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Stability mechanism investigation of emulsion fuels from biomass pyrolysis oil and diesel

Zuogang Guo [a,b], Shurong Wang [b,*], Xiangyu Wang [b]

[a] Guang Dong Electric Power Design Institute, China Energy Engineering Group Co. Ltd., 510663 Guangzhou, China
[b] State Key Laboratory of Clean Energy Utilization, Zhejiang University, Zheda Road 38, 310027 Hangzhou, China

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ABSTRACT

In this paper, emulsion fuels from crude bio-oil and its molecular distillation fractions were prepared by single ultrasonic and ultrasonic-mechanical emulsification. The results showed that the emulsions from crude bio-oil and 0# diesel had the best stability, with a stability time of 31 days. The stability time of the bio-oil middle fraction emulsion was 216 min, while that of the bio-oil heavy fraction emulsion was as low as 14 min. The particle size distributions of the emulsions were analyzed by a Malvern particle size analyzer. Emulsion fuels made from crude bio-oil and the bio-oil middle fraction had a smaller droplet size of 8–60 nm. In contrast, the emulsion fuel from the alcohol-diluted bio-oil heavy fraction had much larger droplet size, reaching up to 6000 nm. Compared with single ultrasonic emulsification, ultrasonic-mechanical emulsification had positive effects on increasing the stability time of the crude bio-oil emulsion, but negative effects on the stability time of the bio-oil middle and heavy fraction emulsions. To explain the above differences, spherical shell mechanism models were proposed according to the composition properties of the crude bio-oil and its fractions.

1. Introduction

Due to environmental pollution and the growing scarcity of fossil fuel, biomass has received increased attention because of its renewability and environmental friendliness [1–3]. Fast pyrolysis technology, a biomass utilization method, can convert solid biomass into liquid bio-oil with higher energy density and better transportation properties. Pyrolysis experiments on empty fruit bunch were conducted to determine the key variables which were required to maximize the liquid bio-oil yield [4]. Results indicated that the maximum liquid yield reached 55.14 wt% at 450 °C with a vapor residence time of 1.03 s. The experiments on non-catalytic and catalytic pyrolysis of cotton seed were investigated by Ersan [5] to determine the influence of MgO catalyst addition on quantity and quality of bio-oil. The addition of MgO catalyst decreased the quantity of bio-oil yet increased the quality of bio-oil in terms of calorific value, hydrocarbon distribution and removal of oxygenated groups. However, compared to fossil fuels such as petroleum, crude bio-oil still has some disadvantages in fuel properties, such as high oxygen content, high water content and instability, which limit its direct application as a high-grade fuel [6,7]. Bio-oil upgrading technologies mainly include catalytic hydrogenation [8,9], catalytic cracking [10,11], catalytic esterification [12] and emulsification [13,14].

Emulsification is the only physical upgrading technology that blends immiscible liquids into homogenous emulsions, through the addition of emulsifiers. Through this method, stable emulsions of bio-oil and diesel can be prepared. The emulsion behaviors between crude bio-oil and 2# diesel was conducted by Ikura et al. [14], and the tests showed that the fuel emulsion had good stability with 10–20% bio-oil content, and the viscosity of the emulsion was substantially lower than pure bio-oil. Yu et al. [15] studied the utilization of emulsion fuels composed of crude bio-oil and 0# diesel. The experimental results showed that the stability time reached 120 h when the content of bio-oil was 10% and the content of emulsifier was between 4 and 6%. The lubricity of bio-oil/diesel emulsions was studied on a High Frequency Reciprocating Test Rig [16]. Results showed that the lubrication ability of the bio-oil/diesel emulsion fuels was better than that of the 0# diesel fuel in China. However, the anti-corrosion and anti-wear properties of the emulsion fuel were not satisfactory in comparison with those of conventional diesel fuel. The combustion performance and emission characteristics of bio-oil/Jatropha methyl ester (JME) emulsion fuels were also investigated in a single cylinder diesel engine [17]. Shorter ignition delay and higher peak cylinder pressure were observed with bio-oil/JME emulsion fuels compared to that of

* Corresponding author. Tel.: +86 571 87952801; fax: +86 571 87951616.
E-mail address: srwang@zju.edu.cn (S. Wang).

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diesel. There was also a significant reduction in the nitric oxide (NO) emissions by 2.5% when fueled with bio-oil/JME emulsion fuels. In our previous research [18,19], mechanical or ultrasound emulsification was used to prepare emulsions from crude bio-oil and diesel. Crude bio-oils from pyrolysis of different biomass resources, such as rice husk, rice straw and algae, were used in those experiments, and it was found that the emulsion fuel from rice straw bio-oil and diesel had the longest stability time of 16 days. In the ultrasonic emulsion fuel preparation, the stability time of 35 h was reached with an emulsion of 5% bio-oil mass content and ultrasonic power of 80 W. In the present work, a comparative investigation between emulsion preparation from crude bio-oil and its fractions was conducted.

As bio-oil is a thermosensitive mixture, it cannot be separated efficiently with traditional distillation without coking problems. To overcome the obstacles in traditional distillation, as well as pushing forward bio-oil fraction research, a KDL-5 molecular distillation apparatus was purchased from UIC company, Germany. We previously reported on our bio-oil separation research using the KDL-5 molecular distillation apparatus, utilizing different separation temperatures [20,21] and pressures [22]. The bio-oil fraction, or its typical components, was converted by catalytic esterification or catalytic cracking [12,23]. In the present work, this type of distillation technology was adopted to separate thermosensitive bio-oil efficiently in terms of obtaining middle and heavy fractions. We also conducted a comparative study on emulsion preparation from crude bio-oil, middle fraction, and heavy fraction using single ultrasound and ultrasound-mechanical emulsification. Mechanism models based on the composition of crude bio-oil and its fractions were proposed to illustrate the variations of emulsion stability.

2. Material and methods

2.1. Bio-oil separation by molecular distillation

The crude bio-oil used in this paper was derived from the fast pyrolysis of pineapple pine at temperatures of 500–550 °C. The bio-oil middle fraction and heavy fraction were obtained by a KDL-5 molecular distillation apparatus manufactured by the UIC Corporation, Germany, under 90 °C temperature and 700 Pa pressure. More detailed information about the molecular distillation equipment and its operating procedure is available in our early papers [18,19].

2.2. Physical property and composition analysis of bio-oil and its fractions

Higher heating values of bio-oil and its fractions were measured with 5E-KC5410 calorimeter. Density was measured under ambient temperature. The compounds in the crude bio-oil and its fractions were identified by gas chromatography and mass spectrometry, using a Trace DSQ-2 GC/MS with a 30 m × 0.25 mm × 0.25 μm Agilent DB-WAX polar capillary column. The oven temperature was first kept at 40 °C for 1 min, then increased to 240 °C with a heating rate of 8 °C/min and maintained for 10 min.

2.3. Fuel emulsion preparation and measurement

0# grade of conventional diesel was bought from commercial petrol station. It has a heating value of 40.20 MJ/kg and a density of 0.845 g/cm^3. Crude bio-oil has a heating value of 16.40 MJ/kg and a density of 1.101 g/cm^3. Commercial surface active agents included Span-80, Tween-80 and Span-85 were mixed at a certain percent to obtain emulsifiers with different HLB (Hydrophile–Lipophile Balance) values.

Ultrasonic and ultrasonic-mechanical emulsification was used to prepare emulsion fuels of crude bio-oil and 0# diesel, as well as bio-oil fractions and 0# diesel. Ultrasonic emulsification was performed with a Sonicator Q700 ultrasonic instrument under the following conditions: operating frequency of 20 kHz, amplitude output of 20% and operating time of 2 min. Mechanical emulsification was conducted with a Fluke F6/10 homogenizer using a speed 5000 rpm and a time of 5 min. During the ultrasonic-mechanical emulsification, emulsion fuels were first ultrasonically mixed for 2 min, and then quickly transferred to the mechanical emulsification equipment for 5 more minutes of mixing. The stability of emulsion fuels was evaluated by stable time, which was defined as the time period from fresh emulsion fuel formation to precipitation appearance.

In our study, crude bio-oil and its middle fraction had good flowability, and were used to prepare emulsion fuels directly. The bio-oil heavy fraction couldn't be directly emulsified with 0# diesel due to its high viscosity. Therefore, methanol or ethanol was used as a diluent to prepare the alcohol-diluted heavy fractions. Several emulsions were prepared with the crude bio-oil and its fractions to obtain their individual optimal HLB value, with a mass ratio of bio-oil (or bio-oil fraction):0# diesel: emulsifier of 10:85:5. The optimal HLB values of the crude bio-oil emulsion fuel, bio-oil middle fraction emulsion, methanol-diluted heavy fraction and ethanol-diluted heavy fraction were 7.0, 4.3, 1.8 and 6.0, respectively. Then, emulsions were prepared by single ultrasonic and ultrasonic-mechanical emulsification using their optimal HLB values. A Malvern nanometer particle size analyzer (Zetasizer Nano S90) was used to analyze the emulsion droplet size distribution.

3. Results and discussion

3.1. Yields and properties of bio-oil fractions

Bio-oil is thermosensitive and suffers from severe coking problems during conventional distillation. Molecular distillation is suitable for the separation of thermosensitive mixtures. Here, a KDL-5 molecular distillation apparatus was used to separate crude bio-oil at 90 °C and 700 Pa without bio-oil coking problems, and the yields and physical properties of the bio-oil fractions were measured. The feeding weight of the bio-oil was 224.82 g during the separation process, and 127.03 g of the distilled middle fraction was collected, with a yield of 56.50 wt%. The water content of crude bio-oil was 23.30 wt%; however, during the separation process most of the water was distilled into the bio-oil middle fraction, resulting in its water content rising up to 35.57 wt%. The water content of the heavy fraction (residual fraction) decreased to 4.20 wt%, due to the removal of water. The redistribution of water had a significant influence on the physical properties of the fractions. The middle fraction concentrated the majority of the water from the crude bio-oil, and its flowability was enhanced. However, the heating value of the middle fraction declined to 12.62 MJ/kg due to the water enrichment, while that of the heavy fraction rose to 20.13 MJ/kg; both from 16.40 MJ/kg of crude bio-oil.

The chemical composition of crude bio-oil and its fractions obtained from molecular distillation was shown in Fig. 1. The bio-oil was comprised of oxygenated chemicals such as ketones, carboxylic acids, aldehydes and sugars. The content of ketones was 24.81%, and that of carboxylic acids was 20.52%. Compared with crude bio-oil, the bio-oil middle fraction still had a higher content of small molecular oxygenated chemicals, such as ketones and carboxylic acids. The considerably increased content of carboxylic acids indicated that carboxylic acids were enriched in the middle fraction during molecular distillation. In comparison with the crude bio-oil and the middle fraction, the content of small molecular ketones and