Synthesis and catalytic evaluation of hematite (α-Fe₂O₃) magnetic nanoparticles from iron sand for waste cooking oil conversion to produce biodiesel through esterification-transesterification method

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Abstract. Indonesia's catalyst needs to reach 2000 tons/year with active period of 1 up to 2 years. The catalyst requirement is largely filled with import catalysts. Iron sand has a potential to be used as a catalyst mainly because of the hematite magnetic mineral content (α-Fe₂O₃). α-Fe₂O₃ can be synthesized from iron sand using coprecipitation and calcination method. Performance of these synthesized catalyst evaluated through the production of biodiesel from waste cooking oil by esterification-transesterification method. The catalyst preparation by chemical coprecipitation method followed with calcination. Catalyst was characterized by using XRD, SEM-EDX, BET, and PSA and tested for biodiesel production. α-Fe₂O₃ phase was obtained at calcination temperature 650°C, 700°C, 750°C and 800°C. The best character is given at temperature 700°C. Biodiesel obtained meets SNI (Standar Nasional Indonesia) based on density, viscosity, and acid number. Yield of biodiesel obtained by using α-Fe₂O₃ calcined at 700°C reaches 86.781% while Fatty Acid Methyl Ester (FAME) content obtained reaches 87.880%.

1. Introduction
Catalyst is a substance that is used to accelerate a reaction, reacts but does not turn into products [1]. Catalysts are important substances in industry, this statement arises because the fact that more than 75% of the chemical production process in the industry is synthesized with the help of catalysts. Indonesia's catalyst needs reach 2,000 tons/year with an active period of around 1 up to 2 years. This large enough catalyst requirement is mostly fulfilled by imported catalysts due to the limited local catalyst industry [2].

Indonesia has many resources that can be developed into catalysts, one of them is iron sand. Indonesia has abundant iron sand with resources of 4,459,586,351 tons and reserves of 808,938,227 tons [3]. Iron sand has the potential to be developed as a catalyst due to hematite (α-Fe₂O₃) as magnetic mineral content. However, the content is not naturally present in iron sand, synthesis process is needed to get the content.

Several studies related to iron sand synthesis have been carried out [4-6]. In these studies, α-Fe₂O₃ has been successfully synthesized from iron sand. Rasheed and Meera [6] used biological and calcination methods in the synthesis process and Mufti et al. [5] and Lubis et al. [4] used coprecipitation and calcination methods. α-Fe₂O₃ was applied to removal of heavy metal contaminants from water/wastewater [6] and α-Fe₂O₃ can also applied as photocatalyst in photodegradation of indigo carmine (IC) dyes [4].
In previous studies have weakness about not yet a lot of optimization process in the synthesis of \( \alpha-Fe_2O_3 \). Considering that the synthesis process is always terminated by calcination, optimization during the calcination process become important to do. Calcination temperature optimization is expected to bring out the best characters of \( \alpha-Fe_2O_3 \). In addition, it has not been widely studied about the catalytic ability of \( \alpha-Fe_2O_3 \) synthesized from iron sand. \( \alpha-Fe_2O_3 \) synthesized from iron sand usually only used as adsorbent, therefore another study through application to determine the catalytic ability of \( \alpha-Fe_2O_3 \) was important. In the other hand, \( \alpha-Fe_2O_3 \) has fairly good catalytic performance in biodiesel production [7-9] but \( \alpha-Fe_2O_3 \) used was prepared from commercial chemicals [7-9]. The results of the study obtained 92.1%, 92.2% and 92% yield of biodiesel. Based on these studies, it can be concluded that \( \alpha-Fe_2O_3 \) can be used as a catalyst in biodiesel production and considering that the \( \alpha-Fe_2O_3 \) used was synthesized from commercial chemicals such as Iron (III) Nitrate Nonahydrate (Fe(NO$_3$)$_3$).9H$_2$O, the use of synthesized \( \alpha-Fe_2O_3 \) was even more synthesized from natural materials such as iron sand to be interesting. Catalysts synthesized from natural materials for biodiesel production have been done before. The CaO catalyst were prepared by limestone, calcium hydroxide and calcium carbonate. The yield of biodiesel obtained from the experiment was 89.98% for the catalyst from limestone; 85.15% for the catalyst Ca(OH)$_2$; and 78.71% for CaCO$_3$ catalyst [10]. This proves that the catalyst synthesized from natural materials has good catalytic ability.

Indonesia has natural materials that can be developed to hematite like iron sand. In this study iron sand was carried out by using chemical precipitation and calcination method. The objective of the research was studied to bring out the best characters of \( \alpha-Fe_2O_3 \) by using synthesized from natural materials for biodiesel production have been done before. The CaO catalyst were prepared by limestone, calcium hydroxide and calcium carbonate. The yield of biodiesel obtained from the experiment was 89.98% for the catalyst from limestone; 85.15% for the catalyst Ca(OH)$_2$; and 78.71% for CaCO$_3$ catalyst [10]. This proves that the catalyst synthesized from natural materials has good catalytic ability.

2. Experimental Methods

2.1. Tools and Materials
The tools used include: beaker glass, electric stove, neodymium magnet, magnetic stirrer, erlenmeyer, Liebig condenser, vacuum oven, vacuum pump, furnace, boiling three neck, Quantachrome Instrument, JED 2300 Analysis Station, Bettersize 3000 plus particle size analyser, XRD Instrument, XRF Instrument and GC-MS instrument. The materials used include: Iron sand (taken from Adipala Beach, Cilacap, Central Java), Hydrochloric Acid 37% (HCl 37%, Merck), Ammonium Hydroxide 25% (NH$_3$.OH 25%, Merck), Sulphuric Acid 97% (H$_2$SO$_4$ 97%, Merck), Methanol (CH$_3$OH, Merck) and Polyethylene Glycol 4000 (PEG 4000).

2.2. Iron Sand Characterization and Treatment
Iron sand was characterizing using XRF (X-Ray Fluorescence Spectrometry). If XRF results showed that iron sand containing much impurities, impurities were separated by magnetic separation method to obtain higher iron content.

2.3. Synthesis of Iron Sand and Characterization
Hematite (\( \alpha-Fe_2O_3 \)) synthesis method used referred to be undertaken method [11] with modification. Method used is chemical coprecipitation followed with calcination to obtain hematite phase (\( \alpha-Fe_2O_3 \)).

20 grams of iron sand filled in beaker glass and added 40 mL of HCl 37%. A mixture was stirred at 70°C for 30 min and followed by filtration using Whatman filter paper (no.1). The filtrate was mixed with PEG (Polyethylene Glycol) 4000 which has been melted previously with a volume ratio of 1:5. A mixture was stirred at 70°C for 40 minutes. 30 mL of NH$_3$.OH 25% was added to mixture and stirred at 70°C for 40 min until precipitation forming. The solids product was washed with distilled water. The catalyst was separation by using filtration in vacuum condition. The catalyst was dried in oven at 120°C for 2 hours. The catalyst was calcined in tubing furnace at variation temperature of 650°C, 700°C, 750°C and 800°C. The catalysts were characterized using XRD, BET, PSA and SEM-EDX analyses.
response observed from the analysis are: the appearance of $\alpha$-Fe$_2$O$_3$ phase, morphology, material content, surface area, pores volume and particle size.

2.4. Treatment and Characterization of Waste Cooking Oil
Waste cooking oil taken as much as 1500 mL and heated to 150°C for 40 minutes. Then waste cooking oil was filtered with Whatman filter paper. Waste cooking oil content was analysed by using GC-MS while FFA (Free Fatty Acid) content of waste cooking oil was analysed by using acid-base titration. Free Fatty Acid (FFA) calculated by equation:

$$% \text{FFA} = \frac{\text{Vol NaOH (ml)} \times N \text{ NaOH (N)} \times \text{MW of fatty acid}}{\rho_{\text{WCO}} \times \text{Vol Sample} \times 1000} \times 100\%$$ (1)

2.5. Biodiesel Production

2.5.1. Esterification. Esterification method used refers to undertaken method [12] with slight modifications. This method used methanol and H$_2$SO$_4$ as catalyst to reduce FFA content in waste cooking oil. Waste cooking oil was heated to 70.0±1.0°C temperature then sulphuric acid in methanol was added, which was considered as the starting point of reaction. Esterification performed by using methanol: waste cooking oil molar ratio of 5:1, H$_2$SO$_4$ 1% wt of waste cooking oil at 70°C for 300 minutes. After esterification has done, mixture is moved to separating funnel and washed with warm water. Bottom product which is water discarded. After that excess methanol separated from esterification product. Esterification product taken to be tested Free Fatty Acid (FFA) content by using acid-base titration. FFA calculated by using equation (1). If FFA content is ≥2%, Esterification method repeated (continued to 2nd stage), and if FFA content is ≤2% transesterification method is allowed.

2.5.2. Transesterification. Transesterification method refers to undertaken method [8] with slight modifications. A mixture of waste cooking oil, methanol (molar ratio of 15:1) and catalyst (1% wt of oil) was heated at 65°C for 3 hours. The product was discharged and centrifuged at 3500 rpm to separate the solid catalyst. After catalyst separated, liquid product moved to separating funnel and let to settle to three layers for 12 hours. Glycerol at the bottom layer, Fatty Acid Methyl Ester (FAMEs) at the middle and excess methanol at the top layer. After that FAMEs separated from excess methanol and glycerol.

2.6. Biodiesel Characterization
Product will be characterized based on density, viscosity, acid number, yield and content of methyl esters.

3. Result and Discussion

3.1. Properties and Treatment of Iron Sand
Based on XRF analysis (table 1), element which has the highest content in iron sand is Fe (iron) with a percentage of 43.076%. Besides Fe, there are other elements in iron sand. Because what will be used in this study is Fe, and Fe content is still quite low, magnetic separation was carried out with the aim of increasing the content (purity) of Fe (iron).
Table 1. XRF analysis result.

| Element | Content (%) | Element | Content (%) | Element | Content (%) |
|---------|-------------|---------|-------------|---------|-------------|
| Na      | 0.271       | As      | 0.029       | Ni      | 0.148       |
| Mg      | 0.649       | Se      | 0.030       | Cu      | 0.075       |
| Al      | 1.077       | Br      | 0.031       | Zn      | 0.122       |
| Si      | 4.724       | Rb      | 0.174       | Ga      | 0.032       |
| P       | 2.655       | Sr      | 0.462       | Ge      | 0.023       |
| S       | 3.023       | Zr      | 0.561       | Au      | 0.041       |
| Cl      | 4.426       | Mo      | 0.587       | Hg      | 0.031       |
| K       | 14.237      | Pd      | 0.049       | Ti      | 0.034       |
| Ca      | 3.813       | Ag      | 0.068       | Ba      | 0.661       |
| Sc      | 8.392       | Cd      | 0.097       | Hf      | 0.068       |
| Ti      | 1.619       | In      | 0.111       | Ta      | 0.077       |
| V       | 0.487       | Sn      | 0.164       | W       | 0.067       |
| Cr      | 0.178       | Sb      | 0.209       | Pt      | 0.039       |
| Mn      | 0.537       | Te      | 0.289       | Pb      | 0.034       |
| Fe      | 43.076      | In      | 0.348       | Bi      | 0.051       |
| Co      | 5.056       | Cs      | 0.549       | Ce      | 0.519       |

3.2. Characterization of Synthesized Iron Sand

3.2.1. X-ray Difraction (XRD) Analysis. Fig. 1 shows diffractogram of the synthesized iron sand. From the diffractogram, it can be seen that all patterns show a characteristic XRD pattern of hematite (α-Fe₂O₃) (ICDD cards no. 33-0664) [4, 13]. All observed peaks were indexed according to rhombohedral (hexagonal) structure (space group: R-3C), with lattice constants a=0.5034 nm and c=1.375 nm [14]. This shows that the α-Fe₂O₃ phase has been successfully obtained using coprecipitation and calcination methods. It can also be seen that there are no characteristic peaks indexed except α-Fe₂O₃ (usually there are impurities such as γ-Fe₂O₃ and Fe₃O₄). Narrow sharp peaks indicate that α-Fe₂O₃ has a high crystallinity, implying that the purity of α-Fe₂O₃ is high.

![Figure 1. XRD pattern of synthesized iron sand.](image-url)
Besides being able to show the phase, through XRD analysis can also be known the particle size. The method used to measure particle size from XRD analysis is called the Scherer method. This method is actually used to determine crystal size, not particle size. However, for nanometer-sized particles, usually one particle only contains one crystal so that the calculated crystal size can be a particle size [15]. The particle size of crystal is shown in Fig. 2.

![Figure 2. Crystal (particle) size of synthesized iron sand.](image)

Based on the difference in calcination temperature, it can be seen that the greater the calcination temperature, the greater the size of the crystal (particles). This can occur due to the sintering of nanoparticles. There are two mechanisms for sintering of nanoparticles: particle migration and coalescence (PMC) and Ostwald Ripening (OR). PMC involves the mobility of particles in a Brownian-like motion, with subsequent coalescence leading to nanoparticle growth. In contrast, OR involves the migration of atoms or mobile molecular species, driven by differences in free energy. PMC and OR could occur, especially at high temperatures [16]. The higher the temperature, the possibility of sintering of nanoparticles (PMC and OR) will be even greater.

3.2.2. Scanning Electron Microscope Energy Dispersive X-ray Spectrometer (SEM – EDX) Analysis.

Fig. 3 shows the results of SEM analysis of iron sand that has been synthesized. The results show that particles form clusters with polymorphic structures. Cluster formation is likely due to the magnetic relationship of the particles so that they tend to group. It can also be seen that the particles are evenly distributed but have a less homogeneous particle shape and size, some of which have rounded spherical shapes, some of which form almost cubic structures. There was no significant difference due to an increase in calcination temperature.

Based on the results of EDX analysis (table 2), the most elements found in particles are Fe with content above 56% (% mass). This proves that with magnetic separation and also chemical co-precipitation, the purity of Fe can increase which previously only contained 43.076% in raw materials. In the particles it was also detected other elements such as Mg, Al, Ti, Si, Cu and Zn. The presence of these elements is indicated due to the raw material of iron sand. The element O appears due to the oxidation process. While element C is most likely to come from contamination of analytic equipment.

Based on the difference in calcination temperature, it can be seen that the content of C increases with increasing calcination temperature. This is probably due to the use of carbon-based containers when calcination so that the possibility of causing contamination, and the higher the calcination temperature, the higher the possibility of carbon sticking and carrying. For other content the phenomenon of the effect of calcination temperature cannot be explained.
Figure 3. SEM Analysis Results with Magnification of 7.500x (a)650°C (b)700°C (c)750°C (d)800°C.

Table 2 EDX analysis results.

| Element (% mass) | Calcination Temp. |
|------------------|-------------------|
|                  | 650°C | 700°C | 750°C | 800°C |
| Al               | 1.11   | 2.39  | 3.54  | 1.85  |
| Fe               | 64.88  | 62.92 | 59.02 | 56.22 |
| Si               | 0.24   | -     | -     | -     |
| Cu               | 0.92   | -     | -     | 0.93  |
| Zn               | 0.67   | -     | -     | -     |
| Mg               | -      | 0.76  | 1.25  | 0.51  |
| Ti               | 3.77   | 4.5   | 4.3   | 3.73  |

3.2.3. Brunauer, Emmett and Teller (BET) Analysis. BET analysis is used to find out surface area and pore volume of $\alpha$-Fe$_2$O$_3$. The pore and surface characters are presented in table 3. Surface area and pore volume represent the active surface which can occur in contact with the reactants in the process reaction. The greater the active surface of the catalyst, the better catalyst activity is expected [17].

Based on the calcination temperature differences, it can be seen that when the calcination temperature is more than 700°C, surface area and pore volume of $\alpha$-Fe$_2$O$_3$ will decreases. Particles will change at temperatures higher than 700°C. This is because at high temperatures, kinetic energy will increase and then the constituent atoms will diffuse with particles adjacent to each other and mutually binding (agglomeration) [18].

Table 3. BET analysis results.

| Calcination Temp. | Surface Area (m$^2$/g) | Pore Volume (cc/g) |
|-------------------|------------------------|--------------------|
| 650°C             | 19.332                 | 0.031              |
| 700°C             | 22.988                 | 0.040              |
| 750°C             | 14.358                 | 0.022              |
| 800°C             | 10.547                 | 0.016              |
3.2.4. Particle Size Analyser. Fig. 4 shows the particle size distribution based on cumulative volume expressed in percent distribution. Based on the results of the PSA analysis, it was found that the particles have a micro size, this result is different from the results obtained in the use of XRD analysis. From the difference in calcination temperature also cannot be concluded the relationship between the calcination temperature and particle size. The particle size tends to increase from the calcination temperature of 650°C to 700°C, then there is a very extreme increase at a temperature of 750°C, and then decreases at a temperature of 800°C.

The cause of the different results between PSA and XRD and also the phenomena that cannot be concluded is probably due to the occurrence of particle agglomeration at the time of PSA analysis. In PSA analysis, water is used as dispersion medium, so the chance of small particles joining together causes by water is very large.

The emergence of this indication is strengthened due to the report stated that in water-Fe$_3$O$_4$ nanofluid preparations, dispersants or surfactants must be added to get a stabilization mechanism. This stabilization aims to prevent flocculation. From the report, it can be concluded that Fe$_3$O$_4$ tends to agglomerate if using water as dispersion medium without dispersants or surfactants. It’s also possible to apply to α-Fe$_2$O$_3$ which originates from Fe$_3$O$_4$[19].

![Figure 4. Particle size distribution from PSA analysis.](image)

3.3. Characterization of Biodiesel

Yield of biodiesel obtained in this study is 86.871%. Others characters such as density, acid number and viscosity have values of 888.3 kg/m$^3$, 0.27 mg-KOH/gr, and 5.685 mm$^2$/s. Can be said that biodiesel obtained in this study has good quality because it meets SNI 7182-2015 biodiesel standards (850–890 kg/m$^3$ for density, max 0.5 mg-KOH/gr for acid number and max 6 mm$^2$/s for viscosity) [20].

To determine the content of biodiesel, GC-MS analysis was carried out. The results of the analysis can be seen in Fig. 5. Based on GC-MS analysis can be known that the content of methyl esters is 87.880%. This results is quite high considering that there is no process optimization and also refining biodiesel. It can be said that synthesized α-Fe$_2$O$_3$ has a high enough potential to be used as a catalyst in biodiesel production. This might be caused α-Fe$_2$O$_3$ consist of positively charged metal ions act as electron acceptors and negative oxygen ions as proton acceptors. Methoxide anion in the catalyst will react with triglyceride molecules [21]. The formation of this nanocomposite (metal oxide) increase catalytic activity due to increased catalyst active sites.
4. Conclusion
Hematite (α-Fe₂O₃) has been successfully synthesized using the chemical coprecipitation and calcination method. The calcination temperature that gives the best α-Fe₂O₃ character is 700°C. Biodiesel produced using α-Fe₂O₃ catalyst has density, viscosity and acid number in accordance with SNI (Standar Nasional Indonesia). Yield of biodiesel obtained in this study is 86.781% and the content of methyl esters (FAMEs) is 87.880%.

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