Conversion of palm oil sludge to biodiesel using alum and KOH as catalysts

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A B S T R A C T
Conversion of palm oil sludge was studied by esterification and transesterification which used methanol as a reactant. The esterification of palm oil sludge was performed by variation of molar ratios of methanol to palm oil sludge (5:1, 10:1, 15:1, 20:1, and 25:1) and percentages of alum catalyst (3–7 wt%) at 60°C for 3 h with stirring rate 300 rpm. Transesterification was also carried out by variation of KOH (0.5–2.5 wt%) at 60°C and stirring rate 300 rpm for 1 h. The optimum molar ratio of methanol to palm oil sludge was 20:1 (6% alum catalyst). Meanwhile, the optimum concentration for transesterification was 1.5% of KOH. The yield of biodiesel production was 93%, the density and kinematic viscosity were 0.864 g mL and 12.8 mm² s⁻¹, respectively. The existence of ester compounds in the product was shown by Fourier Transform Infrared Spectrometry spectrum data of carbonyl group (C=O) at 1744 cm⁻¹ and C=O of ester at 1234; 1119 and 1026 cm⁻¹. Gas Chromatograph-Mass Spectrometry analysis showed the biodiesel product contains palmitic acid methyl ester (23.4%), trans-methyl oleate (75.5%), cis-methyl oleate (< 0.1%), and methyl stearate (1.2%).

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1. Introduction

Energy is one of important thing in the human life. For many years, the fuel such as petroleum, natural gas, and coal has been explored in excess. As a nonrenewable material, it will be exhausted in the future if the fuel is consumed continually. Indonesian government has to solve the problem with the release of the President Regulation No. 5/2006 about National Energy Policy and the President Regulation No. 1/2014 about National Energy General Plan Making Guidance.

One of fuel interest to the government, industry sector, researcher, and engineer is biodiesel, which is a renewable alternative fuel. Biodiesel is defined as a mixture of monoalkyl esters of biodegradable long chain fatty acids, contains insignificant amounts of sulfur, and it is nontoxic and renewable [1–3]. Biodiesel can be produced from vegetable oil or animal fat as raw materials by esterification and transesterification reaction with alcohol (methanol, CH₃OH), in the presence of a catalyst in acid or base condition [4].

The raw material which is the most perspective to be developed in Indonesia is crude palm oil (CPO), as industrial plants have been spread in the almost region of Indonesia, especially in South Kalimantan [5]. On the other hand, the usage of CPO for foodstuff is important. Hence, it needs other alternative raw materials for biodiesel production. The alternative material is palm oil sludge (POS), which is a waste of crude palm oil industry. The low quality of POS as non-edible oil is due to its high value of free fatty acids (FFAs) (> 20%).

In this work, alum (Al₂(SO₄)₃·14H₂O) was used as acid catalyst. Alum is cheap, easily available, acidic, and solid form. The heterogeneity of alum with reaction mixture could facilitate separation easily. Besides that, the heterogeneous catalyst can reduce the corrosion for equipment [6]. Another catalyst which was used in this research is KOH. The advantages of using KOH in transesterification reaction are low cost, high activity, and safe for the environment [7,8]. The esterification of POS using alum catalyst had been studied with 94.7% yield at reaction condition 65°C, 5 h, SPO to methanol ratio 1:20, and catalyst quantity 3 wt% [9]. The utilization of waste cooking oil with high FFAs was studied at 60°C,
1.5 wt% of a heterogeneous catalyst (silica sulfuric acid), 6:1 M ratio of methanol to oil and at 300 rpm. It achieved the conversion up to 90% [10]. Another raw material also investigated on esterification of palm fatty acid distillate with high FFAs at 60 °C, the molar ratio of methanol to distillate was 12:1 with stirring rate of 500 rpm for 4 h [11]. The 83.7% yield of methyl ester was achieved through transesterification of POS, molar ratio of methanol to POS 10:1, at 60 °C, 60 min, stirring rate of 400 rpm, and KOH 1 wt% [12].

It is interesting to evaluate biodiesel production from POS. There are many factors affecting biodiesel production from POS, including the type of catalyst. Biodiesel production in this work is different as compared with the previous works. Usman et al. [9] used only alum as a catalyst, while Hayyan et al. [12] used H2SO4 and KOH as catalysts. Commonly, biodiesel production uses only acid catalyst which needs more time than basic. Therefore, Hayyan et al. [12] used strong acid in the first step and KOH as the second catalyst in biodiesel production. Biodiesel production from POS in this work used alum in the first step and KOH in the second step. Thus, it is expected that producing biodiesel from POS can be done in a shorter time with favorable quality. The biodiesel production was carried out with variable of molar ratio of methanol to POS (5:1, 10:1, 15:1, 20:1, and 25:1), alum catalyst concentrations (3, 4, 5, 6, and 7 wt%), and KOH catalyst concentrations (0.5, 1.0, 1.5, 2.0, and 2.5 wt%). The overall reaction was performed on 60 °C for 3 h for esterification and 1 h for transesterification. The biodiesel physical properties such as density and kinematic viscosity and chemical property for FFA analysis were also evaluated. Meanwhile, a qualitative analysis for biodiesel was observed by Fourier Transform Infrared Spectrometry (FTIR) in order to identify functional groups and Gas Chromatography–Mass Spectrometry (GC–MS) to identify compounds in biodiesel. Determination of optimum condition in this work also considered in terms of efficiency aspect in the usage of materials (methanol and catalyst).

2. Materials and methods

2.1. Materials

POS was obtained from Asian Indo Holdings Pte with alum from PT. Indonesian Acids Industry, South Kalimantan, Indonesia. The analytical grade of methanol, KOH, NaOH, oxalic acid dihydrate ((COOH)2-2H2O), phenolphthalein was used (Merck), with n-hexane and Alum in technical grade.

2.2. POS treatment

POS (15 g) was poured into beaker glass which contains n-hexane (20 mL). The addition of POS to n-hexane forms two layers in a separating funnel. The upper layer was separated from the lower, then was poured into the distillation flask to evaporate n-hexane. Furthermore, POS was heated on a hot plate until reached a constant weight, cooled at room temperature and then analyzed for FFA, kinematic viscosity, and density.

2.3. Esterification of POS

20 g of POS was poured into the three-neck flask and methanol and catalyst were added. The mixture was heated at a temperature of 60 °C at 300 rpm for 3 h. After reaction finished, the mixture was poured into the separation funnel and allowed to settle for 20 h. The upper layer (biodiesel) then was purified from the residual methanol at a temperature of 70 °C by heating for 30 min. Subsequently, biodiesel was washed with distilled water until pH neutral reached. The residual of water was evaporated to obtain a constant weight of biodiesel.

2.4. Esterification–transesterification of POS

POS (20 g), methanol, and alum catalyst were added into the mixture. The amount of methanol and alum in this step was an optimum condition from the previous step. The mixture was heated at a temperature of 60 °C at 300 rpm for 3 h. Subsequently, the reaction was continued by transesterification for 1 h by adding KOH as a catalyst in the mixture of reaction. Transesterification was conducted under the same reaction conditions as with esterification include washing and evaporation steps.

2.5. Determining of molar ratio and percentage of alum catalyst

Determining the optimum molar ratio of methanol to the POS was conducted by the variance of 5:1, 10:1, 15:1, 20:1, and 25:1. Determining the optimum percentage of alum catalyst for esterification was carried out by the variance of 3–7 wt%. The optimum molar ratio of methanol to the POS and alum catalyst percentage were determined by the lowest value of FFAs.

2.6. Determining of percentage of KOH as catalyst

Determining the optimum of KOH catalyst percentage for transesterification was studied by variance of 0.5–2.5 wt%. The optimum KOH catalyst percentage was determined by the lowest value of kinematic viscosity and density.

2.7. Biodiesel characterization

Biodiesel was characterized by determination of FFA, specific density, and kinematic viscosity according to Indonesia National Standard for biodiesel as SNI 7182:2012. FTIR (Shimadzu., Kyoto, Japan, Prestige 21) was used for the identification of the functional groups on the product. Biodiesel products were analyzed using a GC–MS (Shimadzu, Kyoto, Japan) with an HP-5 capillary column (0.25 mm ID, 30 m long, with 0.25 µm film thickness; Hewlett-Packard, USA) equipped with a flame ionization detector. Helium was used as a carrier gas at a flow rate of 3 mL min⁻¹, the split ratio was 67.5.

3. Results and discussion

3.1. Pretreatment of POS

POS slurry from wastewater treatment containing water and dirt was extracted by addition of n-hexane. As a nonpolar solvent, n-hexane can dissolve the oil and separate non-oil material easily. The extracted of POS was analyzed by determination of FFA content, kinematic viscosity, and density. The results of raw material are: FFA 36.7%; and density 0.90 g mL⁻¹. Other researcher reported FFA value of POS being 74.8% [9] and 22.3% [12]. Kinematic viscosity of SPO this work is 46.63 mm² s⁻¹. The viscosity of vegetable oils is between 23.2 and 53.0 mm² s⁻¹ [13]. Therefore the POS can be used in biodiesel production. Demirbas and Karcioglu [13] reported that an increase in density of oil from 0.848 to 0.885 g mL⁻¹ has a significant impact on increased viscosity of biodiesel from 2.8 to 5.1 mm² s⁻¹. The density of the POS in the current study is 0.90 g mL⁻¹. This value indicates that biodiesel from this work should yield higher viscosity.

The high content of FFA in POS can lead the formation of soap in the transesterification step. Therefore, FFA in the POS must be reduced by esterification using an acid catalyst. Alum was chosen as a catalyst due to the acidic nature of sulfate ion [14]. The hydrogen ion then interacts with fatty acid molecules as a catalyst [9].
3.2. Effect of molar ratio of methanol to POS

The molar ratio of methanol to POS will affect the conversion of FFAs into a methyl ester. Fig. 1a presents the variations in the molar ratio of methanol to POS. The result shows that the conversion increases with increasing ratio.

Esterification was performed to convert the carboxylic acid to esters. The reaction also produces water but it can be overcome by using an excess of methanol. Water from esterification process will be dissolved in methanol so that it does not inhibit the reaction process [15]. Based on Fig. 1a, the molar ratio of methanol to POS with the highest FFA conversion (87.3%) is 25:1, at a ratio of 20:1, the conversion is 87.1%. Since there is no obvious change between these two conditions, the molar ratio of 20:1 is considered to be the optimum ratio due to minimum methanol consumption. Some researchers also reported similar results, e.g., Usman et al. [9] and Arora et al. [16] reported that the optimum molar ratio of methanol to oil (POS and rice bran oil) is 20:1. In another case, the researcher using waste cooking oil also reported that 20:1 was the optimum condition [17,18]. Meanwhile, there was used carbon-based catalyst derived from starch and H3PW12O40·6H2O as catalyst which need higher concentration of molar ratio methanol to oil (waste frying oil and waste cooking oil) of 30:1 and 70:1, respectively [19,20]. The molar ratios of their works are higher than alum as catalyst.

3.3. Effect of concentration of alum as catalyst

The alum as a heterogeneous catalyst is more desirable because it can be easily separated from the mixture if it is compared with homogeneous catalysts. Beside, acidic alum will add positively charged (protonated) to the carbonyl group of FAAs, that can catalyze the esterification reaction with methanol (weak nucleophilic) [21]. However, the increased concentration of the catalyst is not always followed by an increase of conversion. Increasing of alum more than optimum percentage will add cost and reaction time. In addition, more reaction time was needed for separation of the catalyst from the product. Therefore, variation in the percentage of the catalyst is needed to determine the optimum condition in order to produce biodiesel with a catalyst efficiently.

Fig. 1b shows that esterification conversion of FFA with 6% and 7% of alum is almost the same about 98%. Hence, the 6% of alum concentration in this work was chosen as the optimum condition. The 98% esterification with 6% of alum as a catalyst resulted in FFA value of 0.82% compared to the original POS value of 36.7%. The POS with low FFA (< 1.0%) is essential for the production of biodiesel through transesterification step [10,21]. Hayyan et al. [12] set 2% as limit maximum of FFA for all esterification experiments for obtaining biodiesel. Therefore, the esterified POS from this work should be good for subsequent transesterification process.

3.4. Effect of KOH concentration in transesterification of POS

Fig. 2 depicts the highest yield of methyl esters with 1.5% of KOH is 93%. This concentration corresponds to previous work which produced biodiesel from chlorella protothecosis oil and argemone oil [22,23]. The yield of methyl ester is 76% when 2% of KOH catalyst was used. The lowest yield of 55% in this experiment is at 2.5% KOH. A decreasing yield by increasing of catalyst percentage may be due to the impact of soap forming. The existence of soap can dissolve products in water, complicate the separation of biodiesel with glycerol, and will also increase the viscosity of biodiesel [24] (Fig. 3).

3.5. Physical properties of biodiesel product

The viscosity of fuel for diesel engines needs to be restricted. The fuel with too low viscosity does not provide sufficient lubrication on the oil injection pump, resulting in leaks in the fuel injection pump, while high viscosity leads to the formation of large droplets on injection resulting in poor combustion and, hence, higher exhaust...
smoke and emissions [25]. Table 1 shows that kinematic viscosity of biodiesel byproducts decreases with increased KOH, except for 2.0% and 2.5% of KOH. Transesterification which uses a high concentration of KOH will react with the residual of FAAs in the esterification reaction and could cause a saponification reaction. Additionally, soap from the transesterification will increase the viscosity of biodiesel and present difficulty in the glycerol separation [26]. The lowest viscosity of biodiesel in this work is 12.8 mm² s⁻¹, exceeding biodiesel quality standard (2.3–6.0 mm² s⁻¹) according to SNI 7182:2012. This viscosity value is higher than that generated by Usman et al. [9]. However, biodiesel produced in this research can be used as fuel, because biodiesel is always mixed with petroleum diesel in engine application [27].

Table 1 Physical property of biodiesel product.

<table>
<thead>
<tr>
<th>Concentration of KOH (wt%)</th>
<th>Kinematic viscosity (mm² s⁻¹)</th>
<th>Specific density (g mL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>20.8</td>
<td>0.865</td>
</tr>
<tr>
<td>1.0</td>
<td>17.9</td>
<td>0.865</td>
</tr>
<tr>
<td>1.5</td>
<td>12.8</td>
<td>0.864</td>
</tr>
<tr>
<td>2.0</td>
<td>16.8</td>
<td>0.867</td>
</tr>
<tr>
<td>2.5</td>
<td>17.5</td>
<td>0.868</td>
</tr>
</tbody>
</table>

3.6. Product analysis of biodiesel

The conversion of triglycerides into three molecules of fatty acid methyl esters through the transesterification process reduces the viscosity to one-eighth of the triglyceride [13,28]. Hence, the high viscosity of the methyl ester (biodiesel) obtained in this study indicates defective transesterification reaction. The initial density of POS was 0.90 g mL⁻¹ and decreases after esterification and transesterification. The density of produced optimum biodiesel was 0.86 g mL⁻¹. This value fulfilled the standard (0.85–0.89 g mL⁻¹) of quality biodiesel according to SNI 7182:2012. The density trend is proportional to the increase in KOH concentration, except for 2.0 and 2.5% of KOH. The high concentration of KOH could increase density as the impact of the presence of glycerol in the biodiesel [29]. The physical property of biodiesel product is shown in Table 1.

The carbonyl group from ester (C=O) at 1744 cm⁻¹, stretching vibration of C=O from ester at 1234, 1119, and 1026 cm⁻¹. The spectra also recorded other functional group peaks in biodiesel such as stretching vibration of sp² C–H at 3194 cm⁻¹, sp³ C–H at 2916, 2855, 2731, and 2677 cm⁻¹ as well as stretching vibration of C–C at 1597 cm⁻¹. Bending vibration of CH₂ at 1458 cm⁻¹, CH₃ at 1373 cm⁻¹, C–C at 872 cm⁻¹, and (CH₂)₃ at 725 cm⁻¹. The peak at 3472 cm⁻¹ could normally be attributed to O–H bands O–H groups which be suspected from FFAs in biodiesel and glycerol residual present in the biodiesel [30,31].

GC-MS analysis of the biodiesel was carried out in order to identify the compounds present in the biodiesel. Fig. 4 presents a chromatogram analysis on biodiesel with the presence of four compounds in biodiesel, which the highest concentration of methyl ester was trans-methyl oleate (75%). Usman et al. [9] reported that compositions of methyl esters biodiesel made from POS from West Kalimantan, Indonesia were palmitic acid methyl ester (49.5%), trans-methyl oleate (41.5%), methyl stearate (6.1%), and methyl myristate (2.0%) [9]. Comparatively, the previous work reported that methyl 9-octadecenoate (44.4%), methyl hexadecanoic (37.1%), methyl octadecanoic (9.6%), and methyl 9,12-octadecadienoate (5.8%) as the major fatty acid methyl esters made from African CPO [32]. The difference occurs due to the fatty acid compositions of natural oils. Among the factors that affect the fatty acid compositions are climate conditions, soil type, growing season, plant maturity, and genetic variation of the plant [33].

![Fig. 3. FT-IR spectra of biodiesel.](image)

![Fig. 4. GC spectrum of biodiesel.](image)
4. Conclusions

Alum can be used as a heterogeneous catalyst in the conversion of POS to biodiesel, with the optimum conditions: 20:1 (molar ratio of methanol to POS); 6% of alum in esterification; 1.5% of KOH in transesterification. The existence of ester compound in the product was shown in FTIR spectra at 1744 cm⁻¹ (C=O ester) and 1234, 1119, and 1026 cm⁻¹ (C–O ester). Compounds in biodiesel from this work were palmitic acid methyl ester, trans-methyl oleate, cis-methyl oleate, and methyl stearate. The density of biodiesel has fulfilled the standard of quality (SNI 7182: 2012), but not for kinematic viscosity.

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