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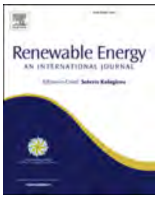

Span80/Tween80 stabilized bio-oil-in-diesel microemulsion: Formation and combustion

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ABSTRACT

A detailed experimental study was conducted to investigate the production and fuel properties of bio-oil-in-diesel microemulsion (BDM) and its emission characteristics. Bio-oil was produced from liquefaction of methanol, castor oil and sewage sludge. Hydrophilic surfactant (Span 80) and hydrophobic surfactant (Tween 80) of different mixing ratio and different co-surfactant (alcohols) were tested to form BDM with higher bio-oil solubility and better stability. The best mixed ratio was proved to be 7/3 (Span 80/Tween 80) with 2% n-hexanol. The principle of “likes dissolve likes” was set as a guiding mechanism on bio-oil solubilization process. The emulsified fuel stabilized by mixed surfactant and co-surfactant, in comparison with other hybrid fuels and diesel, was tested in a single cylinder, four-stroke, water cooling, direct injection, diesel engine to study the emission characteristics. The results show that, compared with diesel, BDM performed well in brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) while reduced CO, CO_2 and NO_X emissions by 21.4%–66.7%, 7.1%–27.3% and 1.5%–14.7%, respectively. This was the first time of using surfactant compound to form bio-oil microemulsion, which provides a possibility for practical application of microemulsion fuels and further benefiting SS utilization.

1. Introduction

Since or even earlier than the oil embargo of 1973, researchers are trying to find the sources of renewable energy [1]. Currently, besides wind and solar energy, bio-energy is one of the widely studied renewable resources [2]. The derivation of bio-energy is extensive, such as agricultural residues, forest debris, animal faeces and municipal sludge [3]. Due to their low production cost and low emissions the study of bio-energy has attracted widespread concerns.

As a developing country, water pollution in China is a serious problem. 1.3 billion populations, large-scale urbanization process, rapid economic growth and so on, all of those aggravate the pollution of water and generate huge amount of sewage sludge (SS) [4,5]. Better quality water requirement and more stringent environmental laws had further intensified this situation [6–9]. The disposal of SS needs to be attached great importance [5,8]. Traditional disposal methods for SS, including agricultural application, landfill and incineration, were restricted by land limitations and stringent regulations [10–12]. A cleaner ways to handle SS is urgent needed.

Preparing bio-energy was an effective way for SS dispose and utilization. One side is to produce bio-char. Leng et al. [13] prepared bio-char by liquefing SS with microalgae and lignocellulosic biomass. They found its product had a good quality in thermal stability and surface porous structure, and also possessed enriched oxygen-functional groups. Peng et al. [14] used hydrothermal carbonization (HTC) of sewage sludge (SS) to produce bio-char. The formed bio-chars, especially sample 260–60, had higher E (activation energy (kJ mol-1)) and A (frequency factor (1/min)) value than SS at first combustion on TGA analysis. Another way is to use

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SS produce bio-oil. Xin et al. [15] discussed the optimum condition for co-pyrolysis of microalgae and SS in bio-oil generation. J. Alvarez et al. [16] produced fast pyrolysis bio-oil by SS in conical spouted bed reactor (CSBR) at the temperature of 450–600 °C. Compared with initial sludge, they found that bio-oil has a great reduction of S, N and O, whereas that of C and H is substantially increase. These studies indicated that low temperature (250–350 °C) and high pressure (5–20 MPa) with solvent participation makes liquefaction a widely used technology for bio-oil production [17].

In this study, a low oil production rate was obtained by direct liquefaction with SS and solvent in pre-experimental stage. In order to increasing oil production rate, castor oil was chosen to be raw material for co-liquefaction. Castor plants were massively planted in china and its product castor oil has a high viscosity which was caused by its high percentage of unsaturated fatty acid [18]. In a previous study, a potential way to use castor oil as fuels was formed by preparing water-in-oil (W/O) microemulsion based on rhamnolipid, and reduced the viscosity of raw materials prominently at same time [19]. This provides the possibility of using castor oil and SS to producing bio-oil. However, vegetable oils during engine test had to meet many problems including operational (starting ability, ignition delay, engine performance and combustion) and durability (the formation of deposit, carbonization of injector tip, ring sticking and lubricating oil dilution) problems [20]. Chen et al. evaluated the characteristic combustion properties of castor pyrolytic oil produced from a thermal pyrolysis process with castor seeds [21]. Their result illustrated that pyrolysed fuels characteristics could devote to improve engine combustion efficiency. In a preliminary experimental stage, castor oil liquefied with or without addition at different conditions had acquired an obvious effect on reducing viscosity. Organic solvents such as short-chain alcohol were suitable for liquefaction, and methanol was proved to have the highest conversion rate as compared with ethanol and acetone [22]. Considering the conversion rate of methanol and ignition point of castor oil (322 °C), 300 °C setting temperature and 20 min retention time was supposed to be ideal conditions for co-liquefaction of SS and castor oil.

Nevertheless, poor quality (such as high viscosity (compared with diesel) and easy aging) was a common problem of bio-oil, which further urges an upgrading as pretreatment process before using it as engine fuels. Emulsification, in contrast with other commonly used approaches to bio-oil upgrading (hydrodeoxygenation, blending and cracking), was confirmed to be more energy saving and easy operation [23,24]. Furthermore, microemulsification could establish more spontaneously and stable fuel than emulsification [25]. Hydrophobic Span 80 was a commonly used surfactant in the formation of emulsion/microemulsion and exhibited good results on upgrading fuel properties [26–28]. Considering the limitation of a single surfactant (mainly was smaller range of HLB value), some researchers used mixed hydrophobic surfactant and hydrophilic surfactant together as emulsifier which proved to get better effects. These studies indicated that emulsions formed by mixed surfactant were benefited in yield more stable emulsion [29], improved combustion efficiency [30], shorten ignition delay time [31] and reduced NO emission [32]. There was no detailed research of using mixed surfactant on bio-oil microemulsion formation, which stimulates us to carry out this study.

To sum up, the main objectives of this study were as follows: (1) Providing a simple approach to transfer SS into available fuels–bio-oil. (2) Screening out a better microemulsion formula with the aid of Span 80 and Tween 80 mixtures. (3) Discussing the potential (fuel properties and pollution emission) of emulsified fuels as engine fuels.

2. Materials &methods

All the used materials were listed below, and the methods of this test were divided into three parts as liquefaction and solubilization of bio-oil, characterization of bio-oil, diesel and emulsified fuels and engine performance and combustion of tested fuels.

2.1. Materials

Sewage sludge was collected from a local sewage disposal works (Changsha, Hunan, China), and screened by 80 mesh sieve after 48 h drying at 105 °C. No.0 diesel was purchased from a local petrol station in Changsha, China. Span 80 (purity>98%) and Tween 80 (purity>98%) were purchased from Qinxi Chemical Industry S&T Co., Ltd (Shanghai, China). Alcohols (purity>99%) were provided by Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd (Tianjin, China). And all other chemicals were analytical grade and used without purification.

2.2. Bio-oil liquefaction and solubilization

2.2.1. Bio-oil production

4/1 (volume ratio) of castor oil and methanol with 12 g SS was chosen to be the liquefaction formula after a comprehensive consideration of getting stable bio-oil and using castor oil as far as possible. The given materials (total volume: 150 mL) were poured into a 500 mL autoclave reactor (GSHA-0.5, China). Temperature was increased constantly until 300 °C and maintained 20 min and then cooled down to room temperature [22]. The product was filtered by vacuum suction filter machine and drip washing by ethyl acetate (EA). According to the boiling point of Water and EA, 150 rpm rotate speed and 75 °C were set for wiped out those impurities by rotatory evaporator. And the residue liquor was bio-oil.

2.2.2. Bio-oil solubilization

Bio-oil solubilization could be prepared by a sequential adding method or a directly blending with all materials. For sequential adding method, certain amounts of Surfactants (either single Span 80 or mixed Span 80 and Tween 80) and diesel were poured into a 10 mL centrifuge tube first. Water (1%, according to a previous study [19])was injected and blended afterwards (help generate micro-explosion for getting better performance in combustion). Co-surfactant (n-alcohol) was dispersed into the mixture of water and diesel drop wisely and the additional amounts were determined by getting the critical points where the epinephelos emulsion became transparent liquid. 10 min of 1000 rpm centrifugal process was to help the formation of smaller water droplets and water grain diameter was measured by particle size analyzer to ensure the type of formed emulsion (retain water-in-oil microemulsion (WDM)) [19,24,33]. After that, bio-oil was added in stabilized WDM and blended into homogeneous liquid—bio-oil-in-diesel microemulsion (BDM). Direct blended was a simillar process as the described one, the only difference was all specified materials poured into centrifuge tube at the same time in this method.

High speed centrifugation was used to determine bio-oil solution amount in this stage. After 10 min at 3000 rpm high speed centrifugation, the fuels were divided into two sections-upper solution (homogeneous solution) and lower solid (excess bio-oil and sediments). The upper liquor, emulsified fuels, was used for further study. In order to evaluate the efficiency of bio-oil solubilization, ***E*** (g/g) which defined as the solubilized bio-oil mass of unit mass of bio-oil was introduced as a parameter [34].

2.3. Characterization of bio-oil, diesel and BDM

C, H, O, N, and S elements analyses were carried out by a Thermo Fisher ARL 3460 Advantage. Carbon residue was measured by national standard method- Kang carbon residue determination method. Pour point was tested on the basis of GB/T3535-2006. A kinematic viscosity analyzer (KD-R0515, China) set at 30 °C was used to measure viscosity. And total acid number (TAN) of BDM was tested through a fully automatic acid value analyzer.

Gas chromatography/mass spectroscopy (GC/MS) analysis was conducted on a GCMS-QP2010 Plus spectrometer (30 m × 0.25 mm × 0.25 μm; Shimadzu, Japan) by using a semi-quantitative analysis of bio-oil yield by Hyun Ju Park [35,36]. The carrier gas flow rate was 2.0 mL/min helium (He). Temperature program was as follows: initial and final temperatures were 30 °C and 290 °C, respectively, while retention times at the initial and final temperatures were 2 and 5min, respectively. The period of temperature rise was divided into two stages with the ramp rate of temperature rise from 30 °C to 190 °C and 190 °C to 290 °C were 8 °C/min and 6 °C/min, respectively. The given sample (oils) was injected at 1 μL with 50:1 split ratio. The injection and interface temperature was 270 °C and 230 °C, respectively. MS was operated in scan mode with mass range from 45 to 700 amu (atomic mass unit). The 2008 version of National Institute of Standardsand Technology (NIST08) was selected as spectrum library to interpret the mass spectra from GC/MS.

All parameters of fuel properties and GC/MS analysis were tested before stability test. Prepared fuels were stored over 90 days at indoor temperature in an attempt to verify its stability.

2.4. Engine performance and combustion of BDM

To study its engine performance and emission characteristics, diesel, BDMs (single surfactant), BDMb (mixed surfactant, without alcohol) and BDM (mixed surfactant with n-hexanol) were combusted in a single cylinder, four-stroke, water cooling, DI (direct injection) engine (ZS1110). Rotate speed, torque and power were measured by a turbulent flow measurement motor (DW25, Sichuan, China). The dynamometer torque rating and the rated power absorption were 120 N•m and 25 kW respectively (torque measuring accuracy: ±0.4% F•S), while the measurable maximum speed could reach 11000 r/min (rotation speed measuring precision: ±1 r/min). The tested fuels were flow down to the cylinder through the fuel consumption minitor (ET2500, Sichuan, China; measurement accuracy: $\pm 8\ \mathrm{g \cdot h^{-1}}$), which could accurately determine the instantaneous fuel consumption and average fuel consumption of the diesel engine. During the experiments, the engine load (brake mean effective power (BMEP)) was set from 0.23 to 0.92 MPa(which was transformed by adjusting torque) with a constant speed of 1200 rpm. This setting conditions were determined by empirical assumption of the used diesel engine [37]. At each load, the emissions of CO, CO_2, and NOx were recorded by an exhaust gas analyzer (FGA-4100, Guangdong, China), while the smoke intensity was collected by an impermeable photometer (FTY-100, Guangdong, China). The concentrations of NO_X was expressed in ppm whereas those of CO and CO_2 were expressed as a percentage volume. And the smoke intensity emission was expressed in m^{-1} (coefficient of optical absorption ***k***). The range and accuracy of measurement for each emission index are as follows: CO: 0–10%, ±5%; CO_2: 0–20%, ±5%; NO_X: 0–0.4%, ±4%; ***k***: 0–16 m^{-1}, ±2%. And significant engine performance parameters such as the brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) were calculated for further explanation. The detailed specification of engine was shown in Table 1 and the schematic diagram of the experimental setup was shown in Fig. 1.

Table 1
Parameters of the ZS1110 diesel engine.

	specifications
Type of engine	Single cylinder, four-stroke, direct injection
Bore × stroke	110 mm × 115 mm
Power (maximum)	14.7 Kw
Speed (maximum)	2200 r/min
Displacement	1.093 L
Compression rate	17:1
Cooling system	Water cooling

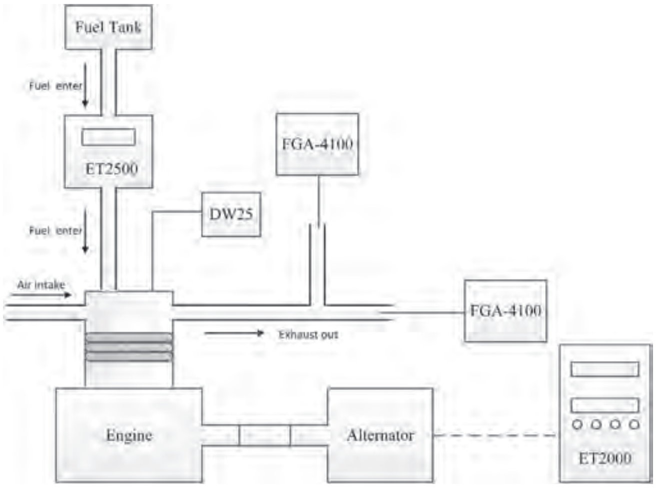

Fig. 1. Schematic layout of combustion test.

3. Result and discussion

3.1. Bio-oil solubilization

The factors affecting on bio-oil solubilization mainly included types of bio-oil, the method of form emulsified fuels, type of surfactant and types of co-surfactant. In this stage, misoperation was the most important reason for experiment deviation. Multiple measurement (not less than three times) was used for eliminating or cutting down this negative effects. And all the data used below were the average value of 3 multiple valid data.

3.1.1. Bio-oil type and BDM formation method

In BDM preparation, the type of bio-oil and formation method played a major role. Initially, direct liquefaction of castor oil and SS was selected to produce bio-oil. After filtration and rotary evaporation, we added it into the prepared diesel microemulsion and find it precipitated quickly, mainly due to the poor oil quality of bio-oil. Normally, liquefied oil performed poorly without purifying and adding an appropriate amount of lower alcohol was beneficial on oil upgrading. Therefore, given mass of methanol was chosen to assist liquefaction.

The sequence of materials was another important factor [28]. As mentioned in Section 2.2.2, we tried to find a better bio-oil addition on two ways; put all materials in a centrifuge tube and shook it into homogeneous liquor or prepared diesel microemulsion first and then bio-oil was added and blended till no sediment appears. The latter one performed better in the experimental process. Directly blending could generate sediment easily. The exact reason was not clear, some unknown connection between bio-oil, surfactants and co-surfactants were formed. Considering the test results, preparing diesel microemulsion first and then adding moderate amount of bio-oil was regarded as a proper approach for BDM formation.

3.1.2. Effect of surfactant type

Bio-oil and diesel can only mix together in a very limited part in nature. It is possible that a slight amount of bio-oil could dissolve into diesel, but sediment appears quickly. Surfactant could prompt them soluble to each other by the formation of microemulsion. During the preparation of microemulsion, surfactant played a major role. It has a hydrophobic and a hydrophilic group. Usually, HLB value acts as an index to evaluate the ability of their affinity on oil-water interface. Higher HLB value means lower hydrophobic of surfactant. Nonionic surfactant Span 80(HLB = 4.3) was the frequently used one for the formation of microemulsion. In the formation of BDM, a critical factor was the capacity of bio-oil. In this study, we blended two surfactants in different ratio (Span 80/Tween 80 ranging from 8/2 to 6/4). As shown in Fig. 2a, we could easily find the value of ***E*** increases first and then drops for all situations when the dosage reaches 0.06 g/mL. The absence of surfactant in lower dosage resulted in bio-oil overdosed, while bio-oil dissolved saturation and superfluous surfactant lack scope for their abilities in higher dosage. The results of those four different recipes illustrated that mixed surfactant, with the proportion of Span 80/Tween 80 equals 7/3, had the highest surfactant use ratio (0.946 g/g). However, the addition of surfactant caused increase of TAN and viscosity in test, this change was not obvious between emulsified fuels. This indicated that mixed surfactant systems had better performance on bio-oil solubility than single surfactant (Span 80) system.

3.1.3. Effect of co-surfactant type

In Fig. 2b, all the alcohols had a positive effect on BDM formation and as the chain-length of the alcohols increased, alcohol consumption and viscosity of BDM rose. N-hexanol displayed the best effect (***E*** = 1.039 g/g) in this study (about 9.8% higher than none co-surfactant participated). There was no obvious increase of n-butanol, n-pentanol and n-hexanol in consumptions (2%) and viscosity on BDM formation. But for n-heptanol and n-octanol, increased dosage (3%) leads to the viscosity rise (not less than 3.6%).

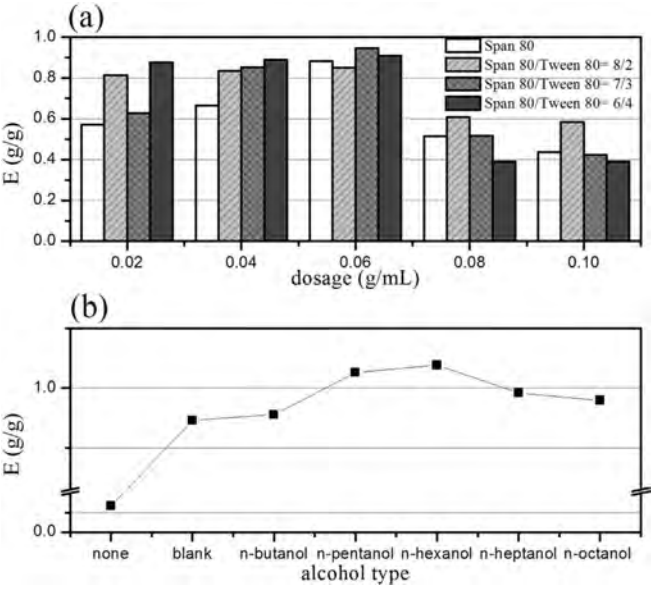

Fig. 2. Effect of surfactant and co-surfactant type on bio-oil solubilization: (a) Effect of different method of surfactant compound on bio-oil solubilization; (b) Effect of alcohol type on bio-oil solubilization: "blank" means a direct blend of bio-oil and diesel. "none" means no alcohols participate.

Furthermore, the major additional amount and chain-length there included might cut down the capacity of soluble bio-oil. Compared with BDMb, the solubilization capacities of BDM were higher, which proved that adding alcohol had a positive influence on solubilization. On bio-oil-diesel interface, the added alcohol might stimulate micelles swelling acting like co-surfactant, enhancing the solubilization of more bio-oil or alcohols (the detailed explanation was shown on Fig. 4) [38].

3.2. Characterization of emulsified fuels and diesel

All test fuels were stored over 90 days to study its stability performance. There is no doubt that diesel was homogeneous and transparent with no sediment and separation after storage. BDM obtained the same phenomenon as diesel while trace amount of sediment appeared on BDMs and BDMb. This indicated that the addition of mixed surfactant and cosurfactant could steady the fuels prepared by microemulsification and indicated that BDM possessed the prerequisites as engine fuel.

The essential fuel properties of diesel and bio-oil were shown in Table 2. For the content of H/C, bio-oil was slightly lower than diesel which leads to a little lower calorific value than diesel. Higher O bio-oil might help reduce the CO emission in combustion, while might also increase CO_2 emission [39] and yield more NO_X [40]. Furthermore, more oxygen could stimulate H_2O_2 generate more and fasten, which could slightly shorten ignition delay while had a slight incrase of CO emissison (however, Fig. 5 indicated this influence was filled by other factors, such as abundant oxygen and the technology of emulsification) [41]. Lower nitrogen content of the bio-oil renders the emulsified fuels have a potential of reducing NO_X emission (as compared with diesel). Slight amount of sulfur (S: 0.16%) and carbon residue (1.62%) of bio-oil might have negative effects on engine. This impact could be reduced by adding less bio-oil into microemulsion and the ability of more efficient combustion emulsified fuels possessed could further mitigate its negative effects. The viscosity of bio-oil was approximately 7 times larger than diesel, but after bio-oil solubilization, the emulsified fuels increased about 39.1% viscosity than diesel. As evaluation index, the consumption of KOH was recorded, and it was found that the more KOH was used, the higher TAN the fuel has. In other words, it suggested the fuel has a lower pH. Obviously, diesel has the lowest TAN. Large TAN of bio-oil (high to 36.90 mg KOH/g) could rule out its possibility as an engine fuel for direct use. Nevertheless, put bio-oil as an additive and solubilize into emulsified fuels could greatly reduce TAN.

GC/MS analysis of bio-oil and BDM was shown in Table 3. The prepared bio-oil was a complex mixture of hydrocarbons (alkane, arene and cycloparaffin), acid, ester, ketone, amine and dyestuff. Similar composition to diesel (mainly contained hydrocarbons) provided a possibility for bio-oil combustion. The complexity of bio-oil leads to an intricate process in the solubilization of bio-oil. From the percentage of each solubilized bio-oil compound in total solubilized bio-oil after microemulsification, we could find that the vast majority of ester (46.59%) and plenty of hydrocarbons (23.82%) were solubilized into emulsified fuels. Little dyestuff and trace amount of ketone and amine could also be found in BDM. This result could offer support for the bio-oil solubilization mechanism.

3.3. Mechanism of bio-oil solubilization

In the formation of emulsion, stable micelle formed by the attractive interaction due to the hydrophobicity between hydrophobic groups of surfactant. In this study, reversed micelles were formed by Span 80 and Tween 80 to build water-in-diesel microemulsion [42]. As shown in Fig. 3a, two surfactants have synergetic

Table 2
Essential fuel properties of diesel and bio-oil.

	diesel	Bio-oil	BDMs	BDMb	BDM
C (%)/H (%)/O (%)/N (%)	78.76/11.57/8.11/1.56	76.78/10.93/11.0/0.98	–[a]	–	–
S (%)	<0.035*	0.16	–	–	–
H/C	1.76	1.71	–	–	–
O/C	0.07	0.11	–	–	–
Viscosity (cst)	3.15	21.98	5.16	5.11	5.18
TAN (mg KOH/g)	<0.07*	36.90	1.85	1.80	1.78
Carbon residue (%)	<0.3*	1.62	–	–	–
Pour point (°C)	−12	−22	–	–	–
Calorific value (MJ/Kg)	42.03	38.84	39.45	39.88	40.57

*The maximum mass percentage set by GB 252-2015 (China). [a] Not detected.

Table 3
Chemical composition of bio-oil and distribution characteristics of solubilized bio-oil compounds in BDM.[a] The peak area of chemical compounds lower than 1%.

compounds	group	peak area (%)	percentage (%)[b]
		bio-oil	BDM
Hexane, 2,2,3,3-tetramethyl-	alkane	3.03	6.94
Decane	alkane	5.41	2.52
pentadecane	alkane	2.87	1.10
Pyrrolidine, 1- (1,6-dioxooctadecyl)-	alkane	2.30	–[c]
N1,N1-Dimethyl-N2- (1-phenyl-ethyl)-ethane-1,2-diamine	amine	5.69	6.14
o-Xylene	arene	1.77	–
Indane	arene	2.03	–
Benzene, butyl-	arene	3.74	–
Benzene, 1-ethenyl-4-ethyl-	arene	4.34	5.36
Benzene, 1-methyl-3-(1-methyl-2-propenyl)-	arene	1.63	–
Benzene, 1-methyl-2- (1-methyl-2-propenyl)-	arene	2.21	3.56
Benzene, pentyl-	arene	1.60	–
Benzene, hexyl-	arene	1.70	–
Cyclodecane	cycloparaffin	1.88	–
Cyclohexane, pentyl-	cycloparaffin	1.49	–
Spiro [3.6]deca-5,7-dien-1-one,5,9,9-trimethyl	cycloparaffin	1.51	–
1-Dodecanesulfonyl chloride	dyestuff	1.49	10.94
Hexanoic acid, methyl ester	ester	8.31	6.89
Octanoic acid, methyl ester	ester	6.10	4.84
Nonanoic acid, methyl ester	ester	5.17	3.42
2-Naphthalenol, 1,2-dihydro-, acetate	ester	4.84	10.94
5-Chlorovaleric acid, 3-pentadecyl ester	ester	3.92	3.58
Undecanoic acid, methyl ester	ester	3.92	–
Cyclobutanecarboxylic acid, 3-phenyl-2-propenyl ester	ester	2.96	10.09
Tridecyl pentafluoropropionate	ester	2.28	–
p-Toluic acid, 5-tridecyl ester	ester	1.92	–
Carbamic acid, phenyl-, dodecyl ester	ester	1.75	–
Tridecanoic acid, methyl ester	ester	1.68	–
Octadecanoic acid, methyl ester	ester	1.82	6.83
Total		**89.83**	
Butanoic acid, 4-oxo-2- (1-piperidyl)-4-(4-tolyl)-	acid	#[a]	3.57
Heptane, 5-ethyl-2-methyl-	alkane	#	–
5-Undecene	alkane	#	–
4-Decene	alkane	#	–
Benzene, propyl-	arene	#	–
Naphthalene, 2-methyl-	arene	#	–
p-Xylene	arene	#	4.34
Cyclohexane, butyl-	cycloparaffin	#	–
Cyclopentane, pentyl-	cycloparaffin	#	–
Cyclotridecane	cycloparaffin	#	–
Ethanone, 1- (1-methylcyclopentyl)-	ketone	#	3.94

[a] The peak area of chemical compounds lower than 1%.

[b] Percentage of each solubilized bio-oil compound in total solubilized bio-oil after microemulsification. It was calculated by the following equation: $Percentage\ (\%)^{b} = \frac{peak\ area\ (\%) of\ one\ bio-oil\ compound}{total\ peak\ area\ (\%) of\ solubilized\ bio-oil\ in\ BDM} \times 100\%$.

[c] chemical compounds not detected in BDM or peak area less than1%.

impacts on building reversed micelle. On one hand, mixed surfactant could broaden the range of dissoluble matters. On the other hand they might increase the oil-water interface properly which could help solubilize more bio-oil. This synergistic effect was confirmed by previous studies. Lv et al. [43] observed a continuous process of W/O emulsion transfer into O/W emulsion gradually (contained a transition stage O/W/O (oil-in-water-in-oil emulsions) multiple emulsion) while adding hydrophilic surfactants (Tween 20) into lipophilic ones (Span 80) formed stable W/O emulsion. Through optical micrograph of transfer progress, Lv et al. build a similar mechanism graph to express synergistic effect of mixed surfactant. As depicted in Fig. 3b, the participation of co-surfactant

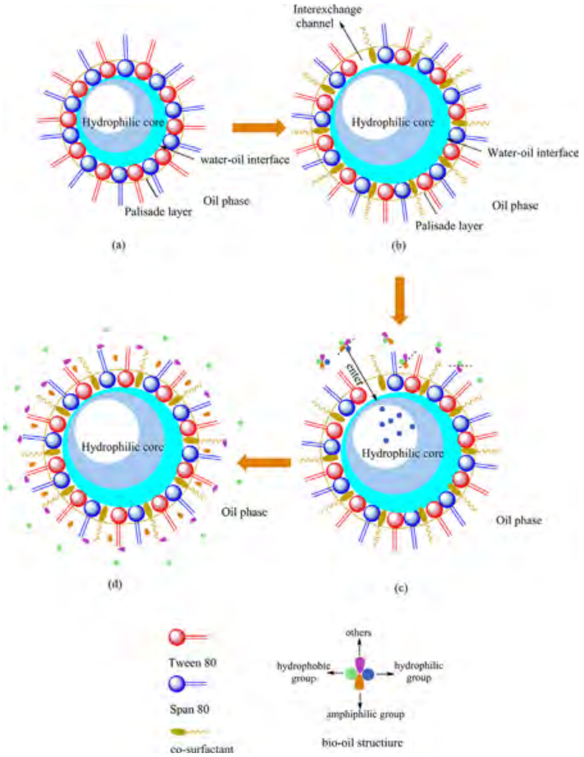

Fig. 3. Mechanism of bio-oil solubilization.

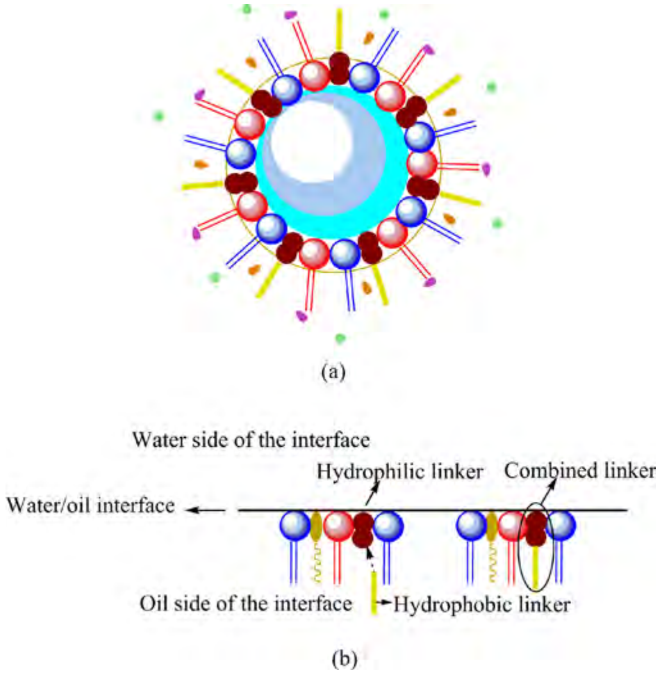

Fig. 4. Solubilization of amphiphilic groups of bio-oil: (a) combined with free surfactant and co-surfactant to build new micelles; (b) self-assembly of linker molecules on water-oil interface.

could further reduce surface tension which prompts the oil-water interface broadened. Bigger oil-water interface should accommodate moreamphiphilic groups (located on palisade layer) and some organic matter (absorbed in reversed micelle surface) which could not dissolve into water. Bio-oil solubilization progress was shown in Fig. 3c and the final result was presented in Fig. 3d. According to the main composition of bio-oil, four approaches of bio-oil solubilization were obtained: 1) hydrophilic groups of bio-oil like acids might tend to enter hydrophilic core; 2)hydrophobic groups of bio-oil, such as hydrocarbons (including alkane, cycloparaffin and arene) were probably solubilized into diesel (oil phase); 3)amphiphilic groups of bio-oil like amine and ester were located on palisade layer (Fig. 4); 4) others component of bio-oil like dyestuff and some organics insoluble in both water phase (hydrophilic core) and oil phase (diesel) might adhere to micellar surface. The guiding principle of those four solubilization stage was “like dissolves like” principle, and the detailed bio-oil solubilize mechanism was similar to our previous studies [24,34,44].

However, the third stage which was about the mechanism of amphiphilic groups solubilization needs detailed description due to its unique properties. There are several researches who pointed that methyl esters could serve as surfactant [34,45]. They might combine free surfactant with co-surfactant to build new micelles in air/oil phase or in diesel (Fig. 4a). This effect could further increase soluble amount. Several studies refers that specific esters and acids of bio-oil might act as linker molecules (play a similar role as surfactant) which possessed hydrophobic and hydrophilic linker could self-assemble into many structures [46–48]. The combined linker, behaved as assemble surfactant, was shown its synergistic effect on bio-oil solubilization (Fig. 4b). Those soluble mechanisms of amphiphilic groups made this stage become the most effective one in all soluble approaches and could get the highest solution amount.

3.4. Engine performance and combustion test of emulsified fuels

BSFC and BTE were used to describe engine performance of tested fuels, and the emission of CO, CO_2, NO_X and smoke intensity were mainly indicated pollution in combustion test. The deviation of this experiment was probably caused by misoperation and the contingency of data. In order to reduce the deviation of experiment and ensure the accuracy of testing result, two continuous measure was necessary at every operating point. And the data used below was the mean data of those two measurement results.

3.4.1. Engine performance of diesel and emulsified fuels

As shown in Fig. 5a, the use of emulsified fuels in cylinder in place of diesel increased fuel consumption at the same engine load, and the minimum BSFC was obtained at 0.46 MPa for all type of fuels. Compared with diesel at 0.46 MPa, BDMs, BDMb and BDM increased BSFC by 12%, 10% and 8%, respectively. The lower heating value of emulsified fuels was one possibly reason [49]. Table 2 illustrated that the aimed microemulsion with 1% water reduce the heating value (approximately 3.5%–6.1% lower than diesel), which lead to small increase of BSFC than diesel eventually. The higher viscosity was another reason [50]. The viscosity of emulsified fuels which was approximately 63.5% higher than diesel required larger fuel consumption for the sake of releasing same energy as that of diesel. Thus, for the same energy output, emulsified fuels consumed more in diesel engine. And as the engine load added, the BSFC of all tested fuels were increase continuously. The excessive engine load at the given speed might diminished the use ratio of fuels, which lead to the rising trend of BSFC.

Fig. 5b illustrates the variation of BTE with engine loads. At lower engine loads, diesel showed its advantage (higher than emulsified fuels) while emulsified fuels got similar BTE (however, the BTE of BDM was a little bigger). The slight variations in BTE of all tested fuels were mainly due to the lower heating value of microemulsions had [51]. And the heat sink effect of emulsified fuels was

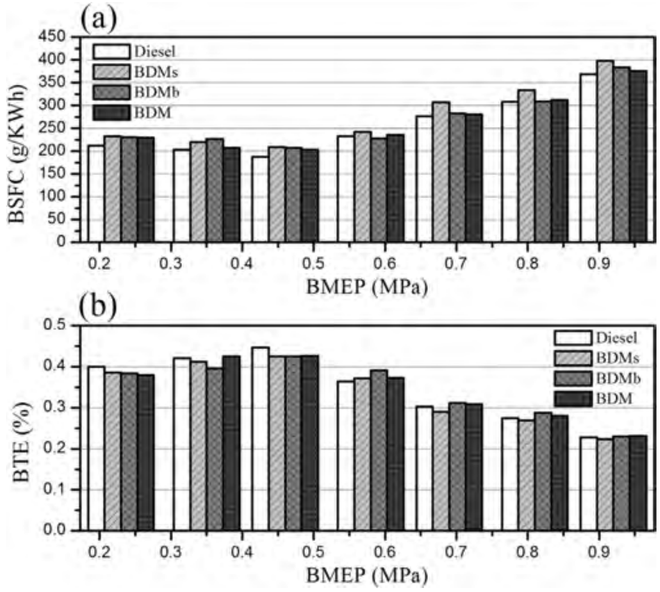

Fig. 5. Engine performance of diesel and emulsified fuels: (a) Comparison of BSFC with respect to engine loads; (b) Comparison of BTE with respect to engine loads.

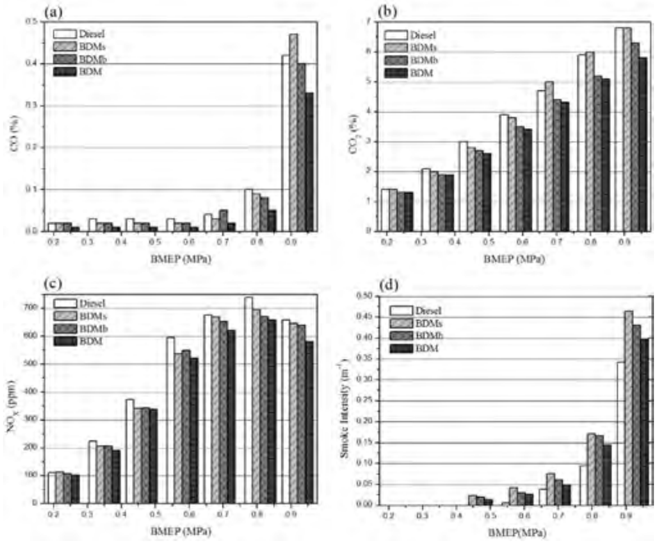

Fig. 6. Emission of diesel and emulsified fuels: (a) Comparison of CO emission with respect to engine loads; (b) Comparison of CO_2 emission with respect to engine loads; (c) Comparison of NO_X emission with respect to engine loads; (d) Comparison of smoke intensity with respect to engine loads.

another potential reason [52]. Water contents in the inner phase partly absorbed the calorific value of the emulsions while heat sink effect occurred, which resulted in the decrease of BTE. At higher engine loads ($\geq$0.58 MPa) emulsified fuels obtained higher BTE than diesel. In this stage, higher oxygen content [53] and micro-explosion [54] which stimulated the combustion process more complete combustion and prompted for higher release of energy, were mainly reasons. The superiority of using mixed surfactant in place of a single surfactant was increased as the engine load went up. Additionally, the added alcohol could further increase BTE slightly.

3.4.2. Emission of diesel and emulsified fuels

Fig. 6a was shown that all samples had steady CO emission load before 0.70 MPa and sharply rose afterwards. Enough oxygen cylinder filling urges CO to transfer into CO_2 at lower engine load while more and more fuel injected into cylinder and caused the lack of oxygen and then resulted in more CO release as engine powers rose [55]. Compared with diesel, microemulsions had a remarkable reduction of CO expect BDMs at 0.92 MPa (0.47% CO emission (percentage on total emissions), 12% higher than diesel). When the variation of BDMs and BDMb were contrasted, about 14.8% lower BDMb discharged than BDMs at 0.92 MPa, implying that mixed surfactant could get a positive effect on the reduction of CO emission [56]. This trend was more remarkable between diesel and BDM (about 66.7% less than diesel before 0.70 MPa, and even with the highest engine load 21.4% CO emissions had also reduced). The positive effect of adding alcohol should be proved from the comparison of the column height between BDMb and BDM(not less than 17.5% reduction of CO emissions). More homogeneous microemulsion formed with n-hexanol that might render fuel distributed better with air in cylinder which could further reduce CO emission [57].

Fig. 6b illustrated that CO_2 emission of each sample added as engine load increased. There was little disparity through each fuel before 0.46 MPa which might owe to the lower temperature in cylinder and limited amount of fuels participate in combustion. As engine load went up, a mass of fuel injected into cylinder and sharply rose inner temperature, which stimulated more CO_2 released. The lowest CO_2 emission was obtained by BDM in all situations (approximately 7.1%–27.3% lower than diesel). Higher O elements and 2% alcohol BDM contained bring more extra Sauerstoff atom injected into cylinder which could generate more CO was the probable reason for partly CO_2 reduction [58]. As compared with diesel, BDMs, BDMb and BDM reduced CO_2 emission not less than 2.7%, 6.4% and 8.5%, respectively (except BDMs at 0.69 MPa and 0.81 MPa). This evident reduction of CO_2 suggested that the superiority of microemulsification exerted. And the analysis result of BDMs, BDMb and BDM indicated that mixed surfactants were effective in reducing CO_2 emission and adding alcohol could further reduce not less than 2% CO_2 emission at higher engine load.

In Fig. 6c, considerable NO_X emission rise could be observed for all fuels before 0.8 MPa and then slightly decline. Lower NO_X emission in 0.92 MPa might owe to the transformation of NO_X which convert back into molecular nitrogen with the help of reverse NO_X mechanism that predominates at fuel rich conditions, which mainly combined hydrocarbon free radicals to generate NO, giving rise to the form of hydrogen cyanide (HCN) [26,59]. The highest NO_X emission diesel had in all situations might owe to the higher nitrogen diesel contained and an obvious advantage emulsified fuels have in flame temperature reduction which was caused by water evaporation, thermal dilution with water and combustion off-phasing [30,60]. Compared with diesel, BDMs, BDMb and BDM reduced NO_X not less than 1.0%, 3.0% and 8%, respectively (except BDMs at 0.23 MPa). This significant decrease of the emulsified fuels illustrated that microemulsification was an effective approach for oil upgrading and emission reduction. Analyzed the column height of BDMs, BDMb and BDM could easily find that the NO_X emission of BDM was the lowest and the highest one was BDMs. This consequence proved that the advantage of mixed surfactant compared to single one and further reduction on NO_X emission of adding alcohol as co-surfactant.

In Fig. 6d, the value of smoke intensity was undetected while the engine loads were lower than 0.46 MPa. The probable reason was the practical smoke intensity was lower than 0.001 m^{-1} (below the minimum which FTY-100 can be detected). Compared the column height of tested fuels we could easily find that there were little smoke intensity generated and the rising tendency was mild with the engine loads increase before 0.81 MPa. Even at the highest engine load, the optical absorption coefficient ($\boldsymbol{k}$) was small (lower than 0.500 m^{-1}) while emulsified fuels were also obtained higher $\boldsymbol{k}$ (approximately 16%–29% higher than diesel) which might be due to the shorter ignition delay and the larger organic matter bio-oil had [61]. Though the emulsified fuels had no superiority in reducing smoke intensity, the result also had some valuable information. As shown in Fig. 6d, the sequence of $\boldsymbol{k}$ for the emulsified fuels was BDMs > BDMb > BDM at each engine load, which indicated that the utilization of mixed surfactant and alcohol have a positive effect in reducing smoke intensity. Using mixed surfactant in micro-emulsion formation could reduce approximately 3%–20% smoke intensity than the one formed by single surfactant, while adding alcohol could further decrease the emission of smoke (not less than 10%). In other words, the thought of using mixed surfactant for oil upgrading was worth spreading.

4. Conclusion

The formed bio-oil (generated by co-liquefying of castor oil, SS and methanol) had similar heating value as compared with diesel (bio-oil: 38.84 MJ/kg, diesel: 42.03 MJ/kg) while contained lower nitrogen and higher oxygen elements which could well reduce CO and NO$_X$ emissions. The best microemulsified formula in this study has proved to be mixed surfactant (Span 80/Tween 80 = 7/3) with the help of 2% n-hexanol. As for bio-oil solubilization, the vast majority of hydrocarbons (23.82%) and plenty of esters (46.59%) were soluble into BDM at the relevant location which was based on the principal of “likes dissolves likes”. Generally, emulsified fuels had higher BSFC and BTE (at higher engine loads) than diesel due to its lower heating value and slight amount of water. This phenomenon also implied that emulsified fuels performed well in engine performance as engine fuels. Furthermore, from the data of emission for main gaseous pollutants, it was found that BDM reduced approximately 21.4%–66.7% (CO), 7.1%–27.3% (CO$_2$) and 1.5%–14.7% (NO$_X$) than diesel, respectively. Engine load and the addition of co-surfactant were common reasons for this difference. In this study, the smoke intensity of emulsified fuels were little higher than diesel. However, as the comparison between different emulsified fuels, we could easily find that the utilization of mixed surfactant and alcohol have a positive effect in reducing smoke intensity. The above result demonstrates that emulsified fuels have the potential of using as engine fuels and microemulsify technology could be an efficient approach on energy conservation and emission reduction.

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