TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC SƯ PHẠM TP HỒ CHÍ MINH
Tập 21, Số 9 (2024): 1668-1681
Website: https://journal.hcmue.edu.vn
ISSN: 2734-9918

HO CHI MINH CITY UNIVERSITY OF EDUCATION
JOURNAL OF SCIENCE
Vol. 21, No. 9 (2024): 1668-1681
https://doi.org/10.54607/hcmue.js.21.9.4213(2024)

Research Article

SYNTHESIS HETEROGENEOUS CATALYST Fe_xO_y/CaO FROM BLUE CRAB SHELL FOR TRANSESTERIFICATION OF FISH FAT OIL

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Received: April 07, 2024; Revised: June 03, 2024; Accepted: July 11, 2024

ABSTRACT

Nowadays, biodiesel attracts much attention since it is renewable, sustainable, and can replace fossil fuels. CaO was a suitable heterogeneous catalyst for transesterification reaction to produce biodiesel. In this study, blue crab shell was recycled as the CaO source. CaO was combined with iron oxide to form a bifunctional catalyst, which was applied for the transesterification of fish fat oil in an autoclave reactor. The catalyst characteristics, i.e. thermal degradation property, morphology, and composition, were studied by TGA and SEM-EDX. The effect of catalyst, temperature, reaction time, and MeOH: oil molar ratio was investigated. The results showed that the addition of Fe can enhance the reaction rate. The reaction temperature and MeOH: oil molar ratio affected the reaction time and catalyst loading more significantly than the FAME yield. The highest FAME yield (84.28%) was achieved at 140℃, 2h, 10wt% Fe_xO_y/CaO catalyst and 20:1 MeOH: oil molar ratio.

Keywords: biodiesel; blue crab shell; calcium oxide; iron oxide; fish fat oil

1. Introduction

Renewable energy attracts numerous research and projects to find alternative energy sources to replace fossil fuels. Biodiesel is a renewable, sustainable, and environment-friendly fuel produced yearly, especially in the EU, Brazil, and the US (Ooi et al., 2021; Spence et al., 2022). Biodiesel has shown remarkable industrial growth in two recent decades since its lower greenhouse gas emissions are biodegradable and nontoxic (Pasha et al., 2021; Talha & Sulaiman, 2016). Raw materials for biodiesel production are very diverse e.g. edible oil (soybean, canola, palm oil, fat…) or inedible oil (waste cooking oil, Jatropha Curcas, rubber seed, microalgae, neem seed…) (Amenaghawon et al., 2022; Amesho et al., 2022;

Cite this article as: Tran Thi To Nga, Trinh Hoai Thanh, Nguyen An Binh, Nguyen Thi Kim Thanh, Ho Tuan Kiet, & Nguyen Phuc My Tran (2024). Synthesis heterogeneous catalyst Fe_xO_y/CaO from blue crab shell for transesterification of fish fat oil. *Ho Chi Minh City University of Education Journal of Science, 21*(9), 1668-1681.

Baloch et al., 2018; Shankar & Jambulingam, 2017). Generally, biodiesel can be produced by transesterification of triglycerides in oil with alcohol in the presence of a catalyst (homogeneous, heterogeneous and enzyme) or without a catalyst (supercritical fluids) (Kosuru et al., 2024; Pasha et al., 2021).

Biodiesel is produced economically *via* transesterification utilising the homogeneous base catalysts, *e.g.* NaOH or KOH. The homogeneous catalyst process has some benefits, i.e. shorter reaction time and inexpensive, but it quickly gets saponification, and there is no way to recycle the catalyst (Kosuru et al., 2024). In contrast, the heterogeneous catalyst has higher efficiency, is eco-friendly, and has no saponification (Talha & Sulaiman, 2016). Numerous solid catalysts were applied in transesterification, such as CaO, CaO/Al_2O_3, MgO, MgO-Li, Fe_3O_4/CaO, Na-SiO_2, zeolite X, SO_4/ZrO_2, etc. (Kosuru et al., 2024). CaO is the most popular heterogeneous catalyst for biodiesel production since it is a strong base catalyst, nontoxic, cheap and insoluble in methanol (Kosuru et al., 2024; Palitsakun et al., 2021). Mainly, CaO can be synthesised from waste sources of food industrial and agriculture, e.g. eggshells (Attari et al., 2022; A.V.S.L.Sai et al., 2020; Yusuff et al., 2022), crab shell (Cardoso et al., 2020; Ismail et al., 2022; Shankar & Jambulingam, 2017), clam shell (Niju et al., 2016; Risso et al., 2018), oyster shell (Hernández-Martínez et al., 2023; Risso et al., 2018), snail shell (Aisien & Aisien, 2023; Phuttawong et al., 2015), etc. Using these raw materials help to reduce not only processing cost but also environmental issues (Hernández-Martínez et al., 2023).

To improve the activity of CaO catalyst, researchers usually combine it with an alkaline, alkali earth metal, or transition metal oxide (Aisien & Aisien, 2023; Hernández-Martínez et al., 2023; Palitsakun et al., 2021; Xia, Hu et al., 2022; Xia, Li et al., 2022). Results showed that the combination of group 1 and 2 metal oxide enhanced the reaction's strong base sites and active site (Hernández-Martínez et al., 2023; Palitsakun et al., 2021). Recent research revealed that the addition of transition metal oxide, e.g. CoO, NiO or Fe_2O_3 enhanced not only the active sites but also the specific surface area of the catalyst, resulting in a higher activity (Amal et al., 2024; Das et al., 2020; Sulaiman et al., 2021; Xia, Li et al., 2022).

In this research work, we added a small amount of Fe (i.e. 6.5 wt%) to CaO catalyst. Then we applied the catalyst for transesterifying fish fat oil to produce fatty acid methyl ester (FAME). CaO was synthesised from the shell of a blue crab (*Portunus pelagicus*), which is very popular in Viet Nam's seafood. Meanwhile, Hu fish (*Pangasius conchophilus*), a common catfish in Vietnam's aquaculture, has a surplus unused amount of fat during fish processing. Utilising these waste materials can produce valuable biodiesel from the fish waste and reduce environmental pollution. Furthermore, the transesterification was carried out in an autoclave reactor to provide a reaction temperature higher than the boiling point of methanol (MeOH) (up to 160°C), increasing the reaction rate.

2. Experiment

2.1. Material

Blue crab shell (BCS) was collected from markets and seafood restaurants around Ho Chi Minh City. The catfish fat was obtained from the local seafood market's waste. $Fe(NO_3)_3 \cdot 6H_2O$ (Reagent, Merck), Methanol (HPLC grade, Fisher), *n*-hexane (Xilong, China), and double-distilled water were used as chemicals in the experiments.

The BCS was washed carefully to remove the contamination, then washed with boiling water three times. The clean BCS was dried under sunlight for 6h and put in the oven at 105°C for 3h. After that, the sample was ground into small pieces (around 1mm). The dried BCS was placed in alumina crucibles and calcined at 900°C for 4h in the muffle furnace (air atmosphere), forming CaO sample. The CaO sample was finally ground and sieved to 0.125mm particles. The brown fine powder was kept in the desiccator for further processing.

The fish fat was washed with water and naturally dried for 1h before oil extraction. The traditional method of extracting oil from fish fat is heating the fat until the yellow oil (FFO-1) was removed from the solid. Moreover, the Soxhlet extraction was applied to extract oil from the fish fat using *n*-hexane as a solvent for 4h. The *n*-hexane was removed from the product by a vacuum evaporator, and then the light-yellow oil was obtained by FFO-2. FFO-2 was extracted with MeOH to remove all polar components and free fatty acid (FFA). This final fish fat oil was named FFO-3. The yield of these oils is listed in Table 1.

Table 1. *The yield of oil extracted from fish fat by different methods.*

Fish fat oil	Yield, wt%
FFO-1	75.15 ± 8.55
FFO-2	91.40 ± 1.35
FFO-3	81.94 ± 0.56

2.2. Catalyst preparation and characterisation

The Fe_xO_y/CaO was prepared with co-precipitation method. The mass ratio of Fe/CaO was fixed at 1/14 (around 6.54 wt% Fe). The CaO was dissolved in 500mL of double-distilled water in a beaker and placed on a stirred hot plate. Solution of $Fe(NO_3)_3$ was dropped slowly into the mixture of CaO and water, set at 60°C. The system was stirred for 4h, then cooled to room temperature, and let the precipitation settled down. The precipitation was filtered and dried at 105°C for 14h. Then, it was ground and calcined at 500°C for 4h. The final Fe_xO_y/CaO catalyst was sieved to 0.125mm particle size and stored in the desiccator for further experiments.

The synthesis catalyst was characterised by TGA-DSC (the simultaneous Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)) and SEM-EDX (Scanning Electron Microscopy and Energy Dispersive X-ray Analysis) to study thermal degradation property, elemental composition, and morphology. TGA-DSC was performed on the TGA/DSC 3+ (Mettler Toledo). The TGA experiment was carried out on a

TGA LABSYS Evo 1600. The samples were placed in the platinum crucible; the oven was raised from room temperature to 800°C (TGA) or 1000°C (TGA-DSC) with a ramp rate of 10°C/min in air. Furthermore, SEM-EDX was applied to study the surface morphology and elemental composition by JSM-IT200 IntouchScope^{TM} SEM-EDX (JEOL - Japan). The sample was sputter coated with a palladium ultrathin layer before SEM-EDX analysis.

2.3. Transesterification reaction

The experiment was conducted in an autoclave reactor. The reactants and catalyst were added to a 100ml Teflon container and then placed inside the stainless-steel reactor. The reaction was carried on inside the muffle furnace with a heating rate of 10°C/min, and the furnace temperature was considered the reaction temperature. After the reactions were completed, the system was gradually cooled to room temperature, condensing the solvent. Then, all the products except the catalyst were transferred to cylinders and kept for one day for gravity settling, leading the catalyst to sink to the bottom. Furthermore, the liquid phases were transferred to the separatory funnel and washed several times with methanol or water to remove all glycerol. The final product was dried in the oven at 105°C for 30 minutes.

The product was analysed with GC-MS (Gas chromatography/mass spectrometry) to calculate the yield of FAME formation. The GC-MS Agilent GC6890 system was applied with HP-5MS (30m x 250µm x 0,25µm) column. The sample was diluted with *n*-hexane, and methyl heptadecanoate was used as the internal standard (ISTD). The inlet was kept at 250°C, with a split ratio 1:50. Helium was used as a carrier gas. The FAME yield was determined by equation (1)

$$H\% = \frac{\Sigma A_{FAME}}{A_{ISTD}} \cdot \frac{m_{ISTD}}{m_s} \cdot 100\% \tag{1}$$

Where: A_{FAME}, A_{ISTD} are the peak areas of FAME and ISTD

m_s, m_{ISTD} , which are the mass of the sample and ISTD in the solution.

3. Results and discussion

3.1. Catalyst characterisation

The simultaneous TGA-DSC curves of BCS showed three mass loss ranges (Figure 1). The first one was from room temperature to 210 °C, corresponding to the evaporation of physically adsorbed water. The second range of 210−500°C showed a mass loss of 23.1%, attaching to an exothermic peak in the DSC curve. This mass loss was assigned to the degradation of organic compounds in BCS. The last mass loss was observed at 815−860°C, which corresponded to the degradation of $CaCO_3$, yielding CaO as the final product. An endothermic peak observed simultaneously at the DSC curve reinforced this phenomenon. The degradation of $CaCO_3$ in this research showed a higher degradation temperature than in other research, such as crab shell (Correia et al., 2014), eggshell (Correia et al., 2014; Rahman et al., 2022; Yusuff et al., 2022) and oyster shell (Hernández-Martínez et al., 2023)… which almost degraded completely before 800°C. However, the chicken eggshell in Attari's research degraded completely at 877°C, higher than this study. The different degradation temperatures of $CaCO_3$ observed from various studies might come from the type of equipment, sample weight, particle size, and the heating program… However, all research had chosen 900°C for the calcination of raw material to synthesise CaO. The mass loss of CO_2 of about 24.5% provided the per cent of $CaCO_3$ in raw BCS about 55.7%, which is lower than another shell type (Correia et al., 2014). This TGA-DSC result set the calcination temperature at 900°C to synthesise CaO from BCS.

The uncalcined Fe_xO_y/CaO was analysed with TGA from room temperature to 800°C in the air; the result is presented in Figure 2. Three main weight losses are observed in the TGA curve corresponding to 3 sharp peaks in the derivative thermogravimetric (DTG) curve. The peak at 117°C was considered as desorption of physisorbed water. At the same time, the decomposition of iron hydroxide and calcium hydroxide was assigned to the peak at 387°C with the mass loss of 7.9%. $Ca(OH)_2$ formed when water was added during preparation. At the same time, $Fe(OH)_3$ precipitate was produced when Fe^{3+} encountered a base medium. The third mass loss at 450°C should be the degradation of nitrate salts. This peak is not high since the Fe percentage in the final catalyst is only 6.48wt%. The last peak at 640°C gave a mass loss of 5.1%, corresponding to the degradation of $CaCO_3$. This carbonate species of Ca had lower degradation temperature than the one in BCS in Figure 1, which two reasons can explain. Firstly, two different TGA equipment analysed BCS and uncalcined Fe_xO_y/CaO. Secondly, this carbonate species was an external coating of $CaCO_3$ formed in an uncalcined Fe_xO_y/CaO sample, which resulted from the recombination of CaO fine particles and CO_2 in the air during the storage, preparation, and calcination processes. These made $CaCO_3$ appear in uncalcined Fe_xO_y/CaO samples with a low amounts and at the outer surface, leading to an earlier degradation peak (Hernández-Martínez et al., 2023).

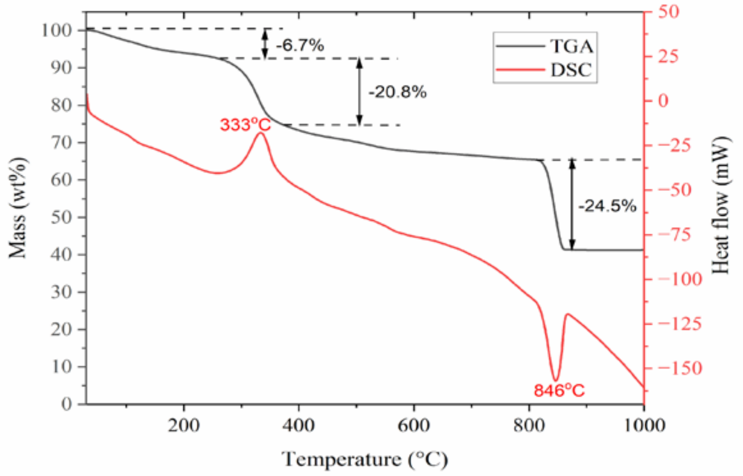

Figure 1. Simultaneous TGA-DSC results of blue crab shell - BCS in air

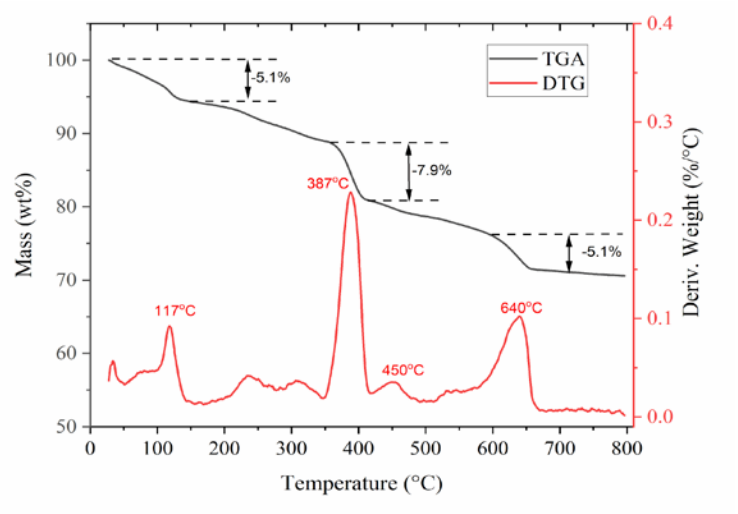

Figure 2. *TGA results of uncalcined Fe_xO_y/CaO in air*

The SEM-EDX results are shown in Figure 3 and Table 2. There was an irregular shape in the morphology of CaO synthesised from BCS. When combined with iron oxide, an agglomeration was detected, making the calcium oxide particles come closer. This phenomenon was observed in other research (Xia et al., 2022). Besides, some fiber-like pieces appeared on the surface of CaO, which might be iron oxide, as in Figure 3b. Figures 3c and d showed that the CaO calcined from BCS contained only Ca, Mg, and O. In addition, the signal appeared at 2 keV, representing the Pd as the coating material. However, there was no P detection, which was different from previous studies on another crab shell (Cardoso et al., 2020; Ismail et al., 2022). In these research works, phosphorous was also detected as a trace in CaO samples. This difference might come from different types of crab shells, and the P was too low to observe in the EDX test.

Table 2. *Elemental composition in CaO from BCS and Fe_xO_y/CaO samples by EDX results*

CaO (BCS)			**Fe_xO_y/CaO**		
Atom	Mass%	Atom%	Atom	Mass%	Atom%
O	50.46	70.97	O	39.48	62.38
Mg	3.29	3.05	Mg	3.71	3.86
Ca	46.25	25.98	Ca	45.11	28.46
Fe	-	-	Fe	11.71	5.30

Table 2 demonstrated Fe mass per cent of 11.71%, which was higher than the calculated data (6.54%). Moreover, the atom% of O doubled the atom% of metals (*i.e.* Ca, Mg, and Fe), which was higher than the stoichiometric of metal oxide formula. Other research also found a similar discrepancy in EDX results (Das et al., 2020; Ismail et al., 2022). This difference might come from oxygen, which has low detector efficiency in the EDX technique, or from the preparation process. In conclusion, SEM-EDX results revealed that iron oxide was successfully attached to CaO and caused some minor changes in the morphology.

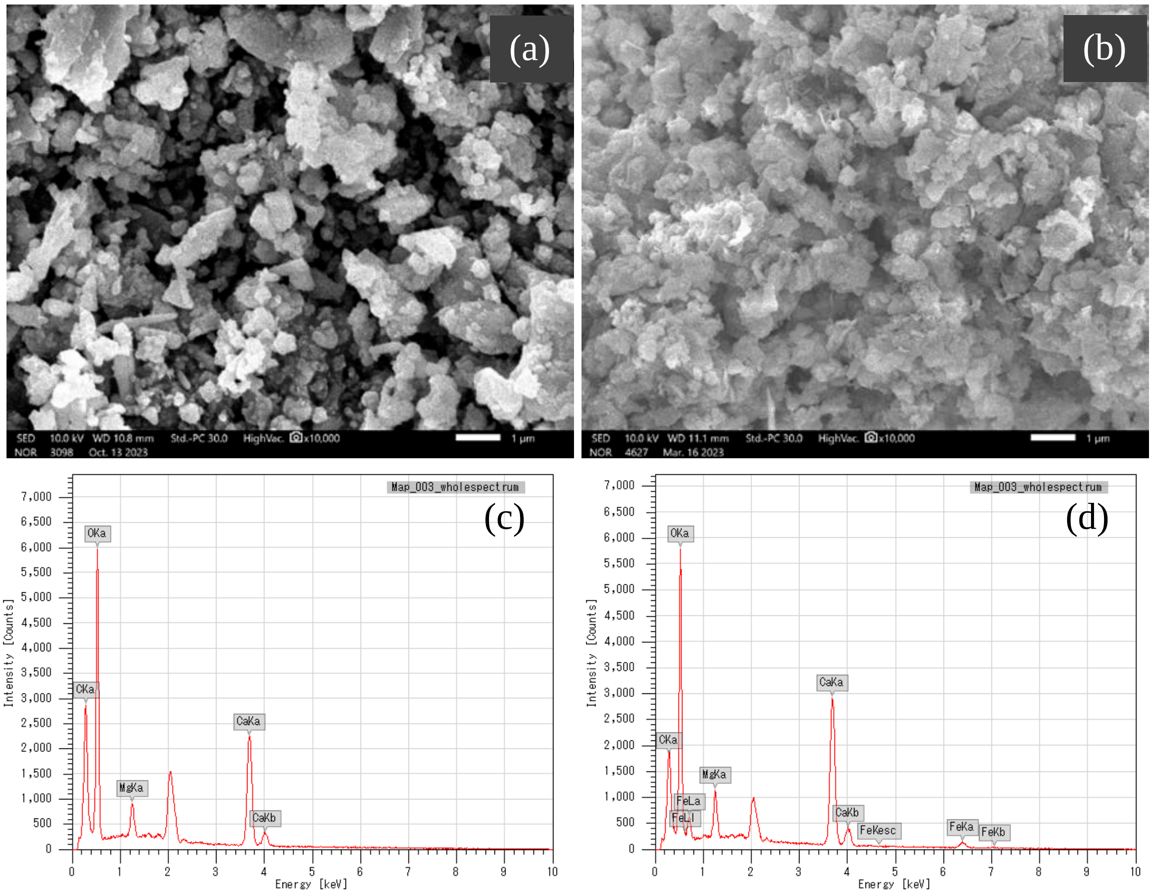

Figure 3. *SEM-EDX images of CaO and Fe_xO_y/CaO samples. a) and b) SEM image of CaO and Fe_xO_y/CaO; c) and d) EDX spectra of CaO and Fe_xO_y/CaO*

3.2. Transesterification experiments

3.2.1. Effect of extraction method

As described above, the oil was extracted from fish fat with three different methods. The oil yield of FFO-3 was around 84%, which was compatible with the fish oil in Lin's research (Lin & Li, 2009). Lin *et al.* produced fish oil from the soapstock of marine fish through cooking, squeezing, centrifugal, clay adsorption, washing, and drying. While Pham *et al.* obtained the fish oil from fish waste/gut (not only the fat) with a yield of 25% using microwave-assisted extraction (Pham et al., 2022). Figure 4 shows the FAME yield obtained from different oils when the reaction temperature changed. The FFO-1 and FFO-2 showed an unpredictable trend and high error in experiment results. Meanwhile, FFO-3 showed a clear relationship between FAME yield and reaction temperature. These can be explained by the contaminant in the FFO-1 and 2, which can be polar components, such as free fatty acid (FFA) (Kara et al., 2018). The polar components could not produce FAME and prevented transesterification, which lowered the yield. Meanwhile, FFA was known as the soap formation source, inhibiting the reaction and decreasing the FAME yield.

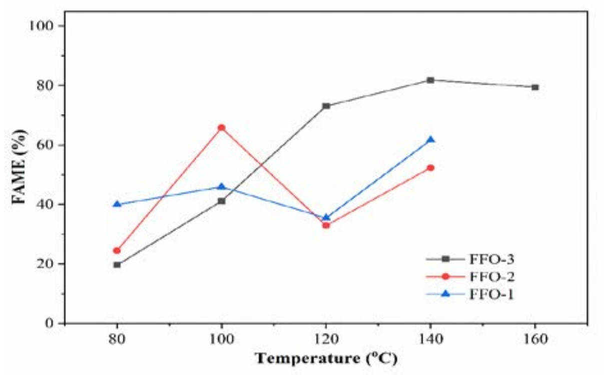

Figure 4. *FAME yields of 3 FFO types using Fe_xO_y/CaO catalyst. Experiment conditions: reaction time 3h, 5wt% catalyst, MeOH:oil molar ratio of 20:1*

Figure 5 shows the GC-MS chromatography of FAME products of three FFO. The chromatography revealed that the FAME produced from fish fat oil contained mainly methyl ester of C16:0 (palmitic acid), C18:0 (stearic acid), C18:1 (oleic acid) and C18:2 (linoleic acid). Moreover, the FFO-1 showed higher low intensity peaks than others, suggesting that it contained more FFA and impurity compounds. Furthermore, FFO-3 has a lighter yellow colour than FFO-1 and 2; these oils were solidification at room temperature after a few days. Biodiesel obtained from FFO-3 has a transparent yellow colour and no observation of solidification, while other products turned to a black colour and solid during storage. So, FFO-3 was chosen as the feedstock for further investigations. Repeat experiments (conditions: 140°C, 20:1 molar ratio, 2h and 10wt% catalyst) were conducted with FFO-3 oil 3 times and showed the standard error was lower than 0.5%.

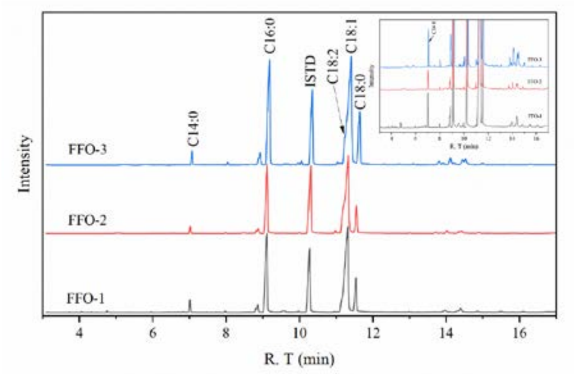

Figure 5. *GC-MS chromatography of 3 FFO types using Fe_xO_y/CaO catalyst. Experiment conditions: 140℃, reaction time 3h, 5wt% catalyst, MeOH:oil molar ratio of 20:1*

3.2.2. Effect of catalyst

Figure 6 compared the FAME yield archived by different catalysts at different reaction temperatures. As the reaction temperature was lower than 120°C, Fe_xO_y/CaO clearly gave a higher FAME yield than the CaO catalyst. When the reaction temperature was higher than 120°C, both catalysts showed almost the same efficiency, with the FAME yield of around

82%. The transesterification reached its equilibrium at 120°C since there was a slight discrepancy in FAME yield when the temperature changed from 120 to 160°C. Even the Fe_xO_y/CaO catalyst showed a decrease in FAME yield at 160°C. CaO showed a slightly higher FAME yield at high temperatures than Fe_xO_y/CaO. However, its FAME yield is very low at lower temperatures, *i.e.* 5%. This revealed that the addition of iron oxide helped decrease the activation energy of the reaction, resulting in higher yield at low temperatures. Fe_xO_y/CaO acted like a bifunctional catalyst in which CaO was the base site while adding iron oxide helped increase the base site number and strength (Amal et al., 2024; Xia et al., 2022).

3.2.3. Effect of reaction temperature

As shown in Figure 6, the higher the temperature, the higher the FAME yield. At low temperatures (<100°C), CaO gives a shallow conversion of triglyceride, while Fe_xO_y/CaO gives a higher FAME yield. The FAME yield increased from 80 to 140°C when the reaction temperature increased. However, the reaction might reach the equilibrium state around 140°C. After reaching the equilibrium state, the transesterification rate became high, and it is not the rate limit factor. At that time, the reaction rate depends on the diffusion of the reactants to the catalyst's surface or the diffusion of the FAME to the environment. The reaction with Fe_xO_y/CaO showed a slight decrease in FAME yield at 160°C. Higher temperature was not applied since it can affect the Teflon material. The autoclave showed advantages such as higher temperatures and pressure than other traditional reactors, e.g., reflux and microtube reactors. Therefore, we can investigate the reaction temperature higher than the boiling point of methanol. However, it also faced some disadvantages, such as no agitation, reactants and catalysts in three different phases, and difficulty controlling temperature. In conclusion, the reaction temperature was set at 140°C to obtain the highest FAME yield.

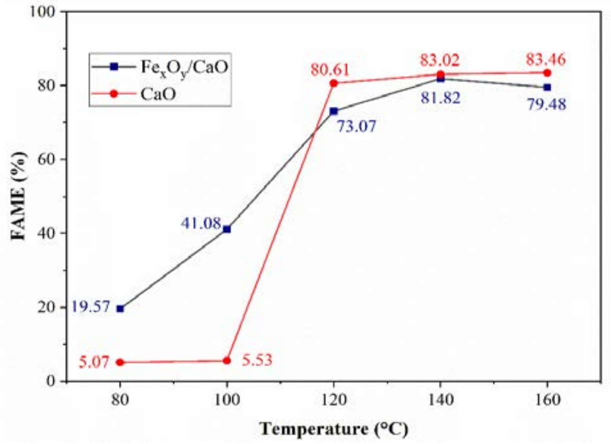

Figure 6. *FAME yields of CaO and Fe_xO_y/CaO catalysts. Experiment conditions: reaction time three h, 5wt% catalyst, MeOH: oil molar ratio of 20:1*

3.2.4. Effect of catalyst loading

To understand the effect of catalyst loading on FAME yield, the catalyst per cent (oil mass base) was varied from 2.5 to 15 wt%, and the result is shown in Figure 7. The amount of catalyst did not affect the FAME yield remarkably. The previous discussions said that this autoclave reactor has a disadvantage in agitation, so the solid catalyst is almost always retained at the bottom of the reactor. The circulation might occur due to the boiling of methanol. Hence, increased catalyst loading did not increase the interface at which the reaction occurred. However, the ten wt% catalyst showed a slightly higher FAME yield than other points and was chosen for further investigation.

3.2.5. Effect of reaction time

The reaction time was counted when the temperature reached the set value with the heating rate fixed at 10°C/min. The effect of reaction time is presented in Figure 8. From the result, the reaction time was not significantly affected by the FAME yield, and 2h showed a slightly higher FAME yield than others. The FFO in our research gave the maximum FAME yields of 84.28%, which is lower than other research even though we had pretreated the oil with MeOH. There might be some contaminants that cannot be transformed into FAME. In summary, the reaction time of 2h was chosen for the subsequent investigation.

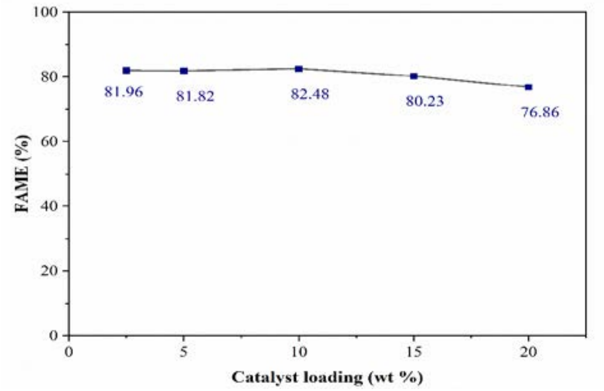

Figure 7. *Effect of catalyst loading to FAME yields. Experiment conditions: reaction temperature 140℃, reaction time 3h, MeOH:oil molar ratio of 20:1, Fe_xO_y/CaO catalyst*

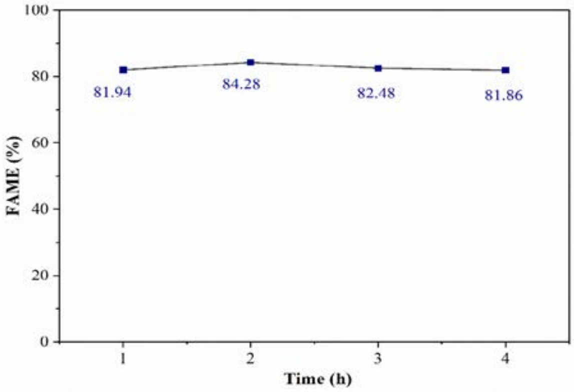

Figure 8. *Effect of reaction time to FAME yields. Experiment conditions: reaction temperature 140℃, 10wt% catalyst, MeOH:oil molar ratio of 20:1, Fe_xO_y/CaO catalyst*

3.2.6. Effect of MeOH: oil molar ratio

The effect of methanol amount was investigated, as shown in Figure 9. As the MeOH: oil molar ratio increased from 5:1 to 30:1, the FAME yield increased from 66.6% to 82%. The stoichiometric ratio for transesterification is 3:1, so a higher reactant ratio could promote the reaction rate. In this batch autoclave reactor, the circulation caused by MeOH boiling is the most efficient factor. Lastly, a higher MeOH: oil ratio was used, and a higher FAME yield was achieved.

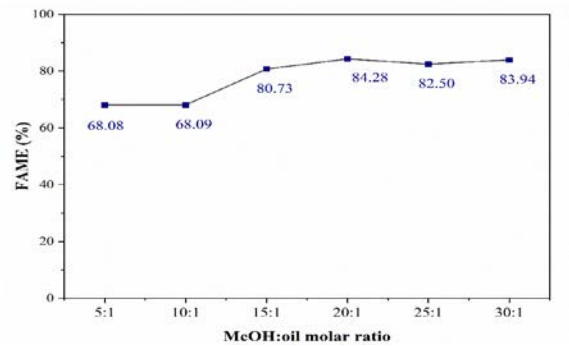

Figure 9. *Effect of MeOH: oil molar ratio to FAME yields. Experiment conditions: reaction temperature 140 ℃, reaction time 2h, 10wt% catalyst,* Fe_xO_y*/CaO catalyst*

4. Conclusions

The transesterification experiments were conducted in an autoclave reactor to reveal whether higher reaction temperatures could improve the FAME yield. Reaction temperature strongly affected the fame yield, while conditions such as catalyst loading, MeOH-ratio, and reaction time were less significant. The fish fat oil needed at least two steps to purify the oil. However, the FAME yield reached a maximum of 84.28%, suggesting that there were still some unreacted components inside the oil. Adding iron oxide to calcine oxide could enhance the reaction rate, leading to lower reaction temperatures.

- ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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TỔNG HỢP XÚC TÁC DỊ THỂ Fe_xO_y/CaO TỪ VỎ GHẸ VÀ ỨNG DỤNG CHO TRANSESTERIFICATION DẦU TỪ MỠ CÁ

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Ngày nhận bài: 07-4-2024; ngày nhận bài sửa: 03-6-2024; ngày duyệt đăng: 11-7-2024

TÓM TẮT

Ngày nay, biodiesel thu hút sự quan tâm lớn vì nó là nguồn nhiên liệu tái tạo, bền vững và có thể thay thế cho nhiên liệu hóa thạch. CaO được xem là một xúc tác dị thể tốt cho phản ứng transesterification để sản xuất biodiesel. Trong nghiên cứu này, vỏ ghe được tái chế để cung cấp CaO. CaO được kết hợp với sắt oxide tạo nên xúc tác hai chức năng để ứng dụng vào phản ứng transesterification cho dầu trích từ mỡ cá trong một thiết bị thủy nhiệt. Các đặc tính của xúc tác như sự phân hủy nhiệt, thành phần nguyên tố và hình thái được nghiên cứu với các phương pháp TGA và SEM-EDX. Sự ảnh hưởng của xúc tác, nhiệt độ, thời gian phản ứng và tỉ lệ mol MeOH:dầu đã được khảo sát. Kết quả cho thấy việc thêm sắt vào CaO đã làm tăng tốc độ phản ứng. Nhiệt độ phản ứng và tỉ lệ mol MeOH:dầu ảnh hưởng đến hiệu suất tạo FAME nhiều hơn là thời gian và phần trăm xúc tác sử dụng. Hiệu suất FAME cao nhất là 84,28% đạt được tại các điều kiện phản ứng 140℃, 2h, 10%KL Fe_xO_y/CaO và MeOH:dầu là 20:1.

***Từ khóa*: biodiesel; vỏ ghẹ; calcium oxide; iron oxide; dầu từ mỡ cá**