased from Kingbuilt.com Inc. of Eau Claire, WI.

Physical Property Measurements. Viscosity was measured on freshly prepared emulsions using a Brookfield DV-E viscometer with spindle s62. Measurements were made on emulsions while in 1/2 pt Ball jars; the uncertainty was ±0.3 cP for all uniformly mixed emulsions. Micelle size distributions were measured by dynamic light scattering using a Zetasizer Nanoseries (Nano-ZS) by Malvern Instruments Ltd. Emulsions were diluted to 0.05% of the original glycerin content using *n*-hexane prior to measurement. Interfacial tension between glycerin and oil was measured using a Cenco Du-Nouy tensiometer by Central Scientific Co. Optical micrographs were taken on a Kaiser Optical Systems Raman workstation using an optical Nikon microscope with 10× objective, a charge-coupled device (CCD) video camera, and Holograms software. Water-soluble blue food dye was added for contrast. Samples were placed on glass slides so that a backlighting configuration could be used. Emulsion stability was measured by monitoring the formation of oil layers after a 7 day period using the "bottle test" in closed 1/2 pt Ball glass jars; this is a previously accepted practice.[27] Volume was measured with an uncertainty of ±1.4 mL. Dispersed and continuous phases were identified by the dilution test.[26] After an emulsion droplet was placed into crude glycerin and also oil, the emulsion dispersed in the solvent, matching its continuous phase.

Due to the length of time required to prepare self-consistent emulsion sets for comparison (i.e., when determining the optimum surfactant HLB number), it was not possible to make true replicates. Therefore, we determined the maximum experimental uncertainty in measuring both viscosity and volume, which are included in the figure captions. Data shown in the figures represent self-consistent sets of emulsions.

Glycerin Composition Measurements. Water content was measured using a Metrohm 831 Karl Fischer coulometer. Ash content was measured using an adaptation of ASTM D874-96[28] and also with a TA Instruments Q500 thermogravimetric analyzer. Soap content was measured by titration using the AOCS Cc 17-95 method with alkalinity correction by the ASTM D4662-08 method.[3,29,30] In addition to in-house testing, crude glycerin samples were also sent to Midwest Laboratories in Omaha, NE, for analysis (see Table 1).

Direct Emulsification Method for Glycerin in Oil Emulsions. Typically 5 mL of surfactant was added to 60 mL of the intended continuous phase (fuel oil) in a 400 mL beaker and mixed with a Hamilton Beach hand-held two-speed blender. Then 75 mL of crude glycerin (or USP grade glycerin and added components) was measured into a graduated cylinder; this was to be the dispersed phase in the final emulsion. The glycerin phase was added in approximately 10 mL increments while being blended on low speed (7150 rpm) for about 10 s for each addition. Typically, the mixture appeared cloudy or "milky", and the viscosity increased with each addition of dispersed phase. After all of the glycerin phase had been added, the emulsion was blended on high speed (12 550 rpm) for 60 s. The final prepared emulsion volumes were 140 mL for most experiments.

Phase Inversion Emulsification Method for Glycerin in Oil Emulsions. Phase inversion emulsification (PIE) proceeded by pouring the intended dispersed phase into a 400 mL beaker. The intended dispersed phase was glycerin–water, glycerin–brine (60 mL of glycerin and 15 mL of 26% NaCl/74% water brine), or 75 mL of crude glycerin. The surfactants were then added to the beaker and mixed with the glycerin phase using a Hamilton Beach hand-held blender at low speed (7150 rpm). The next step was to add the intended continuous phase, such as no. 2 fuel oil, in about five or six increments with low speed (7150 rpm) mixing of each increment for about 10 s before addition of the next. Typically a gradual increase of viscosity was noted with the first two to three additions followed by a sharp increase after the third to fourth addition. Then a sharp decrease in viscosity occurred after the phase inversion point, at which time the glycerin became the dispersed phase and the fuel oil became the continuous phase. Finally, the entire emulsion was mixed at high speed (12 550 rpm) for 60 s. As with direct emulsification, the final prepared emulsion volumes were 140 mL for most experiments.

■ RESULTS AND DISCUSSION

Glycerin Composition Analysis. The contaminants present in crude glycerin can vary depending on the feedstock used in transesterificaton (i.e., soybean oil, used cooking oil, animal fats, etc.).[3] They can also depend on whether the crude glycerin had been refined by removing valuable components (such as methanol and free fatty acids), and if so to what extent they were removed.[1] To better understand the role of contaminants on emulsification, crude glycerin was analyzed in-house for ash content, water content, and viscosity. Methanol had been mostly removed by the supplier; this was confirmed with evaporation tests and thermogravimetric analysis (TGA) and also by outside laboratory analysis. Select

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samples were also sent to Midwest Laboratories (Omaha, NE) for determination of ash, water, specific gravity, glycerin, MONG, and methanol. The results of these analyses are shown in Table 1. By IUPAC convention, MONG is that which remains after subtraction of the glycerin, ash, and water contents and therefore includes all other organics, including methanol. In the analysis presented here, the methanol content was also measured independently of MONG.[31]

The variability in crude glycerin composition posed a difficulty for understanding our observations when attempting to emulsify the samples with fuel oil. Therefore, we prepared reproducible stable surrogates using USP grade glycerin, sodium chloride, and water. We refer to the surrogates as "glycerin−water" and "glycerin−brine", and their compositions are also shown in Table 1. The surrogates effectively modeled the water and ash contents of crude glycerin, and we found them to be sufficient to help in understanding the role of crude glycerin composition in determining emulsion formulations.

Surfactant Composition. Primarily nonionic surfactants were used for glycerin in fuel oil emulsions. Using Span 80 (HLB = 4.3) and Tween 80 (HLB = 15), surfactant mixtures can be prepared over a range of HLB values. Examples of such mixtures are shown in Table 2 and represent similar compositions used in the emulsions. Upon emulsification, emulsion stability was monitored to select the optimum HLB value for surfactants.

Table 2. Surfactant System Compositions

	surfactant composition, %			surfactant composition, %	
HLB	Span 80	Tween 80	HLB	Span 80	Tween 80
4.3	100	0	10.1	46	54
5.1	93	7	11.0	37	63
6.0	84	16	12.1	27	73
7.0	75	25	13.1	18	82
8.1	65	35	14.1	8	92
9.0	56	44	15.0	0	100

Experiments aimed at substituting soybean-derived coproducts for the synthetic surfactants were also performed. Striugas used high-HLB sodium oleate with low-HLB distilled monoglycerides (Palsgaard DMG 0093) in their surfactant mixtures; both can be coproducts from the biodiesel process.[13] We considered the use of glycerol monostearate (GMS) as a low-HLB surfactant, but its waxlike pellets were difficult to handle. However, we successfully performed experiments with TOFA as a surrogate for biodiesel-process-derived free fatty acids (FFAs). TOFA was used in combination with the saponifying amine TEA[12] in place of the high-HLB Tween 80. A 1:1 mole ratio of TEA and TOFA yields an HLB of 12.0. Biodiesel-derived FFA was not available at the time of these experiments but would normally be available in the acidulation step in purification of glycerin.[1,32]

Generally, we have found that ionic surfactants are more likely to be affected by the ash (ion) content of the crude glycerin. Weakly ionic carboxylate surfactants (such as TOFA) are negatively affected by high levels of ionic salts, which serve to counter dissociation of the surfactants.[33] These are often assisted by saponifying amines as with TOFA and TEA above. More strongly ionic surfactants, such as alkyl sulfonates, are less susceptible to suppressed dissociation. Nonionic molecular surfactants (i.e., Tween 80 and Span 80) are more forgiving of varying ash levels since dissociation is not necessary.

Preparation and Analysis of Emulsion Stability. Glycerin in oil emulsions were prepared using the direct emulsification and/or phase inversion emulsification methods (vide supra). The design of experiments to develop stable emulsions included a full range of phase volumes (continuous and dispersed), HLB mixtures, and added water. Immediately after each emulsion preparation, viscosity was measured and the emulsions were stored at ambient laboratory conditions (approximately 22 °C) in 1/2 pt glass jars. Stability was monitored by measuring the volume of oil as a result of settling at regular intervals (7 day stability bottle test). The emulsion composition and HLB value of the surfactants are shown in Table 3 for some representative emulsions. Surfactant

Table 3. Emulsion Compositions

glycerin type	HLB	oil fuel concn, vol %	glycerin-phase concn, vol %	surfactant concn, vol %
glycerin−brine, double water	7.0	42.9	53.6	3.5
crude 2	9.0	42.9	53.6	3.5
crude 3	10.0	41.4	51.7	6.9
glycerin−brine[a]	10.5	41.2	51.5	7.3
glycerin−brine	10.1	42.9	53.6	3.5
glycerin−brine[b]	10.1	42.9	53.6	3.5
crude 1	11.0	42.9	53.6	3.5
glycerin−water	12.1	42.9	53.6	3.5

[a]Surfactants: 2.8% Span 80 + 3.3% TEA−TOFA + 1.2% TEA. [b]Oil fuel: 50% no. 6 fuel oil/50% no. 2 fuel oil.

applications were between 3% and 7% by volume of the final emulsion, which was determined to be adequate for sufficient emulsion stability with little to be gained from higher levels. Surfactant volumes were kept self-consistent within comparisons.

Selection of Surfactants. Measurement of interfacial tension was used to estimate the optimum HLB value for the emulsions. The effect of surfactant HLB on the interfacial tension between USP glycerin and lamp oil (11.1 dyn/cm^2 without surfactant) was measured and is shown by the graph in Figure 1. The large decrease in interfacial tension with the addition of surfactants is significant and illustrates the generally strong surface-active nature of the surfactants, but the relatively flat region of the plots from HLB 4 to HLB 14 indicates a minimal role for interfacial tension in selecting the optimum surfactant HLB. Nevertheless, the plot ultimately agrees with
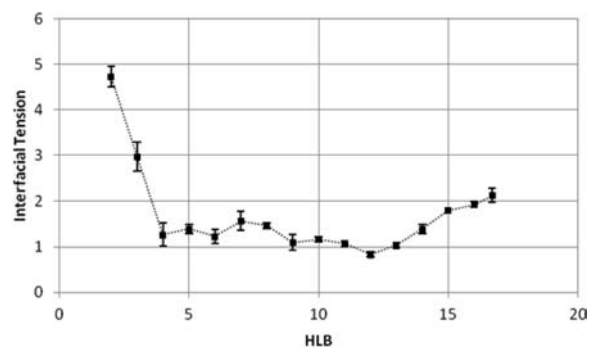

Figure 1. Interfacial tension (dyn/cm^2) vs surfactant HLB for glycerin and lamp oil. Error bars shown are ±1 standard deviation from three replicates.

the optimum HLB values we determined from emulsion stability measurements (vide infra).

Figure 2 shows the results of measuring the clear oil volume after 7 days and compares glycerin—water and glycerin—brine.
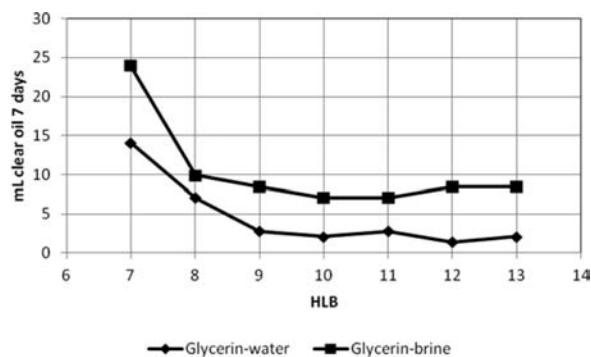

Figure 2. Volume of 7 day clear oil layer vs HLB for reagent grade and glycerin—brine emulsified in no. 2 fuel oil. Uncertainty in volume ±1.4 mL.

The appearance of an oil layer on the top of the emulsion is due to the settling of the glycerin micelles. The plot indicates that the optimum HLB value for glycerin in fuel oil emulsions is in the range of 10—12. This is significantly different from the optimum HLB that has been accepted for water in oil emulsions, which is between 4 and 6.[34,35] This may be due to the difference in affinity of the surfactants for glycerin compared to water; the increase in optimum HLB indicates greater partitioning toward the oil phase and therefore the need for a larger hydrophilic moiety to shift partitioning toward the glycerin—water or glycerin—brine interface. Furthermore, higher water levels such as in crudes 2 and 3 and the double water—glycerin emulsions appear to shift the required HLB closer to that required by water; this is the reverse of the shift mentioned above for glycerin. It is important to note that some water in glycerin was generally necessary to stabilize emulsions; this was not considered an issue since as-received crude glycerin always contains water. Additionally, water serves to significantly depress the freezing point of glycerin, so the presence of water would serve to keep the glycerin micelles in the liquid state at low temperatures.[36] We also note that emulsions containing ash (crude glycerin or glycerin—brine) are generally less stable than those made from USP grade glycerin and water. This can be seen over a range of surfactant HLB values in Figure 2. The presence of salt in crude glycerin from biodiesel catalysts was the most significant destabilizing ingredient for emulsions encountered in this work. Soluble biodiesel catalysts have also been shown to be the source of significant levels of fly ash when burning crude glycerin.[8] The move to solid-state catalysts will ease emulsification parameters as well as reduce emissions issues.

Figure 3 shows oil layer volumes vs HLB for several crude glycerin samples, and some examples of the most stable emulsions are listed in Table 3. Note the shift to lower optimum HLB values of 9.0 and 10.0 for crude glycerins 2 and 3, respectively. As noted above, this is consistent with higher water content. Soap impurities would affect the overall HLB number of the surfactants by serving as a third component in the surfactant mixture. However, the measured levels of soap impurities (i.e., sodium oleate, HLB = 18) are too low to affect the apparent HLB number of the surfactant. For crude glycerin
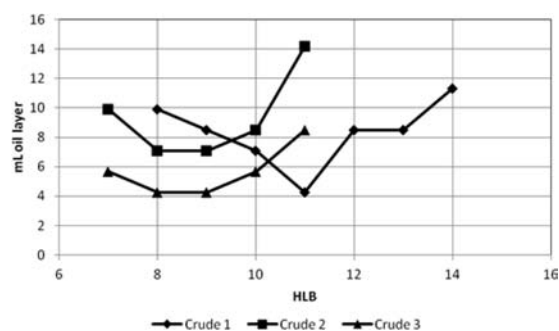

Figure 3. Volume of 7 day clear oil layer vs HLB for three crude glycerin samples emulsified in no. 2 fuel oil. Uncertainty in volume ±1.4 mL.

2 we estimate the soap impurity would raise the actual HLB number by a maximum of 0.5 unit. Crude glycerin 1 showed the best stability at a high HLB compared to the other crude and glycerin—brine samples. This was a more refined sample as indicated by the relatively low ash compared to the other crude and the glycerin—brine.

Direct Emulsification Results. Direct emulsification was performed according to the procedure described above. Figure 4 shows the relationship between viscosity and the concen-
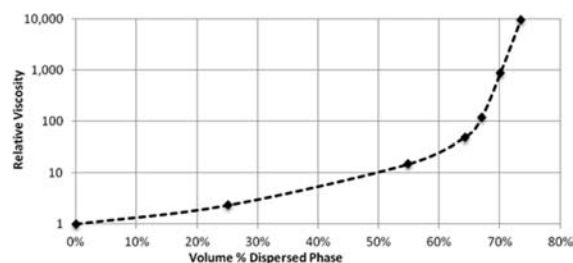

Figure 4. Log(relative viscosity) vs volume of the dispersed phase for a glycerin—brine in no. 2 fuel oil emulsion.

tration (vol %) of the dispersed phase for a glycerin—brine in fuel oil emulsion. This emulsion exhibits fundamental behavior of a steady increase in viscosity as the dispersed-phase volume percent increases, culminating in a sharp viscosity increase near the volume percent approaching the close-packing of micelles (vide supra), i.e., 74 vol %. As the concentration of the dispersed phase increases, the micelles become more tightly packed, resulting in higher viscosity, more stable emulsions with less settling (creaming). This is important due to the high density of glycerin compared to fuel oil; settling of glycerin-phase micelles in no. 2 fuel oil is a larger problem than that of water-phase micelles in no. 2 fuel oil. However, packing too tightly can facilitate coalescence by increasing the interaction among micelles. Coalescence is considered a failure of the emulsion because of the structural breakdown of the micelles, which combine to form fewer micelles with larger diameters.

Stokes law says that particle settling velocity in a liquid is inversely proportional to viscosity.[37] Therefore, higher viscosity continuous phases can lead to an apparent increase in stability by slowing the settling time of glycerin micelles. This was quite likely one of the aspects leading to the excellent stability of the emulsions in the work by Striugas et al.[13] Their emulsions consisted of crude glycerin apparently dispersed in high-viscosity heavy fuel oil (HFO). Accordingly, we prepared emulsions with 50% no. 6/50% no. 2 fuel as the continuous

phase, and the result was a dramatic increase in stability (i.e., oil layers were too small to measure) compared to that of a pure no. 2 fuel oil continuous phase. As an added benefit, no. 6 fuel oil is typically lower in cost compared to no. 2 fuel oil.

Figure 5 shows a Pal–Rhodes type plot of the same emulsion shown in Figure 4. The Pal–Rhodes equation, given below, is
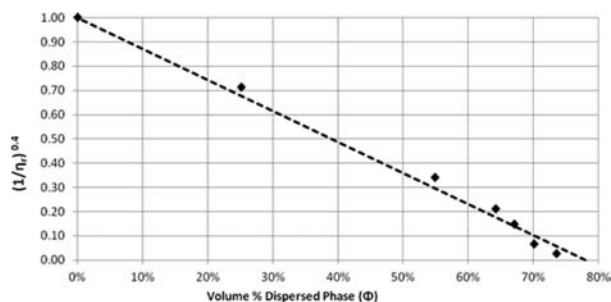

Figure 5. Pal and Rhodes plot for glycerin–brine in no. 2 fuel oil.

an empirical model that can be used to describe both Newtonian and non-Newtonian emulsions.[38] An emulsion viscosity following Newtonian behavior would follow a straight line represented by the following equation:

$$(1/\eta_r)^{0.4} = 1 - K_o K_F(\gamma)\Phi$$

where η_r = ratio of emulsion viscosity to continuous-phase viscosity, Φ = volume fraction of the dispersed phase, K_o = hydration (solvation) factor for the continuous phase clinging to micelles, K_F = flocculation factor, and γ = shear rate. When the volume fraction of the dispersed phase, Φ, is zero, the emulsion viscosity is equal to the continuous-phase viscosity, so $\eta_r = 1.0$. When the dispersed phase is close packed with $\Phi = 0.74$, the viscosity will be very high. If the viscosity becomes infinite with the close-packed micelles, then $(1/\eta_r)^{0.4} = 0$ at $\Phi = 0.74$ and the slope of the correlation line $K_o K_F(\gamma) = 1/0.74 = 1.35$. The slope of the line, $K_o K_F(\gamma)$, was 1.28 for the glycerin–brine/oil, indicating little if any flocculation and little if any solvation of oil around glycerin-phase droplets.

Phase Inversion Emulsification Results. Figure 6 shows the characteristic viscosity increase as the intended continuous phase is added in phase inversion emulsification. For the first three points in the plot, fuel oil is dispersed in glycerin, which is the reverse of the intended arrangement (phase arrangement
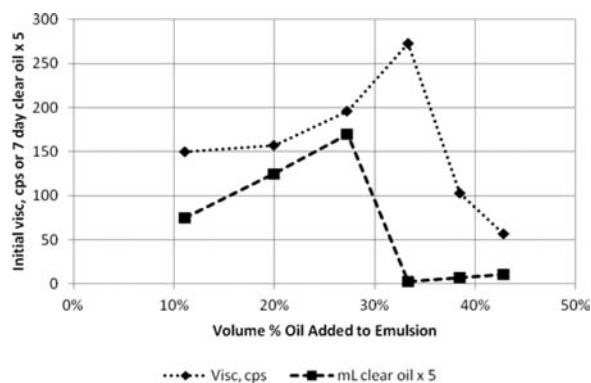

Figure 6. Initial viscosity and volume of the 7 day clear oil layer vs concentration (vol %) of added oil (intended continuous phase) during PIE of glycerin–brine in no. 2 fuel oil. Uncertainty in 7 day oil volume ±1.4 mL and in viscosity ±0.3 cP.

was confirmed by dilution tests). At these three volumes, the intended arrangement would not be geometrically possible because it would exceed the allowed close-packed volumes. Also, the volumes of the 7 day oil layers are very large, indicating a high level of instability. This is because of the unfavorably low HLB for the oil in glycerin arrangement (which requires high-HLB surfactants). However, upon the fourth addition, the glycerin in oil geometry is allowed, and the emulsion phases flip to those matching the low-HLB surfactants. The high viscosity due to the now near-close-packed geometry of glycerin in oil is notable at this point along with the small 7 day oil layer due to the stability from proper matching of the HLB. Adding more oil decreases viscosity (consistent with an oil continuous phase) and slightly increases the oil layer due to Stokes settling. This process has been reported to form small and consistent micelle sizes without high shear mixing.[24]

Figure 7 shows the stability measurement results (oil layer formation at 7 days) for emulsions prepared by the direct
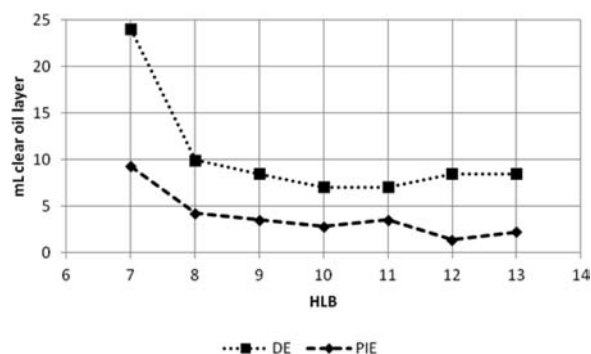

Figure 7. Volume of the 7 day clear oil layer vs HLB: comparison of DE and PIE methods for glycerin–brine in no. 2 fuel oil emulsions. Uncertainty in volume ±1.4 mL.

versus the phase inversion method for glycerin–brine in fuel oil emulsions. The results indicate a substantial decrease in settling for PIE vs direct emulsification (DE). This could be due to smaller micelle sizes, which are reported characteristics of phase inversion compared to direct emulsification.[23−25] Dynamic light scattering analysis of select emulsions was performed and showed a tighter size distribution as well as a lack of micelles above ~250 nm in diameter for PIE compared to DE as shown in Figure 8. Phase inversion emulsions showed micelles centered at approximately ~12 and ~150 nm diameters, while direct emulsions showed a wide range of diameters from ~10 nm to ~5 μm; smaller particles were also seen but may have been dust contamination. Optical micrographs of undiluted, freshly prepared emulsions from DE and PIE methods are shown in Figure 9. The PIE picture shows a more consistent pattern of micelles compared to DE; these micrographs are consistent with the dynamic light scattering (DLS) results. These results support greater stability from smaller micelles.

Figure 10 shows the emulsion viscosity for crude glycerin/fuel oil emulsions prepared by direct emulsification compared to phase inversion emulsification over a range of HLB values. Over the entire range, viscosity from phase inversion is higher than that from direct emulsification with a 4-fold difference at HLB values greater than 11. The emulsions in Figure 10 each had 55% by volume dispersed-phase crude glycerin and
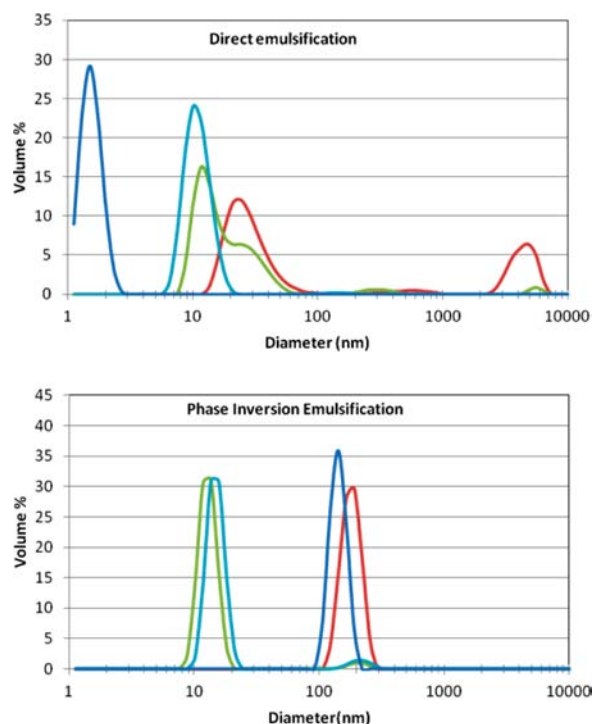
Figure 8. Dynamic light scattering data for emulsions made using DE (top) vs PIE (bottom) methods for glycerin−brine in no. 2 fuel oil with HLB-10 surfactants. Each plot shows the results of four different emulsion samples, thereby indicating the variability seen in the micelle measurement. Emulsions were measured after 2 weeks of destabilization and diluted in hexane.
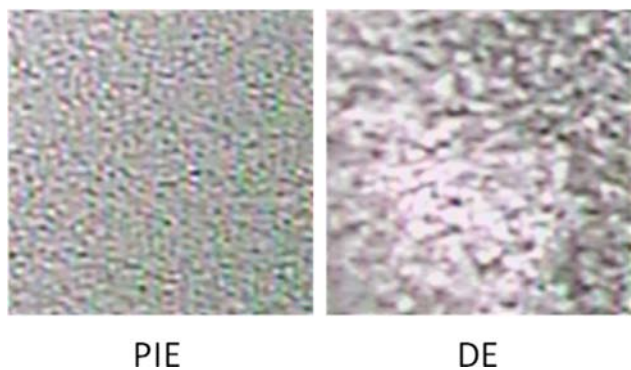

Figure 9. Optical microscopy images of glycerin−brine in fuel oil emulsions prepared with the PIE method and the DE method. Each image is 200 × 200 μm.
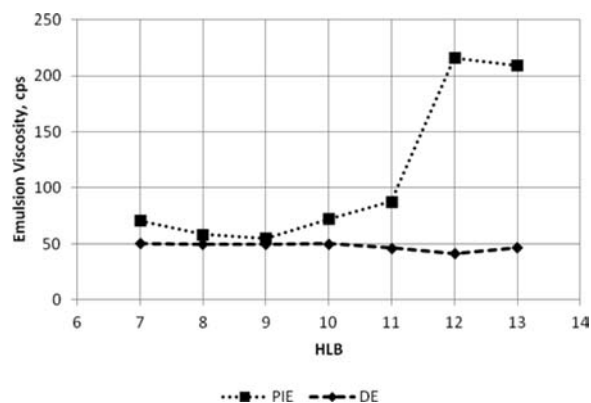

Figure 10. Emulsion viscosity vs HLB: comparison of PIE vs DE for crude glycerin no. 3 in no. 2 fuel oil emulsions. Uncertainty in viscosity ±0.3 cP.
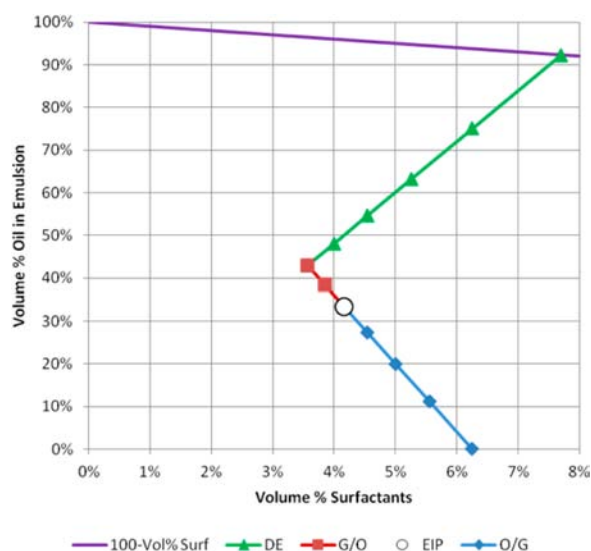

Figure 11. Phase diagram for PIE and DE emulsification of the glycerin phase in fuel oil.

therefore should have the same viscosity according to the Pal−Rhodes relationship. Estimating from Figure 4, a 4-fold increase in viscosity would be equivalent to a change from approximately 55% by volume dispersed phase to 60%. Phase inversion emulsions are known to facilitate multiple-phase micelles,[39,40] which in this case could be in the order of fuel oil/glycerin/fuel oil. This would increase the effective dispersed-phase volume. The corresponding result would be more closely packed micelles which could yield the increased stability shown in Figure 7.

Emulsion Phase Diagram. Phase diagrams are helpful to the understanding of dispersed- and continuous-phase behavior in emulsions.[41] A right triangle phase diagram is shown in Figure 11 showing steps in the formation of emulsions using both direct and phase inversion methods. It is instructive to see that the distinctly different processes of direct and phase inversion emulsification lead to glycerin in oil emulsions of the same composition. However, differences in how micelles are formed lead to apparent stability advantages for phase inversion emulsification.

In direct emulsification, surfactant is added to the continuous phase (fuel oil); the chart shows that the concentrations (vol %) of surfactant and oil decrease upon incremental addition of the dispersed phase (glycerin). As the dispersed phase is added, there is also an increase in viscosity according to Figure 4. With the proper surfactant HLB, a glycerin in oil emulsion can be made by direct addition of glycerin to near the close-packing limit. However, direct emulsification requires mechanical energy from high shear mixing throughout the process to disperse the glycerin into small micelles.[24]

In phase inversion emulsification, surfactant is added first to the intended dispersed phase (glycerin). Then the concentrations (vol %) of surfactant and glycerin decrease as increments of the intended continuous phase (fuel oil) are added; these additions initially make an oil in glycerin emulsion. This initial emulsion is not stable because the HLB of the surfactant is intentionally selected for the glycerin in oil

emulsion. Constant mixing keeps them suspended while increments of oil are added. As shown in Figure 6, there is an increase in viscosity corresponding to the addition of dispersed oil. At the emulsion inversion point (EIP), the phases invert such that oil becomes the continuous phase and glycerin becomes the dispersed phase. Here the geometric argument allows the phases to exist as inverted, which is thermodynamically favorable because the HLB of the surfactant system was chosen for glycerin in oil. Also at the EIP, viscosity is very high due to close packing of glycerin in oil; this is very stable as shown in Figure 6. After the EIP, oil is the continuous phase and further additions dilute the emulsion away from the close-packed arrangement, yielding a lower viscosity. One potential advantage of phase inversion emulsification is the spontaneous micelle formation that occurs during the inversion process, which can reduce the shear intensity required during mixing.[24]

Practical Implications. Emulsification parameters are dependent on the contaminants present in the crude glycerin samples, which vary depending on the source of the crude glycerin. This means that HLB requirements will also vary. A simple and practical method for determining the optimum surfactant mixture is to make a series of small emulsion samples with a range of HLB numbers (according to Table 2) followed by a stability test (i.e., 7 day bottle test) to empirically select the best composition. Once the optimum HLB number for surfactants is determined, emulsification can commence on a larger scale using the direct emulsification or phase inversion method. Analysis of crude glycerin (water, ash, and MONG) would provide additional information to assist practitioners in understanding the HLB requirements, but it is generally not necessary.

Burner Testing. In earlier work, we prepared fuel oil in glycerin—water emulsions and employed them successfully as a single fuel in a waste oil boiler (Kingbuilt.com, Inc.).[26] Subjective observations were made. The dispersed oil volume was 54%, and the viscosity was 549 cP. Emulsions with higher oil content were also used, but most were too viscous for the pumping system. Lower oil content emulsions had difficulty sustaining the flame. The high viscosity (549 cP) caused by the thicker glycerin continuous phase and the close-packing of micelles made fuel pumping difficult. Burner cycling (shutdown and restart) was also problematic. Furthermore, it was very difficult to clean the fueling system to revert to oil fuel.

In the current work, glycerin in fuel oil emulsions were tested as a single fuel using the Kingbuilt waste oil burner. Again, the observations were subjective; tests of heat output and furnace emissions were not done in this work. The emulsions consisted of 53.6% dispersed glycerin—brine in fuel oil (viscosity ∼64 cP) and also 53.6% glycerin—water in fuel oil (viscosity ∼72 cP). The low viscosity and sufficient oil content resulted in a stable flame. Furthermore, the burner shut off and refired several times under thermostat control without problems. This experiment was repeated successfully using a crude glycerin in fuel oil emulsion of 53.6% dispersed crude glycerin 2 in fuel oil (viscosity ∼123 cP), thereby demonstrating the successful application of a crude glycerin in fuel oil emulsion in an oil burner.

Subsequently, a 53.6% glycerin—brine emulsion was diluted in the fuel reservoir with additional no. 2 fuel oil to approximately 30% glycerin. The oil-continuous-phase emulsion dispersed evenly in the additional fuel oil, resulting in a lower viscosity (not measured). With the low viscosity and higher fuel oil content, this emulsion also performed well and

without failure. This demonstrated the ability to prepare a more stable, close-packed emulsion to be stored indefinitely, which could be diluted to meet viscosity requirements immediately prior to use (i.e., using an inline mixer).

After the glycerin in fuel oil emulsions were burned, furnace operation was returned to no. 2 fuel oil. The no. 2 fuel oil effectively purged the fueling system of the emulsion components as the emulsions were soluble in fuel oil. This demonstrated that crude glycerin emulsified into fuel oil can be employed directly as a fuel in an oil burner. Furthermore, the use of these emulsions is interchangeable with pure fuel oil, since they are miscible with one another. Further work should include furnace stack emissions testing, which will be required for permitting industrial burners in many areas. Additionally, a full analysis of heat output is recommended to determine the optimum composition as well as furnace air/fuel settings.

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■ REFERENCES

(1) Van Gerpen, J. Biodiesel Processing and Production. *Fuel Process. Technol.* **2005**, *86*, 1097−1107.
(2) Fan, X.; Burton, R.; Austic, G. Preparation and Characterization of Biodiesel Produced from Recycled Canola Oil. *Open Fuels Energy Sci. J.* **2009**, *2*, 113−118.
(3) Hu, S.; Luo, X.; Wan, C.; Li, Y. Characterization of Crude Glycerol from Biodiesel Plants. *J. Agric. Food Chem.* **2012**, *60*, 5915−5921.
(4) Johnson, D. T.; Taconi, K. A. The Glycerin Glut: Options for the Value-Added Conversion of Crude Glycerol Resulting from Biodiesel Production. *Environ. Prog.* **2007**, *26*, 338−348.
(5) U.S. EPA Renewable Fuel Standard. http://www.epa.gov/otaq/fuels/renewablefuels/index.htm (accessed Nov 11, 2012).
(6) Patzer, R. *Stack Emissions Evaluation: Combustion of Crude Glycerin and Yellow Grease in an Industrial Fire Tube Boiler*; Agricultural Utilization Research Institute: Marshall, MN, 2007; p 12.
(7) Bohon, M. D.; Metzger, B. A.; Linak, W. P.; King, C. J.; Roberts, W. L. Glycerol Combustion and Emissions. *Proc. Combust. Inst.* **2011**, *33*, 2717−2724.
(8) Steinmetz, S. A.; Herrington, J. S.; Winterrowd, C. K.; Roberts, W. L.; Wendt, J. O. L.; Linak, W. P. Crude Glycerol Combustion:

Particulate, Acrolein, and Other Volatile Organic Emissions. *Proc. Combust. Inst.* **2013**, *34*, 2749−2757.

(9) Patterson, C. J.; Setiawan, I.; Schilling, C. H.; Karpovich, D. S. Using Glycerin from Biodiesel Production as a Co-Fuel in a Heating Furnace: Emissions and Efficiency. Presented at the 237th National Meeting of the American Chemical Society, Salt Lake City, UT, March 22−26, 2009; Poster CHED 550.

(10) ASTM 5197-97. *Annual Book of ASTM Standards*; American Society for Testing and Materials (ASTM): West Conshohocken, PA, 1997; Vol. *11.03*.

(11) Wilson, A. L. Triethanolamine Emulsions. *Ind. Eng. Chem.* **1930**, *22*, 143−146.

(12) Petersen, R.; Hamill, R. Studies on Nonaqueous Emulsions. *J. Soc. Cosmet. Chem. Jpn.* **1968**, *19*, 627−640.

(13) Striūgas, N.; Slančiauskas, A.; Makarevičienė, V.; Gumbytė, M.; Janulis, P. Processing of the Glycerol Fraction from Biodiesel Production Plants to Provide New Fuels for Heat Generation. *Energetika (Vilnius, Lith.)* **2008**, *54*, 5−12.

(14) Bombos, D.; Bolocan, I.; Bombos, M.; Vasilievici, G.; Zaharia, E. Glycerol Based Fuel Emulsions. *Chim. Anal. (Bucharest)* **2010**, *61*, 506−510.

(15) Bombos, D.; Mihaescu, L.; Pisa, I.; Bolma, I.; Vasilievici, G.; Zaharia, E. Burning Glycerol Emulsion in Liquid Fossil Fuel. *Chim. Anal. (Bucharest)* **2011**, *62*, 562−566.

(16) Biodiesel Experts International Glycerin/Waste Oil Burner. http://www.biodieselexpertsintl.com/GlycerinWasteOilBurner/tabid/63/Default.aspx (accessed Nov 12, 2012).

(17) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*; Wiley: New York, 1997.

(18) Griffin, W. C. Classification of Surface-Active Agents by "HLB". *J. Soc. Cosmet. Chem.* **1949**, *1*, 311.

(19) Griffin, W. C. Calculation of HLB Values of Non-Ionic Surfactants. *J. Soc. Cosmet. Chem.* **1954**, *5*, 249.

(20) Davies, J. T. A Quantitative Kinetic Theory of Emulsion Type. I. Physical Chemistry of the Emulsifying Agent. *Proc. Int. Congr. Surf. Act.* **1957**, 426−438.

(21) Bancroft, W. D. The Theory of Emulsification, V. *J. Phys. Chem.* **1913**, *17*, 501−519.

(22) Sajjadi, S. Effect of Mixing Protocol on Formation of Fine Emulsions. *Chem. Eng. Sci.* **2006**, *61*, 3009−3017.

(23) Sajjadi, S.; Jahanzad, F.; Brooks, B. W. Miniemulsions by Phase Inversion Emulsification. Presented at the 48th Microsymposium of Prague Meetings on Macromolecules (PMM), Prague, Czech Republic, July 20−24, 2008; Special Lecture SL 17.

(24) Fernandez, P.; André, V.; Rieger, J.; Kühnle, A. Nano-Emulsion Formation by Emulsion Phase Inversion. *Colloids Surf., A* **2004**, *251*, 53−58.

(25) Jahanzad, F.; Crombie, G.; Innes, R.; Sajjadi, S. Catastrophic Phase Inversion via Formation of Multiple Emulsions: A Prerequisite for Formation of Fine Emulsions. *Chem. Eng. Res. Des.* **2009**, *87*, 492−498.

(26) Lucio, A. J.; Patterson, C. J.; Setiawan, I.; Schilling, C.; Karpovich, D. S. Glycerin/Fuel Oil Emulsions for Use in Heating Applications. Presented at the 239th National Meeting of the American Chemical Society, San Francisco, CA, March 21−25, 2010; Poster CHED 712.

(27) Dalmazzone, C.; Seris, H. Use of the DSC Technique To Characterize Water-in-Crude-Oil Emulsions Stability. *Oil Gas Sci. Technol.* **1998**, *53*, 463−471.

(28) ASTM D874-96. *Annual Book of ASTM Methods*; American Society for Testing and Materials (ASTM): West Conshohocken, PA, 1990; Vol. *5.01*.

(29) *AOCS Recommended Practice Cc 17-95: Soap in Oil Titrimetric Method*; American Oil Chemists' Society (AOCS): Urbana, IL, 1997.

(30) ASTM D4662-08. *Standard Test Methods for Polyurethane Raw Materials: Determination of Acid and Alkalinity Numbers of Polyols*; ASTM International: West Conshohocken, PA, 2008.

(31) Hautfenne, A. *Standard Methods for the Analysis of Oils, Fats, and Derivatives. Section III. Glycerines*, 6th ed.; Pergamon Press: New York, 1980; Vol. *52*.

(32) Anitescu, G.; Bruno, T. J. Liquid Biofuels: Fluid Properties To Optimize Feedstock Selection, Processing, Refining/Blending, Storage/Transportation, and Combustion. *Energy Fuels* **2012**, *26*, 324−348.

(33) Kanicky, J. R.; Shah, D. Effect of Degree, Type, and Position of Unsaturation on the pK_a of Long-Chain Fatty Acids. *J. Colloid Interface Sci.* **2002**, *256*, 201−207.

(34) Barrett, R. E.; Mood, J. W.; Lockli, D. W. *Preparation and Firing of Emulsions of No. 2 Fuel Oil and Water*; PH-86-68-84; Columbus Laboratories, Battelle Memorial Institute: Columbus, OH, 1968.

(35) ICI Americas Inc. *The HLB System: A Time-Saving Guide to Emulsifier Selection*; Wilmington, DE, 1976.

(36) Spangler, J.; Davies, E. Freezing Points, Densities, and Refractive Indexes of System Glycerol-Ethylene Glycol-Water. *Ind. Eng. Chem.* **1943**, *15*, 96−99.

(37) Tilton, J. N. *Perry's Chemical Engineers' Handbook. Section 6. Fluid and Particle Dynamics*, 7th ed.; McGraw-Hill: New York, 1997.

(38) Pal, R.; Rhodes, E. Viscosity/Concentration Relationships for Emulsions. *J. Rheol.* **1989**, *33*, 1021.

(39) Sajjadi, S.; Jahanzad, F.; Brooks, B. W. Phase Inversion in Abnormal O/W/O Emulsions: I. Effect of Surfactant Concentration. *Ind. Eng. Chem. Res.* **2002**, *41*, 6033−6041.

(40) Sajjadi, S.; Jahanzad, F.; Yianneskis, M.; Brooks, B. W. Phase Inversion in Abnormal O/W/O Emulsions. 2. Effect of Surfactant Hydrophilic−Lipophilic Balance. *Ind. Eng. Chem. Res.* **2003**, *42*, 3571−3577.

(41) Robbins, L. A.; Cusack, R. W. *Perry's Chemical Engineers' Handbook. Section 15. Liquid-Liquid Extraction Operations and Equipment*, 7th ed.; McGraw-Hill: New York, 1997.