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Synthesis of Zeolite-X from Rice Husk Silica and Aluminum Metal as a Catalyst for Transesterification of Palm Oil

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ABSTRACT

In this study, zeolite-X was synthesized from rice husk silica and aluminum metal as raw materials. The zeolite was then calcined at 550 ° C for 6 h and subsequently tested as a catalyst for transesterification of palm oil with methanol to produce biodiesel.Transesterification experiments demonstrated that the zeolite produced exhibited good activity as a catalyst for conversion of palm oil into biodiesel, as reflected by the composition of the biodiesel according to GC-MS analysis, which are in accordance with the fatty acids contained in palm oil. The catalyst was characterized using XRD, FTIR, and SEM. The XRD revealed that zeolite-X synthesized has a faujasite phase, composing of crystallite shapes of cubic, rectangular, and irregular as seen by SEM. The FTIR analysis revealed the presence of functional groups associated with zeolite.

1. Introduction

Researches on the development of alternative energy sources, especially biodiesel, continue to attract interest around the globe in response to persistent increase of energy demand and depletion of fossil fuels. Biodiesel is produced by transesterification of glyserides composing vegetable oils or animal fats, using simple alcohols, primarily methanol. The reaction of glyserides with methanol will produce fatty acid methylesters (FAMEs), having comparable fuel characteristics with those of conventional diesel. The two reactants involved in the transesterification reaction are known to be non-reactive to each other and for this reason, the use of catalysts is a necessity to accelerate the reaction rate up to a significant level. Various types of catalysts have been used and the most widely used is homogeneous catalyst, either strong mineral acid or strong alkaline. The acid catalyst generally use are hydrochloric acid, sulfuric acid, and nitric acid [1-4]), while common base catalysts are sodium hydroxide and potassium hydroxide [2,5-7]. The use of base homogeneous catalysts is acknowledge to offer several advantages such as simple operating conditions, high activity, and shorter reaction time, and the acid catalyst enable simultaneous esterification and transesterification, therefore suitable for vegetable oils with high content of free fatty acid [8-10]. Despite many advantages, homogeneous catalysts are known to have disadavantages, such as the difficulty of separation of product and catalyst, saponification reaction, the catalyst can not be reused, corrosive, and requires higher molar ratio of alcohol to oil [8,11-12].

To alleviate the problems associated with homogeneous catalysts, currently much interest is focussed on the use of heterogeneous catalysts, since the catalysts of this type of exhibits beneficial characteristics. In principle, the heterogeneous catalyst has the potential to improve the efficiency and effectiveness of the transesterification reaction because the catalyst can be recycled, environmentally friendly, easy to be separated from the reaction products, can be applied in a continuous process, and the product can be used without the need for further purification [8,13]. Various types of heterogeneous catalysts have been developed and assessed, and of particular interest are synthetic zeolites [14-18].

Zeolites are porous, hydrated aluminosilicates, obtained naturally or synthesized from various chemical raw materials. Commercially, synthetic zeolites are more widely used than the natural zeolites, since pure synthetic zeolite can be tailored to have fixed composition and uniform characteristics, such as pore size, and surface morphologies [19-20]. The main components composing synthetic zeolites are silica and alumina, and for this reason, an array of synthetic zeolites has been prepared from different raw materials, such as sodium aluminate and sodium silicate solution [21], silica, aluminum oxide, sodium oxide, hexamethyleneimine (HMI) and tetraethylammonium hydroxide (TEAOH) [15], sodium silicate solution and sodium aluminate solution [22]), sodium aluminate and sodium metasilicate [23], sodium aluminosilicate[24], rice husk ash, sodium aluminate and TEAOH [25], rice husk ash, pellets of sodium hydroxide, tetrapropylammonium bromide (TPABr) [26], and rice husk ash and sodium aluminate solution [27].

Today, a variety of synthetic zeolites with different compositions has been developed, one of them, that has been used for various industrial purposes including catalyst [15], is zeolite- X (SiO_2: Al_2O_3: Na_2O = 2.5: 1: 1) [14,19,21-22]. In this study, zeolite-X was synthesized using rice husk silica extracted by alkaline method [28-29] as a source of Si and aluminum metal as a source of Al. From practical point of view, the use of rice husk silica is advantageous since rice husk is highly available and renewable. In addition, rice husk silica is cheaper than other types of silica commonly used. Direct use of aluminum metal, instead of aluminum salts generally used is another practical reason of this current study. The zeolite produced was subjected to a calcination treatment at 550 ° C for six hours, and then tested as a catalyst for transesterification of palm oil with methanol.

2. Experimental details

2.1. *Extraction of silica*
Rice husk was obtained from local rice milling industry in Bandar Lampung. Extraction of silica from rice husk was carreid out using alkalis extraction method as described in previous studies [28-29]. A typical process was undertaken by mixing 50 grams of dried husk and 500 mL of 1.5% (by weight) NaOH solution, prepared using NaOH pellet purchased from Aldrich. The mixture was placed in an Erlenmeyer flask and boiled for 30 minutes. To optimize the dissolution of the silica, the mixcture was left overnight at room temperature. After the completion of the extraction process, the mixture was filtrated and the filtrate which contains dissolved silica (silica sol) was acidified by dropwise addition of HNO_3 (10%) solution to convert the sol into gel. The gel was repeatly rinsed with hot distilled water to expell the excess of acid, and subsequently oven dried at 110 ^{o}C for 8 hours to produce dry silica.

2.2 *Preparation of zeolite*
For preparation of zeolite-X, sodium hydroxide solution was prepared by dissolving 40 g NaOH in 500 mL of distilled water and then the solution was divided into two parts, with the same volume of 250 mL. The first part was used to prepare aluminum solution, by dissolving 27 grams of Al metal (purchased from CV. Aluminium Jaya Perkasa Jakarta) and the second part was used to dissolve 75 grams of silica. The two solutions were then mixed thoroughly using a blender, and then left at room temperature to allow the transformation of the mixture from sol into gel. The gel was then oven-dried at 90 ^{o}C for 24 hours. Dry solid was ground into powder and subsequently calcined at 550 ° C for 6 hours.

2.3 *Transesterification experiment*
Catalytic activity of the zeolite synthesized was tested for transesterification reaction of palm oil with methanol. Typical transesterification reaction was carried out in 500-mL round bottom flask equipped with a reflux condenser, following the method described elsewhere [30-32] . The reaction mixture prepared by mixing 25 mL palm oil, 50 mL methanol, and 2.5 g catalyst. The transesterification unit was immersed in a water bath situated on top of a magnetic stirrer with heating plate. Transesterification was run at 70 ^{o}C for two hours. After the completion of the experiment, the sample was cooled to room temperature and then filtered into separatory funnel, to separate the catalyst from the liquid product. The sample in the separatory funnel was allowed to settle for six hours to separate the mixture into two layers, and the upper layer which is the biodiesel was collected. The excess of methanol was removed by evaporation and the biodiesel was analyzed using GC-MS technique to identify the components of the sample.

2.4 *Analysis of Transesterification Products using GC-MS*
Identification of FAMEs in the transesterification product was conducted using gas chromathography-mass spectroscopy (GC-MS) technique. The analysis was carried out on GCMS-QP2010 SE SHIMADZU, equipped

with 30 m long and 0.32 mm internal diameter HP SMS 30 m column. The instrument was operated in the EI mode at 70 EV using helium as carrier gas and nitrogen as make up gas to obtain the total flow rate of 60 mL/min. Tentative identification of the components in the sample was done by comparing their mass spectra with those published in the MS Library System NIST62, Wiley 7 database.

2.5 *Characterization of zeolite-X*
2.5.1 *XRD analysis*
Phase and crystallinity of zeolite were identified by XRD instrument, Bruker D8 Advance with Cu Kα radiation at 40 kV and 40 mA. The difractogram was recorded by scanning the sample in the angle (2θ) range of 5–70°.

2.5.2 *FTIR analysis*
Fourier transformed infrared (FTIR) spectrum of the zeolite-X was recorded by Fourier transform infrared (GX, Perkin-Elmer) spectrophotometer. The FTIR spectrum was produced by scanning the sample in the wavenumber range of 4000 cm^{-1} to 400 cm^{-1}.

2.5.3 *SEM analysis*
Scanning electron micrographs (SEM) were obtained on a FEI type Inspect S50 to observe the morphology of catalyst.

3. Results and Discussion

3.1. *Analysis of Transesterification Products using GC-MS*
Typical example of the GC chromatogram of the transesterification product is presented in Figure 1, and the compounds identified with the aid of MS Library System Wiley 229 LIB database are listed in Table 1.
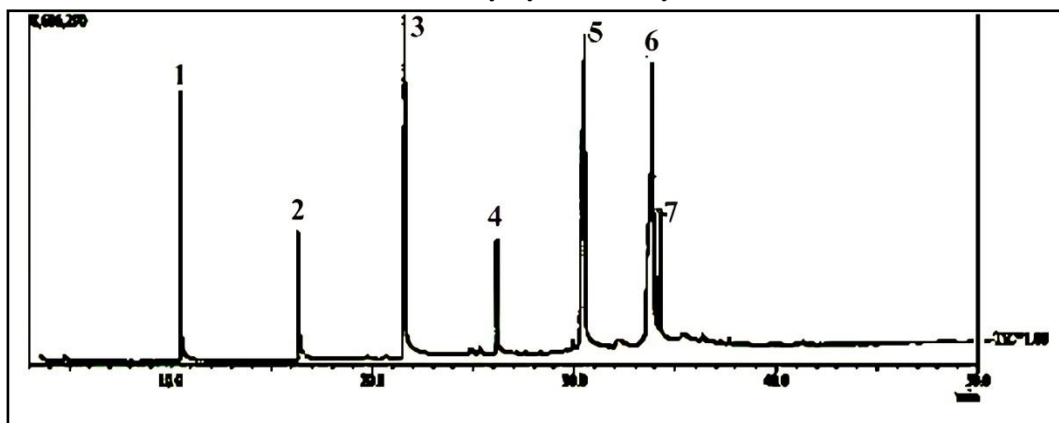

Figure 6: GC chromatogram of the palm oil transesterification product obtained from the experiment using zeolite-X

Table 1: The components of transesterification product of palm oil

Peak number	Retention time (minute)	Relative percentage	Compound name	Molecular formula
1	10.5	8.6	Methyl Caprylate	$C_9H_{18}O_2$
2	16.3	4.2	Methyl Caproate	$C_{11}H_{22}O_2$
3	21.6	17.4	Methyl Laurate	$C_{13}H_{26}O_2$
4	26.1	3.9	Methyl Myristate	$C_{15}H_{30}O_2$
5	30.5	25.8	Methyl Palmitate	$C_{17}H_{34}O_2$
6	33.9	33.7	Methyl oleate	$C_{19}H_{36}O_2$
7	34.2	4.3	Stearic Acid	$C_{19}H_{38}O_2$

As can be seen in Figure 1, seven peaks are observed in the chromatogram, suggesting the presence of seven compounds in the sample. In general, the components display very good peak shapes and they are well separated from each other, except the peak 6 and 7. As listed in Table 1, the compounds identified are methyl

esters of fatty acids commonly found in palm oil, confirming that zeolite-X worked for different kinds of fatty acids as expected. The data also display that methyl oleate and methyl palmitate are the most prominent component of the biodiesel produced, which are in accordance with the existence of oleic acid and palmitic acid as the prominent components of palm oil, as have been reported by others [18,33]. In this respect, the zeolite-X prepared from rice husk silica and aluminum metal exhibited high potential as a heterogeneous catalyst for biodiesel production.

3.2. Characterization of synthetic zeolite by XRD
The formation of zeolite synthesized from rice husk silica and aluminum metal was confirmed by XRD. The XRD patterns of the sample was shown in Figure 2.
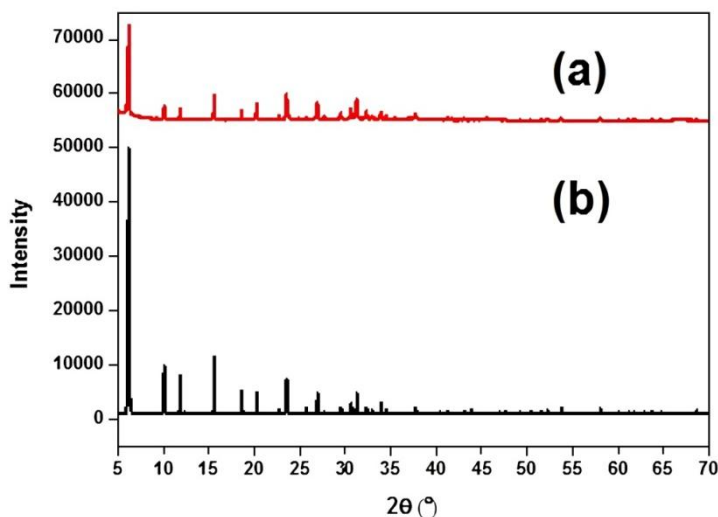

Figure 2: X-ray diffraction patterns of (a) zeolit synthetic from RHS and aluminum and (b) standard of Faujasite

As can be seen, the difractogram of the sample is characterized by the existence of a series of peaks, and four peaks with the highest relative intensities are those located at the angle 2θ (°) of 6.18; 15.60; 23.56 and 31.26. Comparing the difractogram of the sample with those of the standards in the PCPDFWin database, it was concluded that the sample belongs to faujasite with the reference file (PCPDF 430-168). The existence of zeolite-X as a faujasite observed in this study is in agreement with the results reported by others [21,34].

3.3. Characterization of synthetic zeolite by FTIR
Figure 3 is the FTIR spectrum of the zeolite-X prepared, showing the existence of several functional groups in the sample.
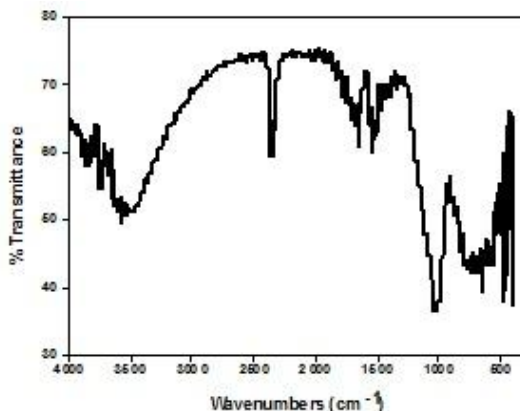

Figure 3: FTIR spectrum of zeolite-X.

A broad absorption band at the wavenumber of 3477 cm^{-1} is characteristic vibration band associated with stretching of -O-H functional group, indicating the presence of bonded -O-H group or adsorbed water molecules in the sample. The presence of adsorbed water molecules is supported by the absorption band located at 1645cm^{-1}, commonly assigned to bending vibration of adsorbed water molecule [35]. Other functional groups exist in the samples are Si-O-Si, indicated by the absorption band at 1020 cm^{-1}, Al-O indicated by the peak at 770 cm^{-1}, and Si-O-Al is indicated by the presence of an absorption band at the region between 420 and 494 cm^{-1}. With respect to the existence of functional groups Si, O, and Al observed in the spectrum, it was then concluded that the formation of zeolite framework was confirmed by the FTIR results.

3.4 Characterization of synthetic zeolite by SEM
Recognizing the role of surface on catalytic activity, the surface morphology of the zeolite-X synthesized was evaluated using SEM. To gain more insight, the micrographs were recorded at different magnifications, and the result are compiled in Figure 4.
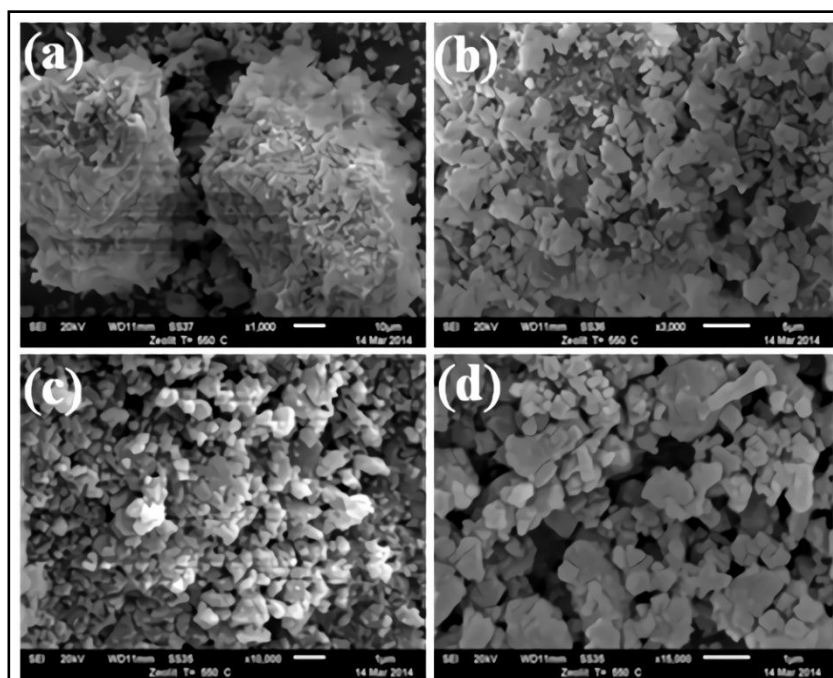

Figure 4: SEM images of zeolite-X with different magnifications (a) 1000 x; (b) 3000 x; (c) 10000 x, and (d) 15000 x

The SEM images of the sample (Figure 4) clearly indicate the existence of the sample as porous material, which is one of the important characteristics of heterogeneous catalyst. The image produced at low magnification (1000 x) indicated the presence of clusters, which has also been reported in previous study [36], most likely as a result of particles agglomeration on the surface of the sample. Closer inspection of the cluster by increasing the magnification to 3000 x, revealed the presence of grains with different sizes and shapes, spread over the surface. Further increased of magnification to 10000 x produced the image which display that in general, three different shapes of the grains can be distinguished, i.e. cubic, rectangular, and irregular. These crystal shapes are more evidently displayed by the image obtained at highest magnification (15000 x). Different crystal shape (octahedral) of zeolite-X crystal was reported by other [34], who synthesized the zeolite from pure mineral silica and alumina using hydrogel method. In this respect, different crystal shapes of zeolite-X is probably associated with different raw materials and preparation methods applied.

Conclusions
The present work demonstrates that it is possible to prepare synthetic zeolites-X from rice husk silica and aluminum metal. The formation of zeolite framework was revealed by the functionality of the sample as seen by the FTIR and the structure by the XRD, as well as microstructure (surface morphology) indicated by SEM. Transesterification experiment demonstrated that zeolite-X exhibited good activity as catalyst for conversion of palm oil into biodiesel, as reflected by the composition of the biodiesel obtained using GC-MS technique.

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