Fuel Processing Technology 118 (2014) 141–147

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Study on the solubilization capacity of bio-oil in diesel by microemulsion technology with Span80 as surfactant

Xue-li Wang [a,b], Xing-zhong Yuan [a,b,*], Hua-jun Huang [a,b], Li-jian Leng [a,b], Hui Li [c,d], Xin Peng [a,b], Hou Wang [a,b], Yan Liu [a,b], Guang-ming Zeng [a,b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environment Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China
[c] Hunan Academy of Forestry, Changsha 410004, PR China
[d] Hunan Engineering Research Centre for Biodiesel, Changsha 410004, PR China

ARTICLE INFO

Article history:
Received 16 March 2013
Received in revised form 22 August 2013
Accepted 30 August 2013
Available online xxxx

Keywords:
Synthetic bio-oil
Diesel
Span80
N-alkanol
Microemulsification

ABSTRACT

Bio-oils obtained from liquefaction/pyrolysis of biomass have undesired properties such as high water content (15–25 wt.%), high oxygen content (low heating value), high corrosiveness (acidity) and instability. Therefore, they cannot be directly adopted for fuel applications. Solubilizing bio-oil in diesel by microemulsion technology is one of the most convenient approaches for further upgrading bio-oil. In this work, a synthetic bio-oil was prepared to overcome the limitation posed by complex nature and instability of crude bio-oil. Effects of several microemulsion parameters on the solubilization capacity of bio-oil in diesel were evaluated, including initial bio-oil/diesel volume ratio (B/D ratio), surfactant concentration (Span80), cosurfactant type (*n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol) and the mass ratio of cosurfactant/surfactant (C/S ratio). The optimum bio-oil/diesel volume ratio was 5:5. The proper concentration of Span80 was 0.36 M. *N*-octanol was certified as an ideal cosurfactant. A proper C/S ratio of 0.40 was suggested. Meanwhile, fuel properties of bio-oil/diesel microemulsion were examined, including heating value, density, kinematic viscosity, cloud point, pour point, water content, corrosivity and stability. Elemental analysis and thermogravimetric analysis of bio-oil/diesel microemulsion were conducted. Compared with the original synthetic bio-oil, the bio-oil/diesel microemulsion had more desirable fuel properties close to diesel.

1. Introduction

The increasing demand for fossil fuel leads to the rapid development in alternative energy sources such as biomass energy. Bio-oil, produced by fast pyrolysis or liquefaction of biomass, is a promising renewable energy source which has received extensive recognition around the world for its characteristics as combustion fuels used in boiler, engines or gas turbines and resources in chemical industries [1]. Bio-oil is typically a kind of dark brown, free-flowing liquid, but it can be black or green in color depending upon the chemical composition and the amount of microcarbon content [2]. The specific composition of bio-oil is related to the feed and process conditions used [3]. In general, a pyrolysis bio-oil contains more than 400 kinds of organic compounds, mainly including acids, alcohols, aldehydes, esters, ketones, phenols, and lignin-derived oligomers with H/C molar ratio higher than 1.5 [1–5]. Bio-oil obtained from direct conversion processes has the following undesired properties for fuel applications: high water content (15–25 wt.%), high oxygen content (low heating value), high corrosiveness (acidity), etc. Overall, bio-oil cannot be directly used in stationary combustion engines and requires further upgrading [1].

Bio-oil can be upgraded in a number of ways: physically, chemically and catalytically. During the past decade, various techniques have been employed to upgrade bio-oil, including hydrodeoxygenation (HDO) [1–7], supercritical fluids (SCFs) [1,4], catalytic cracking [1,2,4–6], steam reforming [1,5], esterification [1,4–6], emulsification or microemulsification [1,6,9–12], and chemical extracting from the bio-oil [1]. Solubilizing bio-oil in diesel using microemulsion technology is one of the most convenient approaches [12]. Microemulsions are isotropic, transparent, thermodynamically stable colloidal systems consisting of aqueous phase, oil phase and sufficient concentrations of an appropriate surfactant in combination with a suitable cosurfactant [13–15]. Usually, short or medium chain alcohols are used as cosurfactants [13].

In particular, several researchers have carried out the bio-oil/diesel emulsions or microemulsions. Ikura et al. [10,11] developed a process for producing stable microemulsions with 5–30% of bio-oil in diesel with CANMET surfactant. Fuel properties such as heating values, cetane number, viscosity and corrosivity were improved obviously compared with crude bio-oil. Jiang and Ellis [16,17] investigated emulsification of bio-oil in bio-diesel with the aid of *n*-octanol. It was unveiled by the

---

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China. Tel.: +86 731 88821413; fax: +86 731 88823701.
E-mail address: yxz@hnu.edu.cn (X. Yuan).

0378-3820/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fuproc.2013.08.020

report that emulsification mechanism was based on the solubilization of nonpolar substances in reverse-micellar emulsion of diesel and polar substances in the water pool of reverse micelles.

Generally, hydrophilic–lipophilic balance (HLB) system was used to select an optimal surfactant. Griffin [18,19] first established the HLB system to classify nonionic surfactants. According to the HLB system, low HLB values were ascribed to lipophilic surfactants, whereas high values to hydrophilic surfactants. With regard to this system, water/oil (W/O) microemulsions were obtained using surfactants with HLB values of 3–8, while oil/water (O/W) microemulsions were formed using surfactants with HLB values of 9–12 [20]. Span80 (sorbitan monooleate) is a nonionic, oil-soluble surfactant with a HLB value of 4 ± 1 [21], being inclined to form W/O microemulsions. However, to the best of the authors' knowledge, the application of Span80 in solubilizing bio-oil into diesel through microemulsion technology was rarely involved.

In this work, Span80 was adopted as surfactant for upgrading bio-oil through microemulsification technology. Diesel and bio-oil were regarded as continuous phase and dispersed phase of the microemulsion, respectively. As for the dispersed phase of microemulsion, bio-oil does change slowly with time. Its viscosity will increase with time because of continued slow secondary reactions in the liquid. This second reactions are associated with the presence of reactive chemical species, notably aldehydes, ketones, carboxylic acids, alkenes and guaiacol-type molecules. Upon prolonged storage, condensation reactions involving these functional groups result in the formation of heavier compounds [6–8]. Considering of instability of bio-oil, solubilization of synthetic bio-oil into diesel was studied in this work.

The proposed mechanism about solubilizing bio-oil into diesel through microemulsions is based on the “like dissolves like” principle, which is similar to that of solvent extraction technology [22]. This principle means that a polar solute is more soluble in a polar solvent, while a nonpolar solute is more soluble in a nonpolar solvent. As a result, the nonpolar substances of bio-oil were extracted directly into the oil phase, while the polar substances were simultaneously extracted into the water pools of micelles.

The overall goal of this work was to solubilize synthetic bio-oil in diesel for fuel application. Thus, there were four objectives: (1) to study the effects of various microemulsifying factors on bio-oil solubilization capacity, such as initial bio-oil/diesel volume ratio (B/D ratio), surfactant concentration, cosurfactant type (*n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol) and cosurfactant/surfactant mass ratio (C/S ratio); (2) to analyze the properties of bio-oil/diesel microemulsion as fuel, including heating value, density, viscosity, cloud point, pour point, water content, corrosivity, stability, elemental composition and thermogravimetric characteristics; (3) to compare properties of the synthetic bio-oil, diesel with the bio-oil/diesel microemulsion; and (4) to explain the mechanism of solubilizing bio-oil into diesel by microemulsion technology.

2. Experimental section

2.1. Materials

Unless otherwise stated, chemicals were analytically pure. Surfactant was Span80 (sorbitan monooleate, purity >98%) with a HLB value of 4 ± 1. A series of normal alcohols (*n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol) were used as cosurfactant. NO.0 diesel was purchased from a local petrol station, in Hunan Province, China.

Synthetic bio-oil is composed of compounds that represent most reactive functional groups and a similar weight percentage of compound classes that are present in bio-oil. In this work, synthetic bio-oil samples were freshly prepared according to a simple formula (i.e., methanol (5 wt.%), acetaldehyde (12 wt.%), acetic acid (14 wt.%), glyoxal (4 wt.%), acetol (8 wt.%), glucose (8 wt.%), guaiacol (17 wt.%), furfural (4 wt.%), vanillin (8 wt.%) and de-ionized water (20 wt.%)) before each experiment [7]. The following method was used for the preparation of synthetic bio-oil [23]. Initially, glucose and vanillin were mixed in water and oscillated with constant temperature of 25 °C for 2 h, so that both solids would be homogeneously mixed with water. After then, methanol, acetic acid, glyoxal, acetol, furfural, and guaiacol were added. Finally, acetaldehyde was added (as a low boiling point of −20.2 °C). The homogeneous mixture was stored in a cool and dry place. The measured pH value was 2.20.

In the study of phase behavior, the critical micelle concentration (CMC) is defined as the concentration of surfactants in the bulk at which micelles start forming. Surface tension has historically provided one of the most popular means for determining CMC [24]. Based on the surface tension measurements, it could be concluded that the CMC of Span80 in diesel solution was 0.15 M. That meant diesel microemulsion would form spontaneously when the concentration of Span80 was above CMC.

2.2. Bio-oil/diesel microemulsion preparation

Initially, certain amounts of bio-oil and diesel were mixed with a total volume of 10 mL. Span80 and cosurfactant (*n*-alkanol) with given concentrations were injected afterwards. After magnetic stirring at 1000 rpm for 15 min, samples were placed in 10 mL graduated cylinders to equilibrate and the levels of interphase were recorded against time. For all of the above mixtures, a quick separation was observed during 5–10 min. Stratification was finished after standing for 3 h. Properties of the upper layer (bio-oil/diesel microemulsion) were examined in subsequent studies. The runs were conducted at room temperature in triple to obtain an average and standard deviation, expressed as error bars.

Two parameters were proposed to indicate the solubilization capacity. One parameter ***S*** (V/V) was defined as bio-oil volume dissolved in unit volume of diesel. The other ***E*** (L/mol) representing surfactant efficiency was defined as bio-oil volume dissolved in per mole surfactant.

2.3. Bio-oil/diesel microemulsion characterization

2.3.1. Elemental analysis

Generally, biomass is composed of elements C, H, O, N, S, and Cl, where the former three are major, representing up to 97–99% of biomass organic mass [25]. Elemental analyses were carried out by vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Germany). The specific standard method used to analyze C, H, N, and S elements was a local one (General rules for elemental analyzer, JY/T 017-1996, State Education Committee of PR China) [26].

2.3.2. Fuel properties

Viscosity of bio-oil/diesel microemulsion was measured using a kinematic viscosity analyzer at 30 °C (KD-R0515, China). The stability of bio-oil/diesel microemulsion was characterized by viscosity index (*VI*) [9]. The lower the viscosity index is, the more stable the liquid is. The viscosity index was defined in the equation below:

$$VI = \frac{\left(\mu_{t_2} - \mu_{t_1}\right)}{\mu_{t_1}} \tag{1}$$

where *VI* is the viscosity index, μ_{t_1} the viscosity at time t_1 (i.e. before storage) and μ_{t_2} the viscosity at time t_2 (i.e. after 24 h storage at 80 °C).

Heating value was measured using a calorimeter (SDACM500, China). The pH value was measured by a pH determinator (PHSJ-5, China). Cloud point is the temperature at which fuel begins to thicken and become cloudy. Pour point is the temperature at which fuel begins to thicken and no longer pour. Both of them are cold properties of fuels, they were determined by observing the samples to thicken and become cloudy at cold temperature [22]. The water content was measured by a moisture tester for petroleum products (SYD-260A, China). The corrosivity was measured with copper strip corrosion test (CSCT) by ASTM Standard Test Methods D 130 [27], which was based on the discoloration of a standard copper strip immersed into a petroleum product at 100 °C for 3 h.

2.3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed in an integrated thermal gravimetric analyzer (TG/DTA 7300, Japan). TGA crucibles were made out of Pt, which was confirmed to be inert in those experiments. As-received sample masses of approximately 20–40 mg were placed in the thermogravimetric analyzer's crucible. Mass loss was determined during heating from room temperature (25 °C) to 600 °C at a constant heating rate of 10 °C/min in nitrogen atmosphere (65 mL/min).

3. Results and discussion

3.1. Effect of initial B/D ratio and cosurfactant type

The effect of initial B/D ratio and cosurfactant type on bio-oil solubilization capacity was displayed in Fig. 1. Concentration of Span80 and C/S ratio were fixed at 0.36 M and 0.40, respectively. Initial B/D ratio varied from 2:8 to 7:3 (V/V). Five normal alcohols (*n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol) were used as cosurfactants. ***S*** values varied dramatically at different B/D ratios. At initial B/D ratio of 2:8, ***S*** values were close to each other at all studied cosurfactant types. The maximum ***S*** value was 0.14 with *n*-hexanol as cosurfactant. At B/D ratio of 3:7, the maximum ***S*** value was observed with *n*-heptanol as cosurfactant. At ratios above 3:7, the maximum ***S*** values were obtained with *n*-octanol as cosurfactant. Among all the experiment groups, the maximum ***S*** value was 0.56, peaked at B/D ratio 7:3 with *n*-octanol as cosurfactant.

As shown in Fig. 1, without the addition of cosurfactant, ***S*** values initially increased with the increase of B/D ratio and leveled off when the B/D ratio was higher than 6:4. With *n*-hexanol as cosurfactant, a similar variation trend was obtained. In the cases of *n*-heptanol and *n*-octanol, ***S*** values continuously increased. However, when *n*-butanol was adopted as cosurfactant, ***S*** values continuously reduced. As regards *n*-pentanol, ***S*** values increased firstly and then declined. Higher B/D ratios meant that the amounts of bio-oil compositions which solubilized in the diesel increased, while the volume of diesel for per unit bio-oil decreased. Therefore, ***S*** values increased initially with the increase of B/D ratio. When B/D ratio exceeded one critical value, ***S*** values trended to steady. The addition of *n*-heptanol and *n*-octanol significantly enhanced the solubilization of bio-oil and so ***S*** values continuously increased. The performance of *n*-butanol and *n*-pentanol were not unsatisfactory, and their ***S*** values were even lower than that obtained without the addition of alcohol.

S values had different variation trends with the increasing B/D ratio among different cosurfactants, which probably were due to the distinct structures of cosurfactant. Linear alcohols with different carbon numbers had different effects on the solubilization capacity of bio-oil. The standard Gibbs free energy of transfer (ΔG_t) of alcohols from continuous oil phase to interfacial region decreases with the increase of the chain length of linear alcohols (C_4–C_8) [28,29]. It was suggested that microemulsion formed most spontaneously with *n*-octanol as cosurfactant. The correlation between ΔG_t and carbon number of linear alcohols had been investigated previously in some microemulsion systems [30–33]. The smaller the ΔG_t was, the more spontaneously the microemulsion could form.

Parameter $\boldsymbol{E_{max}}$ (the maximum ***E*** value in each B/D ratio group) increased as initial B/D ratio increased, reaching a maximum at B/D ratio of 5:5 with *n*-octanol as cosurfactant (as shown in Fig. 1). With further increasing of B/D ratio, $\boldsymbol{E_{max}}$ values were decreased. Therefore, the maximum volume of bio-oil solubilized in per mole Span80 was 0.40 L/mol at B/D ratio 5:5 with *n*-octanol as cosurfactant. In consideration of $\boldsymbol{E_{max}}$, initial B/D ratio of 5:5 and *n*-octanol were suitable, although the maximum ***S*** was obtained at initial B/D ratio of 7:3.

3.2. Effect of surfactant concentration

Surfactant concentration was one of the most important factors influencing the bio-oil solubilization capacity. C/S ratio and initial B/D ratio were fixed at 0.40 and 5:5, respectively. Nine different Span80 concentration gradients (0.19, 0.28, 0.36, 0.43, 0.50, 0.62, 0.73, 0.82 and 0.98 M) were investigated. The concentration of Span80 represented the molarity of Span80 present in total volume of bio-oil, diesel, surfactant and cosurfactant. In Fig. 2, as the concentration of Span80 increased, parameter ***S*** continuously increased. As regards parameter ***E***, an opposite trend was observed. Comprehensive analysis of *S* and *E*, an appropriate concentration of Span80 (0.36 M) was suggested.

In the study of phase behavior, it was hypothesized that microemulsion was a solution of swollen (reverse) micelles at low volume fractions of solubilized oil (or water) [34,35]. Single particle of microemulsion could be regarded as a micelle, which was divided into spherical micelle and reverse micelle (Fig. 3). Many researches had also been carried out based on this structure [36–38]. In this study, W/O (reverse micelles) microemulsion of diesel formed with Span80 as surfactant, and bio-oil was solubilized in oil phase and/or into the hydrophilic core (etc. water pools) of the reverse micelles. It was well established that the location of a solubilized molecule in a micelle relative to the structural components of the surfactant would be determined primarily by the chemical structure of the additive (Fig. 4) [39]. In diesel solutions, polar additives such as water and acetic acid were intimately associated with hydrophilic core of the micelle (Fig. 4a), while slightly polar

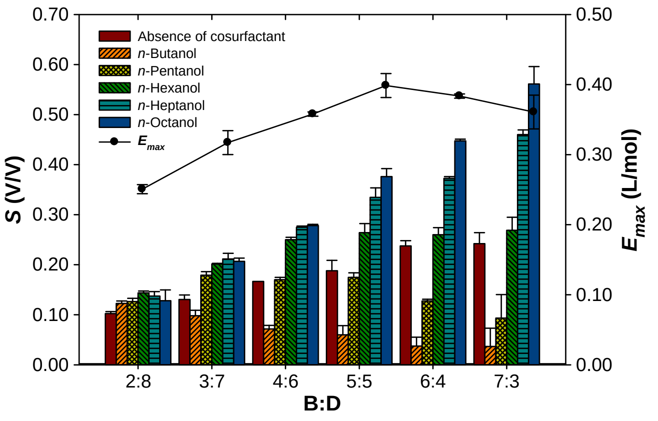

Fig. 1. Effect of initial B/D ratio and cosurfactant type on the bio-oil solubilization capacity.

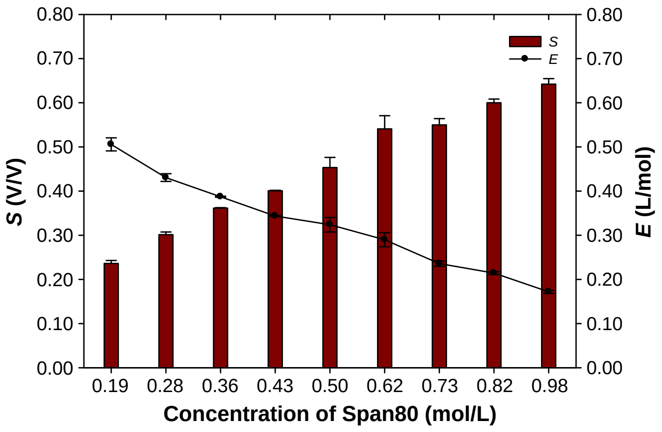

Fig. 2. Effect of Span80 concentration on the bio-oil solubilization capacity.

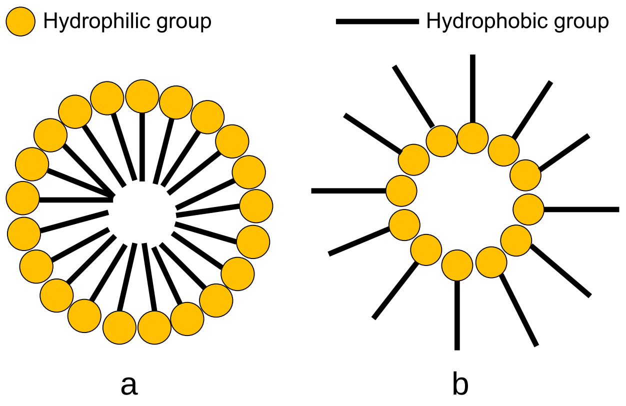

Fig. 3. Two of the proposed micelle shapes: (a) spherical micelle; and (b) reverse micelle.

materials such as long-chain fatty acids and alcohols, esters, amides and the like were usually located in what was termed the "palisades layer" (Fig. 4b) lying near the transition zone between hydrophilic micellar core and the more hydrophobic outer layer of reverse micelle. In addition to the solubilization of additives in micellar core and the core palisades boundary region, those may also be found entirely in the palisades region (Fig. 4c) or on the micellar surface (Fig. 4d).

More specifically, for nonionic surfactant system, the additives would be preferentially located in the palisades region (Fig. 4c) [39]. As the concentration of Span80 increased, superficial area of the palisades region was increased. Therefore, the solubilization capacity of bio-oil in a unit volume of diesel (***S***) was enhanced, and the volume of bio-oil solubilized in per mole surfactant (***E***) was decreased simultaneously.

3.3. Effect of C/S ratio

The effect of C/S ratio on the solubilization capacity of bio-oil in diesel was depicted in Fig. 5. Span80 concentration was fixed at 0.36 M and initial B/D ratio was set at 5:5. *N-octanol* to Span80 ratios varied from 0.00 to 1.20. In Fig. 5, variation tendency of ***S*** was similar to that of ***E***. Both of them were increased with the increase of C/S ratio. Moreover, heating value of bio-oil/diesel microemulsion was measured. As shown in Fig. 5, with the increase of C/S ratio, heating value continuously decreased.

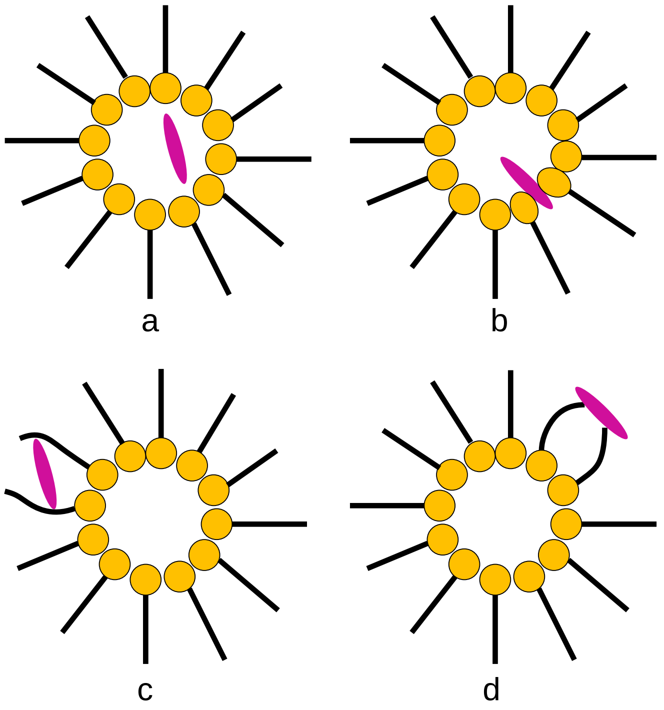

Fig. 4. Location for the solubilization of additives in micelles.

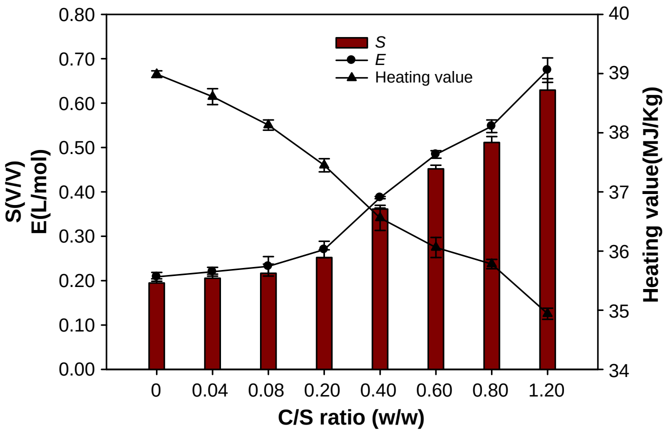

Fig. 5. Effect of C/S ratio (w/w) on the bio-oil solubilization capacity.

Addition of a cosurfactant, usually an alcohol or amine of short or medium chain length, could contribute to reduce interfacial tensions between the two immiscible phases and increase adsorption at the interface [39]. As the relatively large differences in size between the surfactant and cosurfactant, the alcohol molecules, which had a cross-sectional area of only a few square angstroms, could efficiently pack themselves between the larger surfactant chains at the interface. It was supported in Fig. 6 that as the C/S ratio increases, the superficial area of the palisades region was enhanced. As a result, the solubilization capacity of bio-oil in diesel was promoted. So ***S*** and ***E*** values were increased with the increase of C/S ratio.

As shown in Fig. 5, a fact must be noted that the more the amounts of bio-oil solubilized in diesel were, the worse fuel properties of bio-oil/diesel microemulsions would be, which was demonstrated by the significant decrease of heating value. Based on an overall consideration of various factors, the C/S ratio of 0.40 was optimized.

3.4. Property analysis

A comparison of bio-oil/diesel microemulsions with different surfactant concentrations was shown in Fig. 7. As the concentration of Span80 increased, the volume of the lower layer was decreased with color fading. This demonstrated that compounds of bio-oil were solubilized in diesel, and the solubilizing amount rose with the increase of concentration of Span80. This phenomenon occurs because Winsor II systems are formed, comprising a top water-in-oil microemulsion phase in equilibrium with a bottom excess water phase [40,41].

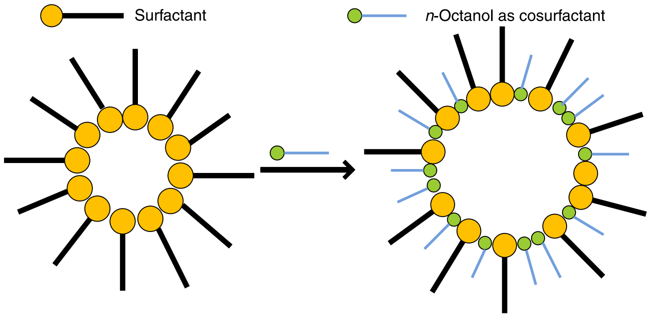

Fig. 6. Proposed mechanism for the role of *n*-octanol as cosurfactant in increased solubilization capacity of diesel microemulsion.

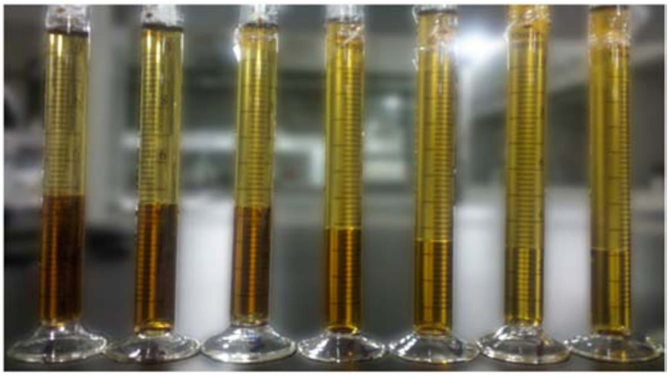

Fig. 7. Bio-oil/diesel blend with different surfactant concentrations.

Properties of bio-oil/diesel microemulsion, synthetic bio-oil and diesel were characterized and systematically compared. Bio-oil/diesel microemulsion examined was obtained under the following conditions: B/D ratio was 5:5 (V/V), concentration of Span80 was 0.36 M, *n*-octanol as cosurfactant and C/S ratio was 0.40.

3.4.1. Elemental analysis

It was indicated in Table 1 that approximately 50% oxygen content was involved in synthetic bio-oil, which was much lower in diesel (8.06%). On the whole, elemental compositions of bio-oil/diesel microemulsion were more similar to those of diesel. Heating values of synthetic bio-oil, diesel and the bio-oil/diesel microemulsion were 16.85, 44.51 and 36.56 MJ/kg, respectively. Due to the solubilization of bio-oil into diesel, heating value of bio-oil/diesel microemulsion decreased a little compared with diesel.

3.4.2. Fuel properties

Fuel properties of synthetic bio-oil, diesel and bio-oil/diesel microemulsion were measured, including density, kinematic viscosity, cloud point, pour point, water content and corrosivity. A viscosity index (*VI*) was proposed to evaluate the stability of the fuel. A summary of these measurements is shown in Table 2.

Kinematic viscosity and viscosity index of bio-oil/diesel microemulsion were much higher than those of bio-oil and diesel, which might be ascribed to the addition of Span80. Because the kinematic viscosity of Span80 reached up to 1000 mm^2/s. Kinematic viscosity of bio-oil/diesel microemulsion was 8.417 mm^2/s, and it was still acceptable compared with the standard value of NO.0 diesel. According to GB252-2011 (national standards of PR China), kinematic viscosity of NO.0 diesel was 3.0–8.0 mm^2/s (20 °C) [42].

Cloud point and pour point of bio-oil/diesel microemulsion were −2 °C and −20 °C, respectively, close to that of diesel (−4 °C and −23 °C), which was promising for fuel applications. Water content of bio-oil/diesel microemulsion was 2.74%, much lower than the original synthetic bio-oil (19.7%), which indicated that most of water in the bio-oil cannot be dispersed in the bio-oil/diesel microemulsion. It was consistent with the Winsor II systems mentioned above. The results of copper strip corrosion test (CSCT) indicated that the corrosivity of bio-oil/diesel microemulsion was reduced to 1a, compared to the bio-oil (1b). With respect to the viscosity index, the lower the viscosity index is, the more stable the liquid is.

In total, compared to the original bio-oil, bio-oil/diesel microemulsion presented more desirable fuel properties which were close to diesel. These above results may indicate that bio-oil/diesel microemulsion formed in this study has great potential to be utilized as fuel.

3.4.3. Thermal analysis

Thermogravimetry (TG) and derivative thermogravimetric (DTG) curves of synthetic bio-oil, diesel, bio-oil/diesel microemulsion and Span80 under nitrogen atmosphere purge of 65 mL/min and heating rate of 10 °C/min were presented in Fig. 8. In Fig. 8a, TG curve of synthetic bio-oil indicated a gradual weight loss from room temperature (25 °C) to 500 °C, which is consistent with a previous study [43]. DTG curve of synthetic bio-oil was indicative of three-step thermal weight loss mechanisms, and peak maximum (i.e. the maximum degradation rate) appeared at 117.7 °C and 46.56% weight loss of sample. The initial weight loss between 25 °C and 130 °C of synthetic bio-oil was attributed to the loss and decomposition of water and highly volatile compounds, such as methanol, acetaldehyde, acetic acid and glyoxal. Compounds with higher cracking energy (acetol, guaiacol and furfural) were decomposed at 130–260 °C. Meanwhile, weight loss at 260–500 °C was assigned to the decomposition of vanillin and glucose.

In Fig. 8b, there was a slight mass loss below 100 °C (weight loss of 3.6%) of diesel, while diesel was mainly decomposed at a narrow temperature ranging from 100 °C to about 280 °C with a narrow evolution profile (weight loss of 96.2%), and peak maximum (i.e. the maximum degradation rate) appeared at 213.9 °C with 67% weight loss.

A comparison of TG–DTG curves of bio-oil/diesel microemulsion with those of bio-oil and diesel could reveal the presence or the absence of certain compounds (Fig. 8c). Weight loss between 25 °C and 130 °C was about 21.1%, which was much lower than the value of synthetic bio-oil in this stage (approx. 53.8%). It was confirmed that a little amount of water and other volatile compounds were solubilized in diesel, and most of them were removed (left in the bio-oil rich phase). About 59% weight loss occurred at a temperature range between 130 °C and 290 °C, which corresponded to a high fraction of diesel present in bio-oil/diesel microemulsion. Moreover, peak maximum appeared at 161.5 °C and 38.03% weight loss of the bio-oil/diesel microemulsion. There was a small peak around 390 °C. Weight loss of bio-oil/diesel microemulsion beyond 290 °C was higher than that of synthetic bio-oil, probably attributing to the participation of Span80. As shown in Fig. 8d, TG–DTG curves of Span80 indicated that it mainly decomposed around 400 °C.

Table 1
Composition and energy content of bio-oil, diesel and bio-oil/diesel microemulsion.

Sample	Elemental analysis (wt.%)				Heating value (MJ/kg)
	C	H	O	N	
Bio-oil	41.55	7.65	49.98	0.82	16.85
Diesel	78.79	11.52	8.06	1.63	44.51
Bio-oil/diesel microemulsion	75.38	10.66	12.70	1.26	36.56

Table 2
Properties of the bio-oil, diesel and bio-oil/diesel microemulsion.

Sample	Density (g/cm^3)	Kinematic viscosity (T = 30 °C) (mm^2/s)	Viscosity index	Cloud point (°C)	Pour point (°C)	Water content (wt %)	pH	CSCT[a]
Bio-oil	1.086	4.030	0.113	–	–	19.7%	2.20	1b
Diesel	0.863	4.178	0.037	−4	−23	0	5.31	1a
Bio-oil/diesel microemulsion	0.914	8.417	0.288	−2	−20	2.74%	3.38	1a

[a] 1 = slight tarnish; a = light orange, almost the same as freshly polished strip; b = dark orange.

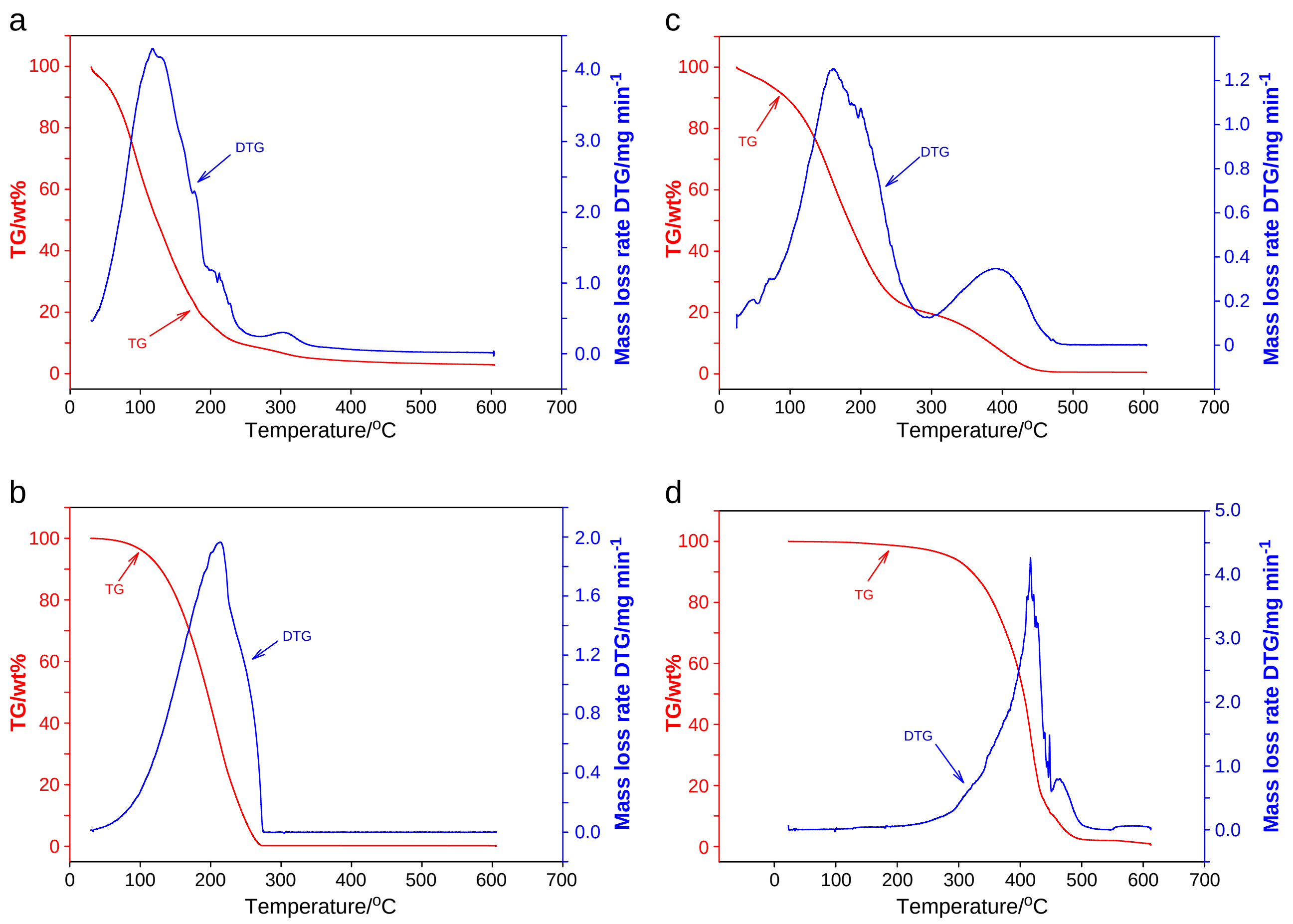

Fig. 8. TG and DTG curves of samples: (a) synthetic bio-oil, (b) diesel, (c) bio-oil/diesel mixture, and (d) Span80.

TG curves of bio-oil/diesel microemulsions with different Span80 concentrations (0, 0.19, 0.36, 0.62 and 0.98 M, respectively) were shown in Fig. 9. Evolution tendency of curves revealed the increment of bio-oil compounds solubilized in diesel with the increase of Span80 concentration. The increase of weight loss between 150 °C and 270 °C may be due to more bio-oil compounds that were solubilized in diesel, such as acetol, guaiacol and furfural which can be decomposed among this temperature range. In addition, the increase of weight loss beyond 270 °C might be attributed to the enhanced solubilization of vanillin, glucose and Span80.

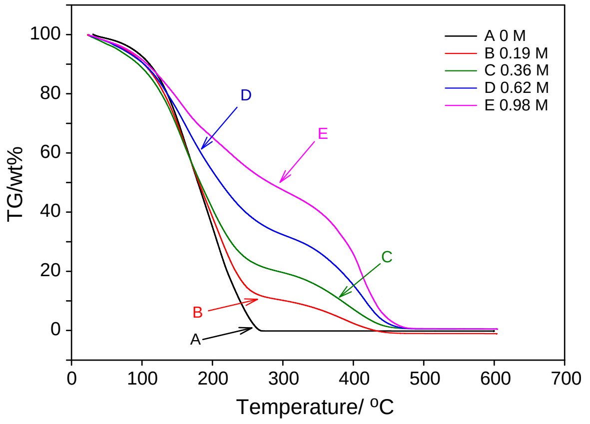

Fig. 9. TG curves of bio-oil/diesel mixtures with different Span80 concentrations.

4. Conclusions

A model compound of bio-oil was applied to produce bio-oil/diesel microemulsion fuels with the aid of Span80. Influences of dominant factors on solubilization capacity of bio-oil in diesel were investigated. Considering the solubilization capacity and fuel properties of bio-oil/diesel microemulsions, modest solubilization conditions of bio-oil/diesel microemulsions were recommended. The optimum bio-oil/diesel volume ratio was 5:5. The proper concentration of Span80 was 0.36 M. *N*-octanol was certified as an ideal cosurfactant. In addition, the solubilization capacity of bio-oil in diesel increased with the increase of cosurfactant/surfactant mass ratio, while the heating value decreased. A proper C/S ratio of 0.40 was suggested. Proposed mechanism of solubilizing bio-oil into diesel could be explained by "like dissolves like" principle and micelle theory. Compared to the original bio-oil, bio-oil/diesel microemulsion presented more desirable fuel properties closed to diesel. Bio-oil was the least expensive liquid fuel obtained from lignocellulosic materials. The processing of emulsifying bio-oil with diesel might be a promising method to extract some of the fuel fractions present into bio-oil for use as an additive to diesel. It provides a short-term approach to the use of bio-oil in diesel engines, which will enhance the economic viability of the bio-oil usage.

Acknowledgments

The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (21276069), the Scientific Research Project Supported by Hunan Provincial Education

Department (11K014), and the Specialized Research Fund for the Doctoral Program of Higher Education (20120161130002).

References

[1] S. Xiu, A. Shahbazi, Bio-oil production and upgrading research: a review, Sustainable Energy Reviews 16 (2012) 4406–4414.

[2] M. Al-Sabawi, J. Chen, Hydroprocessing of biomass-derived oils and their blends with petroleum feedstocks: a review, Energy & Fuels 26 (2012) 5373–5399.

[3] P.M. Mortensen, J.D. Grunwaldt, P.A. Jensen, K.G. Knudsen, A.D. Jensen, A review of catalytic upgrading of bio-oil to engine fuels, Applied Catalysis A 407 (2011) 1–19.

[4] W.N.R.W. Isahak, M.W.M. Hisham, M.A. Yarmo, T. Yun Hin, A review on bio-oil production from biomass by using pyrolysis method, Renewable and Sustainable Energy Reviews 16 (2012) 5910–5923.

[5] L. Ma, T. Wang, Q. Liu, X. Zhang, W. Ma, Q. Zhang, A review of thermal–chemical conversion of lignocellulosic biomass in China, Biotechnology Advances 30 (2012) 859–873.

[6] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy 38 (2012) 68–94.

[7] C.A. Fisk, T. Morgan, Y. Ji, M. Crocker, C. Crofcheck, S.A. Lewis, Bio-oil upgrading over platinum catalysts using in situ generated hydrogen, Applied Catalysis A 358 (2009) 150–156.

[8] J.P. Diebold, A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-oils, Thermalchemie Inc., Lakewood, Colo, 2000.

[9] D. Chiaramonti, M. Bonini, E. Fratini, G. Tondi, K. Gartner, A.V. Bridgwater, H.P. Grimm, I. Soldaini, A. Webster, P. Baglioni, Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines—part 1: emulsion production, Biomass and Bioenergy 25 (2003) 85–99.

[10] M. Ikura, M. Stanciulescu, E. Hogan, Emulsification of pyrolysis derived bio-oil in diesel fuel, Biomass and Bioenergy 24 (2003) 221–232.

[11] M. Ikura, S. Mirmiran, M. Stanciulescu, H. Sawatzky, Pyrolysis liquid-in-diesel oil microemulsions, U.S. Patent 5,820,640, 1998.

[12] Y. Xu, Q. Wang, X. Hu, C. Li, X. Zhu, Characterization of the lubricity of bio-oil/diesel fuel blends by high frequency reciprocating test rig, Energy 35 (2010) 283–287.

[13] L. Djekic, M. Primorac, S. Filipic, D. Agbaba, Investigation of surfactant/cosurfactant synergism impact on ibuprofen solubilization capacity and drug release characteristics of nonionic microemulsions, International Journal of Pharmaceutics 433 (2012) 25–33.

[14] K. Zielińska, K.A. Wilk, A. Jezierski, T. Jesionowski, Microstructure and structural transition in microemulsions stabilized by aldonamide-type surfactants, Journal of Colloid and Interface Science 321 (2008) 408–417.

[15] L. Djekic, M. Primorac, The influence of cosurfactants and oils on the formation of pharmaceutical microemulsions based on PEG-8 caprylic/capric glycerides, International Journal of Pharmaceutics 352 (2008) 231–239.

[16] X. Jiang, N. Ellis, Upgrading bio-oil through emulsification with biodiesel: mixture production, Energy & Fuels 24 (2009) 1358–1364.

[17] X. Jiang, N. Ellis, Upgrading bio-oil through emulsification with biodiesel: thermal stability, Energy & Fuels 24 (2010) 2699–2706.

[18] W.C. Griffin, Classification of surface active agents by HLB, Journal of the Society of Cosmetic Chemists 1 (1949) 311–326.

[19] W.C. Griffin, Calculation of HLB values of non-ionic surfactants, Journal of the Society of Cosmetic Chemists 5 (1954) 249–256.

[20] T. Schmidts, D. Dobler, A.C. Guldan, N. Paulus, F. Runkel, Multiple w/o/w emulsions—using the required HLB for emulsifier evaluation, Colloids and Surfaces A 372 (2010) 48–54.

[21] P.U. Karanjkar, J.W. Lee, J.F. Morris, Surfactant effects on hydrate crystallization at the water–oil interface: hollow-conical crystals, Crystal Growth and Design 12 (2012) 3817–3824.

[22] T. Nguyen, L. Do, D.A. Sabatini, Biodiesel production via peanut oil extraction using diesel-based reverse-micellar microemulsions, Fuel 89 (2010) 2285–2291.

[23] M.M. Tripathi, E.B.M. Hassan, F. Yueh, J.P. Singh, P.H. Steele, Study of the effect of ultraviolet exposure on bio-oil by laser-induced fluorescence spectroscopy, Energy & Fuels 24 (2010) 6187–6192.

[24] Y. Xie, R. Ye, H. Liu, Microstructure studies on biosurfactant-rhamnolipid/n-butanol/water/n-heptane microemulsion system, Colloids and Surfaces A 292 (2007) 189–195.

[25] C. Sheng, J.L.T. Azevedo, Estimating the higher heating value of biomass fuels from basic analysis data, Biomass and Bioenergy 28 (2005) 499–507.

[26] General Rules for Elemental Analyzer, JY/T 017-1996, State Education Committee of P.R. China, Beijing, 1996.

[27] Standard test method for detection of copper corrosion from petroleum products by the copper strip tarnish test, ASTM Standard D 130, American Society for Testing and Methods, West Conshohocken (PA), 2004.

[28] F. Wang, B. Fang, Z. Zhang, S. Zhang, Y. Chen, The effect of alkanol chain on the interfacial composition and thermodynamic properties of diesel oil microemulsion, Fuel 87 (2008) 2517–2522.

[29] A. Bera, K. Ojha, T. Kumar, A. Mandal, Water solubilization capacity, interfacial compositions and thermodynamic parameters of anionic and cationic microemulsions, Colloids and Surfaces A 404 (2012) 70–77.

[30] Y. Bayrak, Interfacial composition and formation of w/o microemulsion with different amphiphiles and oils, Colloids and Surfaces A 247 (2004) 99–103.

[31] L. Digout, K. Bren, R. Palepu, S.P. Moulik, Interfacial composition, structural parameters and thermodynamic properties of water-in-oil microemulsions, Colloid & Polymer Science 279 (2001) 655–663.

[32] R.K. Mitra, B.K. Paul, S.P. Moulik, Phase behavior, interfacial composition and thermodynamic properties of mixed surfactant (CTAB and Brij-58) derived w/o microemulsions with 1-butanol and 1-pentanol as cosurfactants and n-heptane and n-decane as oils, Journal of Colloid and Interface Science 300 (2006) 755–764.

[33] S.P. Moulik, L.G. Digout, W.M. Aylward, R. Palepu, Studies on the interfacial composition and thermodynamic properties of w/o microemulsions, Langmuir 16 (2000) 3101–3106.

[34] Eric W. Kaler, Karl E. Bennett, H. Ted Davis, L.E. Scriven, Toward understanding microemulsion microstructure: a small-angle X-ray scattering study, Journal of Chemical Physics 79 (1983) 5673.

[35] Eric W. Kaler, H. Ted Davis, L.E. Scriven, Toward understanding microemulsion microstructure. II, Journal of Chemical Physics 79 (1983) 5685.

[36] Gurpreet Kaur, Leonardo Chiappisi, Sylvain Prévost, Ralf Schweins, Michael Gradzielski, Surinder K. Mehta, Probing the microstructure of nonionic microemulsions with ethyl oleate by viscosity, ROESY, DLS, SANS, and cyclic voltammetry, Langmuir 28 (2012) 10640–10652.

[37] Aviram Spernath, Abraham Aserin, Amnon C. Sintov, Nissim Garti, Phosphatidylcholine embedded micellar systems: enhanced permeability through rat skin, Journal of Colloid and Interface Science 318 (2008) 421–429.

[38] Saim M. Emin, Pavletta S. Denkova, Karolina I. Papazova, Ceco D. Dushkin, Eiki Adachi, Study of reverse micelles of di-isobutyl-phenoxy-ethoxy-ethyl-dimethyl-benzyl ammonium methacrylate in benzene by nuclear magnetic resonance spectroscopy, Journal of Colloid and Interface Science 305 (2007) 133–141.

[39] D. Myers, Surfactant Science and Technology, Third ed. John Wiley and Sons, Inc., Hoboken, NJ, 2006.

[40] Abhijit Manna, Toyoko Imae, Toshinobu Yogo, Keigo Aoi, Midori Okazaki, Synthesis of gold nanoparticles in a Winsor II type microemulsion and their characterization, Journal of Colloid and Interface Science 256 (2002) 297–303.

[41] Tao Pan, Zhilong Wang, Xu. Jian-He, Wu. Zhenqiang, Hanshi Qi, Stripping of nonionic surfactants from the coacervate phase of cloud point system for lipase separation by Winsor II microemulsion extraction with the direct addition of alcohols, Process Biochemistry 45 (2010) 771–776.

[42] General Diesel Fuels, GB252-2011, National Standards of P.R. China, Beijing, 2011.

[43] T. Ba, A. Chaala, M. Garcia-Perez, C. Roy, Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Storage stability, Energy & Fuels 18 (2003) 188–201.