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Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil Ricky Indra Kusuma, Johan Prabowo Hadinoto,

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19**article info Article history: Received 9 January 2012 Received in revised form** 20 April **2012 Accepted** 26 April **2012 Available online** 12 July **2012 Keywords:**

Biodiesel Transesterification Solid catalyst Zeolite Palm oil abstract The transesterification of palm oil to methyl esters (biodiesel) was studied using KOH/zeolite as solid heterogeneous catalysts. Various process variables such as KOH concentration and reaction time were studied in order

23**to obtain maximum yield of biodiesel.**

2**A series of KOH/zeolite** catalyst was **prepared by impregnation** of zeolite from Pacitan with potassium hydroxide in a various concentration (25 g KOH in 100 mL of distilled water; 50 g KOH in 100 mL of distilled water; 75 g in 100 mL of distilled water; and 100 g in 100 mL of distilled water). The weight ratios between zeolite and KOH solution were 1:4. Trans- esterification was carried out at various reaction times (1 to 4 h). The impregnation of zeolite with KOH concentration of 100 g/100 mL gave maximum yield of biodiesel. The natural zeolite, catalyst, and spent catalysts were characterised by using several techniques such as XRD, EDX, and SEM. © 2012 Elsevier B.V. All rights reserved. 1. Introduction Petroleum-based fuel is still the main source of energy used by all countries in the world. Extensive uses of this un-renewable fuel cause the depletion of petroleum-based fuel sources. Various kinds of alternative energy sources have been explored (Zhou et al., 2011), and one of them is biodiesel. Biodiesel has been considered as an alternative source of petroleum-based fuel due to its similarity to petroleum-based diesel (Noiroj

29**et al.,** 2009). **Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acids**

that can be produced through transesterification process of vegetable oils and animal fats (Leung et al., 2010). This

4**process is usually carried out in the presence of a** homogeneous **base or acid** catalysts **in order to reduce the reaction temperature and to control the product selectivity**

(Benjapornkulaphong et al., 2009). In the homogeneous method, the reactants, catalyst, and FAME are all in the liquid phase, which

3**is difficult to separate the catalyst from the**

after-reaction product (Kansedo et al., 2009). On the other hand, homogeneous base catalysts such as sodium hydroxide cannot be recovered or regenerated after the reaction and also produce toxic wastewater (Soetaredjo et al., 2011). Solid catalysts are a new choice to replace the liquid homogeneous catalyst due to its advantages such as less corrosive, easier to handle and separate, reusable and generating less amount of toxic wastes (Helwani et al., 2009). ⁎ Corresponding author. Tel.: +62 313891264; fax: +62 313891267. E-mail address: suryadiismadji@yahoo.com (S. Ismadji).

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021 Recently, there has been increasing development of heteroge- neous catalyst. Solid catalysts that have been studied and used for transesterification of vegetable oils including alkali and alkali earth metal supported on Al2O3 (Benjapornkulaphong et al., 2009; Noiroj et al., 2009), alum (Aderemi and Hameed,

2009), K2CO3 supported on alumina/silica (Lukic et al., 2009), calcium oxide (Boey et al., 2009), calcium-zinc mixed oxide (Ngamcharussrivichai et al., 2008), quick lime bit (Kouzu et al., 2009), mesoporous molecular sieves MCM-41 (Carmo et al., 2009), and KOH supported on bentonite (Soetaredjo et al., 2011), etc. However, the drawback of using solid materials as catalyst for biodiesel production, especially the synthesized ones, is on its price. To reduce the cost of production, the solid catalyst should be low in price, and available in large quantity. Zeolite is a crystalline aluminosilicate with a three-dimensional framework structure that forms uniform pore size (Cejka et al., 2007). Because of its important chemical properties, this material has been applied in many industrial application such as selective absorbent, ion-exchange resin, and high activity catalyst (Xia et al., 2011; Zhang et al., 2010; Zhou, 2010, 2011). Various kinds of solid materials as mentioned in previous paragraph have been used as heterogeneous catalyst or catalyst supports in biodiesel production, but study about the utilization of natural clay materials such as zeolite as catalyst or catalyst support for biodiesel is still scarce. The present work was focused in modification of natural zeolite- supported KOH prepared through impregnation method as catalyst for transesterification of palm oil. In this study, we used natural zeolite from Pacitan (East Java, Indonesia).

31**To the best of our knowledge, there is no information available** about **the** utilization **of natural** zeolite **as**

catalyst or catalyst support for biodiesel production. In the present study, the zeolite was used as catalyst support; the effects of KOH loading and transesterification conditions

15**on the yield of biodiesel** were also **studied.**

21**2. Materials and methods 2.1. Materials** Natural zeolite **used in this study was obtained from Pacitan, East Java, Indonesia.**

Prior to use, natural zeolite

9**was crushed using a JANKE & KUNKEL micro hammer mill to obtain** zeolite **with particle size of** 170/240 **mesh.**

Subsequently, the zeolite was treated

11**with 30%** of **hydrogen peroxide solution** to remove **the**

organic impurities. Excess

11**hydrogen peroxide** solution **was removed by** gently **heating** in a water bath, and the solution was separated from the zeolite. Subsequently, the purified zeolite was repeatedly washed and dispersed in distilled water. After the water have been separated from zeolite, the purified zeolite was then dried in an oven at 110 °C for 24 h to remove moisture content from its structure. The dried zeolite was finally crushed in a

9**micro hammer mill to obtain powder** zeolite **with particle size of** 170/ 240 **mesh.**

For transesterification study, the

27**refined palm oil** (Bimoli) **was purchased from local market,**

while analytical grade methanol, potassi- um hydroxide, and n-hexane were obtained from Merck, Darmstadt, Germany. The standard fatty acid methyl ester for FAME analysis was

27**purchased from Sigma Aldrich** (Singapore). **2.2. Catalyst preparation**

2**A series of zeolite catalysts** was **prepared by impregnation** with **KOH** at different KOH **concentrations.**

A brief procedure of catalyst preparation is as follows: a known amount of KOH (25, 50, 75, and 100 g) was added into 100 mL distilled water, followed by the addition of zeolite powder into the solution. The weight ratio between zeolite and KOH solution was 1:4. Afterwards, the mixture was removed to three-neck flask equipped with reflux condenser. The mixture of zeolite and KOH solution was

8**stirred at** 60 **°C for** 24 **h.** Subsequently, zeolite **and**

KOH solution was separated by filtration using a vacuum filter system. The zeolite catalyst was then oven-dried at 110 °C for 24 h, and calcined in a furnace at 450 °C for 4 h. 2.3. Material and catalyst characterization Natural zeolite and catalysts were characterized using several methods such as X-ray Diffraction analysis, Energy-Dispersive X-ray (EDX) spectrometry, and scanning electron microscopy (SEM). The X-ray Diffraction analysis was conducted using a Philips X-pert Powder Analytical diffractometer, and as a source for CuKα radiation (1.54056 Å) a 2.2 kW Cu anode was used. The XRD pattern was obtained at operating condition 40 kV and 40 mA with 2θ measure- ments between the ranges of 5° to 90°. Since potassium

26**plays an important role in transesterification of** palm oil into biodiesel, the potassium content both in raw zeolite and catalyst was determined by an

13**Energy-dispersive X-ray (EDX)** spectrometry **(Shimadzu EDX-720/800HS).**

EDX was used in conjunc- tion

18**with scanning electron microscopy (SEM). The EDX technique detects X-rays emitted from the sample during bombardment by** the SEM's **electron beam;**

1**electrons are ejected from the atoms comprising the sample's surface.** The **resulting electron** vacancies are **filled by** electrons **from a higher** state, **and an X-ray is emitted to balance the energy difference between the two electrons'** states. **The EDS X-ray detector measures the** relative abundance **of emitted X-rays versus their energy. The** surface topography **of**

zeolite and catalyst was examined using

5**Cambridge scanning electron microscope (S-360) at an accelerating voltage of 20 kV.**

Zeolite and catalyst samples

5**were mounted on a double-sided tape attached to a metal stub and sputtered with gold** under argon vacuum **in order to make the sample conductive. 2.**

4. Transesterification Transesterification of palm oil into biodiesel was carried out in a 500 mL three-neck flask equipped with reflux condenser, tempera- ture indicator, and controlled water bath heater.

17**The reaction procedure is as follows: mixture of catalyst and methanol was heated to** 60 °C **under continuous stirring at 500 rpm. Subsequently,**

125 mL of palm oil was added to the reactor. Molar ratio of palm oil and methanol used in this study was 1:7, and the amount of catalyst used was 3% weight of palm oil. Transesterification experiment was carried out at reaction time of 1 to 4

20**h. At the end of** the **reaction,** the **reactor was cooled to room temperature and** the **catalyst was separated from** product **mixture**

using vacuum filter. The biodiesel product was separated from glycerol using funnel separator. Subsequently, the

13**excess methanol was removed from the** biodiesel **product using** vacuum **rotary evaporator.**

Biodiesel product was then repeatedly washed using warm distilled water (60 °C). The fatty acid methyl ester or FAME layer (upper layer) was separated from water layer (bottom layer) using funnel separator. Some amount of sodium sulfate was added to the biodiesel product to remove residual water from the fatty acid methyl ester. 2.5. Determination and characterization of FAME contents FAME content in biodiesel product

13**was determined by gas chromatography** analysis **(GC Shimadzu**

2014). The GC was

16**equipped with a DB-** Wax **capillary column (30 m × 0.25 mm i.d. × 0.** 1 **µm film thickness,** Agilent JW **Scientific) and** flame ionization **detector** (FID). Helium **was**

employed as carrier gas at 40 cm/s. The injector temperature was 250 °C at splitless condition. The FID was set at 300 °C. The initial oven temperature was set at 50 °C with equilibra- tion time of 3 min. After isothermal period,

32**oven temperature was increased to** 250 **°C at** heating **rate of 10 °C/min and held for**

8 min. Peaks of methyl esters were identified by comparing them with the reference standard. The yield of biodiesel was determined by the following equation: Yieldð%Þ ¼ ðweight of biodiesel úME in sampleÞ =ðweight of palm oilÞ 100% ð1Þ where FAME is fatty acid methyl esters. Several physical properties of biodiesel product were also determined according to ASTM standard and the results were compared with the Indonesia National Standard for biodiesel. The kinematic viscosity was determined based on ASTM D445-10, 2010, while ASTM standard D.93, 2010 was employed for the determination of flash point. Cetane index and density/specific gravity of biodiesel wereanalyzed according to ASTM D.613, 2010, and ASTM D.1298, 2005, respectively. Table 1 Fatty acid composition of palm oil. Fatty acid %

6**Lauric acid (C12:0) Myristic acid (C14:0) Palmitic acid (C16:0) Palmitoleic acid (C16:1) Stearic acid (C18:0) Oleic acid (C18:1) Linoleic acid (C18:2)** Linolenaic **acid (C18:3)** Arachinoeic **acid**

(C20:0) 0.8 1.2 42.9 0.2 4.7 40.4 9.4 0.1 0.3 R.I. Kusuma et al. / Applied Clay Science 74 (2013) 121–126 123 Fig. 1. The XRD pattern of raw zeolite. 3. Results and discussion 3.1. Characteristic of palm oil The physical and chemical properties of palm oil were determined using standard test methods. These include density (ASTM D1298, 2005), kinematic viscosity (ASTM D445-10, 2010), free fatty acid content, and flash point (ASTM D93, 2010). The results were as follows: the density at 25 °C was 0.9016 g/cm3, kinematic viscosity at 23.4 °C was 70.9 cSt, free fatty acid and flash point were 0.02% and 220 °C, respectively. The chemical composition of palm oil used in this study was analyzed using gas chromatography (GC Shimadzu 2014) and the results are summarized in Table 1. 3.2. Catalyst characterisation 3

25**.2.1. X-ray diffraction (XRD) X-ray diffraction** analysis **was** performed **to identify the** internal structure, bulk **phase,** and crystallinity **of the**

catalyst.

10**The XRD pattern of** raw zeolite **is shown in Fig.**

1. Fig. 1 shows the typical diffraction peaks of zeolite at Bragg angle (2θ) = 12.4°; 19.4°; 29,9°; 37.1°; 45°; 56°; and 60.6°. The pattern also indicates that the raw zeolite used in this study was classified into mordenite. Fig. 2 depicts the XRD pattern of modified zeolite/catalyst. A

28**new phase of K2O can be observed at** Bragg angle **(2θ) = 31°; 39°; 51°; 55°; and 62°.** During calcinations, molecules **of**

potassium hydroxide in zeolite surface and matrix were transformed into K2O. Potassium oxide (K2O) is believed to play an important role during the transesterification of oil into fatty acid methyl esters since it has high catalytic activity.

14**3.2.2. Energy-dispersive X-ray** spectrometry **(EDX)**

Potassium content in raw zeolite, modified zeolite/catalyst, and spent catalyst (after three reaction cycle)

26**was determined using Energy-dispersive X-ray (EDX)** spectrometry, and **the** results were 3.01% (weight) for raw zeolite, 45.34% and 43.80% for fresh catalyst (modified zeolite) and spent catalyst, respectively. The result showed that the potassium content on the modified zeolite increased after the impregnation with KOH. This indicates that potassium molecules Fig. 2. XRD pattern of catalyst.

8**were attached or incorporated into** zeolite **structure or matrix during the** impregnation **process.** Reusability and stability **of**

catalyst for biodiesel synthesis are very important for the industrial application. Potassium molecules should strongly attach on the structure of zeolite to make the catalyst stable. In order to examine the stability of catalyst, three consecutive reaction cycles using the same catalyst were conducted. After three reaction cycle test, the potassium content was also analyzed using EDX, and it was found that the potassium content in catalyst Fig. 3. SEM micrographs of (A) raw zeolite, (B) catalyst, and (C) spent catalyst after three reaction cycles. Biodiesel yield, % 120 100 80 0 60 20 40 60 40 80 100 20 120 0 R3e,a5ctio3n,0tim2e,,5ho2u,r0(s) 1,5 1,0 30 K4O0H c5o0nce6n0tra7ti0on,8g0/10900 100 m L Fig. 4. The effect of catalyst loading and reaction time on the yield of biodiesel (reaction time between 1 and 4 h, amount of catalyst used was 3%, oil to methanol ratio 1:7, and reaction temperature 60 °C, KOH concentration for zeolite impregnation 25–100 g/100 mL). decreased from 45.34% to 43.80%. This evidence indicates that the stability of catalyst is relatively good because only around 3.40% of the potassium content was leached during three reaction cycles. 3

14**.2.3. Scanning electron microscopy (SEM) The surface** topography **of**

raw zeolite, modified zeolite/catalyst, and spent catalyst (after three reaction cycles) was analyzed using

14**scanning electron microscopy (SEM). The** macrostructure **of**

raw zeolite and its modified form remain intact after the calcination process, confirming the high thermal stability of zeolite (Fig. 3A and B). The surface topography of used catalyst also did not change significantly after reused for three reaction cycles (Fig. 3C).

30**3.3. Transesterification reaction The transesterification of palm oil**

using KOH/zeolite as catalyst was performed under following conditions: catalyst amount 3%, ratio of palm oil to methanol 1:7, reaction temperature 60 °C, and stirring speed 700 rpm. Fig. 5. Multiple cycle test of catalyst deactivation (impregnation with 100 g/100 mL KOH, reaction time 2 h, reaction temperature 60 °C, ratio of palm oil and methanol was 1:7, and 3% of catalyst amount). R.I. Kusuma et al. / Applied Clay Science 74 (2013) 121–126 125 Table 2 Comparison of the properties of biodiesel produced from palm oil with KOH/zeolite catalyst with the Indonesia National Standard (SNI-04-7182-2006). Properties Biodiesel produced SNI Density at 15 °C, g/mL Kinematic viscosity at 40 °C, cSt Flash point, °C Cetane number 0.884 ± 0.00343 5.121 ± 0.221 170.417 ± 0.434 58.500 ± 1.525 0.86–0.90 1.9–6.0 Min 65 >45 3.3.1.

2**Effect of KOH loading on** biodiesel yield **To study the effect of potassium hydroxide** (KOH) **loading on** the **yield** of biodiesel, **a series of KOH/zeolite** catalyst was **prepared by** impregnated **zeolite**

with different concentration of KOH. The effect of KOH loading

7**on the yield of biodiesel is shown in Fig. 4.**

This figure reveals that the

2**yield of biodiesel** increased **with the** increase of **KOH** loading. With **the**

increased of KOH loading, the amount of KOH entering the structure of zeolite also increased. During the calcination process, KOH was converted into potassium oxide (K2O) as shown in XRD pattern.

24**As reported by** Noiroj **et al.** (2009) **and** Soetaredjo **et al.**

(2011), K2O has a high catalytic performance for transesterification process. Along with the increased of KOH amount in the structure of zeolite, the formation of K2O which acts as active sites for trans- esterification process was also increased, thus increased the yield of biodiesel. 3

15**3.2.** Effect **of reaction time** on biodiesel yield **The effect of reaction time on the** transesterification **of** palm oil into **biodiesel was studied**

at reaction time between 1 and 4 h. The transesterification reaction consists of three step reactions to convert triglyceride to final product, methyl ester and glycerol. In the first step, the triglycerides react with one molecule of alcohol, produce diglycerides and one molecule of ester. The molecule of diglycerides then reacts with another molecule of alcohol to produce monoglyc- eride and one molecule of ester. Finally, the reaction between monoglyceride and methanol produces methyl ester and glycerol. Therefore, it is important to select a proper transesterification time to ensure the completion of the reaction, especially if heterogeneous catalyst is used.

8**The effect of reaction time on** the **biodiesel** produced **is** also depicted **in Fig.**

4. In the first hour of reaction, only some triglycerides were completely converted into fatty acid methyl ester (biodiesel). Furthermore, the rate of reaction was relatively slow in the first hour due to the problem of mixing and dispersion between palm oil and methanol (Freedman et al., 1986). With increasing of reaction time the

amount of biodiesel produced also increased, and after 2 h of reaction time, the yield of biodiesel was essentially constant with time. The equilibrium condition of

30**transesterification reaction of palm oil with**

methanol has been reached after 2 h. 3.3.3. Catalyst stability and reusability The reusability and stability of heterogeneous catalyst are the most important criteria in the selection of appropriate catalyst for industrial application. Noiroj et al. (2009) mentioned that in

3**heterogeneous catalyst** application **for biodiesel** preparation, **it is important to ensure that the active species are not leached from the solid support of the catalyst** during **the**

process. In this study, the reusability of KOH/zeolite catalyst was determined by carrying out three transesterification reaction cycles. The following reaction conditions were applied: reaction time of 2 h, palm oil to methanol molar ratio was 1:7, catalyst amount of 3% weight of palm oil, reaction temperature of 60 °C, and stirring speed was at 500 rpm. Fig. 6. Proposed reaction mechanism for transesterification of triglycerides using KOH/zeolite solid base catalyst. For fresh catalyst (at KOH concentration of 100 g/100 mL) the maximum conversion was 95.09% as shown in Fig. 5. For subsequent reaction, the biodiesel yield was decreased to 86.08%, and for the third cycle the yield of biodiesel was just only 72.31% (Fig. 5). The decrease of biodiesel yield occurred because some

4**of the active species in** KOH/zeolite **catalyst**

were leached or deactivated during

4**transesterification reaction of** palm **oil with methanol.** This phenom- enon **was**

supported by the EDX result which indicated that the potassium content in catalyst decreased from 45.34% to 43.80%. 3.4. Biodiesel characterisation The physical and chemical properties (density, kinematic viscosity, flash point, and cetane number)

23**of biodiesel** produced **by transesterification of** palm **oil with methanol using** KOH/zeolite **solid catalyst**

were determined by standard analysis as mentioned in Section 3.1 and the results were compared with the Indonesia National Standard for biodiesel, as shown in Table 2. Since it affects the performance of injector, viscosity is the most important property of biodiesels; particularly at low temperatures when an increase in viscosity affects the fluidity

12**of the fuel. The lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets (Islam** and Beg, **2004). The** minimum value **of**

flash point is required for safety and handling of the fuel. It is used to characterize the fire hazards of liquids. Since the flash point of biodiesel produced from this study is high (more than 60.5 °C), therefore, this fuel is safe for handling and storage for some period of time. With a high value of flash point, this biodiesel is considered as combustible. Cetane number relates to the combustion quality of diesel fuel during compression ignition and also the ignition quality of diesel fuels. The cetane index of biodiesel obtained in this study is higher than conventional diesel fuel (45 to 55). This is due to the major contents of this fuel which are the methyl palmitate and methyl stearate which have the cetane index of 59.3 and 85.9, respectively (Rashid et al., 2011). 3.5. Proposed reaction mechanism The transesterification reaction mechanism for biodiesel produc- tion using KOH/zeolite as catalysis is shown in Fig. 6. The mechanism is as follows: the first step of reaction is the formation of methoxide ion (CH3O−) from the reaction between the active site of catalyst (K2O) with methanol. This methoxide ion is a strong base which has high

24**catalytic activity in the transesterification reaction** (Gryglewicz, 1999). In **the** next step, **the**

reactive methoxide ion attacks the carbonyl carbon atom of triglyceride leading to the formation of tetrahedral intermediate. Further rearrangement of tetrahedral intermediate produced one molecule of methyl ester and diglyceride anion. The reconstruction of diglyceride molecule began with the reaction with H+ from the catalyst. On the other hand, the diglyceride anion may also react with methanol and generate reactive methoxide ion (Ma and Hanna, 1999). The catalytic reaction was then followed by the reaction between diglyceride and other methoxide ion to produce monoglyceride molecule and one molecule of methyl ester. Finally, carbonyl carbon atom of monoglyceride was attacked by methoxide ion producing one molecule of methyl ester and one molecule of glycerol. 4. Conclusion Natural zeolite from Pacitan, East Java, Indonesia, was employed as catalyst support for biodiesel production. The catalyst was prepared by impregnating the zeolite with potassium hydroxide solution. The KOH loaded zeolite was then calcined at 450 °C. During calcination, the KOH was converted into K2O, which was believed to be the active site during the transesterification reaction. The maximum yield of biodiesel was 95.09%, and obtained at following operation condition: impregnation with 100 g/100 mL KOH, reaction

3**time of 2 h, reaction temperature of 60 °C** and **ratio of** palm oil **and**

methanol was 1:7, and 3% weight of catalyst amount. During three cycles of transesterification reaction, 3.40% of active site of catalyst was leached from zeolite structure. Acknowledgments The authors would like to acknowledge the support of the Department of Chemical Engineering, Widya Mandala Catholic Univer- sity Surabaya and also

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