

THE SYNTHESIS OF COCONUT METHYL ESTER USING ORGANIC CATALYTIC AGENTS

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ABSTRACT

Biodiesel is one of the biomass materials or renewable energy, which is needed today to replace fuel from fossil energy, which can reduce global warming and has a high renewability cycle. Biodiesel is derived from plants, therefore it is also called biofuel. One type of biodiesel group is coconut methyl ester (CME), which is biodiesel obtained from coconut oil as a raw material. In this study, a synthesis of used coconut oil and methanol has been carried out with an organic catalyst based on coconut coir called the ASK catalyst. The results of transesterification have provided some important information, including: the yield is 15-19.5% after usage of the ASK catalyst consisting of amorphous phase and crystalline phase $ClK_{0.8}Na_{0.2}$, with the density and viscosity of products are 0.788-0.802 g/ml and 0.6-1 mm²/s. These results allow it to provide a distinctive advantage in its application.

Keywords: CME; FAME; biomass; transesterification; organic catalyst

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INTRODUCTION

According to data from the Directorate General of New Renewable Energy and Energy Conservation of the Ministry of Energy and Mineral Resources, it is estimated that there will be a gap in demand for and supply of crude palm oil (CPO) in 2030. For biodiesel, where the demand is estimated to be about 17 million tonnes, whereas the stock or availability is only about 15 million tonnes [1]. To anticipate this, it is possible to develop a diversification to respond to this enormous demand. Biodiesel is one of variables in the government's renewable energy program, whose total energy consumption from all variable value is targeted to increase from 9% MTOE in 2019, to 23% MTOE in 2025 [1]. Coconut as one of edible oils feedstock for biodiesel which had become a potential ogled after palm, both in terms of availability [2] and from a technical point of view because of its physical-chemical properties [3], and its application which tend to be superior to another feedstock [4]. Meanwhile, from an economic standpoint, the use of coconut oil as a raw material in production costs is less competitive

because of the price of raw materials. In view of this situation, cooking oil as a raw material can be taken into account in the production of biodiesel, where numerous studies have been shown successfully [5], [6]. Additionally, all parts of the coconut also have many benefits, such as skin or shell. The use of coconut as a catalytic agent for biodiesel has been carried out by several researchers [7], [8], which provided information that the yield produced is around 90%. Therefore, it is possible to use it on a commercial scale with used coconut cooking oil to support the 3R (reuse, reduction, recycling) program campaign necessary for environmental sustainability.

METHODS

The research flow chart which becomes the reference for this research activity is shown in **Figure 1**. The rectangular symbol represents an activity or process, while the diamond symbol represents a process with a number of conditions for which a decision is required.

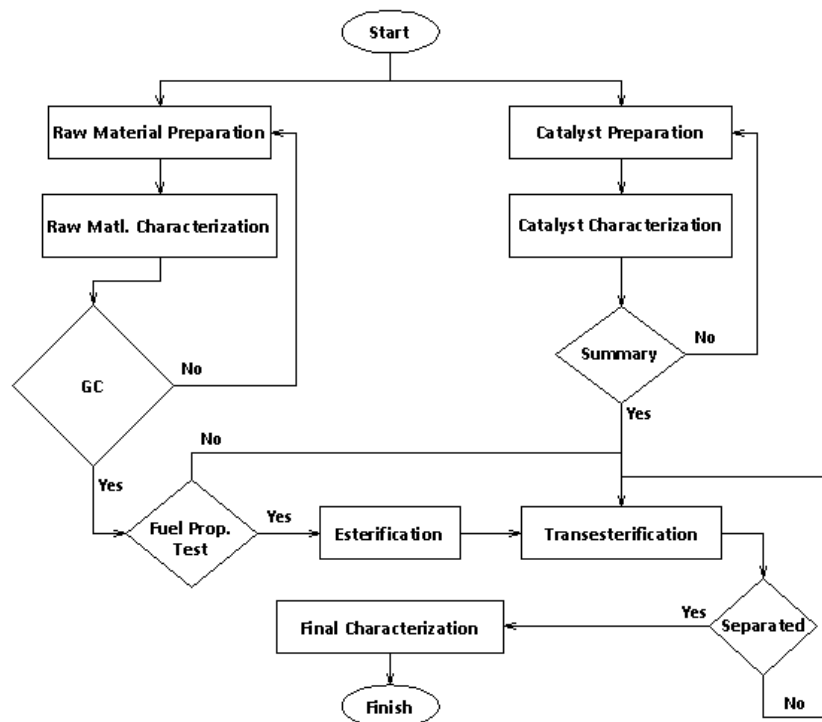


Figure 1. Research flow chart.

Referring to the flowchart in **Figure 1**, research activities in general can be grouped according to the stages of the activity. It consists of preparatory activities, initial characterization, synthesis, final characterization and modelling activities.

When preparing the used oil, we obtained it from the coconut cooking oil that we used for frying for 3 times. The determination of 3 frying times was made as the research limit, so that the stability of the materials should be measured in the same treatment. After being cooled to room temperature, the oil was then filtered to separate it from the remaining food ingredients and collected in the container. During this time, when preparing the ASK catalyst, the moist coconut was first dried in the open air for about 5 hours. After drying, it was heated in a 350°C oven for 1 hour, then cooled and collected in the provided vessel.

Initial characterization activities of used oil using FTIR (Fourier Transform Infra-Red) Spectroscopy and GC (Gas Chromatography) techniques to determine quality of the material. Then Fuel Property Test was done in the form of calculating acid number, iodine number, and density of used oil.

Transesterification of the CME was performed using the following parameters: (1)

volume ratios of oil: methanol was 3:1 and 2:1; (2) variation of catalyst concentration was 5 and 10wt.%; (3) stirring speed was 500 rpm; (4) reaction temperature was 50°C; and (5) reaction time was 1 hour. Upon completion of the reaction time, the material was cooled for 10 minutes before being placed in a separation funnel. Two layers will then be formed, the top layer as CME and the lower layer as glycerol. After approximately 12 hours, the CME was then placed in a beaker glass for weighing and the yield was calculated using the following equation 1 :

$$\% \text{ Yield} = \frac{WP}{WR} \times 100 \quad (1)$$

WP is the weight of separated product (g). WR is total reactant weight (g).

Once the synthesis process with the transesterification technique was completed, the characterisation of the catalyst was continued using the X Ray Fluorescence (XRF) method. and XRD (X Ray Diffraction) as a follow-up analysis. CME products then entered the final characterization stage, by density test, and a kinematic viscosity test using a viscometer, and the best result will be analysed with several physical tests of other fuel products, which are CME with 0.25 wt.% KOH catalyst, PME (*Palm*

Methyl Ester), and B0 or “Solar” as a pure fossil fuel.

RESULTS AND DISCUSSION

Raw Material Characterization

The analysis of **Figure 2** showed several functional groups that appear in peak which can be divided into 3 areas. First, the area of the 500-1500 cm^{-1} wavenumber, which is the fingerprint area. Based on one reference [9], this area was generally overlooked because it contained very complex absorbing forms. This is because all types of molecular bending vibrations absorbed in this region.

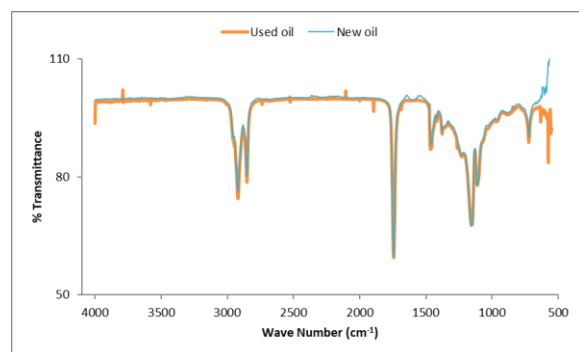


Figure 2. FTIR of used oil compare to new oil.

Table 1. Fuel Property Test of Used Oil.

| | | |
|--------------|-------------------------|--------|
| Appearance | reddish yellow | |
| Acid Value | mg KOH/g | 0.33 |
| Iodine Value | g I ₂ /100 g | 4.4 |
| Density | g/ml | 0.92 |
| Composition | C-8 | 6.22% |
| | C-10 | 5.28% |
| | C-12 | 42.63% |
| | C-14 | 16.94% |
| | C-16 | 12.06% |
| | C-18 | 16.60% |
| | C-18-1 trans | 0.05% |
| | C-20 | 0.23% |

Meanwhile, the second was the area of wave number 1684-1755 cm^{-1} , in this area there was bond stretching, which shows the interpretation of the C=O carbonyl group. Third, the area of wave number 2800-3000 cm^{-1} , in this area there is also a stretching or interpretation of the CH and CH₂ group bonds [9]. The -OH group (indicating the presence of excess water content) which was absorbed from the wave number above 3000 cm^{-1} was not found (+98% transmittance), so it was ensured that the material did not contain water. The significant difference between the new oil and the used oil is that the triglycerides from the new oil showed no absorption at the wave number around 500 cm^{-1} because the hydrolysis process which produced fatty acid was not occurred.

Table 1 showed the composition of chemical bonds in the material which were dominated by saturated fatty acids in the form of lauric acid (C-12) which is 42.63%. Referring to a report [10], it was shown that pure coconut oil was contained 46.5% of lauric acid. Meanwhile, other compositions varied, C-14 acid or myristic acid was 16.94%, C-18 or stearic acid was 16.60%, C-16 acid or palmitic acid was 12.06%, and several other fatty acids. As for unsaturated fatty acids which was C-18-1 trans acid or elaidic acid, the percentage was only 0.05%. These saturated fatty acids indicate the stability of the material, which will be strengthened by the iodine number test.

Furthermore, the acid value of 0.33 mg KOH/g was far below the research reference limit of 5 mg KOH/g [5], [6]. This means that the free fatty acid content of the material was still good, so an esterification process was not required before the transesterification process. While the iodine value or iodine value of 4.4 g I₂/100 g indicates the stability of the used oil, because the more I₂ reacts, the more double bonds or unsaturated bonds in the material. These bonds can make the material easily degraded or oxidized. In comparison, in the another edible oils such as palm oil and olive oil, each of which has an iodine value of 57.5 and 80.2 g I₂/100 g [11] while non-edible oil such as Simarouba glauca (paradise tree) oil has an iodine value of 46 g I₂/100 g [12].

Transesterification

Table 2. Transesterification result.

| CME | Parameter of Transesterification | | |
|-----|----------------------------------|-----------------|-----------|
| | Vol. ratio of oil:methanol | Catalyst (wt.%) | Yield (%) |
| 1 | 3:1 | 5 | 15 |
| 2 | 3:1 | 10 | 16 |
| 3 | 2:1 | 5 | 18.3 |
| 4 | 2:1 | 10 | 19.5 |

The transesterification results are summarized at **Table 2** with parameters as in the methods. It can be seen that the most important yield with a value of 19.5 % occurred at a CME-4 (catalyst concentration of 10 % by weight with an oil:methanol ratio of 2:1). Changes in concentration or volume ratio from 3:1 to 2:1 in the catalyst by 5 wt.% increased yield by 18 percent. The same increase value was also found in the changes in the volume ratio of oil:methanol from 3:1 to 2:1 in the catalytic concentration of 10 wt.%. At the moment, 1 hour reaction time was chosen in the transesterification because it was the entry point or basic data for our catalytic reaction research.

Catalyst Characterization

Table 3. Elements in The ASK catalyst.

| Catalyst | Element (wt%) | | | | | | | | |
|----------|---------------|----|------|------|-----|------|------|------|--------|
| | C | O | Na | Mg | Si | Cl | K | Ca | Others |
| ASK | ND | ND | 8.91 | 0.96 | 1.6 | 2.37 | 7.44 | 1.45 | 1.22 |

Table 4. Oxide compound in The ASK catalyst.

| Catalyst | Stable oxide compound (wt%) | | | | | |
|----------|-----------------------------|------------------|------------------|------|-------------------|--------|
| | MgO | SiO ₂ | K ₂ O | CaO | Na ₂ O | Others |
| ASK | 1.55 | 3.13 | 8.15 | 1.96 | 9.85 | 2.24 |

Characterization using ED (Energy Disperse) XRF presented in the form of elements and their stable oxide compounds as **Table 3** and **Table 4**. Na, K, and Cl, were the dominant elements in the catalyst with an amount of 8.91; 7.44; and 2.37 weight percent, respectively, while the most dominant form of oxide obtained is Na₂O and K₂O with 9.85 and 8.15 weight percent. In the use of ED-XRF, there are several elements whose energy spectrum is not detected (ND), where

were generally elements of organic compounds such as C, H, O and N.

In general, the main elements of catalysts have been identified. These are active elements or compounds that have catalytic properties such as metals, alkaline metals or elements and compounds containing halides [3]. This is also specifically consistent with the reference, where in coconut coir that have been converted into husk ash, one of the constituent elements is a potassium element-based compound [7], [8].

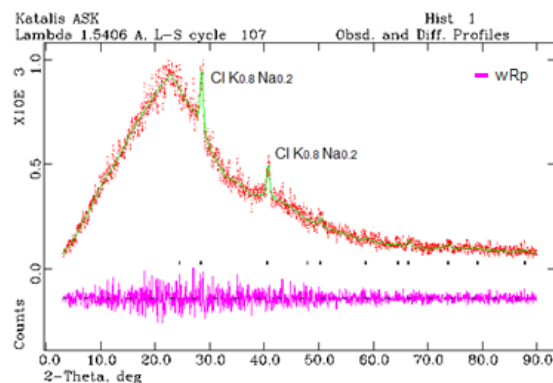


Figure 3. XRD result of The ASK Catalyst.

Figure 3 represents the X-ray diffraction spectrum of the ASK sample data processed through the GSAS software. The graph with red-dot colour represents the main data obtained experimentally, and subsequently equipped with a theoretical graph (green). Whereas the purple path named wRp, which is the residue between the experimental and theoretical intensities. The presence of an amorphous phase was indicated by background data that was mountainous and wide from an angle of $2\theta = 5^\circ$ through 60° . Whereas the presence of a crystalline phase was indicated by the presence of diffraction peaks at 2θ of 29° and 41° diffraction angles. Given the high and wide diffracted background of the pattern, the ASK sample can be assumed to be dominated by the amorphous phase [13]. This is most likely because the dominant chemical elements in the ASK sample are organics like C, O, N, etc that were not detected by XRD because they were lightweight atoms.

The results of GSAS analysis of the ASK catalyst showed that the crystalline phase contained in the ASK sample was the crystalline phase $\text{ClK}_{0.8}\text{Na}_{0.2}$. Another method is necessary to determine the amorphous phase in the ASK samples, which was not performed in this analysis. It can be concluded that the presence of a crystalline phase $\text{ClK}_{0.8}\text{Na}_{0.2}$, and major

compounds like K_2O and Na_2O in the ASK sample have resulted a maximum CME yield of 19.5%. The use of heterogeneous catalysts, as in previous studies, had resulted in the presence of several crystal phases. This can influence the adsorption activity of catalytic elements, in which decreased the FFA (Free Fatty Acid) levels in esterification reactions and increased product performance in transesterification reactions [14], [15].

Product Characterization

The physical properties of the CME resulting from the transesterification reaction are summarized in **Table 5**. These are, in particular, the density and viscosity which were evaluated at 40°C.

Table 5. Physical testing of the CME.

| Sample | Density at 40°C (g/ml) | Viscosity at 40°C (mm ² /s) | Parameter | | |
|--------|------------------------|--|------------|------------|-----------------|
| | | | Vol. ratio | Temp. (°C) | Catalyst (wt.%) |
| CME-1 | 0.802 | 1 | 3:1 | 50 | 10 |
| CME-2 | 0.789 | 0.8 | 2:1 | 50 | 10 |
| CME-3 | 0.798 | 0.8 | 2:1 | 50 | 5 |
| CME-4 | 0.788 | 0.6 | 2:1 | 60 | 5 |

The reaction rate will increase more rapidly as certain parameters increase: the reaction contact surface, the reagent concentration, the reaction temperature and the catalyst. According to **Table 5** above, there is a wedge between the two that was the concentration and the reaction temperature. On this basis, the first effect observed was the concentration of the reagent, represented by the volume of the reagents, on the assumption that the reaction takes place in a first order [16].

It was showed in **Table 5** that a volume addition from a ratio of 2:1 to 3:1 with the fixed parameters: temperature, %catalyst, rpm and reaction time were 50°C, 10%, 500 rpm and 1 hour, respectively, had increased the viscosity value by 20% (0.8 mm²/s to 1 mm²/s) and increased the value of the density by 2% (0.789 g/ml to 0.802 g/ml). On the other hand, decreasing the volume from a ratio of 3:1 to 2:1 had decreased its viscosity and density by the same proportion.

In the same **Table 5**, it was analysed that variations in a temperature increase from 50°C to 60°C with the fixed parameters: volume ratio,

%catalyst, rpm and reaction time were 2:1, 5%, 500 rpm and 1 hour, respectively, will reduce the viscosity by 25% and the density value by 1%. The case is also in line with the density limit of the reactants in connection with the products. The reactant concentration parameters that represented by the volume ratio of oil:methanol and temperature parameters, which were analysed with the product had functioned normally as a result of the first-order reaction.

CME-1 with the highest density and viscosity values was then selected to be compared with the results of physical tests from other fuel samples as be seen at **Figure 4**.

Another three samples were CME with 0.25 wt.% KOH catalyst; PME (Palm Methyl Ester) or B100 palm, and Diesel fuel or B0. The CME product with a 0.25 wt.% KOH catalyst was synthesised according with a product were previously made [17], while the remaining two samples were obtained by a supplier, hence resulting in the summary given in **Table 6**.



Figure 4. Sample product variants include (a) CME with organic catalysts; (b) CME with KOH inorganic catalyst; (c) PME; and (d) B0.

Table 6. Recapitulation of CME with reference fuel.

| Product | CME (ASK catalyst) | CME (KOH catalyst) | B100 PME | B0 |
|--|--------------------|--------------------|----------|-----|
| Yield (%) | 16 | 78 | ND | - |
| Density (kg/m ³) | 802 | 859 | 857 | 837 |
| Kinematic viscosity (mm ² /s) | 1.0 | 3.3 | 4.5 | 3.8 |

Table 6 above shows that CME with ASK catalyst has a lower density and viscosity than CME with KOH catalyst. This is due to the less reactive character of the catalyst compared to KOH catalyst for the same material and time

parameters. Whereas according to the results of the viscosity comparison between products, CME with catalyst KOH and CME with catalyst ASK have viscosity values below PME and B0. Those were advantages that suit with earlier studies, where with a lower viscosity, the fuel stream flows readily to the combustion chamber, causing the fuel to atomize better than other fuels [4], [18] [19], [20], caused a better combustion results and lower hydrocarbon emissions. So, the CME products with the ASK catalyst might be promoted for further research.

CONCLUSION

The synthesis of CME (biodiesel) from used coconut oil through transesterification techniques using the organic catalyst ASK produced yield of about 15% to 19.5%. The CME tends to have lower density and viscosity values than other methyl ester and biodiesel-based products. These features offer an advantage in the application of diesel motors.

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Author Contributions

In this study, MIS, MAEH, and AM are the main contributors, whereas MM is the supporting contributors. All authors reviewed this manuscript.

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