Alginate-CMC/Fe₃O₄-CaO nanocomposite as a catalyst for synthesis of biodiesel from waste cooking oil

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Abstract. Biodiesel as a renewable fuel was found as an environmentally friendly alternative for fossil fuels. In this work, a green heterogeneous catalyst, a combination of Alginate and carboxymethyl cellulose (CMC) biopolymer and Fe₃O₄-CaO supported by Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) was used as a catalyst for biodiesel production from waste cooking oil (WCO) through transesterification reaction. The maximum biodiesel yield obtained was 89.30 % with catalyst loading of 0.9 wt.% and reaction time of 2 h by using Alginate-CMC/Fe₃O₄-CaO nanocomposites. Properties of the obtained biodiesel (density and acid number) were close to the international standards (SNI and ASTM). These results indicate that alginate-CMC biopolymer can be utilized as a support catalyst derived from the biodegradable raw materials and is renewable and green as promising for heterogeneous catalysts in biodiesel production.

Keywords: Biodiesel, biopolymer, heterogeneous catalyst, nanocomposite, waste cooking oil

1. Introduction
Currently, energy demand from petroleum still increasing and it causes the depletion of crude oil resources [1]. British Petroleum Energy reported that about 80 % of the consumed energy in the worldwide came from crude oil, coal and natural gas [2]. The limited availability of the fossil fuels energies makes the use of renewable and sustainable fuels received significant attention, such as biodiesel [3, 4].

Biodiesel is a fatty acid methyl ester and promising alternative fuel that is environmentally friendly because it has several advantages such as non-toxicity, renewable and reduced greenhouse gas emissions [5, 6]. Biodiesel is produced through organic reaction by transesterification of vegetable oils or animal fats with alcohol in the presence of a catalyst to accelerate the reaction of fatty acid methyl ester (FAME) formation, the vegetable oils raw materials used generally, such as soybean oil, coconut and palm oil, and as waste cooking oil (WCO) [7]. Waste cooking oil has low oil quality and less attractive as a source of raw materials, but the use of WCO for biodiesel feedstock can efficiently reduce raw material cost and environmentally friendly [8, 9]. In addition, the reuse of WCO has the advantage of reducing water pollution [10, 11].

Homogeneous catalysts are high active with fast reaction rate, however it is difficult to be separated, regeneration and the resulting biodiesel is not impure, so the heterogeneous catalyst is needed because they are more environmentally friendly and easy for separation from products [12, 13].
The heterogeneous catalyst that is often used is CaO because of its low toxicity, regeneration, high basicity and high catalytic activity [14]. However, the shortcomings possessed by CaO are low thermal stability and low mechanical strength, so it needs to be impregnated with other oxides [15]. Calcium oxide combined with Fe$_3$O$_4$ can be applied as a catalyst in the synthesis of FAME (biodiesel) from palm oil [16]. Modification of carbon with alkaline earth metals as CaO-C can be applied as a heterogeneous catalyst for synthesis biodiesel [17].

In recent years, the combination of biopolymers and inorganic nanoparticles will form nanocomposites that have superior properties [18]. The use of biopolymers can be used as a catalyst support because it has a synergistic effect with inorganic materials [19]. Nano-crystal cellulose (NCC) was isolated from coconut residue by acid hydrolyzed and were supported with polyvinyl alcohol (PVA) can be composited with CaO as an environmentally friendly catalyst for FAME production from waste cooking oil [7].

However, the study of alginate and carboxy methyl cellulose CMC biopolymer combination for a good composite and impregnated with bimetal oxide Fe$_3$O$_4$-CaO are limited. In this study, the combination of Alginate-CMC with Fe$_3$O$_4$-CaO composites into Alginate-CMC/Fe$_3$O$_4$-CaO nanocomposites is investigated as a heterogeneous catalyst for the synthesis of biodiesel from waste cooking oil.

2. Materials and method

2.1. Materials
This research used several materials, namely sodium alginate (Merck), CMC (Merck) and CaCl$_2$.2H$_2$O (Merck) as a Ca$^{2+}$ source for alginate-CMC composites, CaCO$_3$ (Merck) for nano synthesis CaO, FeCl$_3$.6H$_2$O (Merck), FeCl$_2$.4H$_2$O (Merck) for synthesis nanoparticle Fe$_3$O$_4$, NaOH (Merck) as a precipitating agent, methanol (Merck), WCO (household waste) for biodiesel production.

2.2. Synthesis of alginate-CMC composite
Synthesis of Alginate-CMC composites was referred to the previous study [20]. 3 wt.% sodium alginate and 3 wt.% CMC were dissolved in aquadest, respectively. The two solutions were mixed with stirred until homogeneous. The 3 wt.% CaCl$_2$.2H$_2$O solution was added to the mixture using a syringe until a hydrogel was formed. The product in the form of Alginate-CMC hydrogel was dried at 37 °C and the hydrogel was characterized by instrument such as XRD, FTIR and SEM.

2.3. Synthesis of alginate-CMC/Fe$_3$O$_4$-CaO nanocomposite
The synthesis of Alginate-CMC/Fe$_3$O$_4$-CaO nanocomposite was carried out in two stages. The first stage was the synthesis of Fe$_3$O$_4$-CaO composites, and the second stage was the synthesis of Alginate-CMC/Fe$_3$O$_4$-CaO nanocomposites which referred to the study [14]. Fe$_3$O$_4$-CaO composites and Alginate-CMC/Fe$_3$O$_4$-CaO nanocomposites were characterized by FTIR, XRD, SEM and TEM.

2.4. Activity of catalyst
The catalytic activity in this study was carried out by firstly heating WCO to near 60 °C, then added methanol and Alginate-CMC/Fe$_3$O$_4$-CaO as catalyst with variations in the catalyst loading (0.6, 0.9, 1.2 wt.%), reaction time (1, 2, 3 h) and type of catalyst (CaO, Fe$_3$O$_4$-CaO, Alginate-CMC/Fe$_3$O$_4$-CaO). Biodiesel yield was calculated with equation 1 [21]:

$$\text{Yield (\%) = } \frac{\text{Biodiesel obtained (weight)}}{\text{WCO used in reaction (weight)}} \times 100$$
3. Results and discussion

3.1. Characterization by FTIR

Characterization using FTIR to analyze the functional groups is shown in figure 1. Figure 1a shows the spectrum of Alginate-CMC composite featuring an O–H stretch at 3500–3200 cm\(^{-1}\), a C–H stretch at 2925 cm\(^{-1}\), and typical peak at 1621 and 1426 cm\(^{-1}\), respectively showing asymmetric and symmetric stretching of the COO group [22] and at 1050 cm\(^{-1}\) and 937 cm\(^{-1}\) indicating the C–O–C stretch from the glycosidic bond and of C-H stretch from uronic acid [23]. Figure 2b shows Fe\(_2\)O\(_4\)-CaO with a typical peak around 573 cm\(^{-1}\) and 423 cm\(^{-1}\) indicating the Fe-O and Ca-O stretch and the Ca-O bond shown in the sharp peak around 869 cm\(^{-1}\) [14]. Figure 2c shows that the Alginate-CMC/Fe\(_2\)O\(_4\)-CaO nanocomposite featuring the peak that corresponds to the Alginate-CMC composite and the typical peak of the Fe\(_2\)O\(_4\)-CaO composite and there are shifting of each absorption peak.

3.2. Characterization by XRD

The XRD pattern of Alginate-CMC shown in figure 2a featured widen peaks at \(2\theta = 28.23^\circ\) [24] and weak peak at \(2\theta = 38.10^\circ\). Figure 2b shows the diffraction pattern of Fe\(_2\)O\(_4\)-CaO composite indicated the peaks at \(2\theta = 30.29^\circ, 35.64^\circ, 37.69^\circ, 53.95^\circ, 57.51^\circ\) and 63.13\(^\circ\) are typical peaks for Fe\(_2\)O\(_3\) nanoparticles. Whereas the peak at \(2\theta = 30.29^\circ, 35.64^\circ, 43.47^\circ, 46.65^\circ\) and 47.34\(^\circ\) are the typical peaks of CaO nanoparticles. These results are similar to the previous study [13]. Figure 2c shows the diffraction pattern of Alginate-CMC/Fe\(_2\)O\(_4\)-CaO featured the peak that corresponds to the Alginate-CMC composite and the typical peak of the Fe\(_2\)O\(_3\) and CaO and there are shifting of each the diffraction pattern peak. The results of FTIR and XRD support that the Alginate-CMC/Fe\(_2\)O\(_4\)-CaO nanocomposite has been successfully synthesized.

![Figure 1. FTIR Spectrum](image1.png)

![Figure 2. Diffraction pattern](image2.png)
3.3. **Characterization by SEM**

Surface morphology determination performed by SEM is shown in figure 3. The alginate-CMC composite in figure 3b was observed in the fibers form with relatively rough and porous, similar as the previous study [23]. The Fe$_3$O$_4$-CaO composite in figure 3b was observed the spherical non-uniform presence indicating the presence of CaO and Fe$_3$O$_4$ in the Fe$_3$O$_4$/CaO. Then, the presence of Fe$_3$O$_4$-CaO in the form of a spherical irregular spread evenly on the surface of Alginate-CMC can be observed in figure 3c. The distribution of Fe$_3$O$_4$-CaO on the alginate-CMC composite surface was observed by elemental mapping and to determine the mass percentage of each element by SEM-EDS as shown in figure 4.

The results of SEM-Mapping to observe the distribution of elements in Alginate-CMC/Fe$_3$O$_4$-CaO are shown in figure 4. Figure 4a shows the overall distribution of the elements Fe, Ca, O and C in the Alginate-CMC/Fe$_3$O$_4$-CaO. It can be observed that the presence of Fe and Ca element spread evenly on the surface of Alginate-CMC. SEM-EDS analysis was performed to determine the mass percentage of each element in the synthesized compound, as shown in figure 4b. The compositions of O, Ca, Fe and C are 43.2, 33.8, 12.5 and 10.6 wt.%, respectively, which indicates that the nanocomposite was successfully modified by Fe$_3$O$_4$-CaO composite, which spread evenly on the surface of the cellulose. This is supported with the results of the surface morphology of SEM in figure 3. Figure 4c to figure 4f show that the constituent elements of Fe$_3$O$_4$-CaO were evenly distributed on the Alginate-CMC/Fe$_3$O$_4$-CaO surface, which confirmed the successful synthesis of the Alginate-CMC supported catalyst.

![Figure 3](image-url)
Figure 4. Elemental distribution mappings (a) overall element, (b) EDS, (c) Fe, (d) C, (e) Ca, (f) O of Alginate-CMC/Fe$_3$O$_4$-CaO.

3.4. Characterization by TEM

The characterization of Alginate-CMC/Fe$_3$O$_4$-CaO using TEM is to observe the structure of nanocomposites. Figure 5a shows the TEM imaging of Alginate-CMC/Fe$_3$O$_4$-CaO nanocomposite with a 50 nm. The catalyst particles had an irregular shape which can be observed in the gray color of Alginate-CMC and Fe$_3$O$_4$-CaO with dark shade in the form of spherical and hexagonal particles with irregular shape on the surface of Alginate-CMC biopolymer. These results support the SEM-Mapping characteristics. Figure 5b and figure 5c are the high-resolution of TEM images (10 and 5 nm scale)
it can be observed the crystals of Fe$_3$O$_4$-CaO composite and the porous Alginate-CMC of Alginate-CMC/Fe$_3$O$_4$-CaO nanocomposite.

3.5. Catalytic activity

3.5.1. Effect of catalyst loading. Catalytic activity of transesterification reaction from WCO done by varying the parameters were optimized to obtain the maximum yield of biodiesel includes (i) the catalyst loading, (ii) the reaction time and (iii) type of catalyst.

The variation of the yield with the catalyst loading is shown in figure 6. The yield of biodiesel was found to be increase with the increase of the catalyst loading. These data were in line with the results of previous studies [25]. This is due to the increased of catalysts loading, which will increase the number of activated complexes of the catalyst with reactant and will increase the biodiesel product [19]. In this study, the maximum of catalyst loading is 0.9 wt.% with a yield biodiesel of 89.30 %. When the catalysts loading was increased to 1.2 wt.%, there was no significant increase.

![TEM Image](image1.png)

**Figure 5.** TEM image of Alginate-CMC/Fe$_3$O$_4$-CaO (a) 50 nm, (b) 10 nm, and (c) 5 nm scale.

![Yield Chart](image2.png)

**Figure 6.** Effect of the catalyst loading on biodiesel yield.
3.5.2. **Effect of reaction time.** The effect of reaction time on the percent yield of biodiesel from WCO in this work was done in 1 to 3 h as shown in figure 7. The increase in reaction time will affect the collision of particles and the interactions that occur between methanol, catalyst and oil so that the percent yield increases. The optimum biodiesel yield was obtained at 2 h reaction time of 89.30 %. This is faster than that of our previous study for 5 h with a biodiesel yield of 89.2 % using nanocomposite comprising cellulose and nanomagnetite [19]. The combination of Fe$_3$O$_4$-CaO composite with Alginate-CMC biopolymer increased the reaction rate significantly. Further increase to 3 h resulted in the decrease in biodiesel yield to 85.00 %. This is due to the transesterification is a reversible reaction and if the reaction time exceeds the equilibrium time, the reaction will shift towards the reactants so that the biodiesel yield was decreased [19, 26].

3.5.3. **Effect of type of catalyst.** In this study, the effect of the catalyst type to the catalytic activity was also done as a comparison to the Alginate-CMC/Fe$_3$O$_4$-CaO nanocomposite as shown in figure 8. The reaction conditions used a catalyst amount of 0.9 % wt., the reaction temperature was 65 °C, the oil : methanol ratio 1:6 and the reaction time was 2 h. Figure 8 shows that the transesterification reaction from WCO to biodiesel using CaO, Fe$_3$O$_4$-CaO and Alginate-CMC/Fe$_3$O$_4$-CaO nanocomposite as catalyst obtained a biodiesel yield of 70.72 %, 85.00 % and 89.30 %, respectively.

![Figure 7. Effect of the reaction time on biodiesel yield.](image1)

![Figure 8. Effect of type of catalyst on biodiesel yield.](image2)
Table 1. Physical properties of biodiesel

| Properties                        | Results | SNI 7182:2015 | ASTM 6751 |
|-----------------------------------|---------|---------------|-----------|
| Density (g cm\(^{-3}\)) at 25 °C | 0.890   | 0.85–0.90     | 0.85–0.90 |
| Acid number (mg\(_{KOH}\) g\(^{-1}\)) | 0.442   | < 0.50        | < 0.5     |

These results indicated that CaO nanoparticles are the main active site for the transesterification reaction from WCO to biodiesel and the presence of Fe\(_3\)O\(_4\) as a catalyst promoter in the Fe\(_3\)O\(_4\)-CaO composites can increase the catalytic activity. By using the Alginate-CMC/Fe\(_3\)O\(_4\)-CaO nanocomposite catalyst with the mass ratio of Alginate-CMC to Fe\(_3\)O\(_4\)-CaO (2:2), the biodiesel yield was 89.30 %. These results indicated that with the use of alginate-CMC biopolymer a higher percent yield was obtained. This is due to alginate-CMC have porous surface (figure 3) and can be a good supporting catalyst.

3.6. Properties of biodiesel

Analysis of the physical properties of the biodiesel (density and acid number) is shown in table 1. The biodiesel was a slightly yellowish liquid with the density of 0.890 g cm\(^{-3}\) and acid number was 0.442 mg\(_{KOH}\) g\(^{-1}\). The results obtained were very close to the required values ASTM 6751 [1] and SNI 7182:2015 [27].

4. Conclusion

The biopolymer-based catalyst was successfully used as a heterogeneous catalyst for biodiesel preparation from WCO. Alginate-CMC acts as a support catalyst for Fe\(_3\)O\(_4\)-CaO composites and the results are supported by characterization with FTIR, XRD, SEM-Mapping and TEM. The maximum biodiesel yield obtained was 89.30 % with catalyst loading of 0.9 wt.% and reaction time 2 h was applied in Alginate-CMC/ Fe\(_3\)O\(_4\)-CaO nanocomposites. The properties of biodiesel (density and acid number) were close to the international standards (SNI and ASTM). These results indicate that alginate-CMC biopolymer as support catalyst with Fe\(_3\)O\(_4\)-CaO composite can be used as an effective catalyst for biodiesel synthesis from WCO.

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References

[1] Helmiyati H, Budiman Y, Abbas G H, Dini F W and Khalil M, Heliyon 2021 7, e06622
[2] Shimada G B and Cestari A, Renew. Energy. 2020 156, 389-94
[3] di Bitonto L, Reynel-Avila H E, Mendoza-Castillo D I, Bonilla-Petriciolet A, DuránValle C J and Pastore C, Renew. Energy 2020 160, 52-66
[4] Helmiyati, Abbas G H, Budiman Y and Ramadhan S, Rasayan J. Chem. 2020 13, 298-305
[5] Chua S Y, Periasamy L A, Goh C M H, Tan Y H, Mubarak N M, Kansedo J, Khalid M, Walvekar R and Abdullah E C, J. Ind. Eng. Chem. 2020 81, 41-60
[6] Helmiyati H and Suci R P, AIP Conf. Proc. 2019 2168, 020063
[7] Zik N, Sulaiman S, Jamal P Renew. Energy. 2020 155, 267-77
[8] Kumar M and Sharma M P, Renew. Sust. Energy Rev. 2015 44, 814-23
[9] Fawaz E G and Salam D A, Sci. Total Environ. 2018 637-638, 1230-40
[10] Mazubert A, Taylor C, Aubin J and Poux M, Bioresour. Technol. 2014 161, 270-79
[11] Trisnawati L and Helmiyati H, IOP Conf. Ser.: Mater. Sci. Eng. 2020 763, 012012
[12] Huang J, Zou Y, Yaseen M, Qu H, He R and Tong Z, Fuel 2021 290, 119799
[13] Azahra S N A R and Helmiyati, IOP Conf. Ser.: Mater. Sci. Eng. 2020 959, 012016
[14] Helmiyati H and Masriah I, AIP Conf. Proc. 2019 2168, 020062
[15] Ali M A, Al-Hydayi I A and Al-Hattab T A, Bull. Chem. React. Eng. Catal. 2017 12, 460-468
[16] Helwani Z, Ramli M, Saputra, E Bahrudin B, Yolanda D, Fatra W, Idroes G M, Muslem M, Mahlia T M I and Idroes R, Catalysts 2020 10, 164
[17] Jamil F, Kumar P S M, Al-Haj L, Myint M T Z, Al-Muhtaseb A H, Energy Convers. Manag.: X 2020 10, 100047
[18] Helmiyati H and Dini F W, AIP Conf. Proc. 2018 2023, 020101
[19] Helmiyati and Anggraini Y, Int. J. Technol. 2019 10, 798-807
[20] Wu L, Lin X, Zhou X and Luo X, Appl. Surf. Sci. 2016 384, 466-79
[21] Seffati K, Esmaeili H, Honarvar B and Esfandiari N, Renew. Energy 2020 147, 25-34
[22] Salama H E, Aziz M S A and Isehli M, Int. J. Biol. Macromol. 2019 139, 614-20
[23] Ramadhani S and Helmiyati H, AIP Conf. Proc. 2020 2242, 040026
[24] Agarwal C, Narayana S N, Pal K, Pramanik K, Giri S and Banerjee I, Int. J. Biol. Macromol. 2015 75, 409-17
[25] Chingakham C, David A and Sajith V, Chin. J. Chem. Eng. 2019 27, 2835-43
[26] Mansir N, Teo S H, Mijan N and Taufiq-Yap Y H, Catal. Commun. 2021 149, 106201
[27] Widdyaningsih L, Setiawan A, Santoso S P, Soetaredjo F E, Ismadji S, Hartono S B, Ju Y, Tran-Nguyen P L, Yuliana M, Renew. Energy 2020 154, 99-106