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Research Paper

Optimization of the MCM-48 Synthesis Method as a Catalyst in the Esterification of Nyamplung Seed Oil into Biodiesel

La Kolo[1], **La Yusran La Kalamu**[1], **Nunuk Hariani Soekamto**[2], **Paulina Taba**[2], **St. Fauziah**[2], **Maming**[2], **Muhammad Zakir**[2]

[1] Department of Chemistry Education, Universitas Bumi Hijrah, Tidore Kepulauan 97852, Indonesia
[2] Department of Chemistry, Universitas Hasanuddin, Makassar 90245, Indonesia

lakolo1966@gmail.com

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Abstract

This study was conducted to synthesize MCM-48 based on the surfactants (cetyltrimethylammonium bromide (CTAB) and Triton X-100). The effect of surfactant on MCM-48 was studied in the esterification of nyamplung seed oil. Optimization of the amount of surfactant in the MCM-48 catalyst in the esterification of nyamplung seed oil was carried out by washing and calcination methods. Comparison of GC-MS method and acid-base titration was also studied to determine the activity of the MCM-48 catalyst in the esterification. The results of the Mann Whitney statistical test showed that there was no significant difference (Asymp. Sig. (2-tailed) = 0.967) for the two methods. The effect of the active site on the MCM-48 catalyst activity in the esterification was characterized by FTIR and XRD. The catalyst's activity is significantly influenced by both the percentage transmittance of the silanol active site and the surfactant removal method. The MCM-48 catalyst manufactured by calcination (CTAB-MCM-48/650) performed 12.31% better than the washing approach (CTAB-MCM-48/1w). However, the CTAB-MCM-48 catalyst can be applied to the simultaneous reaction (esterification and transesterification) of the conversion of nyamplung seed oil into biodiesel.

Keywords: MCM-48; Surfactant; Esterification; Nyamplung; Biodiesel

1. Introduction

Energy and clean air are essential needs for human survival. The increasing world population causes the demand for energy and clean air to also increase. Fossil fuels are the world's main energy source [1]–[3] however, these fuel reserves are very limited, non-renewable, and unsustainable [4] along with are toxic to the environment [5]–[7]. Therefore, research to find alternative energy sources is needed. One of the renewable and non-toxic alternative energies to the environment is biodiesel from nyamplung seed oil [8]–[10]. Nyamplung seeds are a non-food source of biodiesel and contain 15% higher oil than Jatropha [11], [12], are easily regenerated [13], the seeds can be produced throughout the year [14], and have a fairly wide natural distribution in the world [15].

Generally, biodiesel production from vegetable oil is carried out through esterification [16], [17] and transesterification [18]–[22]. The production stage is strongly influenced by the levels of free fatty acids (FFA) contained in vegetable oils [23]. When using an alkaline catalyst, vegetable oils containing FFA levels greater than 5% [24] need to go through the esterification step before the transesterification stage [25], [26]. In contrast to the base catalyst, the acid catalyst does not need to go through this reaction step, but this catalyst requires a long time [27] and high temperature in the transesterification. This stage is one of the challenges in the production of biodiesel from nyamplung seed oil which contains 29.80% FFA [28]. The use of strong acid homogeneous catalysts (HCl and H_2SO_4) in the esterification is the method most widely used to reduce the FFA levels of these oils. Although this method gives quite good results, the use of a homogeneous catalyst in the esterification has several disadvantages namely, difficult to separate from the product, pollutes the environment [29], cannot be used repeatedly [30], and is not economical [9]. The best solution to overcome this problem is to leave conventional methods and move to modern methods.

One of the modern methods currently being developed is to use heterogeneous catalysts in the production of biodiesel from vegetable oil. The advantages of using this heterogeneous catalyst are easy to separate from the product [31], less waste [32], [33], and reusable [34]. Heterogeneous catalysts that have been used to derive FFA from nyamplung seed oil such as Al/Fe-graphite oxide [16] and CaO support Mobil Composition of Matter No. 48 (MCM-48-CaO) [35]. Al/Fe-graphite oxide catalyst was able to reduce the FFA of nyamplung seed oil from 20% to <2%. MCM-48-CaO catalyst needs two esterifications to reduce the FFA of nyamplung seed oil from 28% to 1.7%. The cost for the synthesis of Al/Fe-graphite oxide catalyst is quite expensive when compared to MCM-48-CaO catalyst. Besides, the MCM-48-CaO catalyst is also not very economical because the synthesis process is still going through the surfactant removal stage. Pirouzmand, et al. [36], proved that the presence of CTAB in the Ca/MCM-41 catalyst can increase the percent conversion of canola oil to biodiesel. It seems that the use of MCM-48 heterogeneous catalysts that still contain CTAB in the esterification gives better results. Apart from that, observations of surfactants in MCM-48 using the calcination method have also been applied to the esterification of nyamplung seed oil. The catalyst calcined at a temperature of 650 °C gave a nyamplung seed oil biodiesel yield of 35.74% and behaved selectively in converting linoleic fatty acids into biodiesel up to 100% [17].

Mesoporous silica synthesized by the washing method will have more silanol groups than the calcination method [37]. The silanol groups in mesoporous silica play an important role in the esterification reaction of nyamplung seed oil [38]. Nyamplung seed oil contains 80% triglycerides and 20% FFA. The silanol group in MCM-48 mesoporous silica is the active site of the catalyst in the esterification reaction of nyamplung seed oil into biodiesel. Apart from that, the active site also functions to minimize the hydrolysis reaction of triglycerides and methyl esters into FFA in the process of converting nyamplung seed oil into biodiesel. Therefore, in this research, gradual observation of the surfactant in the MCM-48 washing method as a catalyst in this reaction will be carried out.

2. Method

2.1. *Materials*

Samples of nyamplung seeds were obtained from Kalauli Hamlet, Leihitu District, Central Maluku Regency, Maluku Province, Indonesia. Phenolphthalein, *n*-hexane, methanol, and H_3PO_4 were from Merck. The chemicals used to synthesize MCM-48 are, ethanol, NaOH, and CH_3COOH from Merck, while Ludox HS40, CTAB, and Triton X-I00 were from Sigma Aldrich. All chemicals were purchased in pro analysis (p.a) grades.

2.2. *Nyamplung Seed Oil*

Nyamplung seed oil was obtained through the Soxhlet method using *n*-hexane as a solvent [39]. The solvent is added as much as 60-70% v/v of the volume of the Soxhlet flask. The oil, produced after the separation from the solvent, is heated in an oven at a temperature of 105 °C for 60 minutes [40]. The oil is then degummed using H_3PO_4 until it becomes suitable for esterification [17], [41].

2.3. *Synthesis of the MCM-48*

The procedure for synthesizing the MCM-48 catalyst followed the report by Taba, et al. [42]. 14.3 g of Ludox HS40 was dissolved in 45.25 g of 1 M NaOH at a temperature of 80 °C for 2 hours. Dissolve 6.12 g CTAB and 1.34 g Triton X-100 in 83.47 g distilled water while heating. After both solutions had cooled, the two solutions were mixed and shaken in a polypropylene bottle. The mixture was heated and shaken occasionally at 100 °C for 24 hours. After cooling, the pH of the mixture was adjusted to 10 using CH_3COOH 30% (w/w). The mixture was heated again in the oven at 100 °C for 24 hours. The mixture was cooled and filtered, then the solid dried in an oven at 120 °C. The surfactant is washed from the solid using an HCl-ethanol mixture. No wash (CTAB-MCM-48), First wash (CTAB-MCM-48/1w), second (CTAB-

MCM-48/2w), third (CTAB-MCM-48/3w), and fourth (CTAB-MCM -48/4w). in addition, the solid was also calcined at 650 °C (CTAB-MCM-48/650) at a rate of 2 °C/min [17]. The presence of surfactant in the MCM-48 catalyst was identified using FTIR and XRD. XRD setting in the range 2θ 2.0-10.0 with 0.01 deg, 2.0 deg/min, Cu Kα, 40.0 kV, and 30.0 mA.

2.4. *Esterification of Nyamplung Seed Oil*

The esterification is carried out inside a 100 mL three-neck flask equipped with an electric heater, thermometer, magnetic stirrer, and cooling system. The reaction temperature is maintained at 62 °C with a stirring rate of 1200 rpm, 2% (w/w) catalyst against methanol, while the oil and methanol ratio is 1: 9 (w/w), and the reaction time is 60 minutes. The three-neck flask was put in an ice cooler to stop the reaction. Next, the mixture is filtered through the Buchner funnel using filter paper. FFA levels in the yield obtained were later identified using the GC-MS method and acid-base titration [17], [43].

3. Results and Discussion

3.1. *Degumming Nyamplung Seed Oil*

The degumming process is carried out to minimize phosphate compounds, carbohydrates, and proteins contained in seed oil [44], [45]. The compounds in the oil will increase the viscosity and density of the resulting biodiesel so that it needs to be purified. Nyamplung seed oil before and after degumming using H_3PO_4 (**Table 1**) shows changes in FFA color, volume, and level. This show that the impurities have been success minimized.

3.2. *Synthesis and Characterization Catalysts*

FTIR is used to describe surfactant-based MCM-48 catalysts. Based on FTIR data (**Figure 1**), it seems likely that the catalyst CTAB-MCM-48 has a surfactant role and has been success made. The peaks of surfactant identified on the CTA-MCM-48 spectrum before washing (**Figure 1a**); -CH stretching (2850 and 2922 cm^{-1}) and -CH bending (1479 cm^{-1}) of the $-CH_3$ cluster as reported in the study [46], [47]. The wide peak at 3453 cm^{-1} and the peak at 1639 cm^{-1} is the absorption of the silanol groups (-Si-OH stretching and bending). The strong (1225 and 1094 cm^{-1}) and weak (966 cm-1 and 802 cm^{-1}) peaks are asymmetric -Si-O-Si- and symmetric stretching vibrations of the silicate lattice [48], [49]. After washing once (**Figure 1b**), twice (**Figure 1c**), three times (**Figure 1d**), and four times (**Figure 1e**) with HCl-ethanol, peaks in the -CH stretching and -CH bending absorption areas continued to decrease the intensity. This indicates that the template (surfactant) removal process for the formation of MCM-48 mesoporous silica has been success carried out. This is support by a peak shift in the -Si-O-Si- stretching vibration region (**Table 2**) to a higher wavenumber. The same finding was previously reported [42]. Compared with the washing method, the calcination method (**Figure 1f**) gives the lowest intensity for both -CH vibrations and almost disappears. This shows that the calcination method is more effective in the surfactant removal process to form MCM-48 mesoporous silica.

The X-ray diffraction pattern of MCM-48 (**Figure 2**) shows two peaks in the 2θ 2-3° region and several peaks with low intensity in the 2θ 4-5° region (usually six peaks). The peaks shifted to a higher 2θ angle after removal of the surfactant from CTAB-MCM-48. There is in line with that reported by Seo, et al. [50] and Taba, et al. [51]. **Figure 2** also shows that the calcination method has an X-ray diffraction peak with higher intensity than the washing method and even disappears for the 2θ 4-5° peak. According to Qian, et al. [52], this phenomenon is an implication of the presence of surfactant covering the pore channels. The presence of this surfactant is supported by FTIR data which can be seen in **Figure 1**. In addition, the low peak intensity in the washing method is probably due to some of the silica having been corrosion by acids [37].

Table 1. Degumming results of seed oil

No.	Variable	Degumming	
		Before	**After**
1.	Volume (mL)	211	183
2.	Color	Turbid yellow	Clear yellow
3.	FFA (%)	23.87*	20.33*

*titration method

Table 2. Shifting of the catalyst active group vibrations after surfactant removal

Catalyst	Group	Vibration	λ (cm^{-1})	Transmittance (%)
CTAB-MCM-48	-Si-OH	S	3425.58	39.56
		B	1637.56	58.81
	-Si-O-Si-	S. Asymmetric	1062.78	24.24
CTAB-MCM-48/1w	-Si-OH	S	3435.22	30.29
		B	1641.42	53.70
	-Si-O-Si-	S. Asymmetric	1064.71	19.80
CTAB-MCM-48/2w	-Si-OH	S	3450.65	12.55
		B	1637.56	34.09
	-Si-O-Si-	S. Asymmetric	1091.71	1.79
CTAB-MCM-48/3w	-Si-OH	S	3452.58	12.89
		B	1637.56	29.98
	-Si-O-Si-	S. Asymmetric	1093.64	5.70
CTAB-MCM-48/4w	-Si-OH	S	3460.30	15.52
		B	1641.42	32.96
	-Si-O-Si-	S. Asymmetric	1093.64	11.15
CTAB-MCM-48/650	-Si-OH	S	3450.65	15.39
		B	1635.63	27.94
	-Si-O-Si-	S. Asymmetric	1082.06	12.30

λ. Wavenumber, S. Stretching, B. Bending

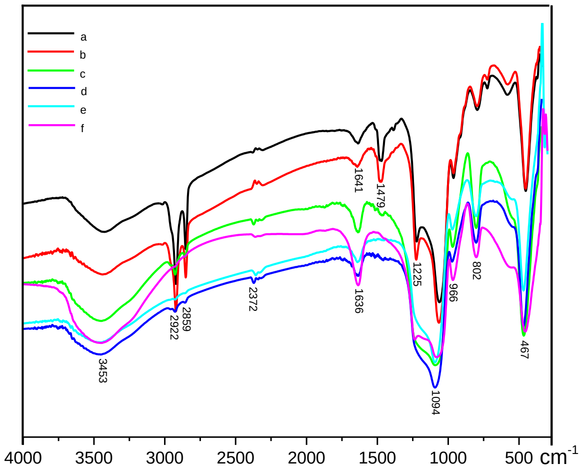

Figure 1. Catalyst FTIR spectrum; a) CTAB-MCM-48, b) CTA-MCM-48/1w, c) CTAB-MCM-48/3w, e) CTAB-MCM-48/4w, and f) CTAB-MCM-48/650

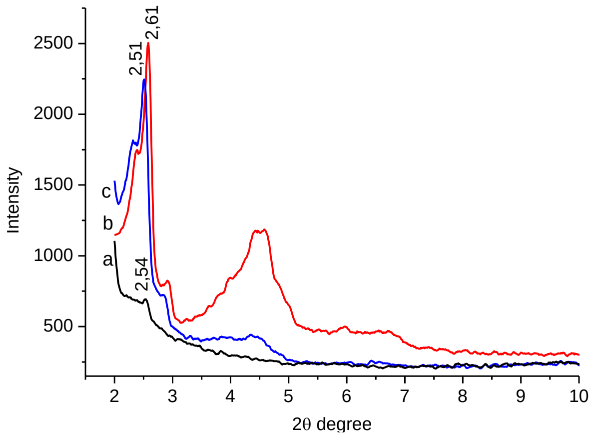

Figure 2. X-ray diffraction patterns; a), CTAB-MCM-48/4W, b) CTAB-MCM-48/650 and c) CTAB-MCM-48

3.3. *Esterification of Nyamplung Seed Oil*

The activity of MCM-48 catalyst as a function of surfactant in the esterification of nyamplung seed oil was identify by determining the methyl esters (ME) level and the reaction yield. If the catalyst activity is show (**Figure 3**) in the esterification of nyamplung seed oil from the highest to the lowest is in the order of CTAB-MCM-48/650 > CTAB-MCM-48/3w > CTAB-MCM-48 > CTAB-MCM-48/1w > CTAB-MCM-48/2w> CTAB-MCM-48/4w. The titration method, the catalyst activity in this reaction is in the order of CTAB-MCM-48/650 > CTAB-MCM-48/1w> CTAB-MCM-48> CTAB-MCM-48/2w > CTAB-MCM-48/3w > CTAB-MCM-48/4w.

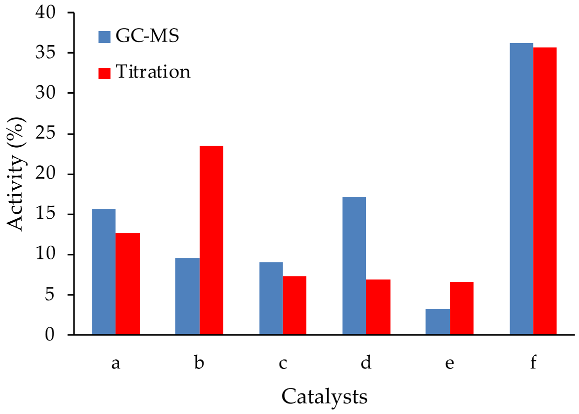

Figure 3. Catalyst activity in the esterification, a) CTAB-MCM-48, b) CTAB-MCM-48/1w, c) CTAB-MCM-48/2w, d) CTAB-MCM-48/3w, e) CTAB-MCM-48/4w, and f) CTAB-MCM-48/650

The disparity in the conversion of catalytic activity may be comper by considering the limitations of the GC-MS approach, which solely enables the identification of volatile chemicals. Furthermore, the calculation only pertains to the MEs and detected FFAs level, as seen in **Figure 4**. In the titration method, the acidity of all components of the compounds is also measured and affects the measurement of FFA levels. The results of the non-parametric statistical test (Mann-Whitney test) proved that there was no significant difference (Asymp. Sig. (2-tailed) = 0.967) for both methods. Therefore, both instruments can be used to identify catalyst activity in esterification. Biodiesel production requires a more economical method, so the choice will be on titration. Besides, this method is easier to apply than the GC-MS.

The percentage of the two active clusters of CTAB-MCM-48 catalysts as surfactant function in the esterification of seed oil (**Figure 5**) is obtained from the percentage of transmittance (**Table 2**); -Si-O-Si- versus the active clusters -Si-OH stretching (blue) and -Si-O-Si- versus -Si-OH bending (red). **Figure 5** shows that in addition to CTA^+ ions from CTAB, the two active groups also play a role in the esterification of seed oil. Similar mechanisms have been reported in the previous study [53], [54]. In the titration method, the rate of catalyst activity decreases as the loss of surfactant and the difference between the two active groups decreases. For CTAB-MCM-48 catalysts that have low activity is thought to be caused by excessive surfactant depravedness. This conjecture is reinforced by the physical and chemical properties of surfactant which has hydrophobic and hydrophilic sites. The existence of surfactant tends to increase the conversion of FFA to biodiesel, but the higher of surfactant can also inactivate the FFA cluster, mediating the mixture of yield with water and glycerol as a by-product of esterification, thereby lowering catalyst activity. This is understandable from the GC-MS characterization results showing the highest hydrocarbon side results (**Figure 4**) on this catalyst. This review provides a clue that surfactant and both active clusters have an optimum composition as in CTAB-MCM-48/1w catalysts. In the catalyst CTAB-MCM-48/650, it proved that MCM-48 without surfactant has higher activity than MCM-48 which still contain surfactant in the esterification of nyamplung seed oil. Moreover, the calcination method provides higher activity than the washing method. The high activity of the MCM-46/650 catalyst is caused by a better pore structure than other catalysts. This shape causes it to have a higher surface area and number of active sites of silanol groups so that its activity is higher. This statement is supported by the FTIR and XRD data of the catalyst. The proposed esterification mechanism that might take place is shown in **Figure 6**.

The results of this study showed that the catalyst CTAB-MCM-48/650 can be used as a candidate to replace homogeneous catalysts strong acid in the esterification of biodiesel raw materials that have FFA levels quite high. However, the CTAB-MCM-48 catalyst is also a possible candidate for a one-step reaction

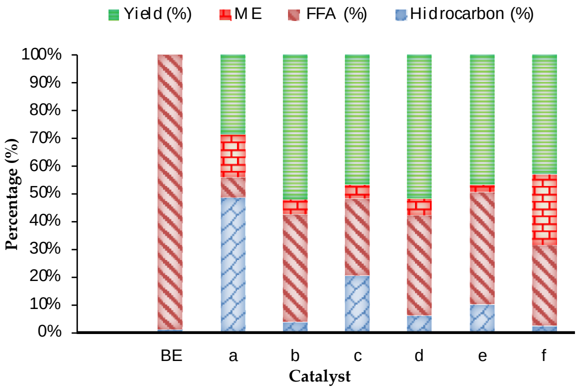

Figure 4. Chemical composition of nyamplung seed oil; before (BE) and after esterification; a) CTAB-MCM-48, b) CTAB-MCM-48/1w, c) CTAB-MCM-48/2w, d) CTAB-MCM-48/3w, e) CTAB-MCM-48/4w, and f) CTAB-MCM-48/650

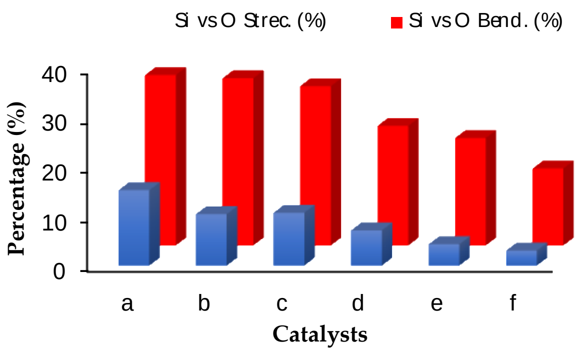

Figure 5. Percentage difference in transmittance; (blue) -Si-O-Si- versus -Si-OH stretching and (red) -Si-O-Si- versus -Si-OH bending, a) CTAB-MCM-48, b) CTAB-MCM-48/1w, c) CTAB-MCM-48/2w, d) CTAB-MCM-48/3w, e) CTAB-MCM-48/4w, and f) CTAB-MCM-48/650.

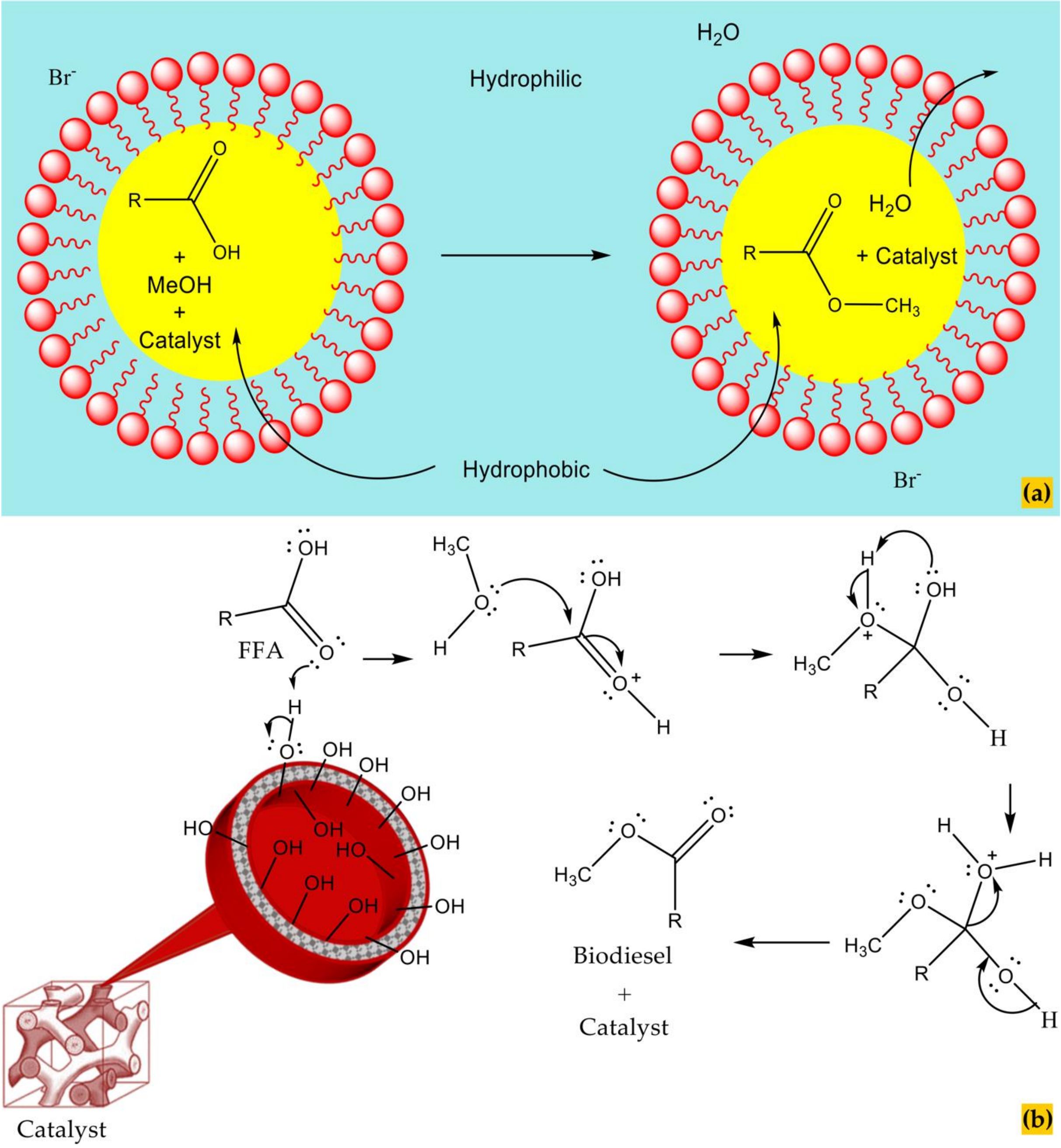

Figure 6. Catalyst activity in the esterification of nyamplung seed oil: a) The reaction takes place in the surfactant medium, and b) The reaction takes place in the hydrophobic part of the surfactant

(esterification-transesterification). The resultant substance may be readily use in diesel engines. The low FFA level in the reaction products may be attributed to the relatively large concentration of hydrocarbons present in biodiesel. In addition, this catalyst will be more active when active sites such as metals.

4. Conclusion

The titration method can be used and is more profitable than the GC-MS method in the production of biodiesel from nyamplung seed oil. The synthesis of the catalyst using the calcination method gave higher catalyst activity (35.74%) than the washing method (23.43%). The titration method can be used and is more profitable than the GC-MS method in producing biodiesel from nyamplung seed oil. The synthesis of the catalyst using the calcination method gave higher catalyst activity (35.74%) than the washing method (23.43%). MCM-48 catalyst without surfactant is more active than MCM-48 catalyst, which still contains CTAB in the esterification of nyamplung seed oil. The smaller the percentage transmittance of the -Si-O-Si- and -Si-OH groups, the greater the percentage of catalyst activity. The CTAB-MCM-48/650 catalyst can be applied to biodiesel feedstock with a high enough FFA level. However, the CTAB-MCM-48 catalyst has a high action to crack the compound components contained in nyamplung seed oil, making it possible for a one-step reaction (cracking-esterification-transesterification) to occur in biodiesel production.

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Author's Declaration

Authors' contributions and responsibilities

The authors made substantial contributions to the conception and design of the study. The authors took responsibility for data analysis, interpretation and discussion of results. The authors read and approved the final manuscript.

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Availability of data and materials

All data are available from the authors.

Competing interests

The authors declare no competing interest.

Additional information

No additional information from the authors.

References

[1] T. M. I. Mahlia *et al.*, "Patent landscape review on biodiesel production: Technology updates," *Renewable and Sustainable Energy Reviews*, vol. 118, no. November 2019, p. 109526, 2020, doi: 10.1016/j.rser.2019.109526.

[2] T. Kivevele, T. Raja, V. Pirouzfar, B. Waluyo, and M. Setiyo, "LPG-Fueled Vehicles: An Overview of Technology and Market Trend," *Automotive Experiences*, vol. 3, no. 1, pp. 6–19, 2020, doi: 10.31603/ae.v3i1.3334.

[3] L. M. Olalekan, O. Olatunde, F. I. Olufemi, and A. A. Olamide, "Mathematical modeling and cost comparison for electricity generation from petrol and liquified petroleum gas (LPG)," *Mechanical Engineering for Society and Industry*, vol. 2, no. 2, pp. 56–62, 2022, doi: 10.31603/mesi.6697.

[4] M. Mofijur, M. M. Hasan, T. M. I. Mahlia, S. M. A. Rahman, A. S. Silitonga, and H. C. Ong, "Performance and Emission Parameters of Homogeneous Charge Compression Ignition (HCCI) Engine: A Review," *Energies*, vol. 12, no. 18, p. 3557, Sep. 2019, doi: 10.3390/en12183557.

[5] R. S. Norhasyima and T. M. I. Mahlia, "Advances in CO_2 utilization technology: A patent landscape review," *Journal of CO2 Utilization*, vol. 26, pp. 323–335, Jul. 2018, doi: 10.1016/j.jcou.2018.05.022.

[6] M. Setiyo and S. Munahar, "AFR and fuel cut-off modeling of LPG-fueled engine based on engine, transmission, and brake system using fuzzy logic controller (FLC)," *Journal of Mechatronics, Electrical Power, and Vehicular Technology*, vol. 8, no. 1, pp. 50–59, 2017, doi: 10.14203/j.mev.2017.v8.50-59.

[7] M. Setiyo, S. Munahar, A. Triwiyatno, and J. D. Setiawan, "Modeling of deceleration Fuel cut-off for LPG fuelled engine using Fuzzy logic controller," *International Journal of Vehicle Structures and Systems*, vol. 9, no. 4, 2017, doi: 10.4273/ijvss.9.4.12.

[8] B. Sajjadi, A. A. A. Raman, and H. Arandiyan, "A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models," *Renewable and Sustainable Energy Reviews*, vol. 63, pp. 62–92, Sep. 2016, doi: 10.1016/j.rser.2016.05.035.

[9] I. Lawan *et al.*, "Synthesis, properties and effects of a multi-functional biodiesel fuel additive," *Fuel Processing Technology*, vol. 198, p. 106228, Feb. 2020, doi: 10.1016/j.fuproc.2019.106228.

[10] S. Pambudi, N. Ilminnafik, S. Junus, and M. N. Kustanto, "Experimental Study on the Effect of Nano Additives γAl2O3 and

Equivalence Ratio to Bunsen Flame Characteristic of Biodiesel from Nyamplung (Calophyllum Inophyllum)," *Automotive Experiences*, vol. 4, no. 2, pp. 51–61, 2021, doi: 10.31603/ae.4569.

[11] M. Fadhlullah, S. N. B. Widiyanto, and E. Restiawaty, "The potential of nyamplung (Calophyllum inophyllum L.) seed oil as biodiesel feedstock: Effect of seed moisture content and particle size on oil yield," *Energy Procedia*, vol. 68, no. 2015, pp. 177–185, 2015.

[12] A. Arumugam and V. Ponnusami, "Biodiesel production from Calophyllum inophyllum oil a potential non-edible feedstock: An overview," *Renewable Energy*, vol. 131, pp. 459–471, 2019, doi: 10.1016/j.renene.2018.07.059.

[13] M. Ranjithkumar, S. Karuppusamy, P. Lakshmanan, D. Ragulnath, K. Saravanan, and A. M. Rameshbabu, "Study on diesel engine combustion parameters using Calophyllum Inophyllum methyl ester and micro algae methyl ester with level addition of Di-Ethyl ether," *Materials Today: Proceedings*, vol. 37, pp. 3388–3392, 2021, doi: 10.1016/j.matpr.2020.09.275.

[14] A. Priyanto, "Eksplorasi nyamplung (Calophyllum inophyllum L.) di sebaran alam Kalimantan Barat (Ketapang) untuk program pemuliaan pohon," *Informasi Teknis*, vol. 11, no. 2, pp. 69–78, 2013.

[15] N. A. Fauzan, E. S. Tan, F. L. Pua, and G. Muthaiyah, "Physiochemical properties evaluation of Calophyllum inophyllum biodiesel for gas turbine application," *South African Journal of Chemical Engineering*, vol. 32, pp. 56–61, 2020, doi: 10.1016/j.sajce.2020.02.001.

[16] T. M. M. Marso, C. S. Kalpage, and M. Y. Udugala-Ganehenege, "Metal modified graphene oxide composite catalyst for the production of biodiesel via pre-esterification of Calophyllum inophyllum oil," *Fuel*, vol. 199, pp. 47–64, Jul. 2017, doi: 10.1016/j.fuel.2017.01.004.

[17] L. Kolo, F. Firdaus, P. Taba, M. Zakir, and N. H. Soekamto, "Selectivity of the New Catalyst ZnO-MCM-48-CaO in Esterification of Calophyllum inophyllum Oil," *Automotive Experiences*, vol. 5, no. 2, pp. 217–229, 2022, doi: 10.31603/ae.6711.

[18] G. P. Benedictto, M. S. Legnoverde, J. C. Tara, R. M. Sotelo, and E. I. Basaldella, "Synthesis of K+/MgO heterogeneous catalysts derived from MgCO3 for biodiesel production," *Materials Letters*, vol. 246, pp. 199–202, Jul. 2019, doi: 10.1016/j.matlet.2019.03.081.

[19] D. Ayu, R. Aulyana, E. W. Astuti, K. Kusmiyati, and N. Hidayati, "Catalytic Transesterification of Used Cooking Oil to Biodiesel: Effect of Oil-Methanol Molar Ratio and Reaction Time," *Automotive Experiences*, vol. 2, no. 3, pp. 73–77, 2019, doi: 10.31603/ae.v2i3.2991.

[20] S. Supriyadi, P. Purwanto, D. D. Anggoro, and H. Hermawan, "The Effects of Sodium Hydroxide (NaOH) Concentration and Reaction Temperature on The Properties of Biodiesel from Philippine Tung (Reutealis Trisperma) Seeds," *Automotive Experiences*, vol. 5, no. 1, pp. 57–67, 2022, doi: 10.31603/ae.5986.

[21] A. Kolakoti, B. Prasadarao, K. Satyanarayana, M. Setiyo, H. Köten, and M. Raghu, "Elemental, Thermal and Physicochemical Investigation of Novel Biodiesel from Wodyetia Bifurcata and Its Properties Optimization using Artificial Neural Network (ANN)," *Automotive Experiences*, vol. 5, no. 1, pp. 3–15, 2022, doi: 10.31603/ae.6171.

[22] A. Kolakoti, M. Setiyo, and B. Waluyo, "Biodiesel Production from Waste Cooking Oil: Characterization, Modeling and Optimization," *Mechanical Engineering for Society and Industry*, vol. 1, no. 1, pp. 22–30, 2021, doi: 10.31603/mesi.5320.

[23] R. Naveenkumar and G. Baskar, "Biodiesel production from Calophyllum inophyllum oil using zinc doped calcium oxide (Plaster of Paris) nanocatalyst," *Bioresource Technology*, vol. 280, pp. 493–496, May 2019, doi: 10.1016/j.biortech.2019.02.078.

[24] M. Rizal, M. D. Supardan, and Y. Syamsyuddin, "Oil Esterification Using High-Free Fatty Acid Acid Using Hydrodynamic Cavitation Process," *IOSR Journal of Applied Chemistry*, vol. 12, no. 10, pp. 1–4, 2019, doi: 10.9790/5736-1210010104.

[25] B. Ashok *et al.*, "An experimental analysis on

the effect of n-pentanol- Calophyllum Inophyllum Biodiesel binary blends in CI engine characteristcis," *Energy*, vol. 173, pp. 290–305, Apr. 2019, doi: 10.1016/j.energy.2019.02.092.

[26] M. AlSharifi and H. Znad, "Development of a lithium based chicken bone (Li-Cb) composite as an efficient catalyst for biodiesel production," *Renewable Energy*, vol. 136, pp. 856–864, Jun. 2019, doi: 10.1016/j.renene.2019.01.052.

[27] Z. Khan *et al.*, "Current developments in esterification reaction: A review on process and parameters," *Journal of Industrial and Engineering Chemistry*, vol. 103, pp. 80–101, Nov. 2021, doi: 10.1016/j.jiec.2021.07.018.

[28] Hartati *et al.*, "Highly selective hierarchical ZSM-5 from kaolin for catalytic cracking of Calophyllum inophyllum oil to biofuel," *Journal of the Energy Institute*, vol. 93, no. 6, pp. 2238–2246, Dec. 2020, doi: 10.1016/j.joei.2020.06.006.

[29] J. Liu, Y. Nan, and L. L. Tavlarides, "Continuous production of ethanol-based biodiesel under subcritical conditions employing trace amount of homogeneous catalysts," *Fuel*, vol. 193, pp. 187–196, Apr. 2017, doi: 10.1016/j.fuel.2016.12.058.

[30] J. Vakros, "Biochars and Their Use as Transesterification Catalysts for Biodiesel Production: A Short Review," *Catalysts*, vol. 8, no. 11, p. 562, Nov. 2018, doi: 10.3390/catal8110562.

[31] E. Dahdah *et al.*, "Biodiesel production from refined sunflower oil over Ca–Mg–Al catalysts: Effect of the composition and the thermal treatment," *Renewable Energy*, vol. 146, pp. 1242–1248, Feb. 2020, doi: 10.1016/j.renene.2019.06.171.

[32] C. Baroi and A. K. Dalai, "Simultaneous esterification, transesterification and chlorophyll removal from green seed canola oil using solid acid catalysts," *Catalysis Today*, vol. 207, pp. 74–85, May 2013, doi: 10.1016/j.cattod.2012.07.003.

[33] Y. M. Sani, W. M. A. W. Daud, and A. R. Abdul Aziz, "Activity of solid acid catalysts for biodiesel production: A critical review," *Applied Catalysis A: General*, vol. 470, pp. 140–161, Jan. 2014, doi: 10.1016/j.apcata.2013.10.052.

[34] N. H. Said, F. N. Ani, and M. F. M. Said, "Review of the Production of Biodiesel from Waste Cooking Oil Using Solid Catalysts," *Journal of Mechanical Engineering and Sciences*, vol. 8, pp. 1302–1311, Jun. 2015, doi: 10.15282/jmes.8.2015.5.0127.

[35] L. Kolo, Firdaus, and P. Taba, "The use of MCM-48-nCaO as catalyst in esterification reaction of nyamplung seed oil (Calophyllum inophyllum L.)," *Indonesia Chimica Acta*, vol. 8, no. 20, pp. 1–10, 2015, doi: 10.20956/ica.v8i2.2466.

[36] M. Pirouzmand, B. Nikzad-kojanag, and S. K. Seyed-Rasulzade, "Surfactant containing Ca/MCM-41 as a highly active, green and reusable catalyst for the transesterification of canola oil," *Catalysis Communications*, vol. 69, pp. 196–201, Sep. 2015, doi: 10.1016/j.catcom.2015.06.021.

[37] P. Dinh Du *et al.*, "Aminopropyl Functionalised MCM-41: Synthesis and Application for Adsorption of Pb(II) and Cd(II)," *Advances in Materials Science and Engineering*, vol. 2019, pp. 1–15, Feb. 2019, doi: 10.1155/2019/8573451.

[38] T. Yokoi, S. Seo, N. Chino, A. Shimojima, and T. Okubo, "Preparation of silica/carbon composites with uniform and well-ordered mesopores by esterification method," *Microporous and Mesoporous Materials*, vol. 124, no. 1–3, pp. 123–130, Aug. 2009, doi: 10.1016/j.micromeso.2009.05.002.

[39] A. B. Fadhil, A. M. Aziz, and M. H. Al-Tamer, "Biodiesel production from Silybum marianum L. seed oil with high FFA content using sulfonated carbon catalyst for esterification and base catalyst for transesterification," *Energy Conversion and Management*, vol. 108, pp. 255–265, Jan. 2016, doi: 10.1016/j.enconman.2015.11.013.

[40] D. O. Onukwuli, L. N. Emembolu, C. N. Ude, S. O. Aliozo, and M. C. Menkiti, "Optimization of biodiesel production from refined cotton seed oil and its characterization," *Egyptian Journal of Petroleum*, vol. 26, no. 1, pp. 103–110, Mar. 2017, doi: 10.1016/j.ejpe.2016.02.001.

[41] M. C. Gomes Souza, M. Firmino de Oliveira, A. T. Vieira, A. Marcio de Faria, and A. C.

Ferreira Batista, "Methylic and ethylic biodiesel production from crambe oil (Crambe abyssinica): New aspects for yield and oxidative stability," *Renewable Energy*, vol. 163, pp. 368–374, Jan. 2021, doi: 10.1016/j.renene.2020.08.073.

[42] P. Taba, P. Budi, and A. Y. Puspitasari, "Adsorption of heavy metals on amine-functionalized MCM-48," *IOP Conference Series: Materials Science and Engineering*, vol. 188, p. 012015, Apr. 2017, doi: 10.1088/1757-899X/188/1/012015.

[43] L. Kolo, N. Soekamto, F. -, and P. Taba, "Synthesis of MCM-48 contains NaCl and Surfactant as Catalyst in the Esterification of Nyamplung Oil (Calophyllum inophyllum L.) to Biodiesel," *Egyptian Journal of Chemistry*, pp. 0–0, May 2022, doi: 10.21608/ejchem.2022.104616.4836.

[44] N. Nurhidayanti, "Studi Kinetika Reaksi Pembuatan Biodiesel dari Minyak Nyamplung Menggunakan Iradiasi Microwave," *Jurnal Tekno Insentif*, vol. 12, no. 2, pp. 1–12, Apr. 2019, doi: 10.36787/jti.v12i2.100.

[45] M. H. Abdellah, C. A. Scholes, L. Liu, and S. E. Kentish, "Efficient degumming of crude canola oil using ultrafiltration membranes and bio-derived solvents," *Innovative Food Science & Emerging Technologies*, vol. 59, p. 102274, Jan. 2020, doi: 10.1016/j.ifset.2019.102274.

[46] J. C. K. Lam *et al.*, "Vibrational spectroscopy of low-k/ultra-low-k dielectric materials on patterned wafers," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 29, no. 5, Sep. 2011, doi: 10.1116/1.3625099.

[47] P. Taba, R. D. P. Mustafa, L. M. Ramang, and A. H. Kasim, "Adsorption of Pb 2+ on Thiol-functionalized Mesoporous Silica, SH-MCM-48," *Journal of Physics: Conference Series*, vol. 979, p. 012058, Mar. 2018, doi: 10.1088/1742-6596/979/1/012058.

[48] M. Fathy, H. Selim, and A. E. L. Shahawy, "Chitosan/MCM-48 nanocomposite as a potential adsorbent for removing phenol from aqueous solution," *RSC Advances*, vol. 10, no. 39, pp. 23417–23430, 2020, doi: 10.1039/D0RA02960B.

[49] E. Elzanati, H. Abdallah, E. Farg, R. S. Ettouney, and M. A. El-Rifai, "Enhancing The Esterification Conversion Using Pervaporation," *Journal of Engineering Science and Technology*, vol. 13, no. 4, pp. 990–1004, 2018.

[50] J. W. Seo, W.-J. Lee, S. Nam, H. Ryoo, J.-N. Kim, and C. H. Ko, "Mesoporous Structure Control of Silica in Room-Temperature Synthesis under Basic Conditions," *Journal of Nanomaterials*, vol. 2015, pp. 1–7, 2015, doi: 10.1155/2015/149654.

[51] P. Taba *et al.*, "Mesoporous Silica Modified With Amino Group (NH2-MCM-48) as Adsorbent of Ag(I) and Cr(III) in Water," *Rasayan Journal of Chemistry*, vol. 14, no. 01, pp. 204–211, 2021, doi: 10.31788/RJC.2021.1415963.

[52] X. Qian *et al.*, "A Simple Strategy To Improve PEI Dispersion on MCM-48 with Long-Alkyl Chains Template for Efficient CO 2 Adsorption," *Industrial & Engineering Chemistry Research*, vol. 58, no. 25, pp. 10975–10983, Jun. 2019, doi: 10.1021/acs.iecr.9b00545.

[53] L. Safiddine, A. Hadj-Ziane Zafour, I. Fofana, A. Skender, F. Guerbas, and A. Boucherit, "Transformer oil reclamation by combining several strategies enhanced by the use of four adsorbents," *IET Generation, Transmission & Distribution*, vol. 11, no. 11, pp. 2912–2920, Aug. 2017, doi: 10.1049/iet-gtd.2016.1995.

[54] Shagufta, I. Ahmad, and R. Dhar, "Sulfonic Acid-Functionalized Solid Acid Catalyst in Esterification and Transesterification Reactions," *Catalysis Surveys from Asia*, vol. 21, no. 2, pp. 53–69, Jun. 2017, doi: 10.1007/s10563-017-9226-1.