Biodiesel Synthesis from Palm Fatty Acid Distillate (PFAD) by Palm Oil Industry Product using Metal-Hydroxyapatite Catalyst

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Abstract. Hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂), has been successfully synthesized hydrothermally from eggshells or shells through the formation of Precipitate Calcium Carbonate (PCC). For biomedical applications, some synthesized HAp are still calcium deficient (HApdc), so they do not meet specifications as implants or fillers of bone and teeth. Because it is resistant to high temperatures and has pores, in this study HApdc used as a catalyst for the synthesis of biodiesel from palm fatty acid (PFAD). In the initial stage, HAp is impregnated with metals: Cu, Co and Ni and produces catalysts Cu-HAp, Co-HAp and Ni-HAp. Furthermore, the metal-HAp catalyst is used in the PFAD esterification process into biodiesel. PFAD has free fatty acid (ALB) levels reaching 90%. Cu-HAp catalyst, giving the highest conversion yield of biodiesel (94.4%), with specific gravity 0.84 g/ml (40 °C, viscosity 4,811 Cst, acid number 0.5533 gr KOH / gr oil, flash point 120 °C and a calorific value of 9813 Kcal/kg in accordance with ISO standards-04-7182-2006. Analysis of the chemical components in the form of biodiesel from PFAD: Methyl Ester Hexadecanoat (53.1%); ME 9, Octadecenoat (32.81%); ME octadecanoic (2.59 %) and ME 9,12, Octadecadienoic (5.93%) and a little Hexadecanoic Acid (5.57%).

1. Introduction
In the refining process of Crude Palm Oil (CPO) as a raw material for oleochemical-based downstream industries, 95% Refined, Bleached and Deodorized Palm Oil (RBDPO) and 5% Palm Fatty Acid Distillate (PFAD) are produced as by-products. PFAD as a by-product, is known to have high levels of free fatty acids (>85%), so it is very feasible to be used as raw material for producing alternative fuels such as biodiesel [1]. The availability of PFAD as a raw material for producing biodiesel in Indonesia, is very profitable. According to GAPKI, in 2017 Indonesia's CPO production reached 42 million tons, and in the next few years it is estimated to penetrate 50 million tons. The high CPO production indirectly impacts the PFAD produced by the CPO processing industry. According to Lintas News the by-product of the CPO processing industry in the form of PFAD reaches more than one million tons/year [2,3].

Biodiesel synthesis (FAME, Fatty Acid Methyl Ether) can be carried out using oil or fat raw materials through the transesterification process with a homogeneous catalyst NaOH or KOH, if the FFA content in oil is <2%. A two-step process, namely esterification and continued with transesterification, is carried out if the oil FFA level is>5%, with an acid catalyst such as HCl or H₂SO₄ in the esterification process. However, the use of heterogeneous catalysts for biodiesel
production, is more advantageous than homogeneous catalysts. For example, sulphonated glucose acid catalyst [4] and heterogeneous sulphonated kenaf seed cake (SO$_3$H-KSC) catalyst [5] is used in biodiesel production from PFAD. Natural zeolite pre-heated with KNO$_3$ has utilized as a catalyst for producing biodiesel from rice bran [6]. The use of hydroxyapatite in addition to being a coating and filler in bone and dental implants, has also been used as an adsorbent and catalyst or catalyst support. Large surface area, causing synthetic hydroxyapatite is very beneficial when used as catalyst adsorbent or catalyst support [7, 8, 9].

In this study, HAp nanoparticles created through the formation of Precipitated Calcium Carbonate (PCC) from shells, were impregnated with transition metals Cu, Co and Ni to produce catalysts Cu-HAp, Co-HAp and Ni-HAp. The resulting catalyst is used in the biodiesel production from PFAD. The use of HAp as a catalyst is basically very beneficial, because this material has pores, has a large surface area and is chemically resistant and to high temperatures up to 1200 °C [10].

2. Methodology

2.1. Materials and Tools
The material used is PFAD obtained from PT. Sari DumaiSejati, Synthesized Hydroxyapatite, Ni(NO$_3$)$_2$.6H$_2$O, CuSO$_4$.5H$_2$O, Co(NO$_3$)$_2$.6HO, methanol and aquadest. The main tool used hot plate stirrer, Thermo Haake, an analytical balance, ovens and furnaces. Tools for analysis are X-ray diffraction (X'Pert Powder DY 3688) with Cu Ka radiation, scanning electron microscopy (SEM) linked to energy dispersive X-ray micro analysis (EDX) (JEOL JED 2300), and the surface area of the metal-hydroxyapatite were characterized using BET measurements Surface Area Analyzer (SAA, Quantachrome NovaWin2).

2.2. Metal Impregnation on HApParticles
To produce a metal-HAp catalyst that is 0.15 grams of metal from its salt and 4.85 grams of HAp mixed into a 250 ml beaker with a 50 ml aquadest added Stirring using a hotplate stirrer with a stirring speed of 350 rpm, at room temperature for 24 hours. Furthermore, a paste is produced. The resulting paste is dried and in an oven at 105°C (± for 90 minutes). Then the catalyst is activated in the furnace at a temperature of 500°C for 3 hours [11].

2.3. Esterification Process
In the esterification process, PFAD was weighed as much as 25 grams, while the metal-HAp catalyst was 0.25 grams, and the ratio of methanol: PFAD = 10: 1. PFAD and the metal-HAp catalyst mixture with methanol were heated to 50°C each for ± 15 minutes. Perform the PFAD esterification and methanol reaction for 2, 3, and 4 hours at 60°C and the stirring speed of 250, 300 and 350 rpm.

2.4. Catalyst and Biodiesel Analysis
Impregnation metal catalyst-Hapanalyze by X-ray diffraction, SEM-EDX analysis and Surface Area Analyzer (SAA). The characteristics of biodiesel produced were analyze by GC-MS (Gas Chromatography-Mass Spectroscopy). Subsequently test several physical properties of biodiesel such as water content, density, viscosity, acid number, heating value and chemical characterization of the biodiesel obtained using analysis.

3. Results and Discussion
Hydroxyapatite used as catalyst or catalyst support is taken from the results of formerly research [10, 12]. In the Cu, Co and Ni metals, 3, 6 and 12% HAp, respectively, Cu-HAp, Co-HAp and Ni-HAp catalysts were produced. The results of the analysis using X-ray diffraction, found no significant differences in the X-ray diffraction patterns for HAp, Cu-HAp, Co-HAp and Ni-HAp at various concentrations of the metal being developed. Figure 1 shows the diffraction pattern of X-HAp rays with Cu-HAp 3%.
SEM-EDX analysis results, showed significantly different results in the morphology of all the catalysts produced. Figure 2 below shows the morphology of the catalysts produced which will be used in biodiesel production, known as hydroxy apatite and Cu-HAp.

The results of the analysis of the surface area of HAp after impregnation, obtained the largest increase in surface area found in Cu-HAp 3%, from the surface area of HAp 17.753 m²/g to Cu-HAp of 31.138 m²/g. The three types of catalysts produced are then used in biodiesel production. In the initial stage, the PFAD to be used was analyzed using GC-MS equipment to determine the types of fatty acid components making up the PFAD. From the results of GC-MS analysis, the main components in PFAD were palmitic acid (C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>) 59.4%, 9-Hexadecenoic Acid (C<sub>16</sub>H<sub>30</sub>O<sub>2</sub>) 37.14 and Squalene (C<sub>30</sub>H<sub>50</sub>) amounted to 3.46%.
From the results of biodiesel production, Cu-HAp catalyst was obtained better than three other catalysts used such as HAp, Co-HAp and Ni-HAp. Based on GC-MS analysis, the use of Cu-HAp as a catalyst resulted in a conversion of about 94.4% biodiesel with Fatty Acid Methyl Ester (FAME) components in the form of Methyl Ester Hexadecanoate 53.1%, Methyl Esters 9-Octadecadienoate 5.93%, Methyl Esters 9-Octadecenoate 32.81%, Methyl Esters Octadecanoate 2.59%. The use of HAp as a catalyst produces FAME around 10.67%, Co-HAp around 26% and Ni-HAp around 34.33%.

The use of 3% Cu-HAp catalyst, then carried out by varying the stirring speed (250, 300 and 350 rpm) and reaction time (2, 3 and 4 hours). The highest yield is obtained at a stirring speed of 300 rpm with a reaction time of two hours, shown in Figure 3.

![Figure 3.](image)

**Figure 3.** Effect of stirring speed and reaction time on biodiesel yield

Some of the characteristics of biodiesel from PFAD base material using Cu-HAp catalyst are shown in Table 1 below. The results of the characterization of some physical properties of biodiesel from PFAD were compared with biodiesel standards according to SNI-04-7182-2006.

| Characteristics          | Biodiesel from research results | SNI Biodiesel          |
|--------------------------|---------------------------------|------------------------|
| Moisture content (% vol)| 0.036-0.066                     | 0.05 max               |
| Density (g / ml)         | 0.862-0.902                     | 0.86-0.89              |
| Viscosity (cSt)          | 4.181-5.029                     | 2.3-6.0                |
| Acidity rate (grKOH / gr oil) | 0.553-1.661                     | Max 0.8                |
| Heating value (kCal / kg)| 9048-9813                       | 9938.76 max            |

4. **Conclusion**

This research succeeded in utilizing calcium-deficient hydroxyapatite, synthesized from eggshell waste and calcium-rich shells, as a catalyst in the synthesis of biodiesel from PFAD by-products of the palm oil industry. Of the three types of catalysts made, Cu-HAp catalysts are better than HAp, Co-HAp or Ni-HAp catalysts in converting PFAD to biodiesel (FAME). The use of 3% Cu-HAp catalyst with a reaction time of two hours and a stirring speed of 300 rpm gave a yield of 63%.

4. **Reference**

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