



## Transesterification of Waste Cooking Oil Using $\text{NH}_2/\text{MCM-41}$ Base Catalyst: Effect of Methanol/Oil Mole Ratio and Catalyst/Oil Weight Ratio towards Conversion of Ester

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Transesterification of waste cooking oil (WCO) using  $\text{NH}_2/\text{MCM-41}$  base catalyst has been carried out. The MCM-41 was synthesized by hydrothermal method using the silica from Sidoarjo mud and cetyltrimethylammonium bromide (CTAB) as a template and calcined at 540 °C for 5 h. The MCM-41 was modified by adding (3-aminopropyl) trimethoxysilane using 5 mol percent of N/Si to produce  $\text{NH}_2/\text{MCM-41}$  base catalyst. Transesterification of waste cooking oil was carried out under variation of methanol/WCO mole ratio of 6, 9, 12, 15 and 18 using 10 wt. % of catalyst towards oil and weight ratio of catalyst/WCO of 2, 4, 6, 8, 10 wt. % using methanol/waste cooking oil mole ratio of 15. The result showed that the purity of silica from Sidoarjo mud was 93.40 wt. %. The highest product of methyl ester was 49.98 wt. % obtained using 4 wt. % of catalyst/WCO weight ratio in methanol/oil mole ratio of 15.

**Keywords:** Sidoarjo mud, Base catalyst, Transesterification, Waste cooking oil.

### INTRODUCTION

Diesel fuels are used in many areas and importance for the economic development in a country, however the diesel fuels source from fossil is limited. So, it is necessary to find another alternative fuel, such as biodiesel. Biodiesel is a biodegradable, renewable and environmentally friendly liquid biofuels that has proven itself commercially, with international standards all around the world [1,2]. Transesterification of vegetable oils constitutes an efficient method that provides a biodiesel. Transesterification of vegetable oils can be carried out using homogeneous or heterogeneous catalysts [3]. Biodiesel production costs are highly dependent on feedstock costs. So, to lower the costs of biodiesel production, used cooking oil can be used in synthesizing biodiesel because of its low cost and also it can be a way to solve the oil waste problem [4].

The most common method to carry out oil transesterification is by homogenous basic catalysis. Homogeneous catalyst presents several disadvantages such that they cannot be recovered at the end of the reaction and the presence of water in the reactants or a high acid index of the oil reduces the effectiveness of the process. Heterogeneous catalysis appears as an alternative to solve the problem of using homogenous catalyst. Heterogeneous catalysts are less corrosive, easier to handle and can be separated at the end of the reaction

by simple filtration and reused [5,6]. Zeolite is one of heterogeneous catalysts that can often be used in biodiesel production [7]. Now MCM-41 has become an interesting mesoporous material that can be used as heterogeneous catalyst.

Mobile composition of matter number 41 (MCM-41) is a mesoporous material that consists of uniformly and highly ordered network of silica that forms hexagonal shape [8,9]. The pore diameter of MCM-41 is 15–100 Å depending on the template, organic compounds addition and parameter of reaction [10]. The MCM-41 can be synthesized by hydrothermal method at 100–120 °C [11]. Due to its highly ordered pores and high surface area, MCM-41 can be used as catalyst and adsorbent [12]. The pure silicate substances, such as sodium silicate and tetraethylorthosilicate (TEOS) usually were used as a silica source in the MCM-41 synthesis [13]. Due to the high silica content in Sidoarjo mud (44.24 %), it can be used as a silica source in the MCM-41 synthesis.

Based on the above consideration, the authors have undertaken to synthesize MCM-41 material using silica from Sidoarjo mud and TEOS as a template. To improve MCM-41 activity as a catalyst, it was modified using 3-aminopropyl trimethoxysilane (3-APTMS) by grafting method to produce  $\text{NH}_2/\text{MCM-41}$  base catalyst [14,15]. This catalyst was then applied in transesterification of waste cooking oil (WCO) using methanol. The variables in transesterification of vegetable oils are type of alcohol, molar ratio, type and amount of catalyst and reaction

temperature [16,17]. In the present work, the catalyst/oil weight ratio and methanol/oil mole ratio were varied.

## EXPERIMENTAL

The materials used in this research were: Sidoarjo mud, hydrochloric acid (Merck), sodium hydroxide (NaOH, Merck), cetyltrimethyl ammonium bromide (CTAB, Merck), 3-aminopropyltrimethoxysilane (3-APTMS, Sigma-Aldrich), methanol, toluene and used cooking oil.

The equipment used in this research were chemical laboratory glassware, X-ray fluorescence (XRF, MiniPal 4 PANalytical), X-ray diffractometer (XRD, Shimadzu XRD-6000), fourier transform-infrared (FT-IR, Shimadzu Prestige-21), transmission electron microscopy (TEM, Pixel Sprometer-X 39173) and gas chromatography-mass spectroscopy (GC-MS, Shimadzu QP2010S).

**Extraction of silica from Sidoarjo mud:** Extraction of silica from Sidoarjo mud was carried out by batch method. The dried Sidoarjo mud was sieved to 100 mesh. The mud was washed with water for 24 h and dried. The mud was refluxed with HCl (6 M) solution at 90 °C for 3 h, then washed with water up to pH 7 followed by refluxed with 6 M solution of NaOH at 90 °C for 16 h. The filtrate was separated, then HCl 3 M solution was dropped to the filtrate until pH 8. The formed precipitate was filtered, washed with distilled water and dried at 80 °C for 24 h. The dry precipitate was an extracted silica and analyzed by XRF.

**Synthesis of MCM-41:** The MCM-41 was synthesized by hydrothermal method. The CTAB (2.3 g) was dissolved into 47 mL of distilled water at 40 °C. The sodium silicate solution was prepared by dissolving 4.2 g of silica into 140 mL of 1.5 M NaOH solution. The sodium silicate solution was added dropwise to the CTAB solution under vigorous stirring. After 1 h, the pH was adjusted to 11 by adding dropwise 3 M HCl solution and the mixture was stirred for 4 h in a static condition. The formed silica-surfactant gel was hydrothermally treated at 100 °C in a Teflon-lined stainless steel autoclave for 24 h. After cooling down to room temperature, the formed solid product was washed with distilled water until neutral and then dried at 80 °C for 24 h. The CTAB was removed through calcination at 540 °C for 5 h with heating rate of 5 °C/min. Then the sample was analyzed by XRD, FTIR and TEM.

**Synthesis of NH<sub>2</sub>/MCM-41:** The NH<sub>2</sub>/MCM-41 was synthesized by grafting method. The calcined MCM-41 (0.5 g) was refluxed in 20 mL of toluene containing 5 mol % N/Si of 3-APTMS for 5 h. The powder of NH<sub>2</sub>/MCM-41 was collected by centrifuge, washed with toluene and methanol was then dried at 50 °C for 24 h. Then the sample was analyzed by FTIR.

**Transesterification of waste cooking oil (WCO):** Transesterification of the WCO was carried out by refluxing in various methanol/oil mole ratio of 6:1, 9:1, 12:1, 15:1 and 18:1 with 10 wt. % of the NH<sub>2</sub>/MCM-41 base catalyst towards oil at 65 °C for 2 h, then the reactor was cooled to room temperature and the catalyst was separated from the product mixture using centrifuge. The biodiesel product was added with *n*-hexane and washed with warm distilled water. Then *n*-hexane was evaporated to get the product. The product was analyzed by GC-MS. Using the same method, the transesterification of WCO

was carried out by refluxing the WCO and methanol under 1:15 molar ratio using NH<sub>2</sub>/MCM-41 catalyst in the weight ratio of the catalyst towards the WCO of 2, 4, 6, 8 and 10 wt. %.

## RESULTS AND DISCUSSION

**Extraction of silica from Sidoarjo mud:** The concentration of SiO<sub>2</sub> in Sidoarjo mud after washing with water is 21.00 %. After refluxed with 6 M HCl and 6 M NaOH solution, the SiO<sub>2</sub> purity increased to 93.40 %. It proved that Sidoarjo mud has high SiO<sub>2</sub> content so that it can be used in synthesis of material based on silica.

**X-ray diffractogram:** Fig. 1 showed the XRD patterns of synthesized MCM-41. It was seen that the MCM-41 diffractogram exhibits two peaks at  $2\theta = 1.77-2^\circ$  which can be indexed as 100 and 110 and  $\pm 57 \text{ \AA}$  of lattice parameter ( $a_0$ , calculated by formula of  $a_0 = 2d_{100}/\sqrt{3}$ ). According to the previous research, the main peak at  $2\theta = 2-3^\circ$  assigned the ordered hexagonal structure of MCM-41, while the other weak peaks at  $2\theta = 4-7^\circ$  assigned the highly ordered structure of MCM-41 [9,18].

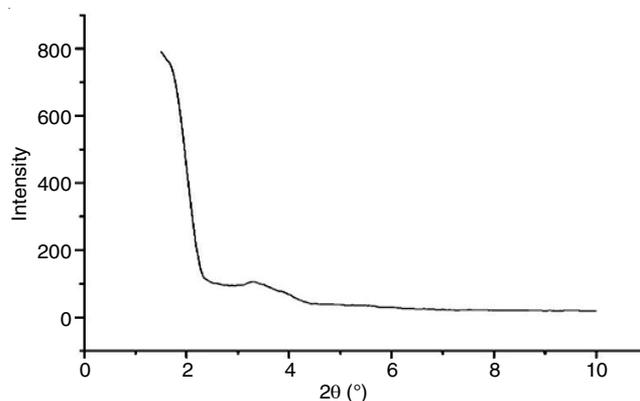


Fig. 1. Diffractogram of synthesized MCM-41

**FTIR:** Fig. 2 showed the FTIR spectra of calcined MCM-41 and NH<sub>2</sub>/MCM-41 at 4000-400 cm<sup>-1</sup> of wave number region. The characteristic of aminopropyl group showed by the band of stretching vibration of -CH<sub>2</sub>- at 2990 and 2890 cm<sup>-1</sup>, vibration of C-N at 1000-1200 cm<sup>-1</sup> and scissoring vibration of NH<sub>2</sub> at 1100-1630 cm<sup>-1</sup> [19,20]. Those bands in Fig. 2 indicate that 3-APTMS was successfully grafted into MCM-41 and produced NH<sub>2</sub>/MCM-41.

**TEM:** High-resolution transmission electron microscopy (TEM) in Fig. 3 characterized the structure of synthesized MCM-41 consists of amorphous silicate that has uniformly highly ordered mesoporous structure in hexagonal shaped [12,21].

**Gas sorption analyzer:** Figs. 4 and 5 showed that the synthesized MCM-41 and NH<sub>2</sub>/MCM-41 were included in isotherm type IV. The hysteresis loop in P/P<sub>0</sub> 0.2-0.4 showed mesopores structures [22]. The surface area, pore diameter and pore volume of MCM-41 are 830.823 m<sup>2</sup>/g, 3.19 nm and 0.248 cc/g, respectively. The surface area, pore diameter and pore volume of NH<sub>2</sub>/MCM-41 are 379.578 m<sup>2</sup>/g, 2.49 nm and 0.123 cc/g, respectively. The surface area, pore diameter and pore volume decreased due to the attachment of amino-silane on the inner and outer surface of MCM-41 pores. This phenomenon indicated that the grafting of 3-APTMS onto the MCM-41 material was successful.

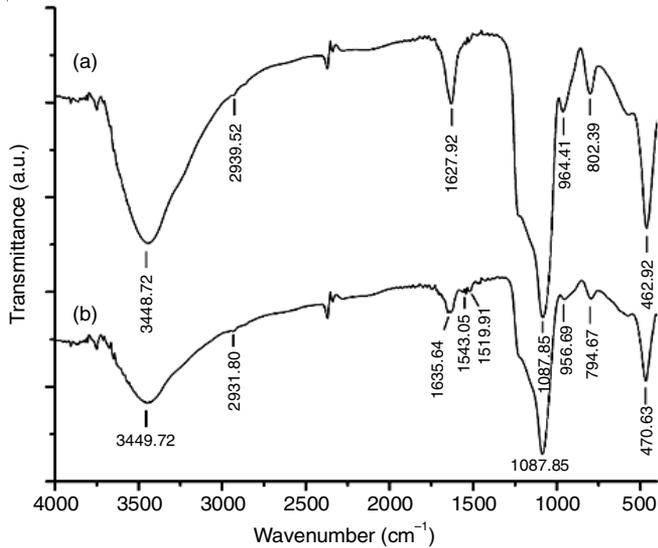
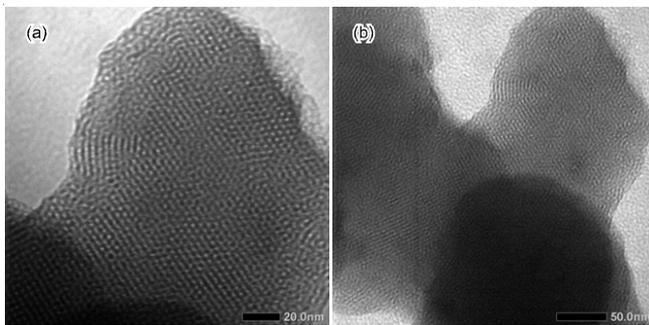
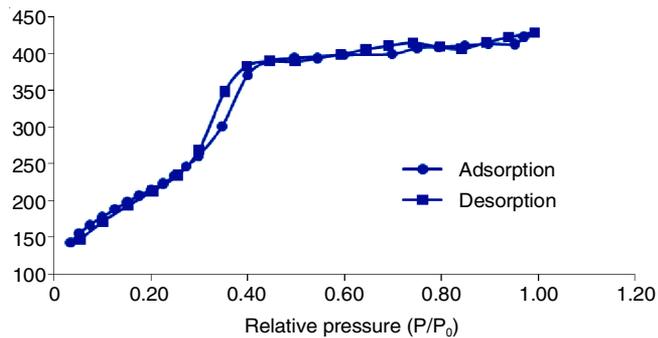
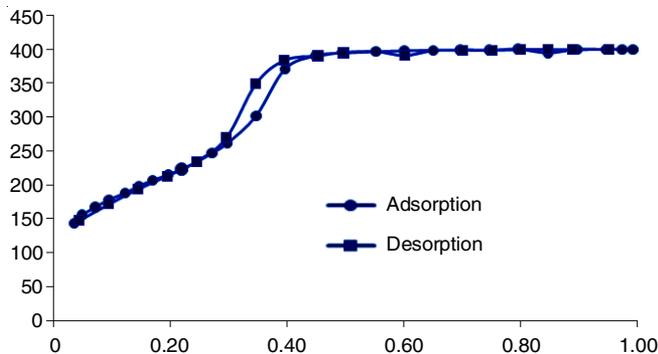
Fig. 2. FTIR spectra of (a) calcined MCM-41 and (b)  $\text{NH}_2/\text{MCM-41}$ 

Fig. 3. TEM micrograph of the MCM-41 sample, (a) 20 nm, (b) 50 nm

Fig. 4.  $\text{N}_2$  adsorption-desorption isotherm of MCM-41Fig. 5.  $\text{N}_2$  adsorption-desorption isotherm of calcined  $\text{NH}_2/\text{MCM-41}$ 

Figs. 6 and 7 showed pore diameter distribution based on the analysis of  $\text{N}_2$  desorption. Pore diameter distributions of the MCM-41 and  $\text{NH}_2/\text{MCM-41}$  were dominantly in the narrow range of 3–4 nm. It was pursuant to the pore diameter distribution of MCM-41 synthesized in the previous study [14,20]. This result indicated that the synthesized MCM-41 and  $\text{NH}_2/\text{MCM-41}$  have the homogeneous pore diameter.

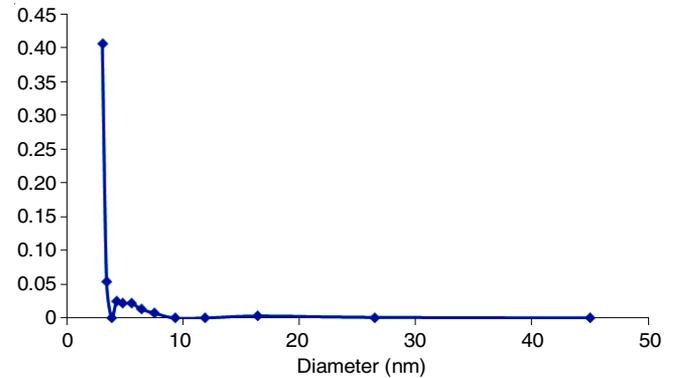
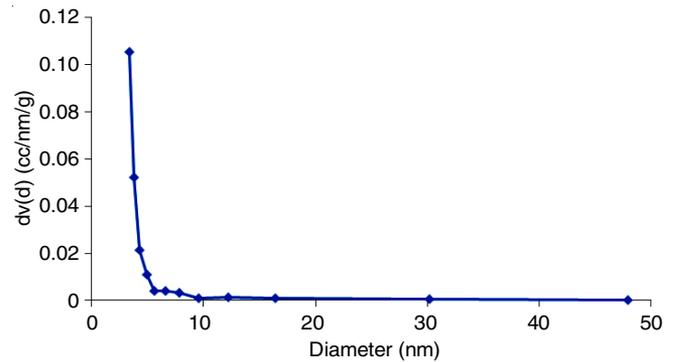


Fig. 6. Pore diameter distribution of synthesized MCM-41

Fig. 7. Pore diameter distribution of  $\text{NH}_2/\text{MCM-41}$ 

**Transesterification of waste cooking oil:** The free fatty acid content in the waste cooking oil is about 0.40 %. If free fatty acid content is above 0.50 %, preesterification is needed [23,24]. The free fatty acid composition in this waste cooking oil is under 0.50 %, thus pre-esterification treatment was not carried out in this research.

**Effect of methanol/oil mole ratio:** Mole ratio of methanol to oil is one of the most significant factors affecting the conversion efficiency. Since the mole ratio of methanol to oil for transesterification is 3:1 and the reaction is reversible, higher mole ratio is required to increase miscibility and to enhance the contact between the methanol molecule and the triglyceride. To shift the reaction towards completion, the mole ratio should be higher than that of the stoichiometric ratio. Further to break the glycerin-fatty acid linkages during transesterification of triglycerides to biodiesel, excess methanol is required [25]. Therefore, higher methanol to oil mole ratio gives rise to greater methyl ester conversion in a shorter time. Experiments were performed using various mole ratio methanol/oil (6:1, 9:1, 12:1, 15:1 and 18:1).

Fig. 8 showed the methyl ester conversion of the WCO in various methanol/oil mole ratio. However, according to Fig. 8, excess methanol was only effective to a certain extent

only in increasing the conversion of methyl ester. The conversion of methyl ester using mole ratio of methanol/oil 6:1, 9:1, 12:1, 15:1 and 18:1 are 40.78; 40.98; 42.47; 41.53; and 32.86 %, respectively. The methanol/oil mole ratio of 12:1 resulted in the highest ester conversion, then a decrease in methyl ester conversion was observed after the ratio of 12:1. This phenomenon was thought to occur because there are several possibilities. The first possibility is because large amounts of methanol will dilute oil and reduce reaction rate. The second possibility is because of excess methanol at the ratio may decrease the concentration of catalyst in the solution. The reduced concentration of catalyst in the solution can reduce the amount of methoxide that attacks the triglyceride, so that the amount of methyl ester conversion decreased [26]. The third possibility is a decrease in percent conversion of methyl ester which can be due to catalyst deactivation. The catalyst deactivation was caused by the molecular absorption of water by the catalyst and the resulting pores of the catalyst are covered by the water molecules. A decrease in methyl ester conversion also indicates a decrease in the quality of fatty acid methyl ester (FAME) and allows the reaction to occur at low temperature [27].

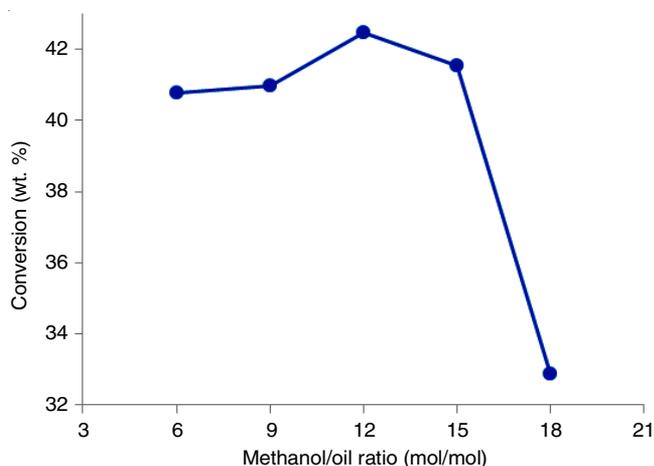


Fig. 8. Methyl ester conversion of waste cooking oil transesterification

The methyl ester products have been shown in Table-1. The main components of ester products were methyl palmitate, methyl linoleate, methyl oleate and methyl stearate. Based on Table-1, it shown that methyl oleate was the main ester for methanol/oil ratio mole of 16:1, 12:1 and 18:1 and then methyl palmitate was the main composition for methanol/oil ratio mole of 9:1 and 15:1. This result was obtained because the main contents in palm oil are palmitic acid and oleic acid.

**Effect of catalyst/oil weight ratio:** Transesterification of the WCO in various of catalyst/oil weight ratio (2, 4, 6, 8 and 10 wt. %) has also been done to find out the effect of catalyst/oil weight ratio towards the conversion of methyl ester. The products of transesterification were analyzed by GC-MS. The methyl ester products have been shown in Table-2. The main components of ester product were methyl palmitate, methyl linoleate, methyl oleate and methyl stearate.

Fig. 8 showed the methyl ester conversion of waste cooking oil in variation of the  $\text{NH}_2/\text{MCM-41}/\text{oil}$  weight ratio towards ester conversion. According to Fig. 5, the utilization

Product	Content of ester products of various ratio methanol/oil (%)				
	6:1	9:1	12:1	15:1	18:1
Methyl palmitate (C16:0)	17.09	15.66	22.20	13.87	20.26
Methyl linoleate (C18:2)	6.48	4.84	7.47	4.06	18.28
Methyl oleate (C18:1)	18.17	15.62	24.09	13.69	27.39
Methyl stearate (C18:0)	2.82	2.09	2.96	1.78	5.81

Product	Content of ester products (%)				
	Catalyst/oil weight ratio				
	2 %	4 %	6 %	8 %	10 %
Methyl palmitate (C16:0)	4.42	12.79	4.03	4.68	4.73
Methyl linoleate (C18:2)	2.70	4.55	1.93	2.23	2.11
Methyl oleate (C18:1)	5.42	21.08	4.64	5.11	4.93
Methyl stearate (C18:0)	0.94	3.76	0.61	0.79	0.80

of 2 %  $\text{NH}_2/\text{MCM-41}$  catalyst yields 40.15 % of ester conversion. The utilization of 4 %  $\text{NH}_2/\text{MCM-41}$  catalyst yields 49.98 % of ester conversion which is the highest conversion. The conversion decreases when using 6, 8 and 10 % of  $\text{NH}_2/\text{MCM-41}$  catalyst of 41.42, 39.94 and 39.25 %, respectively. The increased amount of catalyst makes more active site that will give more chance for methyl ester formation. This might be caused by the excessive amount of catalyst which supported the saponification reaction. In saponification, the reaction can take the formed methyl ester and the methyl ester might get trapped in the formed emulsion [28]. If the amount of catalyst used in transesterification reaction is less than 1 % of oil weight, maximum production yield could not be reached. On the other hand, if the amount of catalyst is more than 10 % of oil weight, the mixture of catalyst and reactant become too viscous, so maximum production yield could not be reached too [29,30]. The reduction of production yield also can be caused by the presence of impurities in the waste cooking oil that can use part of the catalyst in other parallel or competitive reactions, such as free fatty acid neutralization or even, to the presence of oxidative reactions and hydrolytic reactions [5]. The higher amount of catalyst makes excess catalyst in the reaction, so it could not enhance the conversion of methyl ester but led to a reduction in the product yield [31].

Fig. 8 gives the information of the products of methyl ester influenced by methanol/WCO mole ratio and catalyst/WCO weight ratio. The higher the methanol/WCO mole ratio, the less catalyst is needed to produce the methyl ester.

## Conclusion

Synthesis of MCM-41 using silica from Sidoarjo mud produces the MCM-41 material that has ordered pores in hexagonal shape. The highest product of methyl ester was 49.98 % produced by using 4 wt. % of  $\text{NH}_2/\text{MCM-41}/\text{waste cooking oil}$  weight ratio in methanol/waste cooking oil mole ratio of 15.

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