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Upgrading Bio-oil through Emulsification with Biodiesel: Mixture Production

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There has been increasing interest in alternative fuels made from biomass, which is abundant and renewable. Bio-oil produced by fast pyrolysis of biomass is highly viscous and acidic and has a high water content. To overcome these problems as a fuel, a method of emulsifying bio-oil with biodiesel has been investigated. In the present study, various effects on the mixture stability have been examined. The optimal conditions for obtaining a stable mixture between bio-oil and biodiesel are with an octanol surfactant dosage of 4% by volume, initial bio-oil/biodiesel ratio of 4:6 by volume, stirring intensity of 1200 rpm, mixing time of 15 min, and emulsifying temperature at 30 °C. Furthermore, selected fuel properties, such as viscosity, density, water content, acid number, and average molecular weight, are measured for characterizing the bio-oil/biodiesel mixture. Thermogravimetric analysis (TGA) has been used to further evaluate the thermal properties. Data from the TGA and Fourier transform infrared (FTIR) analyses confirm the presence or absence of a certain group of chemical compounds in the mixture. The kinetic parameters for the thermal decomposition of the bio-oil, bio-oil/biodiesel-rich phase, and pyrolytic lignin-rich phase were obtained from the TGA experiments.

Introduction

There are a number of waste and biomass sources being considered as potential sources of fuels and chemical feedstock. Pyrolysis is a thermo-chemical process that converts biomass into liquid, char, and noncondensable gases by heating biomass to about 750 K in the absence of oxygen. The process can be adjusted to favour char, pyrolytic oil (bio-oil), or gas production with a fuel to feed efficiency of up to 95%.[1] As a consequence, the yield and composition of liquid products obtained from the pyrolysis of cellulose and various forms of biomass have received considerable attention.[2−4]

The benefits of bio-oil lie not only as a greenhouse-gas-neutral energy source but also as an opportunity to reduce reliance on fossil fuels and to support sustainable forest development. However, the complex chemical composition of bio-oil results in a multiphase, dark brown, relatively polar material, with an oxygen content between 33 and 45 wt %, high viscosity, and high acid number.[5−8] All of these make bio-oil a difficult fuel to burn. To overcome these disadvantages, several physical and chemical bio-oil upgrading technologies,

such as catalytic cracking,[9−13] hydrotreatment,[5,6] blending bio-oils with organic solvents,[7−20] emulsification with petroleum diesel,[1,21,22] and steam reforming,[23−25] have been tested at a bench scale. Additionally, emulsification of bio-oil with diesel fuel has shown to be an economical and viable fuel choice in diesel engines without the need for much modification.[1,21]

One of the methods in using bio-oil as a combustion fuel in transportation or boilers is to produce an emulsion with other fuel sources. Upgrading of bio-oil through emulsification with

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(1) Chiaramonti, D.; Bonini, M.; Fratini, E.; Tondi, G.; Gartner, K.; Bridgwater, A. V.; Grimm, H. P.; Soldaini, I.; Webster, A.; Baglioni, P. *Biomass Bioenergy* **2003**, *1*, 85–99.
(2) Boateng, A. A.; Mullen, C. A.; Goldberg, N.; Hicks, K. B.; Jung, H. G.; Lamb, J. F. S. *Ind. Eng. Chem. Res.* **2008**, *12*, 4115–4122.
(3) Boateng, A. A.; Daugaard, D. E.; Goldberg, N. M.; Hicks, K. B. *Ind. Eng. Chem. Res.* **2007**, *7*, 1891–1897.
(4) Boateng, A. A.; Mullen, C. A.; Goldberg, N. M.; Hicks, K. B.; McMahan, C. M.; Whalen, M. C.; Cornish, K. *Fuel* **2009**, *11*, 2207–2215.
(5) Garcia-Perez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Rodrigue, D.; Roy, C. *Energy Fuels* **2006**, *1*, 364–375.
(6) Garcia-Perez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Rodrigue, D.; Roy, C. *Energy Fuels* **2006**, *2*, 786–795.
(7) Garcia-Perez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Roy, C. *Biomass Bioenergy* **2007**, *4*, 222–242.
(8) Branca, C.; Di Blasi, C. *Ind. Eng. Chem. Res.* **2006**, *17*, 5891–5899.
(9) Vitolo, S.; Seggiani, M.; Frediani, P.; Ambrosini, G.; Politi, L. *Fuel* **1999**, *10*, 1147–1159.
(10) Zhang, Q.; Chang, J.; Wang, T.; Xu, Y. *Energy Fuels* **2006**, *6*, 2717–2720.
(11) Zhang, S.; Yan, Y.; Li, T.; Ren, Z. *Bioresour. Technol.* **2005**, *5*, 545–550.
(12) Vitolo, S.; Bresci, B.; Seggiani, M.; Gallo, M. G. *Fuel* **2001**, *1*, 17–26.
(13) Nokkosmaki, M. I.; Kuoppala, E. T.; Leppamaki, E. A.; Krause, A. O. I. *J. Anal. Appl. Pyrolysis* **2000**, *1*, 119–131.
(14) Pindoria, R. V.; Lim, J.; Hawkes, J. E.; Lazaro, M.; Herod, A. A.; Kandiyoti, R. *Fuel* **1997**, *11*, 1013–1023.
(15) Pindoria, R. V.; Megaritis, A.; Herod, A. A.; Kandiyoti, R. *Fuel* **1998**, *15*, 1715–1726.
(16) Senol, O. I.; Viljava, T. R.; Krause, A. O. I. *Catal. Today* **2005**, *3−4*, 331–335.
(17) Elliott, D. C. *Energy Fuels* **2007**, *3*, 1792–1815.
(18) Chiaramonti, D.; Oasmaa, A.; Solantausta, Y. *Renewable Sustainable Energy Rev.* **2007**, *6*, 1056–1086.
(19) Scholze, B.; Hanser, C.; Meier, D. *J. Anal. Appl. Pyrolysis* **2001**, *58−59*, 387–400.
(20) Scholze, B.; Meier, D. *J. Anal. Appl. Pyrolysis* **2001**, *1*, 41–54.
(21) Chiaramonti, D.; Bonini, M.; Fratini, E.; Tondi, G.; Gartner, K.; Bridgwater, A. V.; Grimm, H. P.; Soldaini, I.; Webster, A.; Baglioni, P. *Biomass Bioenergy* **2003**, *1*, 101–111.
(22) Ikura, M.; Stanciulescu, M.; Hogan, E. *Biomass Bioenergy* **2003**, *3*, 221–232.
(23) Basagiannis, A. C.; Verykios, X. E. *Catal. Today* **2007**, *1−4*, 256–264.
(24) Rioche, C.; Kulkarni, S.; Meunier, F. C.; Breen, J. P.; Burch, R. *Appl. Catal., B* **2005**, *1−2*, 130–139.
(25) Takanabe, K.; Aika, K.; Seshan, K.; Lefferts, L. *J. Catal.* **2004**, *227*, 101–108.

diesel oil decreases the viscosity and increases the calorific value and the cetane number as a liquid fuel. Chiaramonti et al.[1] studied the emulsion of bio-oil by the ratios of 25, 50, and 75 wt % with diesel fuel, resulting in more stable emulsions compared to the original bio-oil alone. The reduction in viscosity and corrosivity of the emulsion reported by Ikura et al.[22] is encouraging.

Another component of the bio-oil adding complexity to the mixture is the pyrolytic lignin, a mixture of high molecule compounds originating from the lignin in biomass. Several potential uses for pyrolytic lignin have been proposed,[19,20] which can increase the economic viability of the bio-oil. The easiest method of extraction is to take out the precipitate in water. However, this method leaves the remaining components of bio-oil in the aqueous phase, which is not desirable for use as fuel. To overcome this problem, this study investigates the bio-oil emulsification with biodiesel while leaving the pyrolytic lignin phase behind.

Biodiesel is comprised of monoalkyl esters of fatty acids derived from natural and renewable sources, such as animal fats and vegetable oils. It is registered as a fuel additive with the United States Environmental Protection Agency and meets clean diesel standards. Biodiesel is also a renewable fuel derived from triglycerides. It is environmentally innocuous, safe to handle, and has a relatively high flash point. The characteristics, such as heating value, density, and viscosity are comparable to #2 diesel from petroleum. Biodiesel presents a very promising prospect of functioning as an alternative fuel to fossil diesel. The properties of biodiesel can be compared favourably to the characteristics required for internal combustion engine fuels.[26,27] The resulting bio-oil/biodiesel mixtures are characterized on the basis of mixture stability and fuel properties. Upgrading bio-oil through emulsification with biodiesel explores the possibility of attaining independence from petroleum-based fuels. The fuel properties of bio-oil/biodiesel mixtures are studied as an approach for using bio-oil as a diesel extender for combustion in diesel engines.

An emulsion is defined as two immiscible liquids, wherein droplets of one phase (the dispersed or internal phase) are encapsulated within a layer of another phase (the continuous or external phase). For a stable emulsion to form, three basic conditions must be met:[28−30] (a) the two liquids must be immiscible or mutually insoluble in each other; (b) sufficient agitation must be applied to disperse one liquid into the other; and (c) an emulsifying agent or a combination of emulsions may be required.

The most significant parameter that can be varied to produce different emulsions is the stirring intensity. More efficient agitation gives better emulsion. It has been found that the interfacial area increases with an increasing rotational speed.[31] The temperature often has indirect effects on emulsification because it alters the interfacial tension, viscosity, and adsorption of the emulsifier. Both viscosity and interfacial

Table 1. Typical Composition and Energy Content of Bio-oil, Biodiesel, and Upper Layer Mixture (Initial 40 vol % Bio-oil)

	elemental analysis (wt %)				
	C	H	O	N	HHV[a] (MJ/kg)
bio-oil	39.96	7.74	52.19	0.11	15.275
biodiesel	77.54	11.75	9.71	1.00	41.431
upper layer (40 vol % bio-oil)	66.48	11.89	21.50	0.13	35.761

[a] The heating values were calculated from elemental analysis data by equation: HHV (MJ/kg) = $[338.2 \times \%C + 1442.8 \times (\%H - (\%O/8))] \times 0.001$.

tension decrease with the increase in temperature; thus, a higher temperature is favourable for emulsification.

This paper examines the effects of several process variables, such as surfactant dosage, ratio of bio-oil/biodiesel, stirring intensity, emulsifying temperature, and mixing time on the stability of emulsion formation studied over 24 h. Furthermore, the resulting mixture is characterized on the basis of the viscosity, acid value, water content, molecular weight, and functional groups.

Experimental Section

Sample Preparation. The bio-oil produced from fast pyrolysis of softwood residue was supplied from VTT, Finland. Soybean-based biodiesel was supplied from World Energy, Worcester, MA. Octanol was used as the emulsifier. Initially, the effects of the emulsifier concentration, initial bio-oil/biodiesel volume ratio, stirring intensity, mixing time, and temperature were examined. In the present study, the stability of the emulsion was characterized by a parameter *S* defined as the volume of bio-oil dissolved in a unit volume of biodiesel. Initial mixtures of bio-oil and biodiesel were prepared by adding 20, 30, 40, and 50% (by volume) bio-oil into biodiesel and mixed in conical flasks with a homogenizer. After mixing for 15 min, samples were placed in 100 mL graduated cylinders to record the levels of interphase against time. For all of the above mixtures, a quick separation on the order of a few minutes was observed and the stratification stopped in about 10 h. The properties of the upper layer (biodiesel-rich phase) were then characterized. Experiments were repeated at least 3 times to obtain the average and standard deviation, expressed as error bars.

Sample Characterization. The ultimate analysis result was obtained on the basis of "as received" according to American Society for Testing and Materials (ASTM) D-5291 using Carlo Erba Elemental Analyzer EA 1108. The water content and acid number of the mixtures were determined by Metrohm 794 Basic Titrino. The viscosity of the samples was measured using an Advanced Rheometer 2000. The shear rate was $100 \, s^{-1}$, with the measuring temperature at 25 °C. The average molecular weight was measured by gel permeation chromatography (GPC) with a refractive index detector using Agilent 1100 series and RID model G1362A. Tetrahydrofuran (THF) was used as a solvent at a flow rate of 0.5 mL/min. The functional groups of the samples were measured by IR spectra. The attenuated total reflectance (ATR) method was used with a Varian Fourier transform infrared (FTIR) 3100 spectrometer to record the spectra. The samples were applied as a film to the zinc selenide crystal. Thermogravimetric analysis (TGA) was performed on a simultaneous TGA/DSC, SDT Q600, TA Instruments. Samples of 15−20 mg were heated from room temperature (RT) to 600 °C at a constant heating rate of 20 °C/min under nitrogen, at a flow of 30 mL/min.

Results and Discussion

Ultimate Analysis. The results from the ultimate analysis of bio-oil, biodiesel, and emulsion (40 vol % bio-oil) are

(26) Meher, L. C.; Dharmagadda, V. S. S.; Naik, S. N. *Bioresour. Technol.* **2006**, *12*, 1392–1397.

(27) Barnwal, B. K.; Sharma, M. P. *Renewable Sustainable Energy Rev.* **2005**, *4*, 363–378.

(28) Stiegler, U. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2000**, *1*, 197–200.

(29) Saunders, H. G.; Kamke, F. A. *For. Prod. J.* **1996**, *3*, 56–62.

(30) Nakashima, T.; Shimizu, M.; Kukizaki, M. *Adv. Drug Delivery Rev.* **2000**, *1*, 47–56.

(31) Verbich, S. V.; Dukhin, S. S.; Tarovski, A.; Holt, Ø.; Saether, Ø.; Sjoblom, J. *Colloids Surf., A* **1997**, *141*, 209–223.
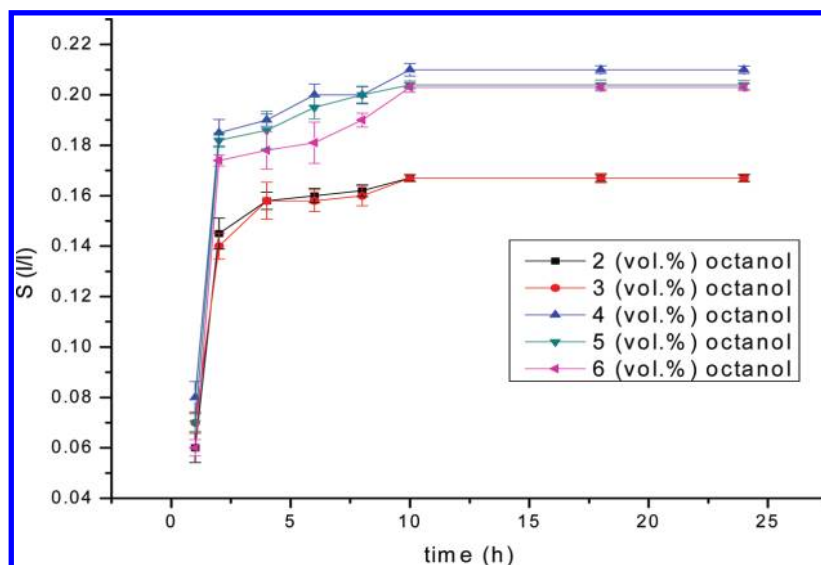
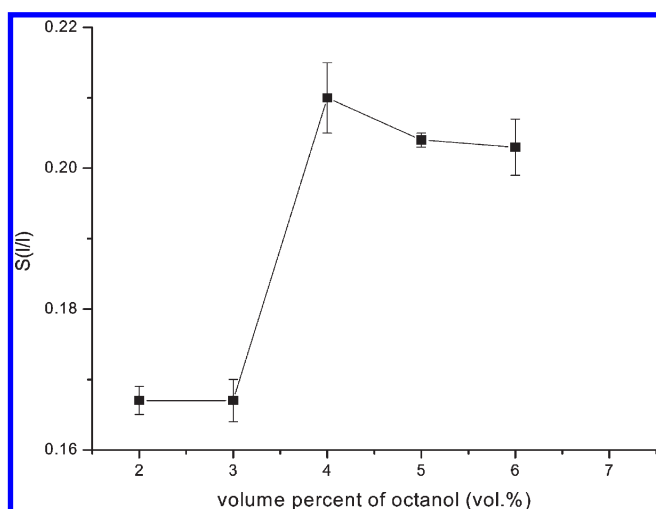**Figure 1.** Effect of the octanol concentration on *S* values.

Figure 2. Effect of the octanol concentration on the *S* value at 10 h.

Figure 3. Effect of the initial volume percent of bio-oil on emulsification.

shown in Table 1, indicating that the bio-oil contains approximately 50% oxygen, which is much lower in biodiesel (9.71%). The calculated high heating values (HHVs) of bio-oil, biodiesel, and bio-oil/biodiesel emulsion (initial 40 vol % bio-oil) are 15.28, 41.43, and 35.76 kJ kg^{-1}, respectively.

Effect of the Emulsifier Concentration on Mixture Stability. The surfactant concentration is one of the most important factors influencing of the stability of emulsions.[32] A typical *S* value curve with time, representing the stability of emulsion shown in Figure 1 indicates that after 10 h a stable mixture is obtained. Once stirring is stopped, the dispersed droplets cool to room temperature and coalesce, while the pyrolytic lignin-rich phase settles to the bottom. When the effect of the emulsifier concentration is examined, the *S* values at 10 h are compared, as shown in Figure 2. There exists an optimal concentration range of octanol producing stable mixtures. At low surfactant concentrations, the mixture is not stable because of agglomeration of the oil droplets, while at higher concentrations, the emulsion
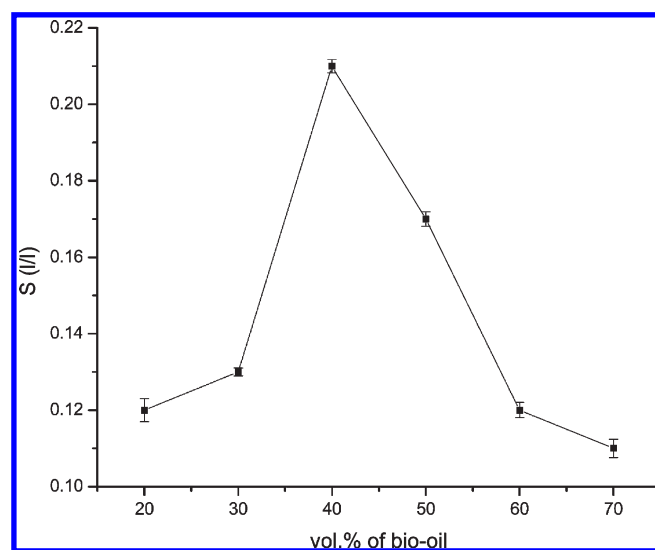
destabilizes as a result of rapid coalescence.[33] The optimal emulsifier dosage is determined to be 4 vol %, which is used for the following experiments.

Effect of the Initial Bio-oil/Biodiesel Ratio and Mixing Temperature. By mixing various volumetric ratios of bio-oil/biodiesel and observing the emulsion stability, Figure 3 is obtained, where the optimum volumetric ratio is 4:6. The *S* value was essentially constant over a period of 24 h, indicating that, once formed, the mixture was very stable, as exemplified in Figure 1.

To investigate the effect of the mixing temperature on the mixture stability, the *S* value was determined at different temperatures ranging between 25 and 50 °C. The mixture was stirred for 15 min at a set temperature, followed by observing the emulsion stability over time. In general, both viscosity and interfacial tension decrease with increasing temperature, which makes the emulsification easier.[32] However, an excessive increase of temperature > 40 °C should be

(32) Ostberg, G.; Bergenstahl, B.; Hulden, M. *Colloids Surf., A* **1995**, *2−3*, 161–171.

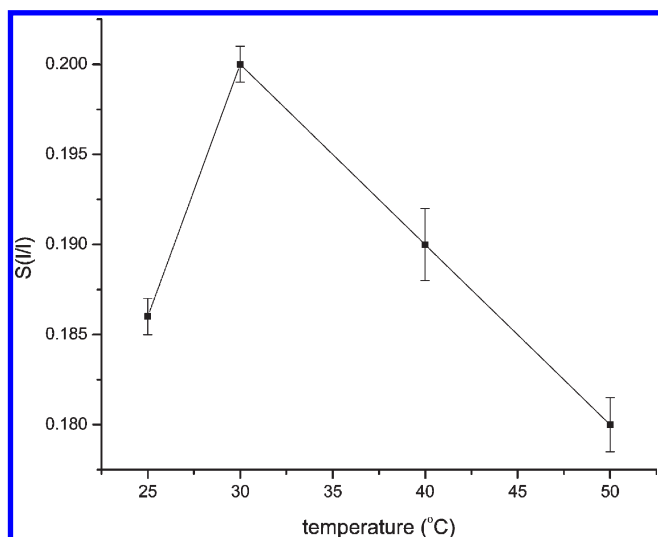(33) Chen, G.; Tao, D. *Fuel Process. Technol.* **2005**, *5*, 499–508.

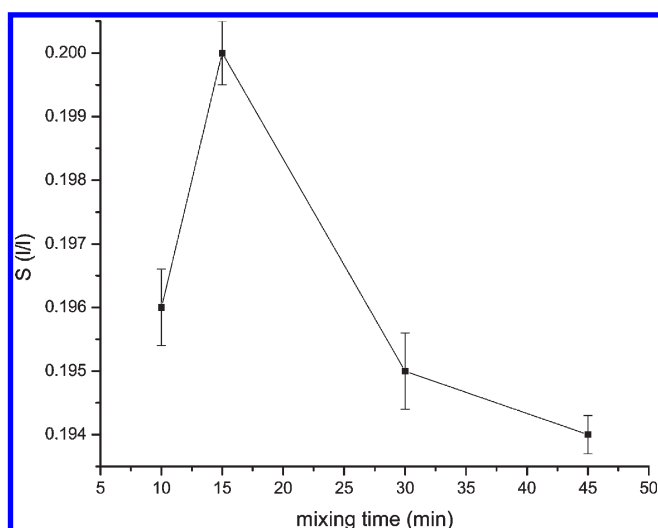**Figure 4.** Effect of the mixing temperature on the *S* value at 10 h.

Figure 5. Effect of the mixing time on the *S* value at 10 h.

avoided because it tends to coagulate the droplets, causing destabilization of the emulsion. Furthermore, the interfacial adsorption of the emulsifier is affected to some extent by increasing the temperature. The surfactant adsorbed on the interface will separate out from the emulsion, increasing the probability of collision and coalescence, thus deteriorating the stability of the emulsion.[33] As shown in Figure 4, the temperature difference had very little effect on the mixture stability yet 30 °C was the optimal when octanol was used as the emulsifier.

Effect of the Mixing Time and Intensity. The mixing time is another important factor for emulsification. In general, the radii of droplets in the emulsion decrease with an increasing stirring speed and emulsifying time.[31] The emulsifier becomes more effective with an increased mixing time. However, if the mixing time is too long, the effect on the emulsifier will be decreased because the intense stirring will cause the emulsifier to drop out from the bio-oil/biodiesel interface. From the *S* values shown in Figure 5, the optimum mixing time was determined to be 15 min.

Emulsification is usually achieved by the application of mechanical energy. A comparison of the emulsion stability with stirring intensity ranging between 500 and 1200 rpm
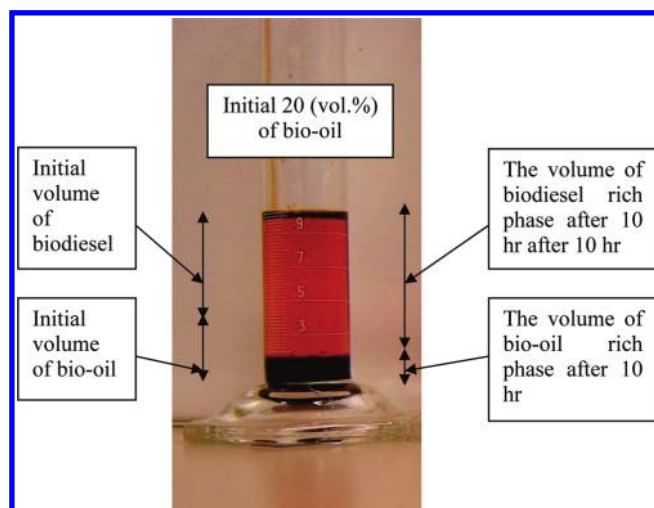

Figure 6. Relationship of the volume of bio-oil and biodiesel at 0 and 10 h.

indicated that, the higher the stirring intensity, the higher the *S* value. Thus, the highest stirring setting was chosen for producing the emulsions.

Properties of Bio-oil, Biodiesel, and Emulsion Phase. As shown in Figure 6, once a stable emulsion is produced, there formed two layers: the biodiesel-rich upper layer and the pyrolytic lignin-rich lower layer. The volume of the biodiesel-rich phase increases from the initial volume percent biodiesel, owing to the emulsification of bio-oil and biodiesel, with the fraction of bio-oil dissolving in the biodiesel phase. The phases examined in this section are made under the following conditions unless otherwise specified: the initial ratio of bio-oil/biodiesel of 4:6 by volume, the octanol content of 4% by volume, the stirring intensity at 1200 rpm, the mixing time of 15 min, and the emulsifying temperature at 30 °C.

Table 2 summarizes the properties of the bio-oil, biodiesel, and the top emulsion phase, with the numbers representing the average of triplicate analyses. The viscosity of the biodiesel-rich phase has decreased remarkably compared to that of bio-oil. Owing to the certain acid compounds of bio-oil mixing with biodiesel, the acid value of the emulsion increases with an increasing bio-oil content. From the lower water content of the emulsion compared to the original bio-oil, it is confirmed that the water remains with the pyrolytic lignin-rich layer. This makes the top emulsion phase desirable for use as fuel.

Thermal Analysis. Thermogravimetry (TG) and derivative thermogravimetric (DTG) curves of the bio-oil, biodiesel, and the mixture under nitrogen purge of 30 mL/min and heating rate of 20 °C/min are presented in Figure 7. The TG curve of the bio-oil indicated a gradual weight loss of the mixture upon heating with N_2 between 50 and 500 °C. This is consistent with a previous study that reported the TG curves for bio-oil and its fractions.[34] The initial weight loss between 50 and 100 °C of bio-oil is attributed to the loss and decomposition of water and highly volatile compounds, such as formaldehyde, acetone, methanol, and ethanol. At temperatures between 130 and 250 °C, many of the compounds with higher cracking energy are decomposed. Lastly, the weight loss at 400−475 °C is assigned to the decomposition of the pyrolytic lignin fraction.[34]

(34) Ba, T.; Chaala, A.; Garcia-Perez, M.; Rodrigue, D.; Roy, C. *Energy Fuels* **2004**, *18*, 704–712.

Table 2. Properties of the Bio-oil, Biodiesel, and Biodiesel-Rich Phase Mixture

method (initial vol % bio-oil)	products	viscosity ($T = 25$ °C) ($\times 10^{-3}$ Pa s)	density (g/cm^3)	acid value (mg of KOH/g)	volume ratio of upper and bottom layer	average molecular weight (M_w)	water content (wt %)
raw materials	bio-oil	67.39	1.200	79.23		421	28.05
	biodiesel	6.590	0.881	0.55		280	0.1607
20 vol % bio-oil	upper layer	4.217	0.891	9.31	90:10	303	0.3785
30 vol % bio-oil	upper layer	4.514	0.892	11.24	72:28	307	0.3857
40 vol % bio-oil	upper layer	4.665	0.895	14.01	73:27	311	0.4558
50 vol % bio-oil	upper layer	4.917	0.897	13.08	60:40	312	0.4634
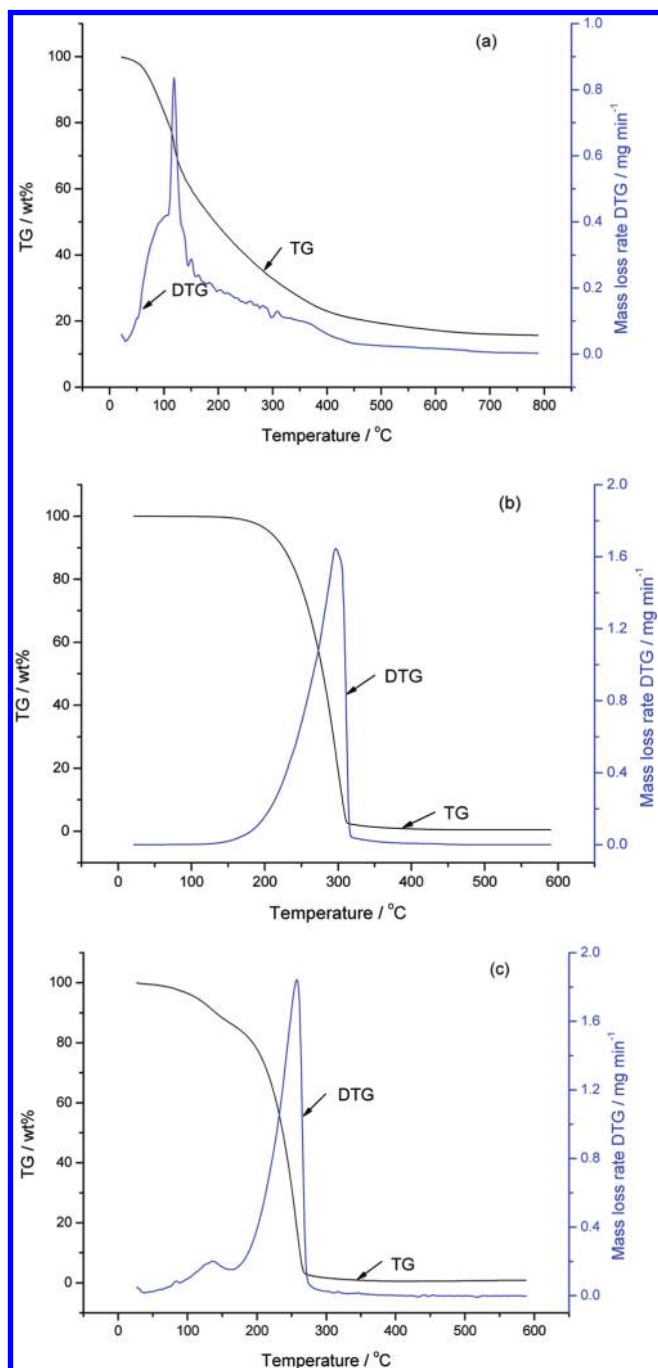
Figure 7. TG and DTG curves of emulsion of (a) bio-oil, (b) biodiesel, and (c) mixture with an initial 40 vol % bio-oil.

A comparison of the DTG curves of the mixture to those of bio-oil and biodiesel reveals the presence or the absence
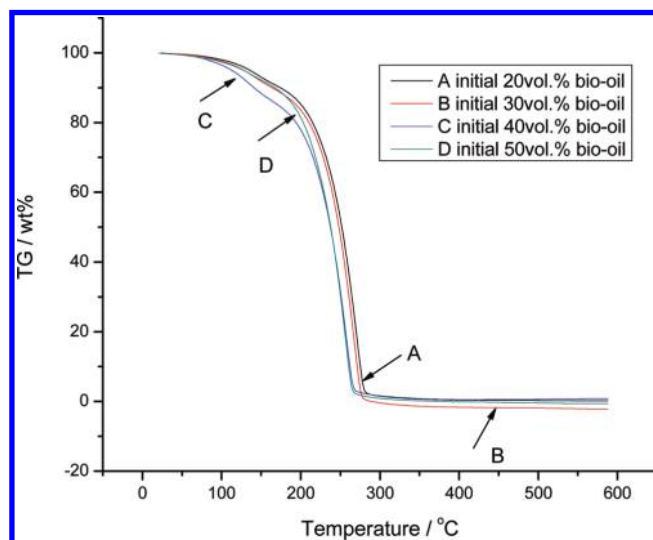
Figure 8. TG curves of mixtures with a different initial volume percent of bio-oil.

of certain compounds. For example, the strong DTG peak around 50−100 °C is absent in the DTG of the mixture, further confirming that most water and volatile organic compounds are removed (left in the bio-oil-rich phase). The small DTG peaks around 130 °C can be attributed to the monolignols and furans according to Garcia-Perez et al.[35] The absence of any weight loss beyond 280 °C from the DTG curves of the mixtures shown in Figure 7 confirms the absence of pyrolytic lignin. The maximum weight loss was observed around 260−280 °C, which corresponds to a high fraction of biodiesel present in the mixture.

Figure 8 shows the trend of increasing compounds, such as phenols and furans, that decompose around 100−200 °C with an increasing bio-oil fraction in biodiesel.[35] The increasing trend around 260 °C may be attributed to the increasing oligomers fraction as explained by Garcia-Perez et al.[35] As summarized in Table 3, the initial and peak temperatures (defined in the footnote to Table 3) for 20−50 vol % bio-oil emulsion decrease with an increasing bio-oil concentration, further reflecting these points.

Figure 9 shows the IR spectra of the bio-oil, biodiesel, and bio-oil/biodiesel mixture of an initial 40 vol % bio-oil. The large band at 3400 cm^{-1} for bio-oil is from the intermolecular hydrogen bonds O−H stretching from the presence of

(35) Garcia-Perez, M.; Adams, T. T.; Goodrum, J. W.; Geller, D. P.; Das, K. C. *Energy Fuels* **2007**, *21*, 2363−2372.
(36) Ozbay, N.; Putun, A. E.; Putun, E. *Int. J. Energy Res.* **2006**, *30*, 501−510.

Table 3. TGA Results of the Mixtures with a Different Initial Volume Percent of Bio-oil[a]

parameters	initial 20 vol % bio-oil	initial 30 vol % bio-oil	initial 40 vol % bio-oil	initial 50 vol % bio-oil
T_0	76	72	62	63
T_f	324	278	335	295
T_p	271	268	257	256
R_s	0.15	0.8	0.32	0.6

[a] T_0, temperature (°C) corresponding to 1 wt % emulsion weight loss; T_f, final temperature (°C) corresponding to 99 wt % emulsion weight loss; T_p, peak temperature (°C) corresponding to a maximum weight loss; R_s, final residue (wt %).
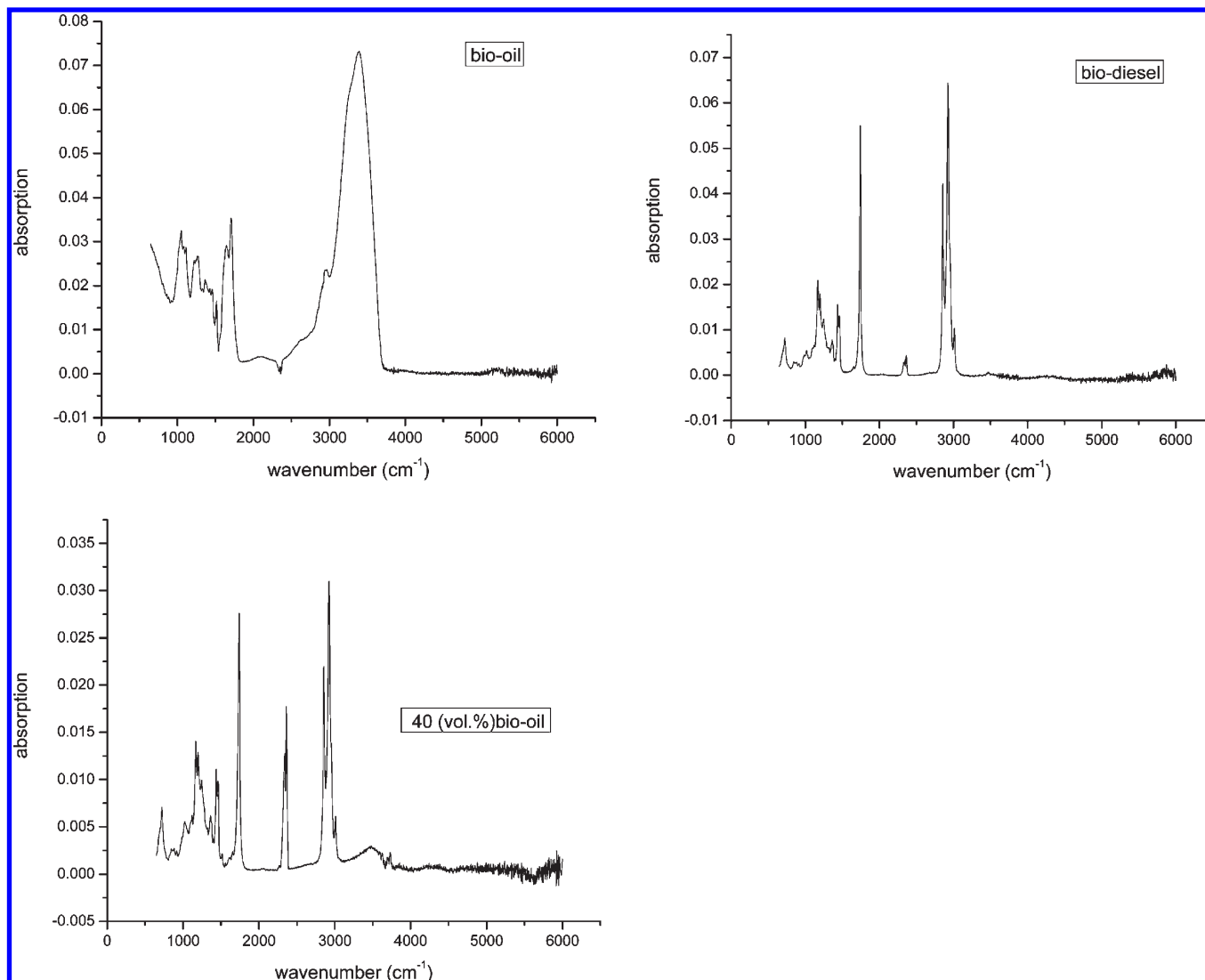
Figure 9. FTIR spectra of bio-oil, biodiesel, and the mixture with an initial 40 vol % bio-oil.

phenols and alcohols.[36] This band is much smaller in the spectra of the mixture. Furthermore, the octanol used as a surfactant in the emulsion may have contributed to the band. The C−H stretching vibration between 2912 and 2929 cm^{-1} results in dominant peaks for biodiesel and the emulsion. The C=O at 1700−1725 cm^{-1} presumably from methyl esters for the biodiesel cannot be distinguished, resulting from the detonic group stretching from the bio-oil sample. The C(=O)−O vibration at around 1200 cm^{-1} shown in the biodiesel sample remains a dominant band in the emulsion.

Thermal Decomposition Kinetics. The nucleation and nuclei growth model (Avrami−Erofeev equation, $n = 1$) are applied to characterize the thermal decomposition kinetics of the bio-oil/biodiesel mixture. The kinetic parameters

were calculated on the basis of weight loss data from room temperature to 600 °C at a 20 °C min^{-1} heating rate. A typical model for a kinetic process can be expressed as

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where $d\alpha/dt$ is the decomposition rate, $\alpha = (w_0 - w)/(w_0 - w_c)$, k is the decomposition rate constant, and $f(\alpha)$ is the differential expression of a kinetic model function; here, $f(\alpha) = 1 - \alpha$. The temperature dependence of the rate constant k can be described in the Arrhenius equation

$$k = A \exp(-E_a/RT) \tag{2}$$

where A is the pre-exponential factor (min^{-1}), assumed to be independent of the temperature.

Table 4. Kinetics Parameters of Different Samples Calculated by the Doyle Method

samples	decomposition stages	E_a (kJ mol^{-1})	A (min)	r
bio-oil	RT−200 °C	12.497	5.7×10^6	0.99103
	200−600 °C	33.335	4.4×10^{12}	0.98673
pyrolytic lignin-rich phase	RT−200 °C	9.236	1.6×10^6	0.99327
	200−600 °C	29.063	3.6×10^{11}	0.99616
bio-oil/biodiesel-rich phase	RT−200 °C	34.089	1.2×10^{11}	0.98915
	200−600 °C	55.141	2.5×10^{16}	0.99832

With the constant heating rate $\beta = \mathrm{d}T/\mathrm{d}t$, a combination of eqs 1 and 2 leads to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\exp(-E_a/RT)f(\alpha) \qquad (3)$$

Variable separation and integration of eq 3 from an initial temperature T_0, corresponding to a degree of conversion α_0, to the peak temperature, T_p, where $\alpha = \alpha_p$, gives

$$F(\alpha) = \int_{\alpha_0}^{\alpha_p} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_p}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \qquad (4)$$

where $F(\alpha)$ is the integral function of conversion, here, $F(\alpha) = \ln(\ln(1/(1-x)))$.

At last, the Doyle method is expressed as

$$\ln\left(\ln\left(\frac{1}{1-x}\right)\right) = -1.0516\frac{E}{R}\frac{1}{T} + \ln\frac{AE}{R\beta} - 5.33 \qquad (5)$$

The same method can be applied to the pyrolytic lignin-rich phase and the whole bio-oil.

Table 4 shows a summary of kinetic parameters of different samples. The activation energies in the second stage are generally higher than the first stage, owing to the progress of cracking and/or pyrolysis of organic compounds.

Conclusions

A stable bio-oil/biodiesel emulsion was produced using octanol as an emulsifier. The best emulsifier concentration was 4% by volume. At a higher concentration, rapid coalescence of the droplets was observed, while at a lower emulsifier dosage, a stable emulsion was not obtained. The optimal initial ratio of bio-oil/biodiesel was 4:6 by volume. Higher stirring intensity at 1200 rpm resulted in a more stable emulsion. A higher temperature induced the stability of emulsion, with the optimal temperature at 30 °C. The best mixing time was 15 min, beyond which the stability decreased because of the surfactant dropping out from the bio-oil/biodiesel interface.

The processing of emulsifying bio-oil with biodiesel is a novel method to extract some of the best fuel fractions present in bio-oil for use as an additive to transportation fuel. Various properties of the emulsion have shown more desirable values in acid number, viscosity, and water content compared to the original bio-oil. Bio-oil is the least expensive liquid fuel obtained from lignocellulosic materials. Further exploration of the pyrolytic lignin-rich phase to value-added chemicals will enhance the economic viability of the bio-oil usage. The thermal decomposition behaviour of bio-oil, bio-oil/biodiesel emulsion, and pyrolytic lignin-rich phase using TGA has shown at least two identifiable stages.

Nomenclature

A = pre-exponential factor, min^{-1}
E_a = activation energy, kJ/mol
$f(\alpha)$ = differential expression of a kinetic model function
$F(\alpha)$ = integral function of conversion
HHV = high heating value, calculated by the formula in Table 1
k = decomposition rate constant
r = correlation coefficient
R = gas constant, 8.314 J mol^{-1} K^{-1}
R_s = final residue, wt %
T = temperature, °C
T_0 = temperature corresponding to 1 wt % emulsion weight loss, °C
T_f = temperature corresponding to 99 wt % emulsion weight loss, °C
T_p = peak temperature corresponding to a maximum weight loss, °C
w_0 = initial weight of the samples, mg
w_c = final weight of the samples, mg
w = actual weight of the sample, mg
α = degree of decomposition, reaction ratio
β = heating rate, °C/min