



## Note

## KOH/bentonite catalysts for transesterification of palm oil to biodiesel

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## ABSTRACT

A potential application of KOH/bentonite as a catalyst for biodiesel production was studied. A series of KOH/bentonite catalysts was prepared by impregnation of bentonite from Pacitan with potassium hydroxide. The ratios between KOH and bentonite were 1:20, 1:10, 1:5, 1:4, 1:3, and 1:2. The characterization of KOH/bentonite and natural bentonite was conducted by nitrogen adsorption and XRD analysis. The effects of various reaction variables on the yield of biodiesel were investigated. The highest yield of biodiesel over KOH/bentonite catalyst was  $90.70 \pm 2.47\%$ . It was obtained at KOH/bentonite 1:4, reaction time of 3 h, 3% catalyst, methanol to oil ratio of 6, and the reaction temperature at 60 °C.

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## 1. Introduction

Biodiesel development has gained the attention of researchers in recent years because of the rate of depletion of fossil fuel (Zhou et al., 2008). Biodiesel is noteworthy for its similarity to petroleum-based diesel. It can be used in diesel engines without engine modification. The production of biodiesel is performed either through transesterification of triglycerides using alcohol in the presence of a catalyst (Kim et al., 2010) or deoxygenative ecofining of triglycerides in a non alcohol environment (Ong and Bhatia, 2010). Different catalysts have been explored and used for biodiesel production from seed oils using homogenous bases such as potassium hydroxide and sodium hydroxide (Saravanan et al., 2009; Shiu et al., 2010), homogenous acids such as sulfuric acid (Saravanan et al., 2009; Shiu et al., 2010), heterogeneous solid catalysts such as cation-exchange resin and hydrotalcites (Dhainaut et al., 2010; Feng et al., 2010; Gao et al., 2010; Guo et al., 2010; Liu et al., 2010; Silva et al., 2010; Sun et al., 2010), and enzymes such as *C. antarctica* (Novozym 435) and lipase (Ranganathan et al., 2008; Talukder et al., 2010). The conventional commercial process used for biodiesel production is base catalyzed transesterification. However, homogeneous base catalysts such as sodium hydroxide for the production of biodiesel cannot be recovered or regenerated after the reaction and also produce toxic wastewater.

Heterogeneous solid catalysts have been studied as substitutes for homogeneous catalysts, and have the advantage of being easy to recover and reuse. They are also more environmentally friendly. The

heterogeneous solid catalysts commonly used for biodiesel production are categorized into several types: solid alkali catalyst (Guo et al., 2010; Hsieh et al., 2010; Samart et al., 2010), solid acid catalyst (Leung et al., 2010; Sun et al., 2010), mesoporous silica support catalyst (Dhainaut et al., 2010), and alkali support catalyst (Samart et al., 2010; Zabeti et al., 2010). Solid alkali catalysts commonly used in biodiesel preparation are calcium oxide (Samart et al., 2010), and calcined sodium silicate (Guo et al., 2010). Some of these catalysts are promising while some others still show lower performance than homogeneous catalysts in the terms of activity and FAME yield. Calcined sodium silicate shows excellent catalytic activity in the first run; however a considerable loss in catalytic activity is found when the catalyst is recycled for more than five times (Guo et al., 2010). Sun et al. (2010) reported that the catalytic activity of  $\text{La}_2\text{O}_3$  loaded on  $\text{ZrO}_2$  shows a correlation with their basic properties towards biodiesel production. Other heterogeneous catalysts that show excellent catalytic activity as for biodiesel production are CaO/mesoporous silica (Samart et al., 2010),  $\text{WO}_3/\text{ZrO}_2$  (Park et al., 2010), and sulfonated-multiwalled carbon nanotubes (Shu et al., 2009). Unfortunately, these catalysts are expensive and complicated to prepare, which limits their potential application in industrial scale operation.

Clay materials are ubiquitous in nature while heterogeneous in composition and particle size (Bergaya and Lagaly, 2006; Zhou, 2010; Zhang et al., 2010). Different kinds of solid materials have been employed as heterogeneous catalysts or catalyst supports in biodiesel production as mentioned in the previous paragraph, however, information about the utilization of clay material such as bentonite as the catalyst or catalyst support for biodiesel preparation is very scarce. Therefore, in this study we utilized bentonite from Pacitan (East Java, Indonesia) as a catalyst for the biodiesel production because of its

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abundance. In the present investigation, the preparation of bentonite base catalyst for biodiesel production has been studied by optimizing KOH loading. Palm oil was used as the feedstock in biodiesel production due to its abundance and low price.

## 2. Materials and methods

### 2.1. Materials

Bentonite used in this study was obtained from Pacitan, East Java, Indonesia. The elemental analysis of the bentonite was conducted using an Atomic Absorption Flame Emission Spectrophotometer (AA-6200, Shimadzu), and the results were as follow: Al 38.93%, Si 46.81%, Fe 3.24%, Ca 3.15%, Mg 0.41%, K 0.17%, Na 0.42%, and Mn 0.03%. Initially, the bentonite was immersed in hydrogen peroxide solution (30%) at 30 °C for 24 h to remove organic impurities. The ratio between hydrogen peroxide solutions to bentonite was 2:1. Then the mixture was gently heated in a boiling water bath to remove excess hydrogen peroxide and subsequently the solution was separated from the bentonite. Then the purified bentonite was suspended in distilled water and allowed to settle, the ratio of purified bentonite to distilled water was 1:4. After the water was removed, the purified bentonite was dried in force-circulation oven at 110 °C until its moisture content reached 10%. Subsequently, the dried bentonite was crushed using a JANKE & KUNKEL micro hammer mill to obtain powdered bentonite with particle size 80/100 mesh.

Refined palm oil (Bimoli) was used as raw material for biodiesel production. Analytical grade methanol and potassium hydroxide were obtained from Sigma Aldrich. Methyl heptadecanoate and standard reference for FAME analysis (methyl palmitate, methyl myristate, methyl oleate, methyl stearate and methyl linoleate) were from Fluka.

### 2.2. Catalyst preparation

A series of KOH/bentonite catalysts for biodiesel production was prepared using the following procedure. The ratios between KOH and bentonite were 1:20, 1:10, 1:5, 1:4, 1:3, and 1:2. The preparation of catalysts was conducted in a three-neck round bottom flask (500 mL) equipped with a reflux condenser, temperature indicator, and mechanical stirrer. The impregnation of bentonite with KOH was conducted at a temperature of 60 °C for 24 h under continuous stirring. After completing the impregnation process, the slurry was dried in an oven at 110 °C for 24 h to remove water. The catalyst was then calcined in a tubular muffle furnace at a temperature of 400 °C for 5 h.

### 2.3. Catalyst characterization

Surface analysis of the bentonite and catalysts was examined by nitrogen adsorption at its boiling point using a Quadrasorb SI. Prior to the nitrogen adsorption measurement, the sample was degassed at 150 °C under vacuum condition for 24 h. The BET surface area was calculated using the standard BET equation in the relative pressure ( $p/p_0$ ) range of 0.06 to 0.3. Powder X-ray diffraction (XRD) patterns of bentonite and the catalysts were recorded on a Rigaku Miniflex Goniometer at 30 kV and 15 mA, using Cu K $\alpha$  radiation at a step size of 0.01°. Qualitative analysis of bentonite and the catalysts was conducted by the FTIR method using the KBr technique. FTIR analysis was carried out on a Shimadzu 8400 S FTIR instrument in wavenumber range of 4000–500 cm<sup>-1</sup>.

### 2.4. Transesterification of palm oil

Transesterification of palm oil was carried out in a three-neck round bottom flask (500 mL) equipped with a reflux condenser, temperature indicator, and mechanical stirrer. The reactor was placed in a controlled water bath heater. A known amount of catalyst (3–

27 g) was added to a known volume of methanol. The mixture was then heated to the desired temperature (60 °C) in a controlled temperature water bath. Subsequently, palm oil was added into the mixture under vigorous stirring (500 rpm). The molar ratio of methanol to oil used in this study was 6 and the transesterification reaction was carried out for 1–6 h. At the end of the reaction time, the solution was centrifuged at a relative centrifugal force of 2054 g for 10 min. After centrifugation, the glycerin and biodiesel layers were separated. The biodiesel phase was washed with water (the ratio of wash water to biodiesel was 2), decanted and heated at 105 °C to remove water and methanol.

### 2.5. Determination of biodiesel yield

The composition of the biodiesel produced by transesterification of palm oil and methanol using bentonite as a solid catalyst was determined using gas chromatography (GC-17A Shimadzu fitted with a DB-Wax capillary column (Agilent JW scientific) and FID (flame ionization detector)). Helium was used as the carrier gas. Methyl heptadecanoate was used as the internal standard. Peaks of methyl esters were identified by comparing them with the reference standards. The injector and detector temperatures were 240 °C and 280 °C, respectively. The initial oven temperature was 80 °C with an equilibration time of 3 min. After an isothermal period, the column oven was heated at a rate of 10 °C/min to 270 °C and held for 20 min. The yield of biodiesel was determined using the following equation

$$\text{yield (\%)} = \frac{\text{weight of biodiesel} \times \text{total weight \% of FAME in sample}}{\text{weight of palm oil}} \times 100 \quad (1)$$

where FAME is fatty acid methyl esters. The physical properties of biodiesel produced in this experiment were determined according to the ASTM standard (kinematic viscosity: ASTM D.445-10, 2010; pour point: ASTM D.97, 2010; flash point: ASTM D.93, 2010; cetane index: ASTM D.613, 2010; and specific gravity: ASTM D.1298, 2005).

## 3. Results and discussion

### 3.1. Surface analysis and XRD measurement of bentonite and catalyst

The BET surface area of the catalyst decreased with increasing KOH loading (Fig. 1a). During the impregnation, the KOH molecules filled the available pores in the bentonite, leading to a decrease of the surface area of the catalyst. By increasing the ratio of KOH to bentonite, the number of KOH molecules that occupy the available pores in the bentonite also increased, and this phenomenon significantly decreased the BET surface area of the catalyst. This indicated that the presence of KOH molecules on the surface of the bentonite particles, and on the surface of the pores within the bentonite particles, and some KOH were probably converted to K<sub>2</sub>O during calcination. Narrowing of the hysteresis curve of the adsorption isotherm (Fig. 1a) was an indication of the change in pore structure of bentonite from a mesoporous material to a nonporous structure after loading with KOH.

A shift in pore sizes to larger pore diameters led to a lower catalyst surface area. The major part of the KOH/bentonite catalyst volume was occupied by pores larger than 5 nm (KOH/bentonite 1:20), 8 nm (KOH/bentonite 1:10), and 10 nm for the 1:5, 1:4 and 1:3 catalysts. A nonporous structure was observed for the KOH/bentonite 1:2 catalyst. These pore size distributions (Fig. 1b) are in agreement with the nitrogen adsorption isotherms.

The FTIR spectrum of the bentonite (Fig. 2) reveals the presence of functional groups such as Al(Mg)–O–H stretching (3614 cm<sup>-1</sup>), H–O–H stretching (3360 cm<sup>-1</sup>), H–O–H bending (1670 cm<sup>-1</sup>), Si–O–Si stretching (1061 cm<sup>-1</sup>), OH bending bounded Fe<sup>3+</sup> and Al<sup>3+</sup> (921 cm<sup>-1</sup>), and Si–O stretching (789 cm<sup>-1</sup>). FTIR analysis showed that

the addition of KOH affected the structure of the bentonite network. The intensity of the Al(Mg)–O–H stretching group increased with an increased KOH loading. Also, a shift of absorption band of this group from 3614 cm<sup>-1</sup> to higher wavenumbers indicated the presence of a new functional group in the catalysts being investigated (Al–O–K group or compound). A band at about 3430 cm<sup>-1</sup> indicates the presence of the stretching vibration of the Al–O–K group (Xie and Lie, 2006).

The XRD patterns of raw bentonite and KOH/bentonite catalyst (1:20 and 1:4) are given in Fig. 3. Reflections relative to the planes

(001), (003) and (130–200) confirmed the presence of montmorillonite in the raw bentonite sample (Patel et al., 2007). The d<sub>100</sub> value for raw bentonite was 1.43 nm. As the KOH loading ratio increased, the crystallinity of the catalyst increased. When the loading amount of KOH was increased to 1:20, the XRD pattern of the catalyst was still quite similar to that of the raw bentonite sample, and a new phase of K<sub>2</sub>O began to appear. Here, the structure of bentonite still could be observed, and the d<sub>100</sub> value shifted from 1.43 to 1.67 nm. The formation of K<sub>2</sub>O is a strong indication that the KOH was not well

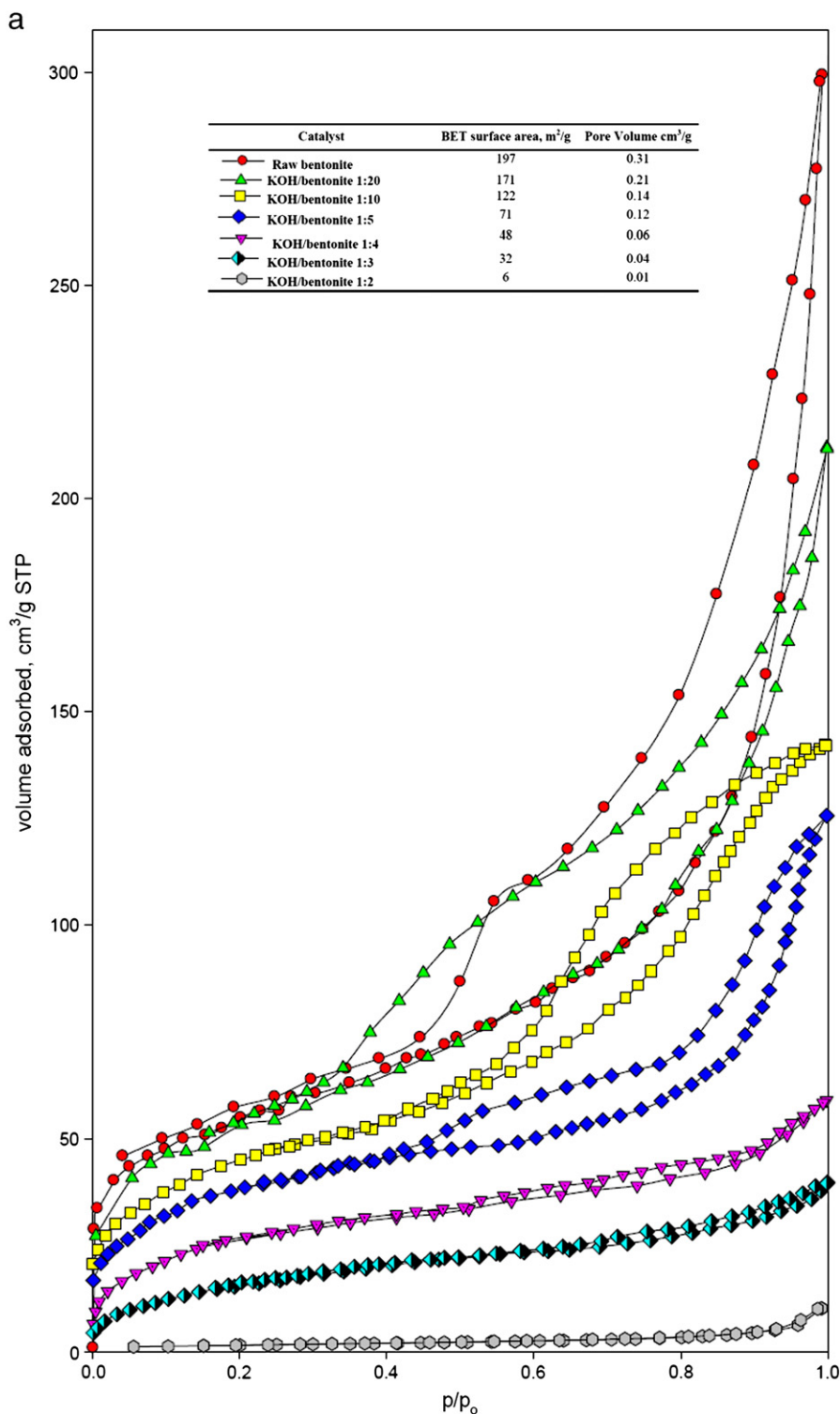


Fig. 1. (a) Nitrogen sorption isotherms of bentonite and KOH/bentonite catalysts, (b) Pore size distribution of bentonite and KOH/bentonite catalysts.

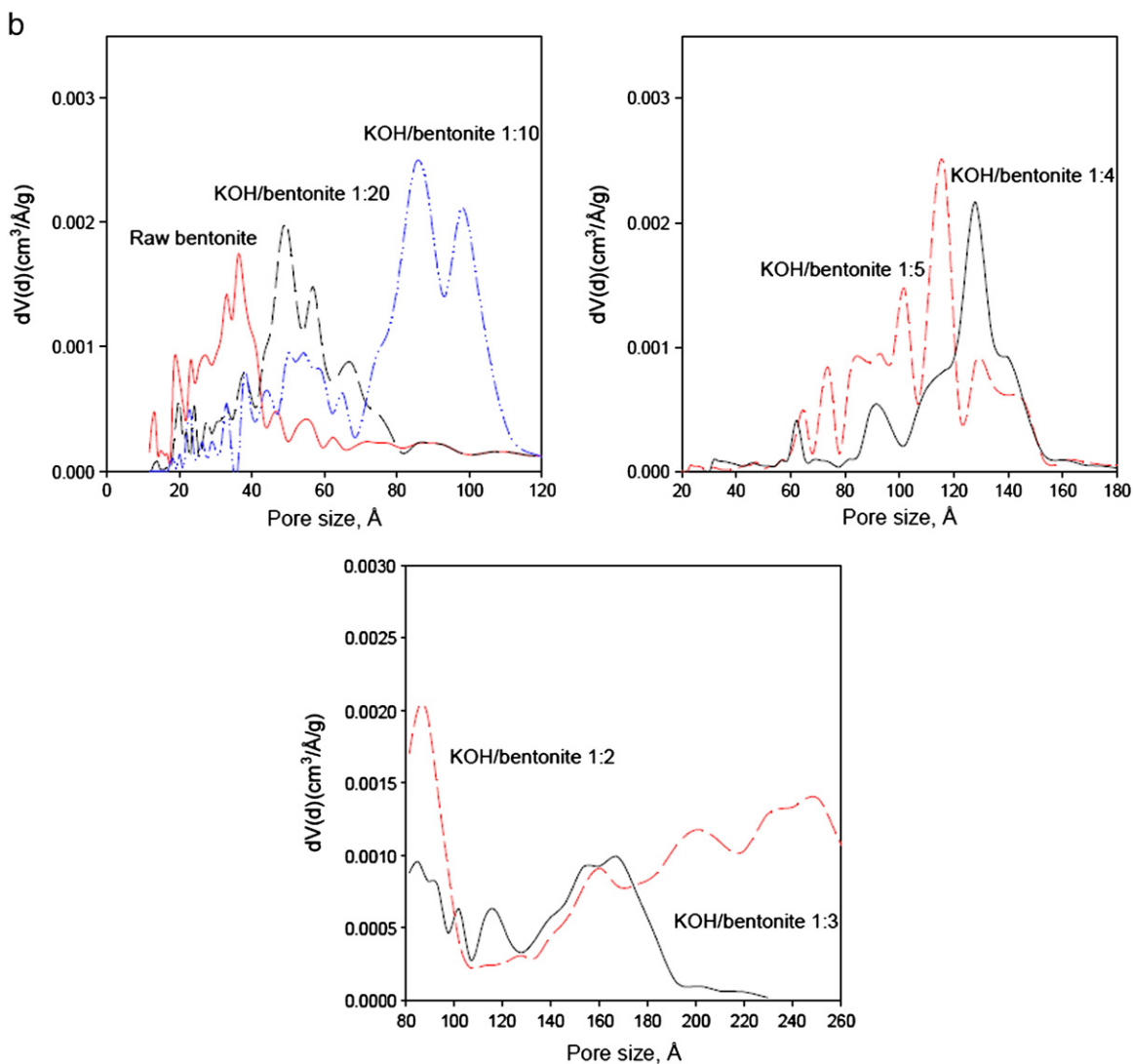


Fig. 1 (continued).

dispersed on the bentonite surface or structure. During calcinations, potassium hydroxide was converted to  $K_2O$  as indicated in the XRD pattern. Reflections observed around  $2\theta = 31^\circ$ ,  $39^\circ$ ,  $51^\circ$ ,  $55^\circ$  and  $62^\circ$  belong to the  $K_2O$  phase (Noiroj et al., 2009).

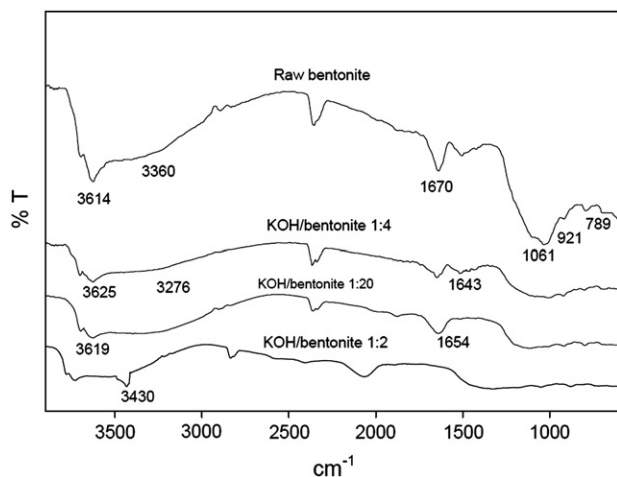


Fig. 2. FTIR spectra of bentonite and KOH/bentonite catalysts.

### 3.2. Activity test of KOH/bentonite

In order to investigate the activity of KOH/bentonite catalyst on the transesterification of palm oil, a series of experiments was conducted. Since the reaction mixture was not fully miscible at  $60^\circ\text{C}$ , the stirrer speed was kept constant at 750 rpm in order to increase the dispersion of the mixture.

#### 3.2.1. Effect of KOH/bentonite loading

The catalytic effect of KOH/bentonite loading on transesterification was investigated from the percentage of yield of fatty acid methyl ester. The experimental conditions for studying the effect of KOH/bentonite loading on the transesterification reaction were: the amount of catalyst at 3% (based on the weight of palm oil), methanol to oil molar ratio of 6:1, reaction time of 3 h, and the reaction temperature at  $60^\circ\text{C}$ . The results clearly indicate that the amount of KOH loaded in bentonite affected the conversion of palm oil into biodiesel (Table 1).

Increasing the loading amount of KOH from 5% (KOH/bentonite 1:20) to 25% (KOH/bentonite 1:4) also increased the yield of biodiesel. However, further increase of the loading amount of KOH/bentonite from 25% to 50% (KOH/bentonite 1:2) significantly decreased the conversion of palm oil into biodiesel. The highest yield (90.7%) was obtained at 25% KOH loading. A similar result was obtained by Noiroj et al. (2009) in the transesterification of palm oil using KOH/ $Al_2O_3$  and KOH/NaY as catalysts.



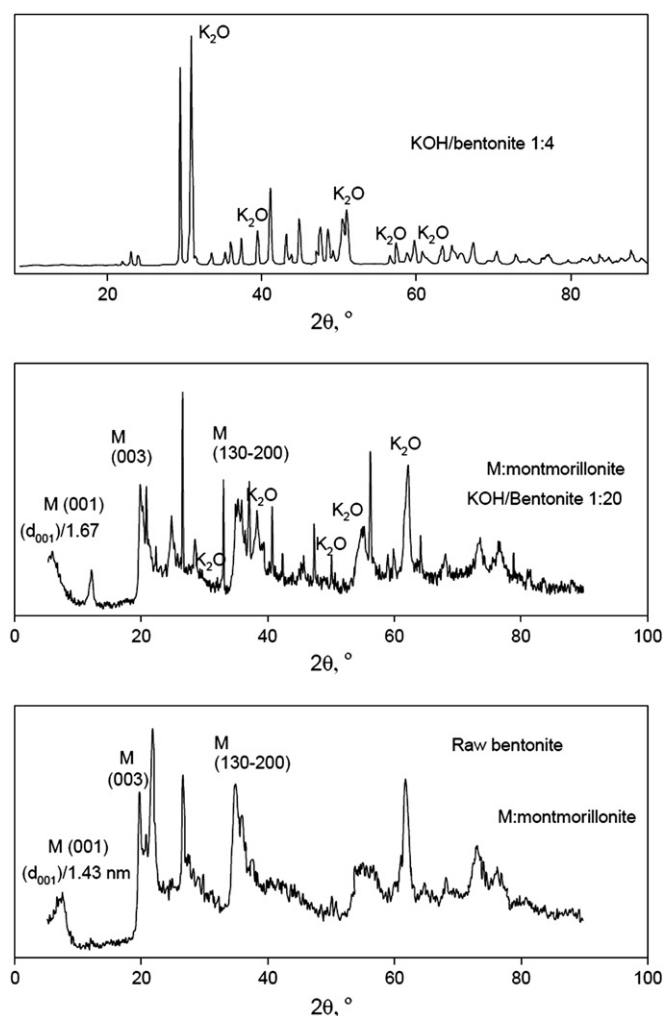


Fig. 3. The XRD patterns for bentonite and KOH/bentonite catalyst.

By increasing the KOH loading from 5% to 25%, the number of  $K_2O$  active sites in the catalyst also increased leading to an increase in the yield of biodiesel. However, further increases in KOH loading (higher

Table 1

The effect of different process variables on the yield of biodiesel.

KOH:bentonite ratio	Reaction time (h)	Amount of catalyst (%)	Yield of biodiesel (%)
1:20	3	3	43.51 ± 3.21
1:10	3	3	57.37 ± 4.11
1:5	3	3	68.46 ± 4.23
1:4	3	3	90.70 ± 2.47
1:3	3	3	81.48 ± 4.92
1:2	3	3	50.21 ± 2.53
1:4	1	3	15.32 ± 2.49
1:4	2	3	64.17 ± 4.58
1:4	3	3	90.70 ± 2.47
1:4	4	3	88.91 ± 3.22
1:4	5	3	90.63 ± 2.50
1:4	6	3	89.48 ± 2.41
1:4	3	1	52.74 ± 5.21
1:4	3	2	79.52 ± 4.32
1:4	3	3	90.70 ± 2.47
1:4	3	4	89.98 ± 3.11
1:4	3	5	90.41 ± 2.05
1:4	3	6	90.83 ± 3.08
1:4	3	7	90.56 ± 3.12
1:4	3	8	90.43 ± 2.97
1:4	3	9	91.22 ± 2.58

Average of three independent measurements.

than 25%) resulted in a decreased yield of biodiesel. With high levels of KOH, the interactions between KOH and the internal layer of bentonite (Al–O–H stretching groups) were excessive and during the calcinations, a new phase of Al–O–K compound was formed. This new phase compound (Al–O–K) has lower catalytic activity and basicity than the  $K_2O$  phase (Noiroj et al., 2009). When a high concentration of the Al–O–K compound was formed, the catalytic activity of the catalyst became lower, leading to a decrease in the biodiesel yield.

### 3.2.2. Effect of reaction time

The operating conditions used to study the effect of reaction time on biodiesel yield were similar to those used in Section 3.2.1. Since the highest yield of biodiesel was obtained with KOH/bentonite 1:4 catalyst, this ratio was used in subsequent experimental studies. The optimum reaction time for the biodiesel production was 3 h. During the first three hours the yield of biodiesel increased with the increase in reaction time (Table 1). After three hours, the yield of biodiesel was almost constant as the equilibrium conversion had been reached.

### 3.2.3. Effect of the catalyst amount

To determine the effect of catalyst on the yield of biodiesel, the amount of catalyst was varied between 1% and 9% by weight based on the amount of palm oil. The yield of biodiesel increased from 52.7% at 1% KOH/bentonite catalyst to 90.7% at 3% catalyst, with little further change in yield between 3% and 9% catalyst (Table 1). The increase in the conversion of palm oil into fatty acid methyl esters between 1% and 3% catalyst addition was due to an increase in the number of active basic sites ( $K_2O$ ) in the reaction system. Furthermore, a slight increase is shown with a change in the amount of catalyst from 3% to 9%. Transesterification reaction of triglyceride with methanol is a reversible reaction; to alter the reaction into the right hand site to produce methyl esters one should consider Le Chatelier's principle. Therefore, when the amount of catalyst provides sufficient basic sites and the reaction has already reached an equilibrium condition, increasing the amount of catalyst does not affect biodiesel yield significantly.

### 3.2.4. Catalyst stability

Reusability and stability are very important criteria for industrial application of KOH/bentonite as a heterogeneous catalyst for biodiesel production (Liu et al., 2007; Silva et al., 2010). In this study the reusability of KOH/bentonite catalyst was examined by carrying out three reaction cycles. For fresh catalyst (KOH/bentonite 1:4) the maximum conversion was 90.7%. After separation from the liquid mixture (biodiesel, glycerin, methanol, and water), the catalyst was repeatedly washed with methanol (at least 4 times) and re-calcined at a temperature of 300 °C for 5 h. A subsequent cycle was started with

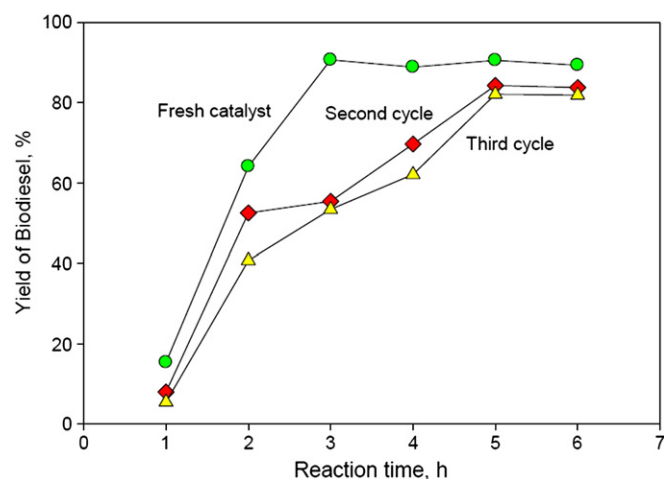


Fig. 4. Multiple cycle test of catalyst deactivation (KOH/bentonite 1:4).

**Table 2**

Comparison of the properties of biodiesel produced in this experiment with the standard issued by Indonesia National Standard (SNI-04-7182-2006).

Properties	Biodiesel produced	SNI
Kinematic viscosity at 40 °C (cSt)	4.2	1.9–6.0
Specific gravity (15 °C)	0.88	0.86–0.90
Cetane index	62	>45
Flash point (°C)	170	Min 65
Pour point (°C)	16	Max 18
Heating value (MJ/kg)	38.1	–

fresh reactants. For the second and the third cycles, the maximum yield of biodiesel was less than 85% (Fig. 4). Here deactivation of basic sites occurred; some of the possible basic sites were poisoned during the transesterification reaction. These results are similar to those obtained by Silva et al. (2010) and Liu et al. (2007).

### 3.3. Biodiesel characteristics

Biodiesel produced from palm oil using KOH/bentonite as a catalyst fulfilled the standard for biodiesel (Table 2). Fuels with low cetane index make the engine starting difficult. There is also an increase of noise and smoke in exhaust gas. Since the cetane index of the biodiesel produced in this experiment was above 45, the diesel engine will operate better using this biodiesel as a fuel. Viscosity of fuel gives a significant effect on the performance of injector and fuel atomization. If the viscosity is lower than 1.9, the fuel may not provide sufficient lubrication for the fuel injection pump, however if the fuel is too viscous it results in larger droplets in injection which can cause poor combustion. Flash point temperature relates to the ignition of the fuel, and the minimum value of this property is required for proper safety and handling of the fuel. Since the flash point of the biodiesel from palm oil with KOH/bentonite as catalyst was higher than the Indonesia National Standard (2006), this fuel is safe for handling and storage for some period of time. Therefore it can be applied as a substitute fuel for diesel engines.

## 4. Conclusion

A heterogeneous catalyst KOH/bentonite can be used as a solid based catalyst for biodiesel production via transesterification of palm oil. The catalyst synthesized with 25% KOH loading gave the best performance for biodiesel production. The operating condition to produce the highest yield of biodiesel was: reaction time 3 h, amount of catalyst 3%, methanol to oil ratio 6, and the reaction temperature at 60 °C.

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