Synthesis of Biodiesel from Palm Oil in Capillary Millichannel Reactor: Effect of Temperature, Methanol to Oil Molar Ratio, and KOH Concentration on FAME Yield

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Abstract

Application of microtube reactor for the continuous synthesis of biodiesel has been widely studied due to excellent performance in liquid-liquid phase reaction. In order to commercialize biodiesel production, integration of microtube reactor is highly recommended. Therefore, in this study, synthesis of biodiesel was carried out in capillary millichannel reactor with inner diameter of 1.59 mm using methanol and potassium hydroxide (KOH) as base catalyst with palm oil as a feedstock. The influences of reaction temperature, methanol to oil molar ratio, and KOH concentration on the production of fatty acid methyl ester (FAME) were examined. The highest FAME yield was achieved at 60 °C with 23:1 methanol to oil molar ratio and 5 wt% of KOH concentration.

1. Introduction

Fossil fuels are non-renewable energy which is limited in supply. It is estimated that petroleum and coal will...
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begradually depleting due to the increase in the population growth and energy consumption. Therefore, research on biodiesel, a renewable and environmentally friendly energy has been widely studied in recent years. Biodiesel or generally known by name of fatty acid alkyl ester is synthesized by transesterification reaction of triglyceride in vegetable oils or animal fats with short-chain alcohol in the presence of a catalyst. Biodiesel has physical properties and energy content that is close to petroleum diesel. In addition, biodiesel is non-toxic, biodegradable, and produces low emissions of carbon monoxide, sulfur dioxide, and unburned hydrocarbon. These properties make biodiesel a good alternative fuel.

A variety of oils (both vegetable oil and animal fats) can be used to produce biodiesel. Typical feedstocks of biodiesel are palm oil, rapeseed oil, soybean oil, sunflower oil, and canola oil. Malaysia is currently the world’s second largest producer of palm oil after Indonesia. Unlike soybean and rapeseed oil, palm oil is a perennial crop which means the production of oil is continuous and uninterrupted. Janaun et al. reported that palm oil has dominated the world’s vegetable oil demand because of its versatile applications from food to consumer product, and now biodiesel. Furthermore, palm oil has the highest fossil energy balance and the lowest production cost relative compared to other feedstocks. Therefore, palm oil-based biodiesel has high potential to be the next sustainable energy.

Microtube reactor with inner diameter less than 1000 μm exhibits excellent performance in biodiesel production. High mass transfer rate due to high interfacial surface area and internal circulation flow in a microtube reactor resulting to high fatty acid methyl esters (FAME) yield. Guan et al. conducted an experiment using a microtube reactor for the continuous production of biodiesel using sunflower oil. The methanol to oil molar ratio is 4.6:1 with 1 wt% of KOH concentration at 60 °C. They reported that substantially 100% oil conversion was achieved within 240 s by using microtube reactor compared to conventional batch reactor which took approximately 600 s. This finding was supported by Sun et al. where they reported that over 95% of methyl yield was obtained with a residence time of about 360 s.

Application of microtube reactor is suggested to be applied in the industry with multiple layer technique. Besides, microtube reactor could be used by individual consumer at home with a simple technique to recycle their waste cooking oil in order to encourage people to preserve the environment. Thus, the application of a microtube reactor for commercial biodiesel production is highly recommended. However, condition parameters for the production of biodiesel in millichannel reactor have not been reported.

In order to expand the scope of microtube reactor, this study is intended to investigate the performance of milli-size reactor. Transesterification of palm oil with methanol was carried out in transparent Teflon with inner diameter of 1.59 mm using KOH catalyst to form FAME. The influences of the reaction temperature, methanol to oil molar ratios, and KOH concentration on the production of biodiesel were studied.

2. Experimental

The transesterification experiment was conducted by using commercial cooking palm oil (Seri Murni) from FFM Berhad, Malaysia as a feedstock. Esterification process is not required in this study due to low acid value in palm oil which is 0.37 mg KOH/g. Meanwhile, methanol, acetic acid, and methyl oleate were supplied by Merck Chemical, German. The potassium hydroxide (KOH) as a catalyst was purchased from R&M Chemicals.

A schematic diagram of the experimental setup is depicted in Fig. 1. The millichannel reactor was made of Teflon tubing with inner diameter of 1.59 mm. Two syringe pumps were used to feed methanol containing KOH and palm oil. The liquids were mixed at T-shaped joint before entering the heated millichannel reactor. The millichannel reactor was placed on the hot plate and covered with glass to prevent heat loss during the experiment. The product was collected after termination of the reaction by acetic acid. The collected product was rinsed with distilled water and centrifuged at 4500 rpm for 15 minutes. This procedure was repeated 3 times to separate unreacted methanol, glycerol, KOH, and acetic acid from the oil phase.
Two series of experiments were conducted at reaction temperatures of 25 and 60 °C by varying the tube length and flow rate as described in Table 1 to study the effect of temperature. The methanol to oil molar ratio and KOH concentration were kept constant at 23:1 and 4 wt%.

Table 1. Experimental condition

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Tube length [mm]</th>
<th>Flowrate [cm³/h]</th>
<th>Residence time [s]</th>
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Furthermore, in this study, more experiments have been conducted to study the effect of methanol to oil molar ratio and KOH concentration on FAME yield.

Each product was analyzed using high performance liquid chromatography (HPLC) from Shimadzu, Japan equipped with refractive index detector (RID). Silica-gel column (Shim-pack CLC-SIL) was used to determine the FAME yield. 100 μL of the rinsed product was diluted in 3 mL of hexane and was injected into HPLC column. The column temperature was maintained at 40 °C and the mobile phase was n-hexane/2-propanol = 99.5/0.5 (v/v).

Two peaks appeared in the liquid chromatogram were attributed to the sum of unreacted glyceride (monoglyceride, diglyceride, and triglyceride) and sum of FAMEs. Methyl oleate was used as standard to determine FAME. The FAME yield was calculated using equation (1) which has been reported by Guan et al.9;

\[
\text{FAME yield} = \left( \frac{C_{\text{FAME}}}{3C_{\text{oil}}} \right) \times 100
\]  

where \(C_{\text{FAME}}\) is the molar concentration of FAME in the product and \(C_{\text{oil}}\) is the molar concentration of triglycerides.
in the feedstock, respectively as described in equation (2) and (3);

\[ C_{\text{FAME}} = \left( \frac{\rho_{\text{ME}}}{\text{MW}_{\text{ME}}} \right) \times \text{Area of FAME} \quad (2) \]

\[ C_{\text{oil}} = \left( \frac{\rho_{\text{oil}}}{\text{MW}_{\text{oil}}} \right) \times \text{Area of methyl oleate} \quad (3) \]

where,

- \( \rho_{\text{ME}} \) is the density of methyl oleate,
- \( \rho_{\text{oil}} \) is the density of palm oil,
- \( \text{MW}_{\text{ME}} \) is the molecular weight of methyl oleate,
- \( \text{MW}_{\text{oil}} \) is the molecular weight of palm oil.

3. Results and Discussion

3.1 Effect of reaction temperature

Fig. 2 shows the effect of reaction temperature on the FAME yield. FAME yield was higher at 60 °C compared to 25 °C. High reaction temperature enhances not only the intrinsic reaction rate but also the mass transfer. High reaction temperature improved the solubility of methanol and triglyceride which enhanced the mass-transfer. Cheng et al.\(^{11}\) and Gunvachai et al.\(^{12}\) found that the solubility between triglyceride and methanol gradually increases with increasing the concentration of FAME. They also mentioned that lower concentration of FAME is needed to achieve a homogeneous phase at 60 °C compared to 20 °C. Temperature plays an important role in improving the solubility of triglyceride and methanol since the solubility is increased with the increased of temperature. This findings also supported by Darnoko et al.\(^{13}\), Vicente et al.\(^{14}\), and Nakpong et al.\(^{15}\) were they reported that the increase in the methyl ester content might have been due to the viscosity of the oil decreasing with an elevation of reaction temperature, which resulted in an increase in the solubility of the oil in the methanol, leading to the improvement in the contact between the oil and methanol.

Fig. 2. Effect of reaction temperature on FAME yield.
(Methanol to oil molar ratio: 23:1, KOH concentration: 4 wt%)
Further increase in reaction temperature higher than boiling point of methanol (64.7 °C) will lead to the formation of bubbles inside the capillary caused by evaporation of methanol. Karaosmanoglu et al. suggested that reaction temperature higher than 60 °C should be avoided because it tends to accelerate saponification of the glycerides and also excessive loss of methanol tends to lower the yield\(^\text{16}\).

### 3.2 Effect of methanol to oil molar ratio

In order to study the effect of methanol to oil molar ratio on FAME yield, experiments were conducted at 5:1, 10:1, 15:1, 20:1, and 23:1 methanol to oil molar ratio. The stoichiometric methanol to oil molar ratio required for a complete transesterification process is 3:1\(^\text{17}\). However, higher molar ratio is required in order to shift the equilibrium to FAME\(^\text{18}\). The molar ratio of methanol to oil was adjusted by changing the liquid flow rates of methanol and oil individually. The 23:1 molar ratio is equal to 1:1 methanol to oil volume ratio.

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**Fig. 3. Effect of methanol to oil molar ratio on FAME yield.**

(KOH concentration: 4 wt%, residence time: 89 s, reaction temperature: 60 °C)

The KOH concentration, residence time, and reaction temperature were kept constant at 4 wt%, 89 s, and 60 °C respectively. It is well-known that the FAME yield will increase by increasing in methanol to oil molar ratio. As shown in Fig. 3, the reaction results obtained from millichannel reactor also exhibited the same trend. It is clearly indicated that the optimum amount required to produce high FAME yield is 23:1 molar ratio which yielded 74%. Guan et al. proposed that due to the reversible reaction of transesterification, the excess amount of methanol shifted the equilibrium to the product side thus increased the oil conversion\(^\text{7}\).

### 3.3 Effect of KOH concentration

Fig. 4 shows the effect of KOH concentration on FAME yield using 500 mm tube length at 60 °C, 23:1 methanol to oil molar ratio, and a residence time of 179 s. The concentration of KOH was varied from 1 to 5 wt% (based on the oil weight). Guan et al. conducted experiment using microtube reactor with 4.5 wt% of KOH concentration\(^\text{10}\). Therefore, maximum KOH concentration used in this study was 5 wt%.

With the increasing of KOH concentration from 1 to 5 wt%, the FAME yield was increased from 16 to 91%. A drastic increase was observed when the KOH concentration from 1 to 3 wt% while a small increment of FAME yield happened when the KOH concentration from 3 to 5 wt%. This finding is supported by Leung et al. as they suggested that, the FAME yield reached an optimal value when the KOH concentration reaches a certain level and
remains relatively constant with a further increase in the KOH concentration. The presence of KOH helps the reaction to proceed more quickly to equilibrium and consequently enhanced the oil conversion. The role of catalyst is important as alcohol is barely soluble in oil and fat. Tomasevic et al. reported that catalyst enhances the solubility of methanol and thus increases the reaction rate. Therefore, increase in KOH concentration will increase the FAME yield.

4. Conclusion

Continuous synthesis of biodiesel from palm oil was carried out in a capillary millichannel reactor. The highest FAME yield that has been achieved in this study was 91%. It was found that the FAME yield is greatly influenced by the reaction temperature, methanol to oil molar ratio, and KOH concentration. At reaction temperature of 60 °C, the solubility of the methanol and triglyceride improved, resulted in high FAME yield. In addition, increasing the methanol to oil molar ratio also increased the FAME yield. The effect of KOH concentration on the FAME yield also showed similar trend.

Acknowledgements

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References