

Transesterification of Used Cooking Oil Using CaO/MCM-41 Catalyst Synthesized from Lapindo Mud by Sonochemical Method

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ABSTRACT

Transesterification of waste cooking oil using CaO/MCM-41 synthesized from Lapindo mud by the sonochemical method has been carried out. The silica was separated from the mud by reflux method used 6 M HCl and 6 M NaOH. The silica was then analyzed by XRF and used as silica source in MCM-41 synthesis. The synthesis of MCM-41 was carried out by the sonochemical method, then analyzed by XRD, Infrared spectrophotometer, SAA, and TEM. The Ca²⁺ was loaded onto the MCM-41 by wet impregnation method under variation of the Ca²⁺ content of 1.15, 1.29, 2.39, and 3.25 wt.% analyzed by ICP produced CaO(1), CaO(2), CaO(3), and CaO(4)/MCM-41 catalyst respectively. Transesterification of used cooking oil was carried out under methanol/oil mole ratio of 15/1, the temperature of 55, 65 and 75 °C, and catalyst/oil weight ratio of 5/100, 10/100 and 15/100 for 2 h by reflux method. The XRD analysis of the MCM-41 showed a characteristic peak at $2\theta = 2-5^\circ$. The MCM-41 has a specific surface area of 1290 m²/g and pore diameter of 3.4 nm. The TEM images of MCM-41 showed ordered pore distribution with a hexagonal shape. The highest conversion of methyl ester was 78.17 wt.% obtained under the reaction conditions at 65 °C and catalyst/oil weight ratio of 15/100 using the CaO(4)/MCM-41. The lifetime CaO(4)/MCM-41 catalyst was 9.8 h.

Keywords: Lapindo mud; sonochemical; MCM-41; transesterification; CaO/MCM-41

ABSTRAK

Telah dilakukan transesterifikasi minyak goreng bekas menggunakan katalis CaO/MCM-41 dari lumpur Lapindo dengan metode sonokimia. Pemisahan lumpur Lapindo dilakukan dengan metode refluks menggunakan HCl 6 M dan NaOH 6 M. Lumpur hasil refluks kemudian dianalisis dengan XRF dan digunakan sebagai sumber silika dalam sintesis MCM-41. MCM-41 disintesis dengan metode sonokimia selama 150 menit dan dianalisis menggunakan XRD, FT-IR, TEM, dan GSA. Katalis Ca diimbangkan pada MCM-41 menggunakan metode impregnasi basah dengan variasi pengembunan 1,15; 1,29; 2,39; dan 3,25% (b/b) yang dianalisis menggunakan ICP. Proses transesterifikasi minyak goreng bekas dilakukan dengan kondisi rasio mol metanol/minyak = 15/1 dan variasi suhu 55, 65, dan 75 °C, serta variasi rasio katalis 5/100, 10/100, dan 15/100 (b/b) terhadap minyak dengan waktu reaksi selama 2 jam. Analisis XRD dari MCM-41 menunjukkan puncak karakteristik $2\theta < 5^\circ$ dengan luas permukaan spesifik dari 1290 m²/g dan diameter pori 3,4 nm. Citra TEM menunjukkan distribusi pori yang teratur dengan bentuk heksagonal seperti sarang lebah. Konversi metil ester tertinggi didapatkan pada kondisi reaksi suhu 65 °C dan rasio katalis umpan 15/100 (b/b) yaitu sebesar 78,17% menggunakan kandungan Ca yang diimbangkan sebesar 3,25% (b/b). Umur katalis CaO(4)/MCM-41 adalah 9,8 jam.

Kata Kunci: lumpur Lapindo; sonokimia; MCM-41; transesterifikasi; CaO/MCM-41

INTRODUCTION

The demand for fuel oil for community activities continues to increase. This condition was expected to increase every year, resulting in the depletion of petroleum supplies. Biodiesel was an alternative fuel that was environmentally friendly, biodegradable, and non-

toxic that can be produced from vegetable oils and animal oils. Biodiesel was a methyl ester as bioenergy or biofuels made from vegetable oil, either new oil or frying and by transesterification process, esterification, or esterification-transesterification process [1-2]

The common method used to convert oil into methyl esters was the transesterification method. The

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transesterification process requires a catalyst, either a homogeneous or heterogeneous catalyst to assist or accelerate the conversion of methyl esters [3]. Heterogeneous catalysts have several advantages such as minimizing the process ie not requiring complex purification of the resulting biodiesel and reusable catalysts [4-5]. Heterogeneous base catalysts one of them was alkaline oxide [6-8]. Calcium oxide was the most promising heterogeneous base catalyst because it was cheap, low solubility and toxicity [9]. Verziu et al. reported the results of transesterification of sunflower oil used a CaO catalyst of 92% after 2 h at 75 °C [10]. CaO as mesoporous silica support in the transesterification of soybean oil yielding 95.2% methyl ester achieved after 8 h when used CaO mesoporous silica [11]. However, a large number of species of Ca released also undergo the formation of Ca diglyceroxide in the presence of glycerol. So to overcome this problem, it was important to investigate a new active and stable heterogeneous base catalyst for transesterification reactions [12].

The MCM-41 material becomes very interesting to study because it was solid with pores composed of amorphous silica but has a regular structure and a uniform cavity [13-14]. The method commonly used by researchers for MCM-41 synthesis was a method with high temperature or called hydrothermally. High temperatures and length of synthesis time become the weakness of the hydrothermal method. The sonochemical method was one of synthesis method that can be used in the various inorganic material. The MCM-41 synthesis process using sonication method was a faster synthesis method than the hydrothermal method. This method produced small particle size and increased wall pore thickness [15-17]. Ventrivel et al. successfully synthesized MCM-41 silica with high solubility under normal conditions via ultrasonic radiation within 5 min, which showed significant time reduction when compared with conventional synthesis methods [18]. Ifah et al. successfully synthesized $\text{NH}_2/\text{MCM-41}$ catalyst with hexagonal pore form using the sonochemical method with best synthesis time were 150 min [19].

Apart from the high temperature and the length of synthesis time, another constraint of MCM-41 synthesis was the high cost of the main raw material of silica. One of the alternative sources of silica that can be utilized was the silica-based sources from nature [20]. Lapindo mud has a silica content of 44.24% [21]. Because of the high silica content makes Lapindo mud has good potential as a supplier of silica-based natural materials for mesoporous material synthesis. Based on the above explanation, the authors undertook to synthesize an MCM-41 material with silica base material from Lapindo mud using the sonochemical method.

In the present work, to increase the catalyst activity in the process of transesterification of used cooking oil

then modified MCM-41 material with Ca metal was carried out. The variation of catalyst/oil weight ratio towards methyl ester conversion in the transesterification of waste cooking oil was also evaluated.

EXPERIMENTAL SECTION

Materials

The chemicals used in this research were Merck products: calcium acetate ($(\text{Ca}(\text{CH}_3\text{COO})_2)$), methanol (CH_3OH), hydrochloric acid (HCl), sodium hydroxide, cetyl trimethyl ammonium bromide (CTAB). Other materials were Lapindo mud and used cooking oil.

Instrumentation

Glass apparatus (Pyrex), hotplate magnetic stirrer (As-one), furnace (Carbolyte), Sonicator (Bransonic 220) for synthesized the MCM-41 by sonochemical method, X-ray Fluorescence Spectrophotometer (PAN Analytical Minipal 4) for elemental analyzes of Lapindo mud, Fourier Transform Infrared Spectrophotometer (Shimadzu model Prestige 21), Transmission Electron Microscope (TEM, JEOL JEM-1400), X-ray Diffractometer (Rigaku Miniflex 600), Inductively Coupled Plasma Spectrophotometer (ICPE-9820), for elemental analyzes of catalysts, Gas Sorption Analyzer (Quantachrome Nova Win Version 11.0) for surface area and porosity measurement and Gas Chromatograph-Mass Spectrophotometer (Shimadzu QP20105).

Procedure

Silica extraction

The method used to extract silica in Lapindo mud was a batch method. Lapindo mud was washed with water for 24 h then dried. The dried sludge was then refluxed with 6 M HCl at 90 °C for 3 h and subsequently refluxed with 6 M NaOH at 90 °C for 16 h. The filtrate was separated, the reflux filtrate was titrated using 3 M HCl until the pH = 8 and white precipitate of silica was formed. Silica was filtered and washed with distilled water, then analyzed by X-Ray Fluorescence (XRF, Minipal 4 PANalytical).

Synthesis of MCM-41 using sonochemical method

The synthesis of MCM-41 was done by the sonochemical method. A total of 1.5 g of silica was dissolved in 50 mL of distilled water containing 3 g NaOH for 2 h (Na_2SiO_3 solution). Elsewhere, a prepared CTAB solution with 2.187 g of CTAB was dissolved in 45 mL distilled water and stirred for 30 min

Table 1. The content of compounds in the Lapindo mud wash with distilled water, HCl, and silica extracted from Lapindo mud

Compound	Content (%)		
	Lapindo mud wash aquadest	Lapindo mud wash HCl	Silica extracted from Lapindo mud
SiO ₂	29.75	60.80	96.70
Al ₂ O ₃	11.01	9.22	-
Fe ₂ O ₃	42.82	16.30	0.84
CaO	6.78	4.48	1.30
Etc	9.64	9.20	3.76
Total	100.00	100.00	100.00

at 50 °C. The Na₂SiO₃ solution was then added to the CTAB solution. Furthermore, 1 M H₂SO₄ solution was added to reach the pH = 11 and the white gel was formed and stirred for 1 h. The white gel solution was sonicated for 150 min. The gel solution was then filtered and neutralized with distilled water until neutral condition. The solid was then dried in an oven at 100 °C for 5 h. The white solid (MCM-41) was then calcined for 5 h at a temperature of 540 °C. The MCM-41 was then characterized using X-ray diffraction (XRD, Rigaku Miniflex600), Fourier Transformation-Infrared (FT-IR, Shimadzu model Prestige 21) spectrophotometer, Transmission Electron Microscope (TEM, JEOL JEM-1400), and Surface Area Analyzer (SAA, Quantachrome NovaWin version 11.0).

Impregnation of Ca²⁺ onto the MCM-41

The Ca²⁺ was supported on the MCM-41 by wetness impregnation technique. One gram of synthesized MCM-41 was introduced into 37.5 mL Ca(CH₃COO)₂ 0.1 M solution and distilled for 3 h at 60 °C, then filtered to produced solid phase. The solid was washed with distilled water and dried at room temperature. The amount of Ca²⁺ was varied in 4, 6, 8, and 10 wt.%. The amount of Ca²⁺ loaded was analyzed using Inducted Coupled Plasma (ICP, ICPE-9820).

Activity and selectivity test of the catalyst

The CaO/MCM-41 catalyst activity test was carried out by transesterification of used cooking oil. The transesterification was carried out by refluxing methanol, used cooking oil, and a catalyst at a temperature of 55, 65, and 75 °C for 2 h. The mole ratio of methanol and used cooking oil of 15:1, and the ratio of catalyst/oil of 5/100, 10/100, and 15/100. After the reflux process, the catalyst was separated using a centrifugation at 2000 rpm for 20 min and the filtrate was washed with warm distilled water. The ester product was analyzed using Gas Chromatography-Mass Spectrometer (GC-MS, Shimadzu QP2010S) to determine the type of ester and its conversion.

The catalyst lifetime determination was performed by reusing the catalyst after has been used in the transesterification of used cooking oil. The catalyst of the

first transesterification process was taken, then washed with distilled water and methanol, then dried at 100 °C for 4 h then reused for the second transesterification process. The transesterification product was analyzed using GC-MS. The transesterification process was repeated with the same catalyst up to 3 repetitions.

RESULT AND DISCUSSION

Silica Extraction from Lapindo Mud

Based on Table 1 about diffractogram of MCM-41 before and after calcination, it was known that the content of SiO₂ and Al₂O₃ compounds in Lapindo mud washed was 29.75 and 11.01 wt.%. Washing successively with HCl and NaOH caused the SiO₂ concentration to be 60.80 and 96.70 wt.%. The change in concentration was due to the reduction of impurity metals after refluxing with HCl and only slightly remaining after refluxing with NaOH. Cl⁻ ions contained in HCl solution bind metal ions such as Ca²⁺, Al³⁺, and Fe³⁺ to form water-soluble chloride salts, which can be separated from the Lapindo mud.

MCM-41 Characterization

XRD analysis was the first method used to indicate MCM-41 material with the presence of diffraction pattern of 2θ = 2-5°. The diffractogram of the MCM-41 material structure before and after the calcination was shown in Fig. 1.

The MCM-41 shown a peak at an angle of 2θ = 2-5 degrees. The MCM-41 before calcination showed a peak at an angle of 2θ = 2.11 (100); 3.51 (110) and 4.19 (200). For the MCM-41 after calcination, the peaks were observed at an angle of 2θ = 2.37 (100) and 4.51 (110). The hkl index that appears on the diffractogram of both materials indicated that the synthesized MCM-41 has a hexagonal structure in accordance with those reported by Kresge et al. [22]. Peak intensity at an angle of 2θ = 2.11 (100) of MCM-41 before calcination was lower than that of an angle of 2θ = 2.37 (100) of MCM-41 after calcination. This result indicated that the crystallinity of MCM-41 after calcination was better and

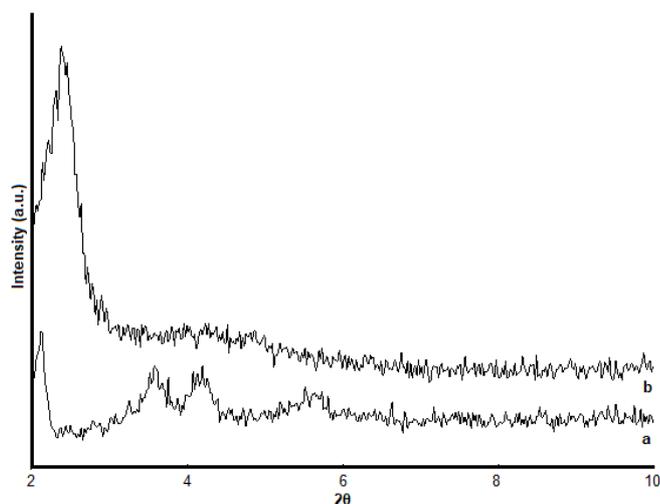


Fig 1. Diffractogram of (a) MCM-41 before and (b) after calcination

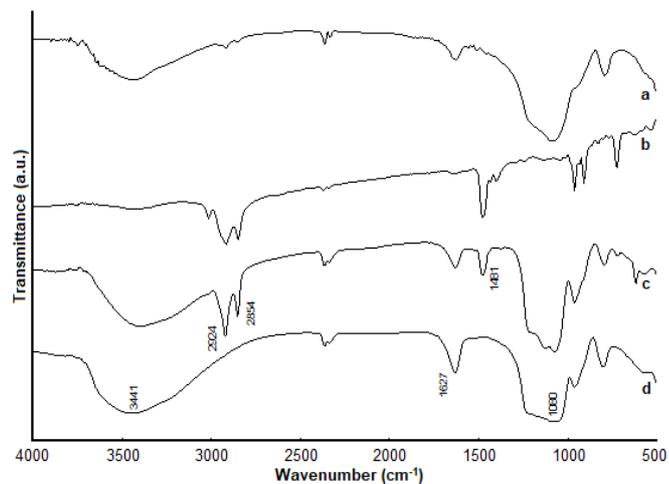


Fig 2. FT-IR spectra of: (a) silica, (b) CTAB, (c) MCM-41 before calcination, and (d) MCM-41 after calcination

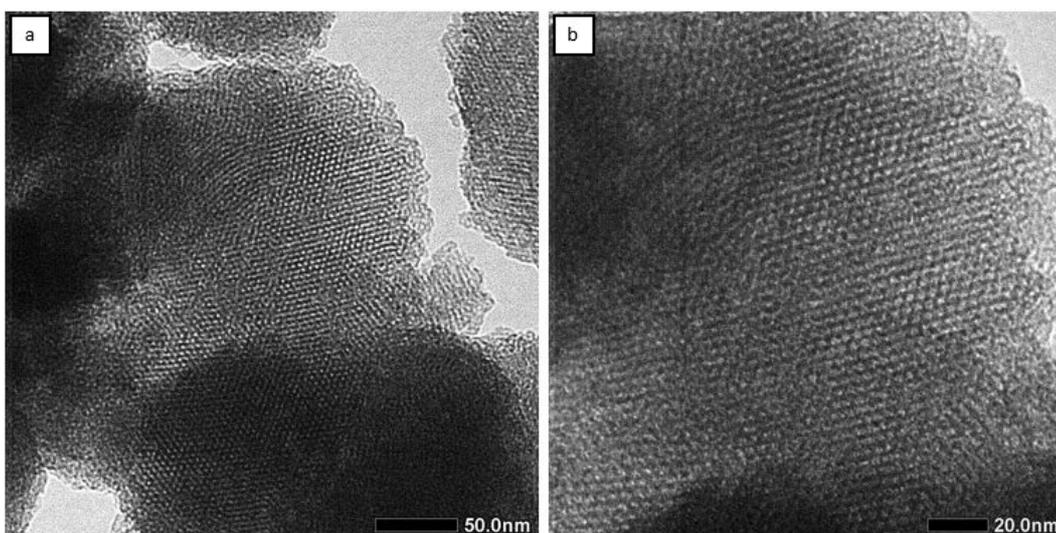


Fig 3. TEM image of MCM-41 mesoporous material with magnification of: (a) 50 and (b) 20 nm

the MCM-41 material has good structure regularity. The increase in crystallinity was due to the loss of CTAB mold in the pore of the MCM-41.

Based on FT-IR spectra in Fig. 2 about FT-IR spectra of silica, CTAB, MCM-41 before calcination, and MCM-41 after calcination, there were some peaks that characteristics to the MCM-41 mesoporous material. The peak at the 1080 cm^{-1} wavenumber indicated the asymmetric stretching vibration of the Si-O-Si group. Peaks in the regions of 964 cm^{-1} and 802 cm^{-1} waves in spectra (d) and 794 cm^{-1} in spectra (c) showed symmetrical vibration of Si-O-Si groups. The Si-O-Si bending vibration appeared in the 455 cm^{-1} regions. There was also a silanol group peak at MCM-41 at a wave number of 3441 cm^{-1} on spectra (d) and 3394 cm^{-1} on spectra (c).

Fig. 2 also showed the existence of the CTAB in the MCM-41 before calcination by a peak at a wave number of 2924 cm^{-1} which was the peak of vibration symmetry for C-H and peak at a wave number of 2854 cm^{-1} which was the asymmetric strain vibration for the C-H group. Bending and vibrating vibrations of the N-H and C-H groups derived from CTAB are shown by peaks at 1481 cm^{-1} . The IR spectra of MCM-41 after calcination showed the loss of all three characteristic peaks of the CTAB. Analysis using TEM provides information about the crystal and porosity order of MCM-41 materials. Based on Fig. 3. about TEM image of MCM-41 mesoporous material with a magnification of 50 and 20 nm, it can be seen that the synthesized MCM-41 material has a honeycomb-like shape structure with the cylindrical hexagonal pore.

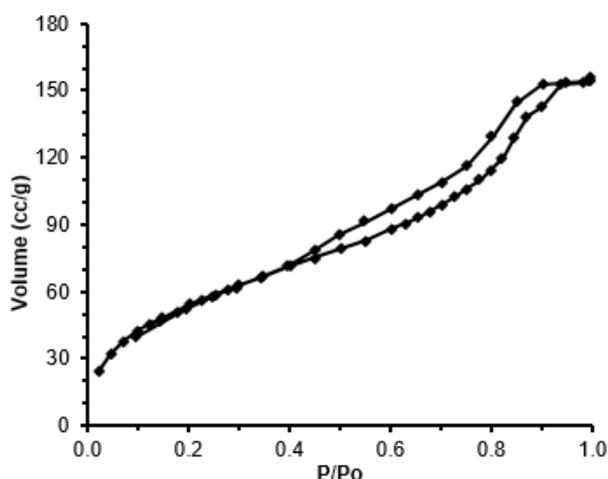
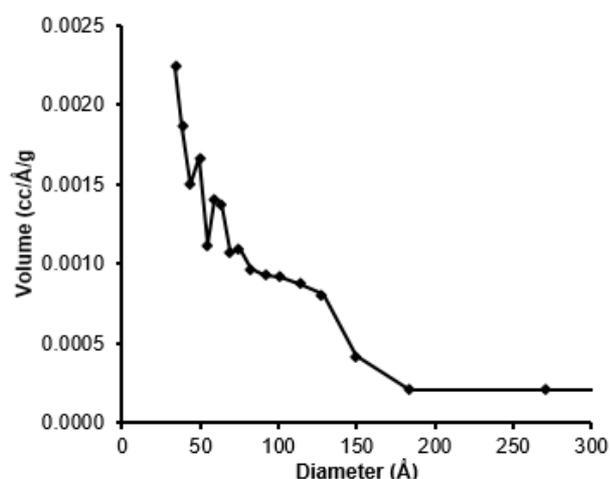
Table 2. The Ca²⁺ content in MCM-41 catalyst

Catalyst	Ca ²⁺ content (%) (w/w)	
	Ca	
MCM-41	0.00	
4% CaO/MCM-41 (CaO(1)/MCM41)	1.15	
6% CaO/MCM-41 (CaO(2)/MCM41)	1.29	
8% CaO/MCM-41 (CaO(3)/MCM41)	2.39	
10% CaO/MCM-41 (CaO(4)/MCM41)	3.25	

Table 3. Surface area analysis of MCM-41 catalyst

Sample	S _{BET} ^{a)} (m ² /g)	V _{total} ^{b)} (cm ³ /g)	Diameter (nm)
MCM-41	1290.27	0.84	3.41
CaO/MCM-41	203.84	0.34	3.41

Information: ^{a)}Specific surface area, ^{b)}Total pore volume

**Fig 4.** Nitrogen Isotherm adsorption-desorption CaO(4)/MCM-41**Fig 5.** The pore size distribution of CaO(4)/ MCM-41 catalyst

Characterization of CaO(4)/MCM-41 Catalyst

The Ca²⁺ content in the catalyst analyzed using ICP was shown in Table 2. Based on the ICP data, the Ca²⁺ content in the MCM-41 was 1.15, 1.29, 2.39, and 3.25 wt.% of CaO(1)/MCM-41, CaO(2)/MCM-41, CaO(3)/MCM-41, and CaO(4)/MCM-41. The isotherm adsorption characterization of N₂ gas was performed to determine the surface area, pore volume, and pore diameter of the MCM-41 material. The results of the Surface Area Analysis (SAA) analysis were presented in Table 3.

From Table 3 it can be seen that the Ca²⁺ loaded onto the MCM-41 caused a decrease in the surface area. This decrease was due to uneven distribution of pores and some small pores were blocked by the CaO in the MCM-41 hexagonal cavity. Fig. 4 showed N₂ isotherm adsorption-desorption of CaO(4)/MCM-41. This separation of adsorption and desorption indicated that the material formed was mesoporous material. The Hysteresis loops of the MCM-41 indicated type H1

where the material was cylindrical and with a uniform distribution. This hysteresis loops pattern occurs due to differences in the amount of gas volume adsorption and the volume of desorbed gas in the pore. This pattern was also caused by a large pore size or the wide pore size distribution. Fig. 5 provided the pore size distribution of CaO(4)/MCM-41 catalyst. It was seen that the majority of pore diameter was distributed at of 3.4 nm. This data indicated the CaO(4)/MCM-41 was mesoporous material.

Activity and Selectivity Test

The methyl ester conversion results for variations of Ca²⁺ content on the MCM-41 material were shown in Fig. 6. Fig. 6 showed the highest yield of methyl ester was 75.68% produced by CaO(4)/MCM-41. Based on the data from the Fig. 7, the highest amount of methyl ester was produced by transesterification of used cooking oil at 65 °C (75.68%), while the lowest methyl ester amount was produced at 55 °C (63.74%). Fig. 8

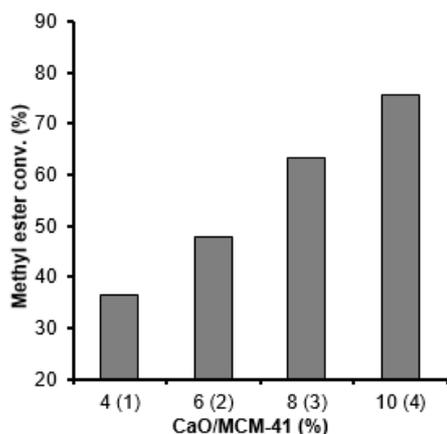


Fig 6. Conversion of methyl esters of the transesterification of used cooking oil using CaO/MCM-41 catalyst

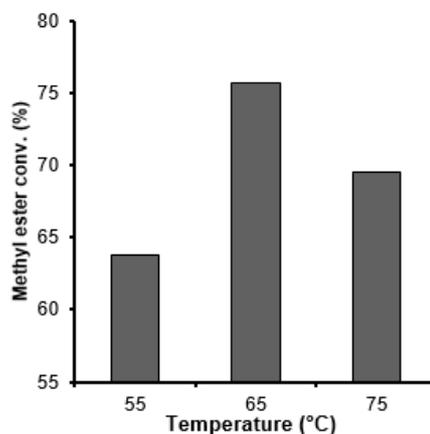


Fig 7. Methyl ester conversion of transesterification of used cooking oil in a variation of temperature reaction

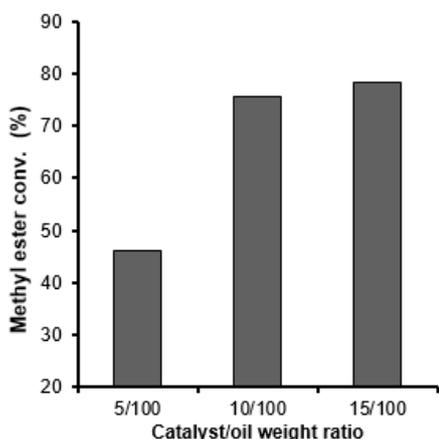


Fig 8. Methyl ester conversion of transesterification of used cooking oil in variation of catalyst/oil weight ratio

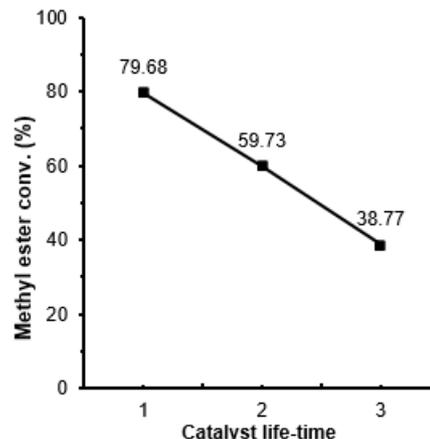


Fig 9. Methyl ester conversion of transesterification of used cooking oil for catalyst lifetime evaluation

showed the highest conversion of methyl ester used cooking oil was obtained with a catalyst/oil weight ratio of 15/100 with a yield of 78.17%. This result was due to the increase in the number of catalysts active sites that promote by the Ca^{2+} in the MCM-41. This provides more opportunities for the formation of methyl esters.

The catalyst lifetime evaluation of CaO(4)/MCM-41 catalyst was shown in Fig. 9. The evaluation was performed in 3 times runs of the transesterification using the same catalyst in 2 h of each run at a temperature of 65 °C for each reaction process. After 3 times of the transesterification processes, the yield of methyl ester was decreased. This indicated the activity of the catalyst was continuously decreased in the 3 times runs. This decrease was due to the blocking of the active sites of CaO(4)/MCM41 catalyst by glycerol as a by-product of the transesterification. The glycerol attached to the catalyst caused the active sites and some pore of the catalyst to be covered, allowing the catalyst's ability to convert the oil into methyl ester was decreased and

further to be deactivated. The linear regression equation calculated from Fig. 9 was $Y = -10.228X + 100.3$. When $Y = 0$, $X = 9.8$. The lifetime of CaO(4)/MCM-41 catalyst was 9.8h.

CONCLUSION

The MCM-41 material synthesized with silica source from Lapindo mud has a regular hexagonal structure and uniform pore shape with the specific surface area, pore volume and pore diameter of 1290.27 m^2/g , 0.84 cm^3/g , and 3.41 nm respectively. The CaO(4)/MCM-41 catalyst has a specific surface area, pore volume and pore diameter of 203.84 m^2/g , 0.34 cm^3/g , and 3.41 nm, respectively. The highest conversion of methyl ester product was 78.17% obtained by CaO(4)/MCM-41 catalyst at 65 °C and at catalyst/oil weight ratio of 15/100. The lifetime of CaO(4)/MCM-41 catalyst was 9.8 h.

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