THE USE OF MCM-48-nCaO AS CATALYST IN ESTERIFICATION REACTION OF NYAMPLUNG SEED OIL *(Calophyllum inophyllum L.)*

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Abstrak. Penelitian penggunaan MCM-48-nCaO sebagai katalis pada reaksi esterifikasi minyak biji nyamplung (*Calophyllum inophyllum* L.) telah dilakukan. Hasil karakterisasi XRF, XRD, dan FTIR menunjukkan keberhasilan dalam proses sintesis katalis heterogen MCM-48-nCaO dengan menggunakan metode *grinding*-impregnasi. Melalui reaksi esterifikasi menggunakan katalis ini kadar FFA yang terkandung di dalam minyak biji nyamplung berkurang dari 28% menjadi 1,7%.

Kata Kunci : minyak biji nyamplung, MCM-48-nCaO, esterifikasi.

Abstract. A study on the use of MCM-48-nCaO as a catalyst in the esterification reaction of nyamplung seed oil (*Calophyllum inophyllum* L.) has been carried out. The characterization results of XRF, XRD and FTIR showed the success in the synthesis of heterogeneous catalysts, MCM-48-nCaO, using a grinding-impregnation method. Through esterification reaction using the catalysts, FFA content in the seed oil of nyamplung reduced from 28 to 1.7%.

Keywords: nyamplung seed oil, MCM-48-nCaO, esterification.

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I. Introduction

Excessive and prolonged exploitation of crude oil causes the continuous decrease of oil resources [1]. Therefore, researches on seeking, optimizing and using alternative energy resources become a very important matter. One alternative renewable energy resource is biodiesel [2] Biodiesel can be obtained from foodstuffs. However, the use of the sources will compete with human food needs. As a consequence, non-foodstuffs sources, such as *nyamplung* seeds are required.

One of the factors that influence the acquisition of biodiesel is the content of free fatty acids or free fatty acid (FFA) present in vegetable oils; the lower the levels of FFA, the higher the biodiesel that can be obtained [3]. *Nyamplung* seed oil contains high levels of FFA, around 22 % [2]. Efforts to reduce the FFA content of vegetable oils can be done through esterification reaction by using a strong acid catalyst [1]. FFA levels of *nyamplung* seed oil was lowered through esterification reactions using homogeneous catalysts, such as, H_2SO_4 and HCl [3.4]. Although this method gives good results, the use of homogeneous catalysts in the esterification reaction has several weaknesses, e.g. it is difficult to separate the catalysts from the product, they can create pollution to the environment, and the method is not economical [5.6]. In order to solve the problem, heterogeneous catalysts are utilized. Enggawati and Ediati [2] reported the use of CaO supported in fly ash as a catalyst in producing biodiesel from *nyamplung* seed oil. However, the rendamen of biodiesel was just about 48.75%. Lee *et al*. [7] reported that the use of Al-MCM-41 in the esterification reaction can lower FFA levels of *nyamplung* seed oil from 21.4 to 0.7%. MCM-48 is a heterogeneous catalyst that is more effective in reducing the concentration of FFA vegetable oil compared to MCM-41[8]. It seems that the use of heterogeneous catalysts of MCM-48 in the esterification reaction gives a better expectation.

Based on the above reason, an effort was undertaken in this research to reduce the level of FFA in *nyamplung* seed oil through esterification reaction using heterogeneous catalysts of CaO supported in MCM-48 (MCM-48-nCaO). The selection of MCM-48 as catalyst supports of heterogeneous CaO in this study was based on a three dimensional channel of MCM-48 that allows the proper diffusion of the reactants to form the product and reduces blocking pore [9].

II. Methods

a. Instrument and materials

1. Instruments

The Instruments used in this study were a set of Soxhlet extraction apparatus (Pyrex), Buchner funnel, oven (Gen Lab), hot plate (Cimarec), bottles of polypropylene, furnace (6000-Barnstead Thermolyse), vacuum pump (Sargent-Welch Co. model 1400), analytical balance (Mettler Toledo), rotary evaporator (Heizbad Hei-VAP), FTIR (Shimadzu 8300), XRD (Philips Expert), XRF (PANalytical, MiniPal 4), and some glassware (pyrex) that commonly used in laboratories.

2. Materials

The materials used in this study were the seed of *nyamplung* taken from Kalauli Village, Leihitu District of Maluku province, *n*-hexane pa (E. Merck), $Ca(CH_3COO)\ 2.H_2O$ p.a. (E. Merck), NaOH p.a. (E. Merck), Na_2SO_4 anhydrous p.a. (E. Merck), Ludox HS40 ($\geq 14.5 \leq 50$ % w/w SiO2, $\geq 0.05 \leq 0.6$ % w/w NaOH, $\geq 50 \leq 86$ % w/w H2O and a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one with 2-methyl-2H-isotiazol-3-one (3: 1) is < 0.003 %) were obtained from Sigma Aldrich, cetyltrimethyl ammonium bromide (CTAB) were obtained from Sigma Aldrich, Triton X-I00 (Sigma Aldrich), CH_3COOH p.a. (E. Merck), HCl p.a. (E. Merck), isopropanol p.a. (E. Merck), indicator PP p.a. (E. Merck), methanol p.a. (E. Merck), ethanol p.a. (E. Merck), and H_3PO_4 p.a. (E. Merck).

b. Procedure

1. Isolation Nyamplung Seed Oil

Isolation of *nyamplung* seed oil were conducted according to the procedure of Pamata [10] and Rokua [11]. Dry powder of *nyamplung* seed as many as 133.3 g was wrapped in a filter paper and at the seed was covered with cotton. The wrapped sample was placed in a Soxhlet extraction apparatus. Furthermore, *n*-hexane as many as 60 % of the volume of the extraction flask was put in the flask. The sample was extracted at a temperature of 70 °C until the liquid came out from the Soxhlet turning clear or colorless. The extract obtained was then poured into the Erlenmeyer, added with anhydrous Na_2SO_4. The Erlenmeyer was covered with a filter paper and stored for 12 hours. Subsequently, the mixture was filtered and the solvent was evaporated using a rotary evaporator.

2. Degumming

A degumming process of *nyamplung* seed oil was conducted using the procedure of Mustafa and Purwanti [7], and Enggawati and Ediati [2]. *Nyamplung* oil was heated at a temperature of 65 °C, 5 % (v/v) of 85% phosphoric acid was then added into the oil, and stirred for 1 hour. Subsequently, the mixture was allowed to stand for 12 hours, and decanted. Oil obtained from the degumming was then washed with hot water (60-80 °C) until the pH of the waste water from the washing process was neutral. The neutral oil was then dried with anhydrous Na_2SO_4 and allowed to stand for 12 hours at room temperature. Furthermore, the mixture was filtered with a paper filter through a Buchner funnel.

3. Synthesis of MCM-48

Synthesis of MCM-48 was conducted following the procedure of Taba [12]. Ludox HS40 solution as many as 14.3 g was mixed with 45.25 g of 1 M of aqueous NaOH solution. The surfactant mixture was prepared by dissolving 6.12 g of CTAB and 1.34 g of Triton X-100 simultaneously in 83.47 g of distilled water with heating. After cooling the sodium tetrasilicate solution and the surfactant solution to room temperature, both solutions were mixed quickly in a large polypropylene bottle. The bottle was immediately capped and shaken vigorously. The gel mixture obtained was heated under static condition at 373 K for 24 h. At this stage, the surfactant-silica mesophases were formed. To avoid separation of the mesophases at an early stage of heating, the bottle containing the mixture was sometimes agitated. The reaction mixture was then cooled to room temperature and acetic acid (30 wt %) was added subsequently into the mixture in order to adjust the pH to 10. After the pH adjustment, the mixture was heated again at 100^{o}C for 24 h and cooled to room temperature. As-synthesized MCM-48 was then filtered, washed with doubly distilled water and dried at 393 K in an oven. The surfactant was removed from the white product by washing with HCl-ethanol mixture until the surfactant left as small as possible

4. Synthesis of MCM-48-nCaO

Synthesis of MCM-48-nCaO was conducted according to the procedure of Albuquerque [13], Pouretedal and Ahmadi [14], and Pouretedal and Saedi [15]. A total number of n % w/w CaO (n = 14 and 20) to MCM-48 was hardly grounded in a mortar at room temperature. The catalyst was then dried in an oven at 100°C for 4 hours and calcined at 850°C with a heating rate of 2°C/min for 6 hours. After the calcination process being completed, the resulting catalyst was stored in a desiccator to maintain the catalyst remains dry. The catalyst obtained was then characterized by FTIR, XRD, and XRF.

5. Determination of Levels of FFA

The FFA content in the seed oil was determined according to the procedure of Enggawati and Ediati [2]. The *nyamplung* seed oil as many as 2 g was dissolved in 25 mL of hot isopropanol that had been previously neutralized with NaOH. Then, 2 drops of the PP indicator were added to the solution and the solution was titrated with NaOH until the purplish color in solution was not disappeared up to 10 seconds. The FFA content was then calculated using the following equation.

$$\%\mathrm{FFA} = \frac{\mathrm{V_{NaOH}\ \ x\ N_{NaOH}\ \ x\ MW}}{\mathrm{Oil\ sample\ mass}}\ \mathrm{x}\ 100\%$$

6. *Esterification*

Esterification of *nyamplung* seed oil was performed according to the procedure of Albuquerque *et. al*. [16], Kartika and Widyaningsih [17], and Enggawati and Ediati [2]. *Nyamplung* oil esterification was conducted in a 500 mL three neck flask equipped with an electric heater, a thermometer, a magnetic stirrer, and a cooling system. The reaction temperature was maintained at 60 °C with a stirring rate of 1200 rpm, the catalyst molar ratio to methanol of 2% (w/w), the oil molar ratio to methanol of 1: 9 and a reaction time of 60 minutes. The reaction was stopped by immersing the three neck flask in an ice bath. Furthermore, the mixture was filtered through a Buchner funnel using a filter paper. The percentage of FFA in the results obtained was then calculated. The esterification reaction was done to obtain the oil of *nyamplung* seed with the FFA content of < 2 %.

III. Results and Discussion

1. Isolation Nyamplung Seed Oil

Isolation of nyamplung oil using n-hexane in a Soxhletation process produced an extract of 67.79 % (90.37 g) from 133.3 g of the fine powder of *nyamplung* seed. The result obtained was in the form of a clear yellow liquid with a specific smell of *nyamplung* seed oil.

2. Degumming

The degumming process using H_3PO_4 produced 9.32 g latex and 80.07 g of pure *nyamplung* oil. The *Nyamplung* pure oil was obtained in the form of brownish yellow liquid with a specific smell of *nyamplung* seed oil.

3. Characterization of MCM-48 and Catalysts Heterogeneous MCM-48-nCaO

The success of the synthesis of MCM-48 can be seen from the results of characterization using XRD. X-ray diffraction pattern of MCM-48 is shown in Figure 1. X-ray diffraction pattern of MCM-48 showed peaks at 2.4° 2 theta and several peaks with low intensity.

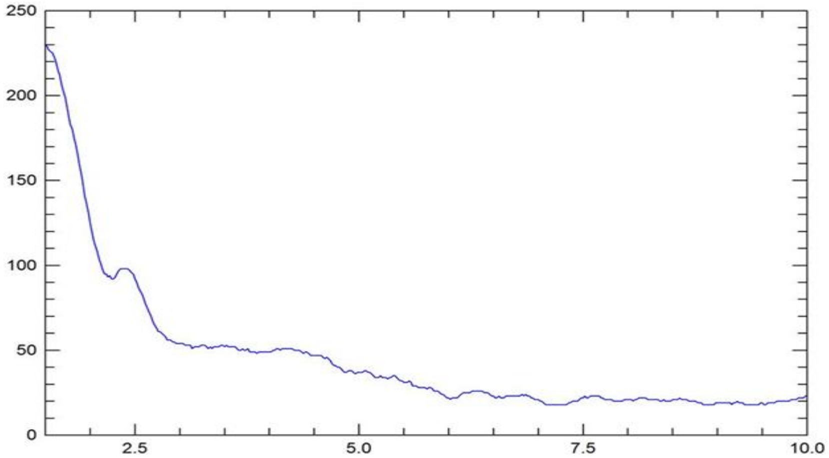

Figure 1. XRD pattern of as-synthesized MCM-48

The X-ray diffraction pattern of MCM-48 showed a strong peak at 2 theta of 2.54^o and seven other peaks with low intensity [18]. In this study, peaks appear at the diffractogram has an intensity that is much lower than that obtained in previous studies and some of the peaks are not clearly visible. This happens because in this study, the measurement was conducted at 2 theta of 1.5 to 10^o whereas in the previous studies, the measurement was performed at 2 theta of 0.8 to 10^o.

Before MCM-48 was used as catalyst supports for heterogeneous CaO, surfactant present should be removed by washing using HCl-ethanol (0.1 M HCl in 50 % ethanol). The success of the washing process was monitored by using FTIR. FTIR spectra of MCM-48 before and after washing are presented in Figures 2a and 2b, respectively.

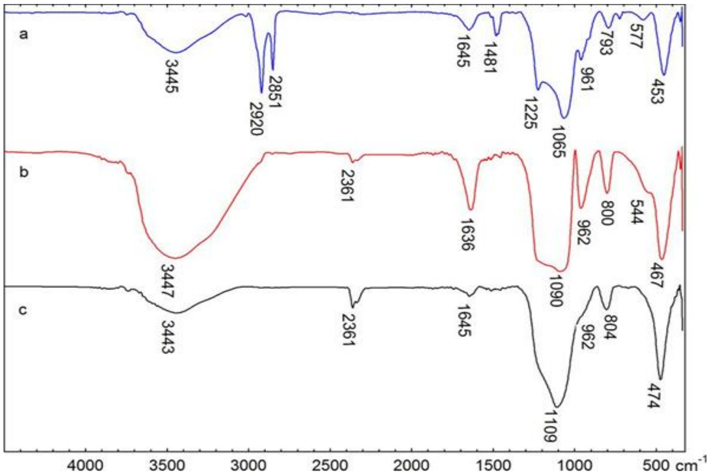

Figure 2. FTIR spectra of a) MCM-48 before washing, b) MCM-48 after washing, and c) MCM-48-20CaO

Two specific areas for organic molecules derived from the surfactant (cetyltrimethyl ammonium bromide) was observed in the spectrum of MCM-48 before washing (Figure 2a); CH stretching (between 2800 cm^{-1} and 3010 cm^{-1}) and CH bending, (between 1300 cm^{-1} and 1500 cm^{-1}). A broad peak at 3445 cm^{-1} and a peak at 1645 cm^{-1} are also observed. These peaks are the contribution of silanol and water physically adsorbed by MCM-48. A strong peak at 1225 cm^{-1} and 1065 cm^{-1} and weak peaks at 961 cm^{-1} and 793 cm^{-1} can be assigned to the Si-O stretching vibration of the silicate lattice. After washing with HCI-ethanol 3 times (Figure 2b) peaks, the peaks of C-H stretching and bending almost disappear. This indicates that most of the surfactant has been lost. This is supported by the shift of peaks at 1225 cm^{-1} and 1065 cm^{-1} to larger wave numbers. The peak shift occurs due to lattice contraction during template (surfactant) removal as has been reported in previous studies [12.14.15].

Figure 2c is a FTIR spectrum of MCM-48-20CaO. There is a decline in the intensity of the peaks at wavenumbers of 962 cm^{-1}, 3447 cm^{-1}, and 1636 cm^{-1}. It is caused by the reaction of CaO with silanol groups on the MCM-48 [19.20]. The decrease in the intensity occurred due to a change of Si-O-H into Si-O-Ca bonds [21.22]. At a high temperature, CaO can react with Si-OH of MCM-48 to form $CaSiO_3$ or $CaSiO_4$ [23]. The assumption is also supported by the shift of a peak at a wavenumber of 1090 cm^{-1} (Figure 2b) to that of 1109 cm^{-1} (Figure 2c). The peaks belong to the asymmetrical stretching vibration of Si-O and Si-O-Si, respectively.

Synthesis of MCM-48-nCaO was conducted by using a grinding-impregnation method. CaO source was obtained from a precursor of $Ca(CH_3COO)$ $2.H_2O$. The characterization results of the heterogeneous catalysts using XRF are presented in Table 1. The results show that only half of the amount of $Ca(CH_3COO)$ $2.H_2O$ entering into MCM-48. This is due to the conversion of $Ca(CH_3COO)$ $2.H_2O$ into CaO after calcination at a temperature of 850 °C for 6 hours. The success of the synthesis of MCM-48-nCaO was also supported by the results of characterization using FTIR method (Figure 2c).

Table 1. Characterization results of MCM-48-nCaO materials using XRF

No.	**Catalyst**	**Ratio (%-w/w)**		**XRF (%-w/w)**	
		MCM-48	**$Ca(CH_3COO)_2.H_2O$**	**SiO_2**	**CaO**
1.	MCM-48-14CaO	86	14	92.69	7.25
2.	MCM-48-20CaO	80	20	89.54	10.19

1. *FFA Content of Nyamplung Seed Oil*

The FFA content in *nyamplung* seed oil before and after esterification reaction (twice) is presented in Table 2.

Table 2. FFA content of *nyamplung* seed oil before and after esterification process

No.	**Reaction**	**Catalysts**	**FFA (%)**	**Rendamen (%)**
1.	Before esterification	-	28	-
2.	First esterification	MCM-48-20CaO	9	95.12
3.	Second esterification	MCM-48-14CaO	1.7	87.59

The first esterification process lowers the FFA of *nyamplung* seed oil from 28 to 9 % whereas the second process lower it from 9 to 1.7 %. The esterification results show that the heterogeneous catalysts of MCM-48-14CaO and MCM-48-20CaO have the ability to reduce the FFA content. This is caused by presence of silanol groups in MCM-48. The silanol groups can interact with C=O groups of FFA via the hydrogen bond [24] as can be seen in Figure 3.

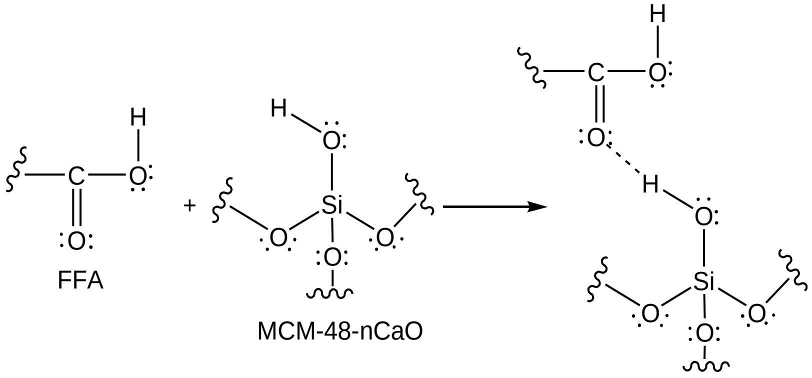

Figure 3. Interaction of silanol groups in with FFA

In addition, the presence of Ca also affects the activity of heterogeneous catalysts MCM-48-nCaO in lowering levels of FFA in *nyamplung* seed oil. This is caused by the increase of the Lewis acid of MCM-48 after the presence of Ca in the framework [25.26].

IV. Conclusion

Heterogeneous catalysts of MCM-48-nCaO was able to lower FFA levels contained in the oil of nyamplung seed from 28 to 9 % and from 9 to 1.7 % after the first and second esterification processes, respectively.

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