Biohydrocarbon production for jet fuel from palm oil derivative products

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Abstract. Jet biofuel can be produced from vegetable oils and fats that are rich in lauric acid and myristic acid. Palm kernel oil is known to contain 47.8% lauric acid and 16.3% myristic acid. Jet biofuel production by the thermochemical method through decarboxylation of basic soap made from palm kernel oil has been extensively investigated. The objective of this study was to produce jet biofuel from basic soap made from palm kernel oil. Several metal compounds from the acetate group were selected for use in making basic soap. Decarboxylation of soap was carried out at 350°C and atmospheric pressure for 5 hours in the semi-batch reactor. Zinc metal enhances the yield of jet biofuel after decarboxylation of soap. Approximately 40 and 62 weight% of the jets biofuel had been obtained in this experiment.

1. Introduction
Today, most of the energy we use comes from fossil fuel. According to the definition of chemistry, fossil fuels consist of hydrocarbon molecules. Petroleum is the fossil fuel that is most in danger of running out. According to Demirbas [1] peak in global oil (petroleum), production may occur between 2015 and 2030. Figure 1 shows global oil production scenarios based on today’s production.
The increase in the rate of consumption of fossil fuels was triggered by the rapid growth of the manufacturing and transportation industries. To ensure the availability of liquid fuels for various industries of the future, of course, the production of fossil replacement fuels needs to be done. There are today many reasons for search and find the replacement of fossil fuel, that is: 1) The limited oil reserves that are estimated to remain for the needs of 80-100 years [1]; 2) uncertain of fossil fuel price; and 3) environmental protection [2]. Renewable fuels are also often called alternative fuels that have a big potential for meeting the future needs of liquid fuel [3]. Renewable fuel is a promising alternative solution because it is clean and environmentally safe. It also has a source that is more evenly distributed than fossil resources [4]. Biomass of vegetable oils and fats has been shown may produce renewable fuel by converting it into bio-hydrocarbon that compatible with fossil fuel [5]. However, Fossil fuels can also be termed biomass since they are the fossilized remains of plants that grew millions of years ago [6]. The use of vegetable oils as fuel for internal combustion engines is not new. Rudolf Diesel, the inventor of the diesel engine, used peanut oil to fuel one of his engines at the Paris Exhibition of 1900 [7]. It is possible because the vegetable oils and fats are components of triglycerides that contain fatty acids that have a molecular structure similar to hydrocarbons (fossil fuels); however, contaminated with oxygen. Such similarity is shown through the molecular structure of lauric acid and dodecane hydrocarbons below [8]:

![Figure 2. Molecular structure of: (a) lauric acid and (b) dodecane](image)

According to Mancini et al. [9], palm kernel oils contain many fatty acid components, especially lauric acid (47.8%) and myristic acid (16.3%). The two types of fatty acids mentioned above can be sources of biohydrocarbon production, especially for jet fuels [10]. However, to obtain biohydrocarbons from fatty acids, oxygen in the chain of molecules of fatty acids must be removed. Two reaction pathways that have commercial applications are decarboxylation [11] and hydrodeoxygenation [12] already been proved to be effective in eliminating oxygen from fatty acid molecules. Nevertheless, the more expected technology is to have a minimum to moderate production capacity, relatively easy to operate, and have a broad implementation scope to various regions producing raw materials. The Hydrodeoxygenation reaction pathway consumes a lot of hydrogen gas to suppress or force the oxygen to form water molecules and leaving fatty acid molecules in the form of biohydrocarbon. Its reaction
can only take place effectively under high-pressure conditions in the presence of Pd and Pt catalysts [13]. Meanwhile, the decarboxylation reaction pathway for converting basic soap (derivatives of fatty acids) can be effective without Pd and Pt catalysts, not consuming hydrogen and operating well under atmospheric conditions [14]. With the reaction pathway, the catalytic process of basic soap is effectively carried out by various alkaline earth and transition metals used for soap making. The yield and characteristics of biohydrocarbon products obtained through decarboxylation of basic soap are largely determined by the type and combination of metals and model compounds (the type of vegetable oil) that used for produce of the basic soap [10]. The objective of this study was to investigate the biohydrocarbon production for jet fuel from palm oil derivative products.

2. Material and Method

2.1. Materials and reagents
Magnesium acetate tetrahydrate [Mg(OOC\(_2\)H\(_5\))\(_2\).4H\(_2\)O] and zinc acetate dihydrate [Zn(OOC\(_2\)H\(_5\))\(_2\).2H\(_2\)O] supplied by Merck (analytical grade) were used to prepare the metal soaps. The C\(_{12/14}\) and C\(_{12/16}\) methyl esters derived from palm kernel oils were purchased from PT. Ecogreen Batam-Indonesia. The ultrahigh-purity (>99.999%) N\(_2\), and He used in the analysis of the gas and liquid products were purchased from PT. Brataco, Indonesia. Ethanol (purity ≥ 96%) and sodium hydroxide (anhydrous, pro analysis) were purchased from PT. Brataco, Indonesia.

2.2. Experimental set-up
Two types of methyl esters derived from palm kernel oil have been used in this study are C\(_{12/14}\) and C\(_{12/16}\). The composition of C\(_{12/14}\) and C\(_{12/16}\) methyl esters were identified by fragmentation patterns from a Shimadzu 2010 Plus Mass Spectrometric (MS) detector and by matching gas chromatography retention times with known standards. Product separation was achieved using a restex-5 capillary column with a length of 30 m and an inner diameter of 0.25 mm. The injector and detector port temperature was 300 °C. The column temperatures were programmed from 150 to 200 °C at a rate of 5 °C/min and then raised to 290 °C at a rate 10 °C/min and were kept at that temperature until no appearance of peak. The biohydrocarbons production was performed by decarboxylation process of the basic soaps which has been resulted from saponification process. Basically, the order of each step included in biohydrocarbons production can be explained as follows: the ME was firstly mixed with hot ethanol in a glass batch reactor with a stirrer to get a uniform mixture. Subsequently, an aqueous solution of sodium hydroxide at 20% by weight was added to the mixture while continue stirring. As soon as the mixture reaches a good level of consistency, a solution consists of magnesium – zinc acetate combination at a ratio of 9:1 in distilled water was gradually added to the mixture while stirring. The Mg-Zn basic soaps produced by ion exchange were insoluble in water and easily separated from their soluble sodium counterparts. The produced basic soaps from this process were filtered, washed with hot water, and then dried in an oven at 70 °C for about 48 hr. The dried basic soaps were subsequently used as the material for decarboxylation process. The Mg-Zn basic soap decarboxylation process was performed under a condition of destructive distillation at 350 °C and atmospheric pressure in a glass batch reactor for 5 hours without any catalysts. The catalytic activities of Mg-Zn combination in basic soaps were evaluated by determining the yield of liquid jets biofuel (or bio-hydrocarbons) and their fraction distribution. The fraction distribution was analyzed by gas chromatography Shimadzu 2010 equipped with a flame ion detector (FID) and a restex-1 capillary column, using Helium as a carrier gas. The injection port temperature and the temperature program were the same as those used with the GC-MS. Standard alkane of n-C\(_2\), n-C\(_{16}\), and n-C\(_{18}\) was used for identification of retention times and calibration of response. The analysis method of GC-FID was used to quantify the biohydrocarbon concentration of liquid product (sample). The determination of the freezing point has been tested with ASTM D-2500 procedures.
3. Results and Discussion

3.1. Main content of fatty acids in the model compounds

The analysis results of fatty acids content in $\text{C}_{12/14}$ and $\text{C}_{12/16}$ methyl esters are presented in Table 1. The results show that the contents of dodecanoate ($\text{C}_{12:0}$) as main fatty acid in $\text{C}_{12/14}$ methyl esters are 74.3 wt%, while those in $\text{C}_{12/16}$ methyl esters are 67.1 wt%. Therefore, the content of dodecanoate in $\text{C}_{12/14}$ methyl esters 7.2 wt% higher than $\text{C}_{12/16}$ methyl esters. Otherwise, $\text{C}_{12/14}$ methyl esters have the content of hexadecanoic ($\text{C}_{16:0}$) fatty acid lower than $\text{C}_{12/16}$ methyl esters. Meanwhile, both $\text{C}_{12/14}$ and $\text{C}_{12/16}$ methyl esters have relatively the same tetradecanoate content. The data in Table 1 show that the two types of methyl esters are renewable feedstock which suitable to be converted into hydrocarbons that are compatible with jet fuel (consist of $\text{C}_{10}$-$\text{C}_{14}$ hydrocarbons).

| Model compounds | Fatty acids, (wt %) |
|-----------------|---------------------|
| $\text{ME C}_{12/14}$ | $74.3$ $25.1$ $0.4$ |
| $\text{ME C}_{12/16}$ | $67.1$ $25.5$ $7.4$ |

3.2. GC-FID chromatograms of liquid product sample

GC-FID chromatograms of the liquid bio-hydrocarbons product sample are shown in Figure 3. According to chromatograms the liquid bio-hydrocarbons that were resulted by basic soaps had a relatively wide range of carbon chain length, i.e., between $\text{C}_8$ - $\text{C}_{18}$. It shows that Mg-Zn metals combination which was expected to act as a catalyst in basic soap decarboxylation do not selective to only the main product i.e., n-undecane ($\text{n-C}_{11}$).

![Figure 3. GC-FID chromatograms of biohydrocarbon derived from $\text{C}_{12/16}$ ME basic soaps](image)

Variation of the carbon chain length in the liquid bio-hydrocarbon suggested that the conversion process of basic soaps $\text{Mg-Zn(OH)(ME C}_{12/16})$ were predicted to not only involve the decarboxylation process, but also others processes such as cracking (generating the small and light products), dehydrogenation (generating unsaturated bio-hydrocarbons) and polymerization (generating long-chain bio-hydrocarbons).

3.3. Effect of metal types in the basic soap on the yield of biohydrocarbon (jet biofuel)

The influence the metal types in the basic soap on the yield of jet biofuel products were studied in these experiments. The analysis results of jet biofuel yield of basic soap decarboxylation which produced from
some types of metal are shown in Figure 4. The result shows that the effect of zinc metal in basic soap is relatively significant, while those in other metals are insignificant. The data in Figure 4 show that the catalytic effect of zinc metal enhances the yield of liquid biohydrocarbons of basic soap decarboxylation. Therefore, from the catalysis point of view, the metal which has high catalytic activity for basic soap decarboxylation was Zn metal.

![Pareto chart of the metals effect](image)

**Figure 4.** Pareto chart of the metals effect (respons is Yield of jet biofuel, α=0.05)

3.4. Yield of jet biofuel from decarboxylation of methyl esters soaps

Both ME compounds with profiles as presented in Table 1, had been converted to basic soaps and were decomposed through a series of decarboxylation process to result in jets biofuel. Experiment result showed that there was a significant difference on the yield of liquid biohydrocarbons derived from decarboxylation of basic soap C_{12/14} and C_{12/16} (Figure 5). Percent yield is the percent ratio of actual yield to the theoretical yield. It is calculated to be the experimental yield divided by the theoretical yield multiplied by 100%, as indicated by the equation below:

\[ Y = \frac{y(\text{actual})}{y(\text{theoretical})} \times 100\% \]  

(1)

The highest yield of jets biofuel was generated by basic soap decarboxylation of the Mg-Zn(OH)(ME C_{12/16}) i.e. 62.17 wt% than the Mg-Zn(OH)(ME C_{12/14}) i.e. 40.06 wt%. These difference may has correlated with the lauric acid (C_{12:0}) and Palmitic acid (C_{16:0}) content in methyl esters. Apparently, the yield of jets biofuel increases when methyl esters contain significant palmitic acids. While, the yield of jets biofuel are relatively low with increasing lauric acids content.
3.5. Distribution of carbon chain length from the n-alkane fractions

The n-alkane content according to the carbon chain length is shown in Figure 6. The results show that the n-alkane content in the liquid biohydrocarbons of both (Mg-Zn(OH)(ME C_{12/14})) and Mg-Zn(OH)(ME C_{12/16}) basic soaps tend to be similar. However, for the Mg-Zn (OH)(ME C_{12/16}) basic soap, the yield of n-C_{11} was found the highest followed by n-C_{15}. Whereas for the Mg-Zn(OH)(ME C_{12/16}) basic soap, the yield of n-C_{15} was found highest and followed by n-C_{11}. It seemed that the short-chain n-paraffin compounds, e.g., n-C_{8}, n-C_{9}, and n-C_{10}, which was found the highest was generated by decarboxylation of the Mg-Zn(OH)(ME C_{12/14}) basic soap. The behavior of increasing the yield of n-C_{8} to n-C_{11} and n-C_{15} alkanes chain length shown in Figure 6 can be explained as follows: lauric acid (C_{12:0}) is the main component of ME C_{12/14} and ME C_{12/16} (see Table 1). Ideally, it can be decarboxylated to produce n-C_{11} hydrocarbons. However, if cracking accompanies the decarboxylation reaction, then short n-alkane hydrocarbons such as n-C_{10}, n-C_{9} and n-C_{8}, even n-C_{7}, n-C_{6}, and n-C_{5} can be produced.

![Figure 5. Biohydrocarbon (jets biofuel) of basic soap decarboxylation](image)

![Figure 6. Relationship between yield and chain length of the n-alkane](image)
hydrocarbon is the result of hexadecanoate (C_{16:0}) decarboxylation, especially from ME C_{12/16} as well. These analysis results indicated that the secondary reaction such as cracking had accompanied the decarboxylation process of Mg-Zn(OH)(ME C_{12/14}) basic soap. In that case, the cracking reaction producing more short n-alkane (< n-C_8) was most likely to occur slowly; therefore, n-C_{10} was still found more than other short n-alkanes. On the other hand, for Mg-Zn (OH)(ME C_{12/16}) basic soap, it was very likely that other reactions such as cracking and polymerization had occurred rapidly as soon as the decarboxylation process began. As a result, n-C_{15} products were the most resulted (by polymerization) as well as the small and light n-alkanes products under n-C_8 (by cracking); thus it reduced the yield of the n-C_{11} and n-C_{10}.

3.6. Grouping of liquid biohydrocarbons fraction

The grouping of liquid biohydrocarbons according to the alkane and alkenes fractions is shown in Figure 7.

![Figure 7. Fraction of alkane and alkenes in biohydrocarbons](image)

The data in Figure 7 show that the alkane fraction in liquid biohydrocarbons of basic soap decarboxylation much higher than alkenes. The results mentioned above, corresponding to the product expected from the basic soap decarboxylation, as shown by the reaction equation scheme follow:

$$\text{(RCOO)}\text{M(OH)} \rightarrow \text{RH} + \text{MCO}_3$$  \hspace{1cm} (2)

Where \(\text{M}\) are metal or metal combination.

4. Conclusion

Thermal decarboxylation of methyl esters basic soaps derived from palm kernel oils under 350°C and atmospheric pressure yielding liquid bio-hydrocarbons corresponding to the jets biofuel. Decarboxylation reactions have been effective in this study, evidenced by the formation of n-alkanes in large numbers. The basic soaps decarboxylation reaction was always accompanied by cracking and polymerization reactions. Mg-Zn(OH)(ME C_{12/14}) basic soap was a better choice as decarboxylation feed because it resulted in liquid bio-hydrocarbons that contain more n-undecane as the main components of jets biofuel. This study has proven that the production of jet biofuel can take place without consuming hydrogen and operating at atmospheric pressure.

Acknowledgments

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