Research on the Upgrading of Bio-Oil Based on Low-Carbon Alcohol Solvents and Ultrasonic-Emulsification

Rundong Liu,[a] Jinliang Yan,[a] Zhiyu Li,[a,b,c,]* Yuchun Zhang,[a] Chunyan Tian,[a] Peng Fu,[a,]* Xuebing Li,[c] Ling Zhou,[d] and Xiwei Xu [e,]*

Effects of the emulsifier type, hydrophilic-lipophilic balance (HLB) value, bio-oil ratio, ultrasonic power density, and ultrasonic time were tested relative to the physicochemical properties and stability of emulsified oils to broaden the use of bio-oil and overcome its defects. The results showed that the turbidity and stabilization times of the emulsified oils reached the maximum values of 184 NTU and 84 min (Span 80 and Tween 80), 191 NTU and 92 min (HLB value of 5), 280 NTU and 92 min (bio-oil ratio of 5%), 191 NTU and 81 min (ultrasonic power density of 0.96 w/mL), 273 NTU and 97 min (ultrasonic time of 20 min), respectively. When the bio-oil to methanol ratio was 1:1, the turbidity value of the emulsified oil reached a maximum value of 664 NTU and the stability time was greater than 24 h. The Fourier transform infrared (FTIR) analysis indicated that the emulsified oil did not delaminate after 30 d, and the uniformity and stability of the emulsified oil were improved.

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*Contact information: a: School of Agricultural Engineering and Food Science, Shandong University of Technology, Zibo 255000, China; b: China Postdoctoral Innovation (Jiangmen) Demonstration Center, Jiangmen, 529000, China; c: Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China; d: College of Mechanic and Electrical Engineering, Tarim University, Alar 843300, China; e: College of Materials and Energy, South China Agricultural University, Guangzhou 510640, China; *Correspondence author: tarmlizhiyu@hotmail.com; fupeng@sdut.edu.cn; xuxiwei200801@hotmail.com*

INTRODUCTION

Biomass has attracted increasing attention, as it is renewable and has great potential to replace petroleum in the near future (Zhou *et al*. 2016). Pyrolysis is a crucial thermochemical process used to convert biomass into fuels and chemicals in which feed stocks are pyrolyzed in a non-oxidative atmosphere at temperatures of 400 to 800 °C and bio-oils are the main products. Bio-oils, if produced sustainably, can be regarded as environmentally friendly alternatives to fossil fuels (Lin *et al*. 2016). However, bio-oil cannot be directly used as a transportation fuel due to its undesirable properties of high viscosity, high corrosiveness, high oxygen-content, low heating value, and instability (Yuan *et al*. 2018). For these reasons, bio-oils cannot be utilized directly as high-grade fuels such as gasoline or diesel and need to be upgraded (de Luna *et al*. 2017). In this aspect, hydrotreating, hydro-cracking, steam reforming, esterification, emulsification, and chemical extraction have been developed to improve bio-oil properties such as viscosity, calorific value, density, instability, water content, and oxygen content (Xu *et al*. 2018).

Emulsification is a convenient, simple, inexpensive, and effective physical method used to upgrade bio-oils for mixing with diesel to use as a fuel (Lin *et al*. 2016). According to Van de Beld *et al.* (2013), pyrolyzed oil treated by emulsification could combust easily and emit less carbon monoxide (CO). In addition, bio-oil emulsion can introduce some improvements in engine performance and exhaust emissions (Van de Beld *et al*. 2013).

It has been reported that increasing the bio-oil content in diesel could effectively reduce nitrogen oxide (NO_x) emissions compared with those from petroleum-based diesel (Indudhar *et al*. 2019). The addition of an emulsifier (also called an emulsifying agent) into two immiscible streams (*e.g.* bio-oil and diesel) with the help of agitation is an essential step in implementing emulsification (Martin *et al*. 2014).

Ultrasound is a kind of wave, so it can be used as a carrier to load and detect information. However, ultrasound is also a form of energy that accelerates chemical reactions or triggers a new reaction channel (Sivaramakrishnan and Incharoensakdi 2018). Ultrasound is a technology frequently used to intensify liquid-liquid processes (Zhao *et al*. 2018). Ultrasound induces acoustic cavitation as well as streaming phenomena into liquids, which can greatly enhance the dispersion and mass transfer rate between immiscible liquids (Dong *et al*. 2016; Zhao *et al*. 2017). Research has shown that many liquid-liquid emulsification, extraction, and reaction processes could be intensified by the mechanical effect of ultrasound (Cintas 2016; Krasulya *et al*. 2016).

Emulsions are systems that contain two immiscible liquids, with one dispersed as droplets (dispersed phase) throughout the other (continuous phase) (Kaci *et al*. 2017). The preparation of an emulsion requires a very large phase interface to greatly increase the system. Therefore, a certain amount of energy is needed to complete the preparation, and ultrasonication of the liquid can induce the spread of an important phenomenon, namely, causing bubbles or cavities to constantly be generated, grow, and implode in liquids. In the medium to micro amount of time required to form a hot spot, its temperature can rise to above 500 K and the pressure can reach the level of several hundred to several thousand atmospheres. This can accelerate the reaction speed for chemical reactions that require enormous energy (Sivaramakrishnan and Incharoensakdi 2018). Compared with other emulsifying technologies, ultrasonic emulsification can make droplets disperse more thinly and narrowly, achieving higher efficiency, better dispersion, and increased emulsion stability (Xu *et al*. 2018).

In the literature, several studies concerning the emulsification of bio-oils and diesel using a variety of emulsifiers such as Span 80, Tween 85, and Brji 72 have been reported. When emulsions are produced from bio-oils and diesel, two important factors will influence the performance of the emulsification – the type and hydrophilic-lipophilic balance (HLB) value of the emulsifier (Martin *et al*. 2014; Lin *et al*. 2016). However, relatively little research has been performed on the effect of the HLB value on a bio-oil/diesel emulsion system, especially concerning the relationship between bio-oil properties and the emulsifier HLB value in stabilizing emulsified fuels. In addition, ultrasonic technology is only considered an aid for improving the synthesis efficiency, and the influence of ultrasonic parameters on the stability of emulsified biodiesel is rarely considered. For this reason, the present study aimed to explore the influence of the emulsifier type, emulsifier HLB value, bio-oil ratio, ultrasonic power density, and time on the stability of emulsification. The effect of added low-carbon alcohols methanol on the emulsion stability of bio-oil was also studied. Through the research of two emulsion systems for biodiesel and alcohol oil, the aim was to broaden new approaches for the industrial application of bio-oil.

EXPERIMENTAL

Reagents

The absolute ethanol (AR) and methanol (AR) were obtained from Shanghai Runjie Chemical Reagent Co. (Shanghai, China). Sorbitan monooleate was obtained as Span 80 (CP) from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). Polyoxyethylene sorbitan monooleate 80 (Tween 80 (CP)) and polyethylene glycol (PEG400 (AR)) were obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). Polyoxyethylene sorbitan monooleate 60 (Tween 60 (CP)) and potassium bromide (KBr, SP) were obtained from Tianjin Komi Chemical Reagent Co. (Tianjin, China).

Ultrasonic-Emulsification Technology

Preparation of the composite emulsifier

In this paper, the non-ionic surfactants Span 80 (sorbitan monooleate, HLB value of 4.3) and Tween 80 (sorbitan monooleate polyoxyethylene ether, HLB value of 15), which have the advantages of non-toxicity and good biodegradability, were used in the emulsification experiment. Since biomass tar is used as the dispersed phase, diesel is the continuous phase and biomass tar is dispersed in the diesel fuel as tiny droplets. Therefore, the emulsifier used should be a water-in-oil (W/O) emulsifier with an HLB value equal to 15 (Yu *et al*. 2018). The HLB value of the composite surfactant was determined by the formula for the HLB value proposed by Griffin (1949). The formula can be seen in Eq. 1,

$$HLB = \frac{w_1 \bullet HLB_1 + w_2 \bullet HLB_2}{w_1 + w_2} \tag{1}$$

where HLB_1 and HLB_2 represent the HLB values of emulsifiers 1 and 2, respectively, and w_1 (g) and w_1 (g) represent the masses of emulsifiers 1 and 2, respectively. The compound emulsifiers with different HLB values were configured for use according to Eq. 1.

Ultrasonic-emulsification test

First, the bio-oil and the composite emulsifier (or composite emulsifier and additive) were mixed in a predetermined ratio and uniformly stirred in a constant-temperature water bath. At the same time, the diesel oil was added to the treated bio-oil at a predetermined ratio with stirring, and the mixture was finally emulsified in an FS-300N ultrasonic processor (Shanghai ShengXi Ultrasonic Instrument Co., Shanghai, China). The addition ratio of the composite emulsifier was 5 wt%. The collected emulsified oil was assessed for turbidity, stabilization time, water content, density, calorific value, pH, and viscosity. Thermogravimetric analysis (TGA) and Fourier-transform infrared (FTIR) analysis were performed.

Analysis of the Emulsified Bio-Oil

Turbidity method ESI1

In this experiment, two methods were used to evaluate the stability of emulsified oil (Emulsification Stability Index, ESI). The turbidity method was used to evaluate the stability of the emulsified oil. The main principle is measuring the change of the turbidity of the emulsion relative to the standing time. The turbidity of the emulsion is a function of the particle size and concentration, so the turbidity reflects changes in the particle size and concentration of the emulsion. This measurement can be used to characterize the demulsification process (Patil and Gogate 2018). Ultrasonic emulsification experiments were carried out as follows. The emulsified oil fuel was prepared at room temperature. A small amount was diluted 50 times and then examined with a UV755B spectrophotometer (Yoke, Shanghai, China) at 500 nm measure absorbance values for 0 min and 20 min, and the stability of the emulsification was computed according to Eq. 2 (Wei *et al*. 2013; Xu *et al*. 2017),

$$ESI1 = \frac{A_o \times \Delta t}{\Delta A} \tag{2}$$

where A_o is the absorbance value at 0 min, Δt is the time difference (20 min), and ΔA is the change of the absorbance value.

Stability time ESI2

The observation of deformation or complete stratification as the end points of emulsified oil stability has the disadvantages of requiring a long observation time and limited observation conditions and the human error in this method is too large. Therefore, these attributes are not suitable for use as the end points of demulsification. Oil separation is the beginning of emulsion breakage, involving some emulsified oil droplets. As the bio-oil density is greater than that of diesel oil, diesel oil will float on the upper layer of the emulsion and leave the emulsion system. However, this phenomenon is not stable, and the emulsion can be recovered by shaking slightly. The oil deposition time is easier to observe, so this paper uses it as the stabilization time of the emulsified oil (Patil and Gogate 2018).

Characteristic analysis

The heat value was measured with a bomb calorimeter (Youxin Ltd., Changsha, China), and the viscosity was measured with a petroleum kinematic viscosimeter (SYP1026-II; Tianjin Jingyi Industry and Trade Co., Tianjin, China). The density was determined by measuring the volume with a graduated cylinder and then using the densitometer method to calculate the corresponding value. The water content was measured by Karl Fischer titration using an AKF-2010V moisture instrument (Shanghai HeGong Scientific Instruments Co., Shanghai, China). The pH value was tested by using a Five Easy Plus pH meter (Mettler Toledo, Columbus, OH, USA), and the TGA was carried out with an STA449C Jupiter synchronous thermal analyzer (NETZSCH, Selb, Germany). The sample was confirmed to be stable before each sampling. Approximately 8 mg was weighed out for each sample, the heating rate was set to 10 °C/min, the carrier gas was air, and the flow rate was set to 80 mL/min. The TG curve of the sample during heating was recorded. To investigate the stability of the mixture, samples were taken at the same position of the mixture on the 0th day, the 10th day, and the 20th day for testing. The FTIR analysis was carried out on a Thermo Fisher Nicolet iS10 spectrometer (Waltham, MA, USA). For each analysis, a 0.01 g blended sample was taken by syringe from the middle of the tube, the location was marked on the tube, and the sample was mixed with 1 g of KBr. The sample was then put into a pressure machine and compressed into sheets, which were then used for the FTIR analysis. The scanning was carried out in the range from 450 to 4000 cm^{-1}, with a typical resolution of 1.0 cm^{-1}. For comparison, after 0 d, 10 d, and 20 d, additional samples were taken from the same place in the tube. The measurements on the liquid products were performed using an Agilent 7890B-5977A gas chromatography-mass spectrometer (GC-MS) system (Santa Clara, CA, USA) equipped with a column of Ptx-Wax (Agilent, State of California, USA) with dimensions of 30.00 m × 0.25 mm × 0.25 μm. The above methods are similar to that used in a previous study (Xu *et al.* 2018).

RESULTS AND DISCUSSION

Analysis of Characteristics of the Experimental Materials

The characteristics of the bio-oil

The raw material used in this experiment was wood chip biomass gasification oil, which was obtained from Dongguan Longzhen Environmental Protection Co. (Dongguan, China). The heavy oil is a black, viscous liquid with a pungent odor and poor fluidity. The physical and chemical properties of the bio-oil are shown in Table 1.

As shown in Table 1, carbon was the most abundant component in the heavy oil, at up to 58.04%. Therefore, the bio-oil had a high heat value. The heat value was 22.1 MJ/kg, the water content was 6.68%, and the oxygen content reached 31.3%. A high oxygen content reduces the heat value of a bio-oil, makes it corrosive, and affects the stability of the bio-oil. Table 2 shows the results of the GC-MS analysis of the bio-oil. The results showed that the main components of the bio-oil were benzene and its derivatives and phenol derivatives. The addition of composite emulsifiers with different HLB values and methanol emulsifiers can improve the heating value of bio-oils and reduce their viscosity.

Table 1. Basic Characteristics of the Raw Materials

Raw Material		Heavy oil	Diesel	Methanol
Density (g/mL)		1.28	0.85	0.79
Moisture Content (%)		6.68	0	<0.5%
Heat Value (MJ/kg)		22.12	42.00	0.73
Viscosity (mm^2/s)	30 °C	4,130.70	4.27	0.68
	40 °C	2,278.50	3.63	-
	50 °C	1,470.00	1.68	-
C (%)		58.04	84.07	-
H (%)		6.99	13.38	-
O (%)		31.34	2.55	-
N (%)		3.63	0	-

The characteristics of methanol

The basic characteristics of methanol are shown in Table 1. The moisture content was less than 0.5% and the viscosity was 0.698 mm^2/s (25 °C). Methanol was used as a mutual solvent to improve the heat value and reduce the viscosity of the bio-oil. The FTIR spectrum of methanol, shown in Fig. 1c, was used to examine its functional groups. The characteristic peak at 3390 cm^{-1} was due to O-H stretching vibrations. The spectrum exhibited the presence of water and alcohols. The peak at 2865 cm^{-1}, which occurred due to aliphatic C-H stretching vibrations, was also observed in methanol. The peaks at 1454 and 1345 cm^{-1} were due to C-H-(CH_3) structural bending through symmetrical or asymmetrical vibrations. The peak at 1015 cm^{-1} was attributed to C-O stretching vibrations (Assanvo *et al*. 2015). The TGA curve of methanol is shown in Fig. 1d. Due to the high volatility of methanol, the 25 to 53 °C stage was a fast-weight loss stage, in which the weight loss reached 90%. A small amount of residual non-volatile components was decomposed over 100 °C. The final residue yield was approximately 5%.

The characteristics of the conventional petroleum-based diesel

The 0# diesel was obtained from Zhongyou Bijie Guangdong Petroleum Co. (Guangzhou, China). The physical and chemical properties of the diesel are shown in Table 1. The diesel had a higher heating value of 42.00 MJ/kg, a carbon content of 84.07%, and a low oxygen content of 2.55%, which lends good combustion performance. The FTIR spectroscopy was used to observe the functional groups of diesel oil, as shown in Fig. 1a. The characteristic peaks at 2845 cm^{-1} to 2870 cm^{-1} and 2915 cm^{-1} to 949 cm^{-1}, which occurred due to aliphatic C-H stretching vibrations, were also observed in diesel oil (Lin *et al*. 2016; Xu *et al*. 2018). The peaks at 1446 cm^{-1} to 1486 cm^{-1} and 1371 cm^{-1} to 1382 cm^{-1} were attributed to C-H bending through symmetrical, asymmetrical, or scissoring vibrations (Assanvo *et al*. 2015; Kaci *et al*. 2017). The TG and derivative thermogravimetric (DTG) curves are shown in Fig. 1b. The combustion could be approximated as occurring in only one stage according to the DTG curves. There was a rapid weight loss at 30 °C to 200 °C due to the volatilization and pyrolysis of some organics with low boiling points. The weight loss in the stage below 200 °C reached 87%. The final residue yield was approximately 5%.

Table 2. The GC-MS Analysis of the Bio-Oil

Entry	Retention (time/min)	Area (%)	Library ID
1	7.68	4.4	Acetic acid
2	10.07	1.5	Butanoic acid, 4-hydroxy-
3	10.48	1.62	2-Furanmethanol
4	11.53	1.12	Acetamide
5	12.41	2.47	1,2-Cyclopentanedione, 3-methyl-
6	12.80	6.54	Phenol, 2-methoxy-
7	12.96	0.98	2-Methoxy-5-methylphenol
8	13.92	5.92	Creosol
9	14.52	7.6	Phenol
10	14.97	4.09	Phenol, 4-ethyl-2-methoxy-
11	15.74	3.2	p-Cresol
12	15.88	2.15	Phenol, 3-methyl-
13	16.34	1.62	Phenol, 2-methoxy-4-propyl-
14	17.36	1.73	3-Allyl-6-methoxyphenol
15	17.47	1.27	Phenol, 3,4-dimethyl-
16	18.95	1.63	trans-Isoeugenol
17	19.05	16	Phenol, 2,6-dimethoxy-
18	21.28	1.62	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose
19	21.67	7.87	Benzene, 1,2,3-trimethoxy-5-methyl-
20	22.54	1.18	5-Hydroxymethyldihydrofuran-2-one
21	23.93	2.59	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
22	25.15	1.52	n-Nonadecanol-1
23	25.234	1.54	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
24	25.632	1.62	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-
25	27.023	6.72	Phenol, 2,6-dimethoxy-4-(2-propenyl)-

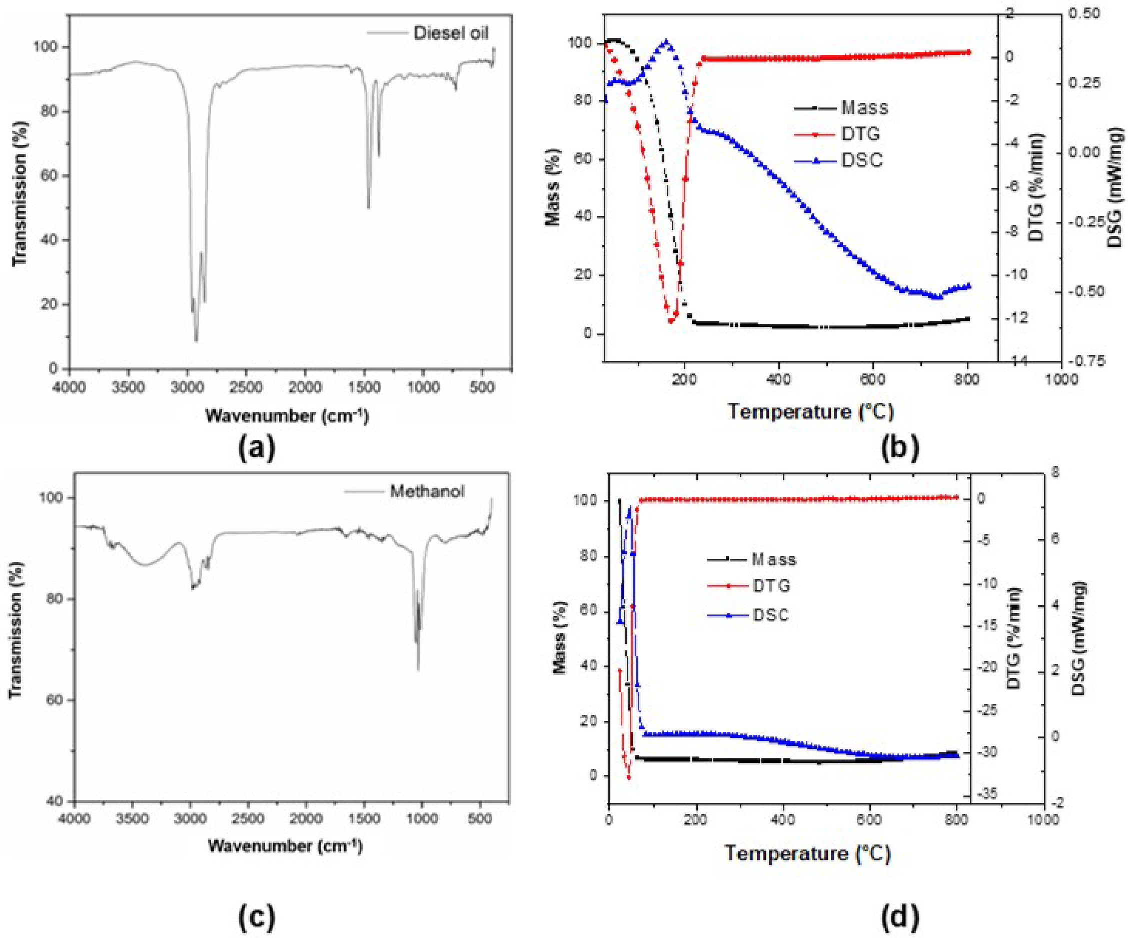


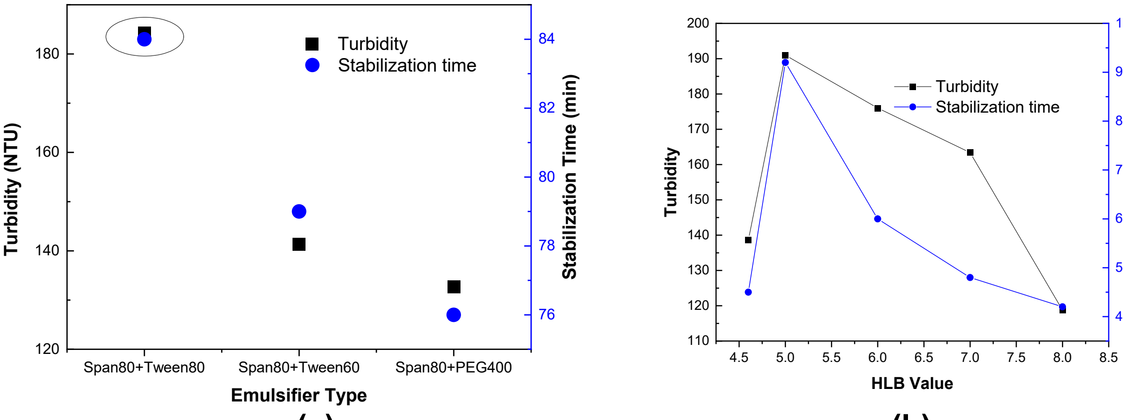
Fig. 1. The a) FTIR spectrum of the diesel, b) TGA of the diesel, c) FTIR spectrum of the methanol, and d) TGA of the methanol

Influence of Emulsifiers on the Emulsified Oils

Influence of emulsifiers

The stability results of the obtained emulsified oils are shown in Fig. 2a. When the emulsifier type was changed from Span80 and Tween80 to Span80 and Tween60 to Span80 and PEG400, the turbidity of the emulsified oil decreased from 184 to 133 NTU and the stabilization time decreased from 84 to 76 min. When the emulsifier was Span80 and Tween80, the emulsified oil had the best stability, and the turbidity and stabilization time both reached maximum values at 184 NTU and 84 min, respectively. This shows that this emulsifier helped to improve the stability of the emulsified oil. These results are mainly attributable to the emulsifier being able to reduce the interfacial tension to different degrees and form an interfacial film. However, different emulsifiers have different abilities to destroy interfacial tension, and composite emulsifiers can increase the viscosity of the continuous phase and enhance the stability of the emulsion. Different composite emulsifiers have different abilities to increase the viscosity of the continuous phase (Zhao *et al*. 2017). The two emulsifiers Tween80 and Span80 contain sorbitan monooleate in their molecular structures, and their hydrocarbon molecular chains can better attract each other, which is beneficial to the stability of the emulsified oil. Therefore, it is most suitable to select such a composite emulsifier (Xu *et al*. 2017).

It can be seen from Table 3 that compared with diesel, the samples of each group showed no obvious effect on the density and heating value after ultrasonic treatment, and the water content and viscosity were higher than those of conventional diesel fuel. The emulsified oil that contained Span80 and Tween80 and bio-oil had a higher viscosity than diesel after ultrasonic treatment. When the temperature was raised from 30 to 50 °C, the viscosity decreased from 5.87 to 4.01 mm^2/s, a decrease of 31.7%. The heating value for diesel dropped from 42.0 to 40.01 MJ/kg, which was a decrease of only 4.74%. The density of the emulsified oil after ultrasonic treatment was the same as that of diesel, and the water content increased from 0% to 0.16%. In summary, the emulsifier of Span80 and Tween80 showed the best performance.



(a) (b)

Fig. 2. The turbidity and stabilization time of emulsified oils based on the a) emulsifier type and b) HLB value

Table 3. Parameters of the Emulsified Oils Under Different Emulsifier Conditions

Item		Density (g/mL)	Water Content (%)	Heat Value (MJ/kg)	Viscosity (mm^2/s)		
					30 °C	40 °C	50 °C
Emulsifier type	Span80+Tween 80	0.85	0.16	40.01	5.87	4.56	4.01
	Span80+Tween 60	0.87	0.16	40.40	5.38	4.93	4.34
	Span80+PEG40 0	0.89	0.13	40.11	5.78	4.60	4.08
HLB value	4.6	0.88	0.15	39.87	5.95	4.51	4.03
	5	0.88	0.19	39.94	5.87	4.56	4.01
	6	0.85	0.17	39.67	5.88	4.84	4.59
	7	0.88	0.16	39.43	5.91	4.91	4.71
	8	0.88	0.13	39.67	5.93	4.98	4.74

Note: a: The ratio of bio-oil and diesel= 5%:95%; the power density and time of ultrasonic: 0.96 w/mL, 15 min; 5% methanol and 5% assisted emulsifier).
b: The ratio of bio-oil and diesel= 5%:95%; the power density and time of ultrasonic: 0.96 w/mL, 15 min; 5% methanol and 5% assisted emulsifier (Span80+Tween80) with HLB values of 4.6, 5, 6, 7, and 8.)

Influence of the HLB values

The effect of different HLB values on the emulsification was studied. The stability results of the obtained emulsified oils are shown in Fig. 3a. As the HLB value increased, the turbidity and stability time of the emulsified oils showed a trend of first increasing and then decreasing. When the HLB value was five, the emulsified oil had the best stability and the turbidity and the stabilization time reached the maximum values of 191.0 NTU and 92 min, respectively. The results showed that when the emulsifier HLB value was five, the emulsification effect was the best. As the HLB value increased, the stability of the emulsified oils gradually deteriorated, which was attributed to the increase of hydrophilic groups and the decrease of lipophilic groups in the emulsifiers. An increase in the amount of bio-oil in each emulsified oil droplet increased the droplet size and decreased the droplet number, which finally led to deterioration of the stability of the emulsified oil droplets. This may be attributed to the demulsification rate of the stable emulsified oil being greater than that of the poor-stability emulsified oil in the early stage (Wei and Wang 2013; Lin *et al*. 2016; Yu *et al*. 2018).

The physicochemical properties of the emulsified oils are shown in Table 4. Compared with conventional diesel, the samples of each group showed no obvious effect on the density and heat value after ultrasonic treatment, and the water content and viscosity were higher than those of diesel. When the HLB value was five, the viscosity after ultrasonic treatment was higher than that of diesel. When the temperature was raised from 30 to 50 °C, the viscosity decreased from 5.87 to 4.01 mm^2/s, a decrease of 31.7%. The heat value of diesel dropped from 42.0 to 39.9 MJ/kg, a decrease of only 4.90%. The density of the emulsified oil after ultrasonic treatment was 3.53% higher than that of diesel, and the water content increased from 0% to 0.19%. In summary, the performance of the HLB value of five was better than that of the other treatment groups.

Influence of Ultrasonication on the Emulsified Oils

Influence of ultrasonic power density

As shown in Fig. 3a, both the turbidity and the stabilization time of the emulsified oils first increased and then decreased with the increase of the ultrasonic power density. The stability of the emulsified oil before ultrasonication was 0.96 w/mL and the turbidity value, ESI 1, and the stable time, ESI 3, of the emulsified oils showed an upward trend as the power density increased. When the ultrasonic power density exceeded 0.96 w/mL, both the turbidity value ESI 1 and the stabilization time ESI 3 of the emulsified oils tended to decrease. The power density of 0.96 w/mL was the best power density value for the preparation of a stable emulsified oil. The emulsified oil had the best stability, and the turbidity and stability time reached the maximum values, which were 191 NTU and 81 min, respectively. Therefore, when the ultrasonic power density was low, the cavitation threshold was not reached such that the cavitation effect was not obvious, and the emulsification could not be completed (Canselier *et al*. 2002; Agarwal *et al*. 2016; Kaci *et al*. 2017; Zhao *et al*. 2017; Kichatov *et al*. 2018; Xu *et al*. 2018). When the intensity of ultrasonication exceeds the cavitation, a further increase in the ultrasound intensity will increase the yield of the chemical reaction and the cavitation effect. However, sound intensity has certain limits beyond which, if the cavitation bubble in the expansion of the ultrasonic phase were to increase, the cavitation bubble could collapse in the compression phase of the sound wave. In this way, the chemical production rate tends to be saturated or even falls under the action of the ultrasound (Wei *et al*. 2013). However, continuing to increase the ultrasonic power density can cause the droplets to coalesce, which can impair the stability of the emulsified oil (Guo *et al*. 2011; Hamidi *et al*. 2015; Hashtjin and Abbasi 2015; Hosseini *et al*. 2015; Kobayashi *et al*. 2015).

It can be seen from Table 4 that compared with conventional diesel, the samples of each group showed no obvious effect on the density and heat value after ultrasonic treatment, and the water content and viscosity were higher than those of diesel. When the ultrasonic power density was 0.96 w/mL, the viscosity after ultrasonic treatment was higher than that of diesel. When the temperature was raised from 30 to 50 °C, the viscosity decreased from 5.87 to 4.01 mm^2/s, a decrease of 31.7%. The heating value of diesel dropped from 42.0 to 39.7 MJ/Kg, a decrease of 5.45%. The density of the emulsified oil after ultrasonic treatment was 3.53% higher than that of diesel, and the water content increased from 0% to 0.55%. In summary, when the ultrasonic power density was 0.96 w/mL, the emulsified oil showed the best performance.

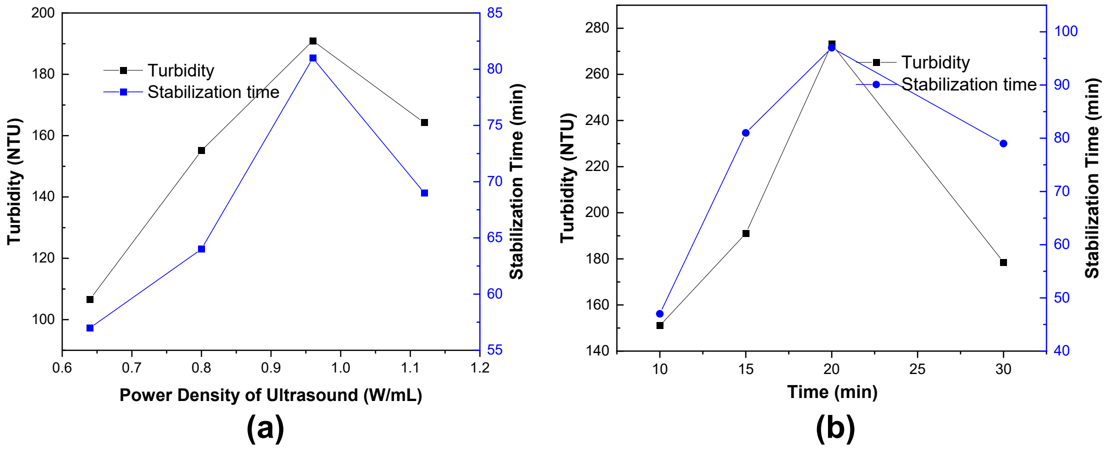


Fig. 3. The turbidity and stabilization time of emulsified oils graphed against the a) ultrasonic power density and b) ultrasonic time.
Note: a: The ratio of bio-oil and diesel= 5%:95%; the power density of ultrasonic: 0.64 w/mL, 0.80 w/mL, 0.96 w/mL, and 1.12 w/mL; the time of ultrasonic: 15 min, 5% methanol and 5% assisted emulsifier (Span80+Tween80) with an HLB value of 5.
b: The ratio of bio-oil and diesel= 5%:95%; the power density of ultrasonic: 0.96 w/mL, the time of ultrasonic: 10 min, 15 min, 20 min, and 30 min; 5% methanol and 5% assisted emulsifier (Span80+Tween80) with an HLB value of 5.

Table 4. Parameters of the Emulsified Oils Under Ultrasonication Conditions

Item		**Density (g/mL)**	**Water Content (%)**	**Heat Value (MJ/kg)**	**Viscosity (mm^2/s)**		
					30 °C	40 °C	50 °C
Power density (w/mL)	0.64	0.88	0.18	39.84	5.32	4.49	4.01
	0.80	0.88	0.29	39.93	5.49	4.84	4.42
	0.96	0.88	0.55	39.71	5.87	4.56	4.01
	1.12	0.89	0.25	39.94	5.81	5.13	4.33
Time (min)	10	0.89	0.31	39.59	5.36	4.46	4.04
	15	0.88	0.31	39.71	5.87	4.56	4.01
	20	0.89	0.32	40.07	6.01	5.10	4.46
	30	0.89	0.39	40.14	5.92	4.49	3.81

Influence of the ultrasonic time

As shown in Fig. 3b, both the turbidity and the stabilization time of the emulsified oil first increased and then decreased with the increase of the ultrasonic time. When the ultrasonic time was less than 20 min, the stability of the emulsified oil increased with time and both the turbidity value ESI 1 and the settling time ESI 3 showed an upward trend. When the ultrasonic time exceeded 20 min, both the turbidity value ESI 1 and the settling time ESI 3 of the emulsified oil showed a downward trend. The results showed that the ultrasonic time of 20 min was the best time to prepare stable emulsified oils. The produced emulsified oil had the best stability, and the turbidity and stabilization time reached the maximum values of 273 NTU and 97 min, respectively. In this work, the emulsion droplets continuously collided during phacoemulsification, causing the possibility of droplet fusion and crushing. When the two opposite processes reached equilibrium, the emulsion remained stable. The optimum ultrasonic time was the time during which the two processes reached equilibrium, at which point the reaction was near equilibrium (Guo *et al*. 2011; Hamidi *et al*. 2015; Hashtjin and Abbasi 2015; Hosseini *et al*. 2015; Kobayashi *et al*. 2015). In addition, since the ultrasonic cavitation process generated a large amount of heat, the treatment time was too long, which caused the temperature of the mixed fuel to rise sharply, and the excessive temperature was also unfavorable for the stability of the emulsified oil. The above results indicated whether the ultrasonic processing time was too short or too long, which was not conducive to improving the emulsion stability (Mohsin and Meribout 2015; Leong *et al*. 2017; van Zwieten *et al*. 2017; Leng *et al*. 2018).

As can be seen in Table 4, the samples of each group showed no obvious effect on the density and heat value after ultrasonic treatment compared with diesel, and the water content and viscosity were higher than those of diesel. This effect may have been because as the emulsification time was further increased, the temperature of the emulsification system also increased. Therefore, the light component was more volatile. At the same time, the moisture content increased, which promoted the homopolymerization reaction to produce an oligomer or a polymer such that the viscosity increased (Xu *et al*. 2018). When the ultrasonic time was 20 min, the viscosity after the ultrasonic treatment was higher than that of diesel. When the temperature was raised from 30 to 50 °C, the viscosity decreased from 6.01 to 4.46 mm^2/s, a decrease of 25.8%. The heat value of diesel dropped from 42.0 to 40.1 mm^2/s, a decrease of 4.6%. The density of the emulsified oil after ultrasonic treatment was 4.7% higher than that of diesel, and the water content increased from 0% to 0.32%. In summary, when the ultrasonic power density was 0.96 w/mL, the emulsified oil showed the best performance.

Influence of the Bio-Oil Ratios on the Emulsified Oils

Influence of the bio-oil ratios

The effect of changing the bio-oil content on the stability of emulsified oil was studied. The stability results of the obtained emulsified oils are shown in Fig. 4a. As the bio-oil dosage increased, the turbidity and stability time of the emulsified oil showed a trend of first increasing and then decreasing. When the bio-oil content was 5%, the emulsified oil had the best stability, and the turbidity and stability time reached the maximum values of 280 NTU and 92 min, respectively. When the bio-oil content was too low, a portion of the diesel oil was not involved in the emulsification, and the condensation of the oil droplets led to poor stability of the emulsion. Since the diesel density was lower than that of the emulsified oil, the diesel oil that had not been involved in the emulsification after a certain period of storage floated on the liquid surface, resulting in an early oil deposition phenomenon. As the bio-oil content increased, the stability of the emulsified oil was strengthened. However, the bio-oil content continued to increase, and the stability of the emulsified oil began to weaken. Concerning the stability time, when the bio-oil content was 5%, the stabilization time was the longest. This indicated that within a certain range, the stabilization time was proportional to the bio-oil content. Meanwhile, the W/O-type droplets that formed in the emulsified oil had almost reached saturation, so the amount of bio-oil was continuously increased and the effect of enhancing the stability of the emulsified oil was not obvious. This indicated that a higher bio-oil content diminishes the stability of the emulsified oil.

The physical and chemical properties of the obtained emulsified oils were obviously different. As the proportion of bio-oil increased, the water content and viscosity of the emulsified oils showed an increasing trend. However, the heat value showed a downward trend. It can be seen from Table 5 that compared with conventional diesel, the samples of each group showed little effect on the density and heat value after ultrasonic treatment and the water content and viscosity were higher than those of diesel. When the bio-oil content was 5%, the viscosity after ultrasonic treatment was higher than that of diesel. When the temperature was raised from 30 to 50 °C, the viscosity decreased from 5.87 to 4.01 mm^2/s, a decrease of 31.7%. The heating value of diesel dropped from 42.0 to 39.5 MJ/kg, a decrease of only 5.93%. The density of the emulsified oil after ultrasonic treatment was 1.18% lower than that of diesel, and the water content increased from 0% to 0.79%.

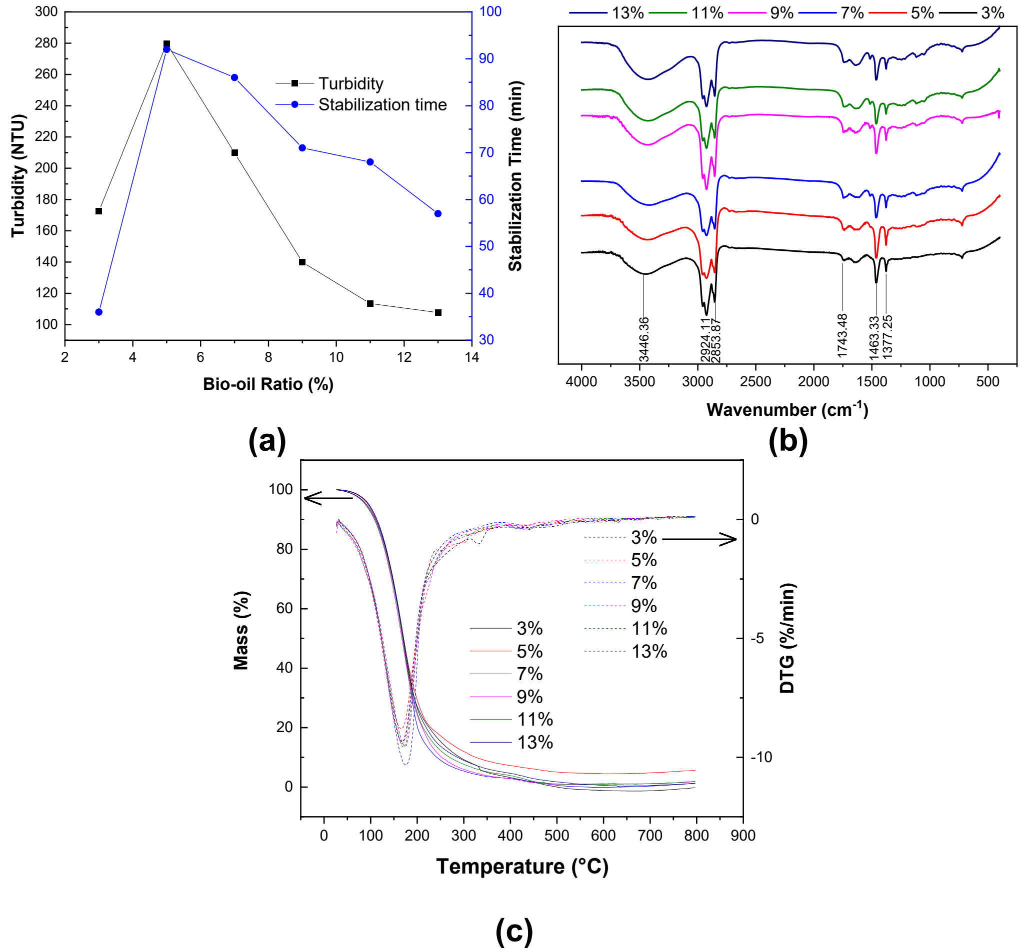


Fig. 4. Graphs of the a) turbidity and stabilization time, b) FTIR analysis, and c) TGA for the different emulsified oils
Note: The ratio of bio-oil and diesel= 3%:97%, 5%:95%, 7%:93%, 9%:91%, 11%:89% and 13%:87%; the power density and time of ultrasonic: 0.96 w/mL, 15 min; 5% methanol and 5% assisted emulsifier (Span80+Tween80) with an HLB value of 5.

Table 5. Parameters of the Emulsified Oils Obtained Under Different Bio-Oil Content Conditions

Ratio (%)	Density (g/mL)	Water Content (%)	Heat Value (MJ/kg)	Viscosity (mm^2/s)		
				30 °C	40 °C	50 °C
3	0.82	0.75	39.88	5.49	4.39	4.00
5	0.84	0.79	39.51	5.87	4.56	4.01
7	0.86	0.91	39.26	6.01	4.81	4.07
9	0.86	1.51	39.08	6.36	5.17	4.20
11	0.87	1.83	38.33	7.60	5.25	4.70
13	0.90	2.11	38.03	11.05	7.94	6.49

FTIR analysis of the emulsified oils

The FTIR spectra of the different bio-oil ratios are shown in Fig. 4b. The characteristic peak at 3446 cm^{-1} was attributed to O-H stretching vibration, the characteristic peak at 2924 cm^{-1} was attributed to aliphatic C stretching vibration, and the characteristic peak observed at 2853 cm^{-1} was the result of stretching of the aliphatic C-H in the emulsion, which indicated the presence of the alkyl group C-H. The C=O stretching corresponds to the ester at 1743 cm^{-1}, and the peak at 1463 cm^{-1} was attributed to the symmetrical bending of C-H-(CH_3) or the complete asymmetry bending of C-H-(CH_2), which indicated the presence of alkyl C-H groups. The final characteristic peak at 1377 cm^{-1} was mainly due to the bending vibrations of the C-H-(CH_3) groups of hydrocarbons in the diesel component (Renuga and Gayathri 2010; Assanvo *et al*. 2015; Lin *et al*. 2016; Xu *et al*. 2018). The FTIR spectrum shown in Fig. 4b depicts that the curves for the six emulsified oils were consistent, which indicated the uniformity and stability of the emulsified oil.

TGA analysis of the emulsified oils

Figure 4c shows the TGA results of the emulsified oils with different bio-oil ratios. As seen in Fig. 4c, the ratio of the bio-oil did not have an obvious effect on the TG changes of the emulsified oils, and the maximum weight-loss rate occurred at approximately 170 °C. The results showed that the emulsified oils can be burned in the middle- and low-temperature stages. When the temperature was 400 °C, the weight loss was above 93% and the characteristics of the emulsified oils were obviously improved.

Influence of Co-Emulsifiers on the Emulsified Bio-Oils

Influence of co-emulsifiers

In general, to improve the stability of emulsified oils, the molecular critical arrangement parameters of the surfactant can be regulated by temperature. For bio-oil emulsifications, the temperature must be adjusted and a small amount of co-emulsifier must be added to promote the formation of a stable emulsified oil. This is mainly related to the complex composition of biofuels (Zhang *et al*. 2009). With the other conditions unchanged, the effects of different oil-to-alcohol ratios (2:3, 1:1, and 3:2) on the stability of the bio-oil were studied. The effects of the co-emulsifier on the stability of the bio-oil are shown in Table 6. The results showed that the stability of the emulsified oil was better under the action of methanol, and the stability time exceeded 24 h. When the oil-to-alcohol ratio was 1:1, the turbidity value of the emulsified oil could reach 664 NTU. Methanol was advantageous for forming a stable bio-oil emulsion, which may be because its oleophilic alkyl chain has a moderate length and is easily linked to the main emulsifier and oil. Therefore, the mechanical strength of the interface film was improved and the stabilization the emulsified oil was achieved (Zhang *et al*. 2009).

When the oil-to-alcohol ratio was 2:3, the emulsified oil with 5% emulsifier added was more stable than was the control. When the emulsifier content was 5%, the oil-to-alcohol ratios were 2:3 and 1:1, which was beneficial for improving the stability of the emulsified oil. However, as the turbidity value increased with the decrease of the oil-to-alcohol ratio, the oil-to-alcohol ratio continued to decrease, and the stability tended to decrease. This is because when the emulsifier content is constant, excessive addition of methanol is not conducive to the homogenization of the emulsion, which leads to an unstable tendency of the emulsified oil (Tan *et al*. 2013; van Zwieten *et al*. 2017).

The effects of the co-emulsifier on the physicochemical properties of bio-oil are shown in Table 6. Compared with bio-oil, the effects on the density, water content, and heating value of each sample were obvious after the ultrasonic treatment. The density, water content, and heating value were lower than those of crude oil, and the heat value decreased. This is because the addition of methanol can dilute the emulsified oil, reduce the viscosity of the bio-oil, and increase the volatile matter and the heat value of the bio-oil. At the same time, changing the microstructure of the emulsified oil can reduce the reaction rate of the bio-oil. Methanol can also react with the active ingredients in the bio-oil to form an ester or an acetal to effectively prevent the formation of a macromolecular polymer, thereby improving the stability of the emulsified oil (Tan *et al*. 2013; Zhang *et al*. 2017).

As can be seen in Table 6, the addition of an emulsifier was beneficial in improving the density, water content, and heating value. This may be because the cavitation, mechanical vibration, and thermal action of the ultrasonic wave have significant influences on the emulsification effect. In addition, alcohols promote decomposition of the polymer under the action of ultrasonic waves. The addition of methanol facilitated the decomposition of bio-oil, the esterification of acidic compounds, and ultimately produced a low-molecular weight polymer, which effectively improved the density, viscosity, and water content of the bio-oil (Guo *et al*. 2011; Agarwal *et al*. 2016; Xu *et al*. 2018; Zhang *et al*. 2018; Zhao *et al*. 2017, 2018).

Table 6. Characteristics of the Bio-Oil and Methanol Emulsions

Bio-Oil: Methanol Ratio	Turbidity	Stabilization Time (h)	Density (g/mL)	Water Content (%)	Heat Value (MJ/kg)
2:3 (0% Emulsifier)	125.85	>24h	1.01	3.48	20.38
2:3 (5% Emulsifier)	274.02	>24h	1.00	3.10	20.48
1:1 (5% Emulsifier)	663.74	>24h	1.05	3.85	20.70
3:2 (5% Emulsifier)	75.64	>24h	1.10	4.34	21.57

Note: The ratio of oil-to-alcohol = 2:3, 1:1, and 3:2; the power density and time of ultrasonic: 0.96 w/mL, 20 min, 5% methanol, and 5% assisted emulsifier (Span80+Tween80) with an HLB value of 5.

As can be seen in Fig. 5a, as the ratio of oil-to-alcohol increased, the viscosity of the emulsified oil tended to increase. However, as the temperature increased, the viscosity of the bio-oil tended to decrease. With the increase of time, the viscosity change of the emulsified oil was not obvious, and the emulsified oil was not stratified. The results showed that the emulsified oil had good stability. When the emulsified oil was stored for 0, 10, 20, and 30 d, the viscosities of the emulsified oil at different temperatures were compared. The viscosity of the treatment group to which the emulsifier was added was larger than that of the treatment group to which the emulsifier was not added, and the viscosity of the emulsified oil continuously increased as the ratio of oil-to-alcohol increased. When the ratio of methanol to bio-oil was 2:3, the viscosity reached a maximum.

From Fig. 5b, when the oil-to-alcohol ratio was 2:3, the emulsified oil with 5% emulsifier showed little difference in the heating value, viscosity, and stabilization time compared with the control emulsified oil. This indicated that the addition of an emulsifier had no obvious effect on the characteristics of the emulsified oil. When 5% emulsifier was added, the differences in the heating value, viscosity, and turbidity of the emulsified oil with different oil-to-alcohol ratios were obvious, which indicated that the effect of the oil-to-alcohol ratio on emulsified oil was obvious. When the oil-to-alcohol ratio was 1:1, the heating value of the emulsified oil was higher than those with the oil-to-alcohol ratios of 2:3 (0% emulsifier) and 2:3 (5% emulsifier) and the turbidity value was higher than those of emulsified oils with the oil-to-alcohol ratios of 2:3 (0% emulsifier), 2:3 (5% emulsifier), and 3:2 (5% emulsifier). This indicated good stability, properties more conducive to storage, and much lower viscosity compared to emulsified oil with an oil-to-alcohol ratio of 3:2 (5% emulsifier).

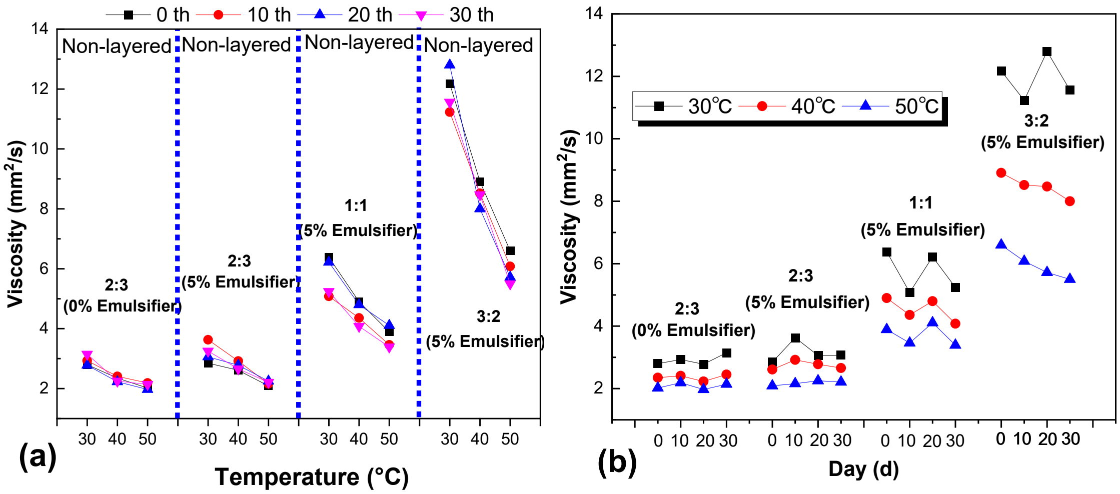


Fig. 5. The viscosity and stratification of the emulsified oils based on the a) temperature and b) time

FTIR analysis of the emulsified oils

The FTIR spectroscopy analysis was performed to observe the changes in the emulsified oil over time. The FTIR spectrum of the emulsified oil after ultrasonic treatment is shown in Fig. 6a. The tensile vibration at 3356 cm^{-1} was observed due to the accumulation of O-H from water, hydroperoxide (ROOH), and their decomposition product alcohol (ROH). The characteristic peak at 2928 cm^{-1} was attributed to the aliphatic C stretching vibration, the C=O stretching corresponded to ester at 1734 cm^{-1}, and the C-C (ring) stretching vibration corresponded to the peak at 1604 cm^{-1}. The characteristic peak at 1465 cm^{-1} was attributed to the symmetrical bending of C-H-(CH_3) or the complete asymmetry bending of C-H-(CH_2), which indicated the presence of alkyl C-H groups. The peak at 1217 cm^{-1} was attributed to the stretching vibrations of C-O (phenol), and the characteristic peak at 1115 cm^{-1} was mainly due to the stretching vibration of the C-O-C groups of esters (Jiang and Ellis 2010; Assanvo *et al*. 2015; Lin *et al*. 2016; Xu *et al*. 2018). The above emulsified oil samples did not separate after standing for 30 d, and spectral changes were not obvious. The results showed that the uniformity and stability of the emulsified oils were good.

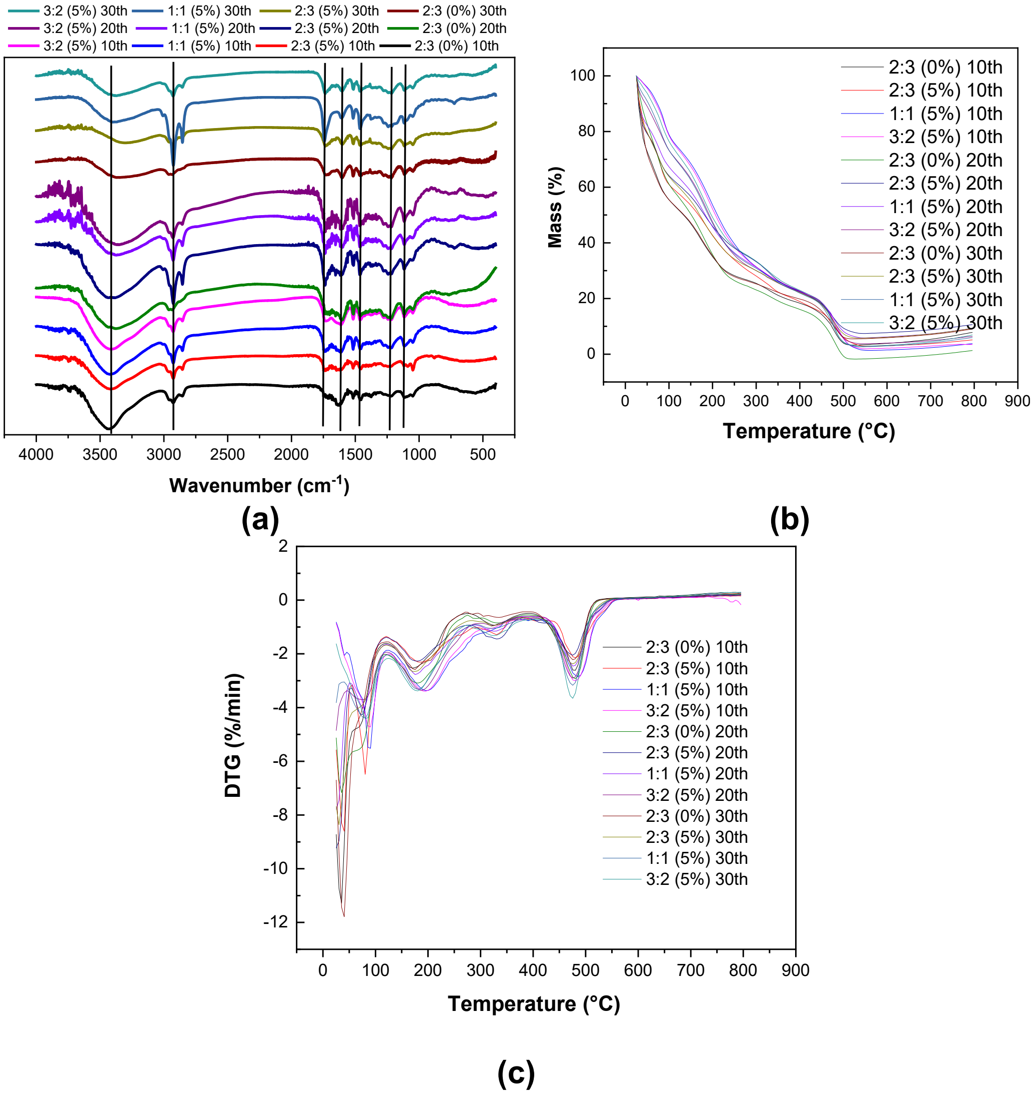


Fig. 6. The a) FTIR, b) TG, and c) DTG graphs of the emulsified oils with different oil-to-alcohol ratios over different time periods.

TGA of the emulsified oils

The TGA curves of different proportions of the emulsified oils are shown in Figs. 6b and 6c. Figure 6c shows that there were four main weight-loss rate peaks and that the maximum weight-loss rates occurred at 81, 188, 331, and 482 °C. The results showed that the emulsified oil had four stages of the combustion process. As can be seen in Fig. 6b, when the temperature exceeded 500 °C, the weight loss was more than 90% and the results showed that most of the substances in the emulsified oil could be completely burned before 500 °C.

The TG data are shown in Table 7. The results showed that the addition of an emulsifier helped to increase the heating value and density of the emulsified oil, making the emulsified oil more easily burned in the high-temperature stage. In the first stage, the weight losses of the 20th and 30th emulsified oils were lower than that of the 10th emulsified oil, which indicated that the 10th emulsified oil contained more macromolecular substances that formed small molecular substances at this stage. However, after 20 and 30 d of storage, the small molecules in the emulsified oil repolymerized to form a macromolecular substance. This indicated that after 10 d of storage, the emulsification effect was obvious and the TG curve gradually shifted to the low-temperature region, which may have been because the macromolecule polymer decomposed to form a small molecular substance, or the acid compound underwent an esterification reaction to generate more water. This caused the bio-oil pyrolysis temperature to shift to a low-temperature region (Xu *et al.* 2017; Xu *et al.* 2018).

Table 7. The TGA of the Emulsified Oils

Emulsified Oil	**First Stage**		**Second Stage**		**Third Stage**		**Fourth Stage**	
	Temp. Range (°C)	Mass Loss (%)	Temp. Range (°C)	Mass Loss (%)	Temperature Range (°C)	Mass Loss (%)	Temp. Range (°C)	Mass Loss (%)
2:3 (0%) 10th	<120.5	47.92	120.5 to 276.5	25.28	276.5 to 393.7	8.18	393.7 to 568.6	15.06
2:3 (5%) 10th	<123.7	42.31	123.7 to 295.5	29.06	295.5 to 376.9	8.05	376.9 to 641.2	17.33
1:1 (5%) 10th	<123.6	26.16	123.6 to 373.5	49.51	373.5 to 628.4	22.68	—	—
3:2 (5%) 10th	<124.9	27.24	124.9 to 412.1	50.85	412.1 to 599.6	19.74	—	—
2:3 (0%) 20th	<116.5	42.80	116.5 to 274.1	32.52	274.1 to 386.2	7.95	386.2 to 574.1	18.28
2:3 (5%) 20th	<120.8	38.97	120.8 to 278.8	25.75	278.8 to 384.1	11.60	384.1 to 643.5	15.56
1:1 (5%) 20th	<121.0	36.23	121.0 to 288.3	31.37	288.3 to 385.4	9.00	385.4 to 641.9	16.81
3:2 (5%) 20th	<122.3	31.07	122.3 to 301.8	39.07	301.8 to 399.5	7.46	399.5 to 647.9	18.10
2:3 (0%) 30th	<123.2	48.16	123.2 to 272.6	25.22	272.6 to 395.0	6.59	395.0 to 658.5	13.53
2:3 (5%) 30th	<120.1	39.70	120.1 to 281.3	28.83	281.3 to 391.5	8.87	391.5 to 564.1	16.74
1:1 (5%) 30th	<123.4	31.78	123.4 to 291.3	36.56	291.3 to 405.3	10.08	405.3 to 583.9	18.74
3:2 (5%) 30th	<123.8	29.10	123.8 to 273.3	34.86	273.3 to 396.7	12.82	396.7 to 583.0	20.16

This also showed that the addition of methanol and an emulsifier can effectively improve the physical and chemical properties of the emulsified oil. In the second stage and third stage, the total weight losses of the 20th and 30th emulsified oils were higher than that of the 10th emulsified oil. In the fourth stage, the 10th emulsified oil had no weight loss and the weight losses of the 20th and 30th emulsified oil increased to over 15%. This indicated that the macromolecular substance was further polymerized, which increased its combustion temperature. The results showed that the 10th emulsified oil was 1:1 (5%) and 3:2 (5%), which was easier to burn in the low-temperature stage. The differences between the weight losses of the two emulsified oils in the first three stages were not obvious, reaching 98.4% and 97.8%, respectively. The results showed that the emulsified oil can be burned in the middle- and low-temperature stages, and its physical and chemical properties could be improved. Considering the viscosity and stability of the emulsified oil, the emulsified oil of 1:1 (5%) was more reasonable.

CONCLUSIONS

1. The effects of the emulsifier type, hydrophile-lipophile balance (HLB) value, ultrasonic power, time, and different bio-oil ratios on the properties and stability of emulsified oils were studied. The results of single factor experiments showed that the turbidity and stabilization time of emulsified oils reached the maximum values of 184.3 NTU and 84 min, 191.0 NTU and 92 min, 279.81 NTU and 92 min, 190.96 NTU and 81 min, and 273.12 NTU and 97 min, respectively, when the conditions were Span80+Tween80 emulsifier, an HLB value of five, a bio-oil ratio of 5%, an ultrasonic power density of 0.96 w/mL, and an ultrasonic time of 20 min, respectively. The FTIR analysis showed that the curves of the emulsified oils of different factors were consistent, and the functional group changes were not obvious, which indicated that the uniformity and stability of the emulsified oils. The thermogravimetric analysis (TGA) results showed that emulsified oils can be burned in the middle- and low-temperature stages. When the temperature was 400 °C, the weight loss was above 93%.
2. The effects of the co-emulsifier methanol on the physical and chemical properties and stability of bio-oil were studied. When the ratio of bio-oil-to-methanol was 1:1, the turbidity value of the emulsified oil was 664 NTU at the maximum and the stabilization time was greater than 24 h, which indicated that the stability was good and storage was more favorable. The FTIR analysis of the stability of the emulsified oils at different treatment times was performed, and the results showed that the emulsified oil was not stratified after 30 d and the spectral change trend was consistent. This indicated that the emulsified oil had good uniformity and stability. The results of the TG experiments showed that the 1:1 (5%) 10th emulsified oil was fully burned in the first three stages and the maximum weight loss was 98.4%.
3. In summary, the physicochemical properties of the emulsified oil obtained from the two emulsion systems of biodiesel and alcohol oil was obviously improved. This indicated that the emulsification method is beneficial to emulsification in industry and provides a new method for the practical application of bio-oil.

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