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Comparison of biodiesel production from crude *Jatropha* oil and *Krating* oil by supercritical methanol transesterification

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ABSTRACT

This work compared the production of biodiesel from two different non-edible oils with relatively high acid values (*Jatropha* oil and *Krating* oil). Using non-catalytic supercritical methanol transesterification, high methyl ester yield (85–90%) can be obtained in a very short time (5–10 min). However, the dependence of fatty acid methyl ester yield on reaction conditions (i.e., temperature and pressure) and the optimum conditions were different by the source of oils and were correlated to the amount of free fatty acids (FFAs) and unsaturated fatty acid content in oils. *Krating* oil, which has higher FFAs and unsaturated fatty acid content, gave higher fatty acid methyl ester yield of 90.4% at 260 °C, 16 MPa, and 10 min whereas biodiesel from *Jatropha* oil gave fatty acid methyl ester yield of 84.6% at 320 °C, 15 MPa and 5 min using the same molar ratio of methanol to oil 40:1. The product quality from crude *Krating* oil met the biodiesel standard. Pre-processing steps such as degumming or oil purification are not necessary.

1. Introduction

Fatty acid alkyl ester or known as biodiesel has been studied as an alternative fuel for diesel engines for over a decade [1–3]. Both catalytic and non-catalytic routes have been employed for the production of biodiesel from different kinds of raw materials. The drawbacks of catalytic transesterification using basic, acid, and enzymatic catalysts usually involve the generation of waste water and by-products, slow process, and high enzyme cost, respectively [4–6]. The non-catalytic transesterification in supercritical alcohol has been proposed as a fast and environmentally friendly method for biodiesel production [7]. Compared to the catalytic processes, the reaction in supercritical alcohol (usually methanol) was found to be completed in a very short time (minutes compared to hours) and product purification is much simpler [8].

Raw material for biodiesel production is one of the important concerns. Besides the quality of raw material, the types of these feedstocks have been on debate. In the early years of biodiesel production, many oil crops came from plants that can also be used as food source such as soybean, rapeseed, sunflower, etc. Due to increasing demand and cost of edible oils and concern about food crisis, the use of non-edible oils for biodiesel production has received more attention. Among many non-edible oils available, *Jatropha* oil has gained popularity as biodiesel feedstock because of the ease of planting at minimal cost. Previous studies have shown that high fatty acid methyl ester (FAME) yield (>93%) can be obtained by double and triple stage transesterification using sodium hydroxide and sulfuric acid catalysts [9–11]. In addition, these biodiesel fuels produced less exhaust emission as compared to high speed diesel [12]. *Calophyllum inophyllum* L. or *Krating* (Thai name) or *Polanga* (Indian name) seed oil is another interesting oil to use as a source of feedstock for biodiesel production. *Krating* oil is a non-edible oil which is obtained from pressing *Krating* seed with mechanical press. It was reported that *Krating* seeds, when dried, gave a great amount of oil roughly 18 kg per 100 kg of dry *Krating* seeds [13]. Unfortunately, the relatively high kinematic viscosity and acid value of *Krating* seed oil make it unsuitable for use in biodiesel production by means of the conventional methods. The technical know-how in using this seed oil as a raw material in biodiesel production via the supercritical methanol process, however, is scarcely found.

Biodiesel production via the non-catalytic supercritical methanol transesterification using *Jatropha* oil as the feedstock has been reported [14] but in less extent comparing to other edible oils such as soybean oil, rapeseed oil, and sunflower oil [7,15–19]. Generally, the presence of water and free fatty acids (FFAs) in oil does not affect the progress of transesterification in supercritical alcohol because transesterification, triglyceride hydrolysis, and alkyl esterification occur simultaneously [7,20,21]. Because alkyl

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esterification is faster than transesterification, complete conversion of FFA to the final FAME products can be achieved [20]. Rathore and Madras [14] attempted to correlate the fatty acids composition to the rate constant of biodiesel synthesis in supercritical methanol transesterification. The study observed that vegetable oil with higher saturated acids composition has higher rate constant than vegetable oil with lower saturated acids for example, coconut oil (~88% saturated acids) has higher rate constant of $5.9 \times 10^{-3}\ s^{-1}$ than *Jatropha* (~26% saturated acids) which has a rate constant of $2.6 \times 10^{-3}\ s^{-1}$. However, an opposite trend has been observed by Bunyakiat et al. [22], in which palm kernel oil (contains lower saturated acids) gave higher conversion than coconut oil (contains higher saturated acids).

In the present study, two types of non-edible oils (*Jatropha* oil and *Krating* oil) containing different amounts of saturated and unsaturated fatty acids were investigated as the feedstock in the biodiesel production via supercritical methanol transesterification. The reaction was carried out at temperature range of 200–350 °C, pressure 8–18 MPa, and molar ratio of methanol:oil 20:1–60:1. The properties of produced biodiesel were compared to the standard specification of biodiesel EN 14214.

2. Experimental

2.1. Materials

Crude *Jatropha* oil and crude *Krating* oil were used as received from pressing the seed with hydraulic press without any further purification. Methanol (98% purity) was supplied by Zenith Science Co., Ltd. Thailand. Standard methyl ester including methyl palmitate, methyl stearate, methyl heptadecanoate, methyl oleate, and methyl linoleate were AR grade and purchased from Sigma–Aldrich USA.

2.2. Methods

The synthesis of biodiesel in supercritical methanol was carried out using an 800 ml stainless steel batch-type reactor. The experimental set-up is illustrated in Fig. 1. The reaction conditions were temperature 200–350 °C, pressure 8–18 MPa, methanol:oil molar ratios 20:1–60:1, and reaction time 5–15 min. First, 90 g of crude oil was mixed with liquid methanol according to the selected molar ratios. This gave the total volume of the oil-methanol mixture no greater than 500 ml (maximum working volume of the reactor vessel is 500 ml). Then poured the mixture into the reactor. After being charged the system was purged with nitrogen gas and closed.

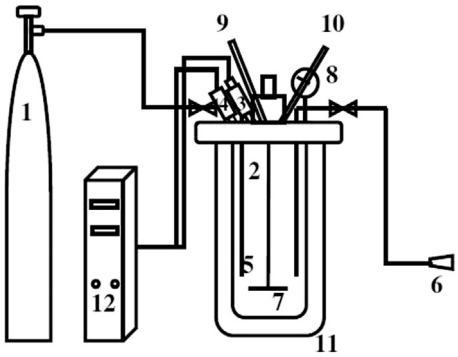

Fig. 1. Experimental set-up for supercritical methanol transesterification. Description: (1) nitrogen tank; (2) reactor; (3) pressure detector; (4) thermocouple; (5) inlet tube; (6) outlet tube; (7) stirrer; (8) pressure gage; (9) cooling water inlet; (10) cooling water outlet; (11) heated jacket; (12) controller.

The desired reaction temperature and pressure were set on the control panel. The pressure and temperature of the reactor can be monitored in real time. Then the heater was turned on. The mixture liquid in the reactor was stirred at a constant rate of 200 rpm in all tests. For the operating condition at low temperature and under high pressure the system could not reach the target pressure. To facilitate pressure build up inside the reactor, partially amount of nitrogen gas was added into the reactor before running the experiment. As the reactor reached the designated temperature and pressure, the recording of the reaction time began. After completion of the set time period, the vessel was depressurized and cooled down to room temperature by cooling water. The products were discharged from the reactor. The mixture products were then evaporated at 40 °C for about 30 min by rotary evaporator to remove an excess of unreacted methanol in the products. Separation of biodiesel and glycerol was done in a separating funnel and allowing the two phases to separate for about 30 min. The upper and the lower phases were fatty acid methyl esters (biodiesel) and glycerol, respectively. The samples were then analyzed for FAME content by a gas chromatography–mass spectroscopy.

2.3. Analysis

The crude *Jatropha* seed oil, *Krating* seed oil and biodiesel product were analyzed for their acid values based on ASTM D664, water content based on EN ISO 12937, iodine number based on EN14111 and saponification value based on AOCS official method Cd-3b-76. The heating value was analyzed according to ASTM D240 and kinematic viscosity according to ASTM D445. Fatty acid methyl ester percentage (%FAME) of biodiesel product was analyzed by gas chromatography–mass spectrometer (GCMS-QP2610, Shimadzu, Japan) based on EN 14103 using a 30 m length and 0.25 mm internal diameter of capillary column lined with a 0.25 μm film thickness of Rtx-5 ms (Rextex). Flame ionization was used as a detector. Methyl heptadecanoate was used as an internal standard. Samples volume of 1 μl was injected with a split/column flow ratio 24:1. The helium was used as the carrier gas at a flow rate of 1 ml/min. The injection temperature was 250 °C and oven temperature was chosen at 250 °C (programmed to start at 120 °C, held at this temperature for 5 min and heated at a rate of 3 °C/min to 250 °C).

3. Results and discussion

3.1. Basic properties of crude Jatropha oil and Krating oil

The basic properties of *Jatropha* oil and *Krating* oil were analyzed and the results are shown in Table 1. Acid value of *Krating* oil was four times higher than *Jatropha* oil, representing high FFA in the oil (FFA content is approximately a half of that of acid value). The presence of FFA is a cause of soap formation in the biodiesel production using basic catalysts but it has negligible effect in the biodiesel production via non-catalytic supercritical methanol transesterification [21]. The lower saponification value of *Jatropha* oil indicates that the *Jatropha* oil contained fatty acid molecules with longer carbon chain than *Krating* oil. The iodine value represents the content of unsaturated fatty acids in oils. The higher the iodine value the greater the content of unsaturated fatty acid. The iodine value of *Krating* oil was slightly higher than *Jatropha* oil. According to Rathore and Madras [14], *Jatropha* oil contained unsaturated fatty acids > 70% (by weight) of total fatty acid. The viscosity of *Krating* oil is twice of that of *Jatropha* oil. However, the viscosity of both oils far exceeds that of standard biodiesel so transesterification reaction is necessary before applying as biodiesel fuels. The heating value represents energy obtained from combustion in engine in which the higher the better. Both *Jatropha*