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Fuel Properties of a Two-Phase Biodiesel Emulsion

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Abstract. Biodiesel is one of the most promising alternative clean fuels to fossil fuel, which can effectively reduce the emissions from fossil fuel burning. The high oxygen content in biodiesel can promote the burning process, but it can also increase NOx formation simultaneously, when biodiesel is used as fuel. Fuel emulsification is considered to be effective in reducing NOx emissions. In this study, soybean oil was used as raw oil to produce biodiesel by transesterification reaction. The biodiesel product was then emulsified with water and emulsifying surfactant to form water-in-oil (w/o) biodiesel emulsion. The biodiesel emulsion composed of 1.5% polyoxyethylated castor oil (EL-12), 0.7% lethicin and 0.5% cetylpyridinium chloride (CPC) was proved to have the better emulsifying activity (EA) and emulsifying stability (ES) values, and higher combustion heat than those of the neat biodiesel and reference biodiesel emulsion (with 2.7% EL-12 as the emulsifying surfactant).

Introduction

Biodiesel is well known due to its high degree of biodegradability, nearly zero toxicity and low emission. The high oxygen content in biodiesel results in the improvement of its burning efficiency, reduction of particulate matter (PM), carbon monoxide (CO), polycyclic aromatic hydrocarbons (PAH) and SOx [1]. Biodiesel, which is produced from vegetable oils, animal fats or used cooking oils, can be used as an alternative fuel for diesel engines. However, burning of neat biodiesel would produce about 10% more NOx than that of petroleum-based diesel [2, 3]. Nitrogen oxides are the precursors of ozone and acid rain which are detrimental to the environment as well as the human respiratory system. The emissions of NOx are critical, especially in ozone non-attainment areas, making the increase with biodiesel problematic to its widespread use.

In order to reduce this adverse effect, investigations have been carried out on different approaches for reducing NOx emission when biodiesel is used. Leung et al. concluded that controlling an individual engine operating parameter cannot acquire satisfactory results on optimizing biodiesel engine emission, and multi-parameter adjustment is required for reducing PAH, NOx and PM emissions [4]. Cetane is used as improving additive and themodified feedstock composition can reduce NOx emissions from biodiesel [5]. The emulsification technique is also being applied to reduce NOx emission and to promote the combustion efficiency for fossil fuels [6, 7]. It has been reported that 15% water in the diesel can give a reduction in NOx emission of up to 35% under regular conditions. The reduction in NOx emissions is explained by the reduction in the combustion temperature caused by the presence of water in the mixture [8, 9]. It is also found that diesel emulsions have lower soot and particulate contents in the exhaust [6]. The reduction in soot emissions is attributed to improved atomization caused by the rapid evaporation of the water drops and to the formation of hydroxyl radicals by water dissociation [9]. Furthermore, diesel emulsion reduced the heat flux, the metal temperatures, thermal loading, and the wear-metal debris in the crankcase oil of

the emulsified diesel [10, 11]. Diesel emulsions, which can be used in internal combustion engines, are easily applicable alternative fuels for the existing vehicle feet, and there is a growing interest in the use of diesel emulsions [12].

Previous studies on diesel emulsions have made some progresses; however, there are also some limitations. For example, too much quantity of surfactant was used (>10%) [13], or thecomposition of the emulsion was complicated [14]. More importantly, the emulsion was often unstable, which restricts its industrial applications [15]. In this study, by mixing a nonionic surfactant polyoxyethylated castor oil (EL-12), a zwitterionic surfactant Lethicin and a cationic surfactant cetylpyridinium chloride (CPC) at certain proportions, we found a biodiesel emulsion which is transparent, stable and with good heating value.

Experiment Details

Production Procedure for Biodiesel

Soybean oil was used as the raw oil. It was mixed with methanol with a molar ratio of 1:6, and the mixture then underwent transesterification reaction in order to produce a biodiesel. At the start of the process, methanol and 1 wt.% of sodium hydroxide (NaOH) of soybean oil were mixed using an electromagnetic stirrer.. The soybean oil with methanol in a reactor was then added with an aqueous mixture of sodium methoxide (CH_3ONa) by a metering pump and stirred by a mechanically homogenizing machine. The temperature was kept at 60℃ and a reflux condensation was used to prevent the methanol vaporization from the reactor. The transesterification reaction completed after about 60 min.

The product mixture was then kept still until the crude biodiesel and glycerol with different specific gravities were separated into two layers. The unreacted methanol was then removed from the coarse biodiesel through distillation at 70℃. Other impurities in the coarse biodiesel are then removed by washing with petroleum benzine (5 wt.% of coarse biodiesel) and water (10 wt.% of coarse biodiesel). The obtained biodiesel product was then added with 1 wt.% hydrogen peroxide (H_2O_2), followed by stirring with a mechanically homogenizing machine for 10 min to improve the fuel characteristics of the biodiesel *via* a peroxidation process.

Preparation of Biodiesel Emulsions

The emulsifying stability (ES), emulsifying activity (EA) of different surfactants were examined to select the most appropriate surfactant or their combination for biodiesel emulsion preparation.

A three-stage emulsification method was used to prepare the w/o biodiesel emulsion. Firstly, a cationic surfactant cetylpyridinium chloride (CPC) was dissolved in water to form solution A. Secondly, a certain amount of nonionic surfactant polyoxyethylated castor oil EL-12 and zwitterionic surfactant Lethicin were added to biodiesel to form solution B. At last, solution A was added into solution B, following by stirring with a mechanically homogenizing machine at a speed of 5000 rpm for 3 min to prepare the biodiesel emulsion [16, 17]. It is reported that adding 5wt. % of water into biodiesel decreased soot content in the flue gas greatly [12], and further addition of water gave only a limited extra reduction. It was reported that adding too much water was not beneficial for combustion because the loss of latent heat became too large for the fuel to burn completely [4]. Therefore, in this study, the water content in the biodiesel emulsion was kept 5 wt. %.

The biodiesel emulsion composed of 1.5% EL-12, 0.7% lethicin and 0.5% CPC was referred to as biodiesel emulsion A. For comparison, the biodiesel emulsion composed of 2.7% EL-12 was referred to as biodiesel emulsion B.**Characterization of Fuel Properties of Prepared Biodiesel Emulsions**

The stability of biodiesel emulsion (ES) was examined by centrifuging at 5000 rpm for 5 min in 15 mL centrifugal test tubes, and recorded the volumes of different layers such as water layer, sedimentation layer, emulsification layer, and oil layer. Another test tube with 15 mL biodiesel emulsions was stand for a preset time to measure the volume ratio of the emulsification layer to the total liquid, and the emulsifying activity (EA) value was defined as the volume ratio of the emulsification layer to the total emulsion in the test tube.

The Brookfield Programmable Viscometer (DV-Ⅱ+Pro, Brookfield Engineering Laboratories, Inc, USA) was used to measure the kinematic viscosity of the biodiesel emulsions at 40℃. The specific gravity of the biodiesel emulsions was measured by a specific gravity meter based on the standard method of ASTM D1298-99e2 [18]. A pH meter (826 pH mobile Meter, Metrohm Ltd., Switzerland) was used to measure the pH value of the emulsions. The oxidation stability of the samples was tested by thermal oxidation stability analyzer. The heating value of the biodiesel samples was analyzed by an oxygen bomb calorimeter (System C200 by IKA Co., Germany).

Results and Discussion

Optimization of Emulsion Formulation

At first, we selected 22 kinds of surfactants (Table 1) at the concentration of 2 wt.% to prepare biodiesel emulsions with 5 wt. % water [19], and recorded the EA and ES values. Since there was separation of water and biodiesel after 24 h for all of the emulsions made of a single surfactant, we tested the ES of the emulsions at 8 h after the biodiesel emulsions prepared. The aim of surfactant addition is to reduce oil and water superficial tension, active their surfaces and maximize the superficial contact area to make small emulsions [19]. This is due to the fact that a surfactant has both a hydrophilic group and a lipophilic group. The lipophilic group in the surfactant will absorb the oil phase while the hydrophilic group will absorb the water phase.

Table 1 The EA and ES values of w/o biodiesel emulsions with different kinds of surfactants

Surfactant	Emulsifying activity (EA)	Emulsifying stability (ES)	Surfactant	Emulsifying activity (EA)	Emulsifying stability (ES)
Tween 20	+	−	SG 6	−	−
Tween 40	+	−	SG 10	−	−
Tween 60	+	−	SG 185	−	−
Tween 80	+	−	MOA-4	−	−
Tween 85	+	−	MOA-7	−	−
EL-10	+	−	MOA-9	−	−
EL-12	+	+	CPC	+	+
EL-40	−	−	CPB	−	−
TX 4	−	−	STAB	+	+
TX 10	−	−	OP-10	−	−
TX 21	−	−	Lethicin	++	+

EL: Ethoxylated castor oil
TX: Polyoxyethylene nonyl phenyl ether
SG: Polyoxyethylene stearate
CPC: Cetylpyridinium chloride
CPB: Cetylpyridinium bromide
STAB: Steartrimonium bromide
"-" for the volumetric proportions of emulsification layer < 70%
"+" for the volumetric proportions of emulsification layer between 70% and 80%
"++" for the volumetric proportions of emulsification layer between 80% and 90%
"+++" for the volumetric proportions of emulsification layer between 90% and 100%

As shown in Table 1, EL-12, Lethicin, CPC and STAB have acceptable EA and/or ES. So we combined these four surfactants to prepare a better emulsion. At first, the surfactants were used pairwise and with each combination at the proportion of 6:1, 4:1, 2:1, 1:1, 1:2, 1:4 and 1:6. As shown in Table 2, we found that EL-12 and Lethicin made the best combination. And when EL-12 and Lethicin were mixed at the proportion of 2:1, the biodiesel emulsion was the most stable one. In this part of the experiment, most of the biodiesel emulsions composed of two or three kind of surfactants were stable for 24 h, so we observed the ES of the emulsions after the biodiesel emulsions prepared for 24 h. Since CPC and STAB are hydrophilic (with HLB value 26 and 15.8), we added CPC or

STAB to water. The solution was then added to biodiesel with EL-12 and Lethicin. As shown in Table 2, the surfactant mixture with 0.5% CPC, 1.3% EL-12 and 0.7% Lethicin is able to produce biodiesel emulsion with the highest emulsification stability among the surfactant mixtures. For at least 3 month, the emulsion is kept stable without obvious phase separation.

Table 2 EA/ES values of biodiesel emulsions with multi-surfactants

		CPC (2-n%)	STAB (2-n%)	Lethicin (2-n%)
EL-12 (n%)	1.7	−/+	−/+	−/+
	1.6	−/−	−/−	−/+
	1.3	−/−	−/−	++/++
	1	−/−	−/−	++/+
	0.7	−/−	−/−	+/−
	0.4	+/−	−/−	+/−
	0.3	+/−	−/−	+/−

		STAB (2-n%)	Lethicin (2-n%)
CPC (n%)	1.7	−/−	−/−
	1.6	−/−	−/−
	1.3	−/−	−/−
	1	−/−	−/−
	0.7	−/−	−/−
	0.4	−/−	+/−
	0.3	−/−	+/−

		Lethicin (2-n%)
STAB (n%)	1.7	−/−
	1.6	−/−
	1.3	−/−
	1	−/−
	0.7	−/−
	0.4	+/−
	0.3	+/−

	CPC (n%)				STAB (n%)			
	0.1	0.3	0.5	0.7	0.1	0.3	0.5	0.7
EL-12 (1.3%) Lethicin (0.7%)	++/++	++/++	++/+++	+/+	+/+	+/+	+/+	+/+

"-" for the volumetric proportions of emulsification layer<70%
"+" for the volumetric proportions of emulsification layer between 70% and 80%
"++" for the volumetric proportions of emulsification layer between 80% and 90%
"+++" for the volumetric proportions of emulsification layer between 90% and 100%

Considering the enormous volume of diesel fuel that is being consumed today, a replacement of just a fraction of regular diesel by w/o biodiesel emulsion would be economic. The EA and ES values could be used as two indices for the quality of the emulsification characteristics for an emulsion [20]. The EA values indicate the capability for a surfactant to form and stabilize an emulsion. The ES property represents the capability of an emulsion to keep the volumetric proportion of its emulsification layer motionless for a period of time or heated at some temperature for a preset time. An emulsion with higher volumetric proportion of emulsification layer or lower sedimentation layer after being kept motionless for a preset period imply a larger value of ES and better capability to prolong its emulsification effects. In this study, the EA and ES values of biodiesel emulsion A with

EL12, CPC and Lethicin as combined surfactant are 86% and 91% respectively. This implies that the existence of Lethicin and CPC in the biodiesel emulsion A promotes the EA and ES of the w/o emulsions prepared from sole EL12 surfactant (reference biodiesel emulsion B).

Viscosity, Specific Gravity, Oxidative Stability and pH Value of Biodiesel Emulsions

As shown in Table 3, the kinematic viscosity values of the neat biodiesel, biodiesel emulsion A and biodiesel emulsion B are 3.73, 4.61 and 4.58 cP, respectively. The kinematic viscosity value of the emulsions increases by 23.5% and 22.7% compared to neat biodiesel. This implies that the presence of water and surfactants in biodiesel emulsion changes its viscosity. The water in biodiesel emulsions increases the emulsion's viscosity primarily because of a larger number of dispersed liquid droplets in the w/o biodiesel emulsions.

The specific gravities of the biodiesel emulsion A and B are relatively comparable and are both larger than the neat biodiesel, which is because of higher specific gravity of water in these emulsions.

Linoleic acid, an example of a polyunsaturated fatty acid, present in soybean oil at a concentration of approximately 0.55 %, is readily to be oxidized, leading to the breakdown of biodiesel and formation of higher concentrations of engine deposits. In this study, addition of surfactants and water reduced oxidative stability value, but the values are all higher than 6.0 h, sufficient for the commercial biodiesel.

The pH value of the neat biodiesel is 7.37. The biodiesel emulsion A has a smaller pH value than that of the neat biodiesel, which is owing to the surfactants in the emulsion (especially CPC, the cationic surfactant).

Table 3 Properties of neat biodiesel, biodiesel emulsions

	Neat biodiesel	Biodiesel emulsion A	Biodiesel emulsion B
Heating value [J/g]	39426.3	37787.7	37297.3
Heating value deducted water content [J/g]	39426.3	40199.7	39678.0
Specific gravity [g/ml]	0.82	0.88	0.88
Kinematic viscosity [cP at 40 ℃]	3.73	4.61	4.58
pH value	7.37	6.67	7.02
Oxidative stability values [h]	12.1	10.7	9.0

Combustion Heat Value of Biodiesel Emulsions

A comparison of fuel properties such as combustion heat value and kinematic viscosity among the neat biodiesel, biodiesel emulsion A and biodiesel emulsion B is shown in Table 3. The neat biodiesel has a larger heating value than the other two kinds of biodiesel emulsions. However, when the 5% wt. % water is deducted from the calculation for the combustion heat value, the biodiesel emulsion has a 5-7 % higher heat value than neat biodiesel. This implies that the biodiesel emulsion has higher fuel economy than the neat biodiesel. The biodiesel emulsion A has the highest heat value after reducing its water content among these three fuels, which is primarily due to the occurrence of a larger extent of the micro-explosion phenomenon which results in a higher combustion efficiency during the burning process of the biodiesel emulsion [21]. The micro-explosion phenomenon from burning emulsified fuel with water has been observed and described in many previous studies [7, 17]. Since the boiling point of water is lower than that for diesel fuel, the enveloped water component explodes through the outer oil layer after it has absorbed sufficient reaction heat for boiling. Hence, the atomized emulsion drops are further atomized into finer oil droplets at a result of micro-explosion,

leading to a stronger degree of mixing and a faster reaction rate between the atomized oil droplets and the surrounding air. Thus, a larger extent of combustion reaction is achieved. In addition, it is reported that the combustion efficiency is enhanced and pollutant emission decreased due to the occurrence of micro-explosions when emulsified fuel is used [16].

Conclusion

The biodiesel produced from soybean oil can be transformed into stable emulsions with water and certain emulsifying surfactants. In this study, the biodiesel emulsion composed of 1.5% EL-12, 0.7% Lethicin and 0.5% CPC has been proved to have the best EA and ES values. Burning of the biodiesel emulsion A produces significantly higher combustion heat than that of the neat biodiesel, if the water content is removed when calculating the amount of heat release.

The specific gravity and kinematic viscosity of the biodiesel emulsion A are larger than those of neat biodiesel. The oxidative stability value of biodiesel emulsion A is the same as that of neat biodiesel. And the pH value of biodiesel emulsion A is lower than the neat biodiesel.

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