Catalytic thermal decarboxylation of palm kernel oil basic soap into drop-in fuel

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Abstract. Catalytic thermal decarboxylation of basic soaps derived from palm kernel oil to produce dropin fuel was investigated. The $C_{12/14}$ and $C_{12/16}$ methyl ester had been used as the model compounds of this study. The purpose of this study was to produce drop-in fuel, especially jets biofuel, by catalytic thermal decarboxylation of basic soaps from palm kernel oils. In this study, two types of Magnesium-Zinc metal combination were used for preparing the basic soaps, both directly have a role as a catalyst. The reaction was carried out at 370°C and atmospheric pressure for 3 hours in the semi-batch reactor. Approximately 41 and 43 weight% of the yield and selectivity of about 97 and 98% toward the jets biofuel had been obtained in both experiments, respectively. The results showed that decarboxylation of basic soaps of $C_{12/14}$ and $C_{12/16}$ methyl ester were converted into drop-in fuel, especially jets biofuel in the relatively good yield of conversion.

1 Introduction

Until now the world only depends on liquid petroleum as the fuel for various motorized vehicle engines. The transportation technology that continues to grow over time had an impact on increasing the need of liquid petroleum fuel [1]. Correspondingly, the petroleum reserves continue to deplete, the purchase prices are increasingly high and the environmental impacts of petroleum fuel on global climate change and air quality continue to increase as well [2].The various weaknesses as mentioned above have emerged as the global issues. The issues have attracted the attention of researchers to find alternate liquid fuel that is compatible with petroleum fuel from renewable sources. One renewable source that has a chemical structure similar to the petroleum fuel is fatty acids contained in vegetable oils and fats [3].Such similarity can be shown through the molecular structure of dodecanoate fatty acid and dodecane hydrocarbons below [4]:


Figure 1. Molecular structure of: (a) dodecanoate fatty acid and (b) dodecane
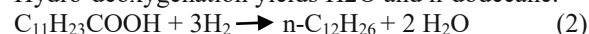
Especially for jets fuel, alternate fuels are expected to fulfill all physicochemical properties and other characteristic required for jets engines. It is known that jet fuel consists of a mixture of hydrocarbons (i.e. paraffin, naphthene and aromatics) in the C_{10}-C_{14} chain length range [5]. Vegetable oils and fats produce jets fuel which preferably contains more dodecanoic fatty acids ($C_{12:0}$). The reason is that when dodecanoic fatty acid or basic soap derived from dodecanoic fatty acid was converted by the hydro-deoxygenation process, it will produce dodecane (nC_{12}) and through the decarboxylation process, undecane (nC_{11}) bio-hydrocarbons will be produced, as shown by the reaction equation 1 and 2 [6].

Decarboxylation yields CO2 and n-undecane:
$$C_{11}H_{23}COOH \longrightarrow n\text{-}C_{11}H_{24} + CO_2 \qquad (1)$$
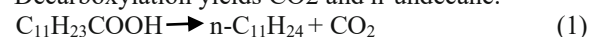
Hydro-deoxygenation yields H2O and n-dodecane:
$$C_{11}H_{23}COOH + 3H_2 \longrightarrow n\text{-}C_{12}H_{26} + 2\,H_2O \qquad (2)$$

Both the direct hydro-deoxygenation and decarboxylation process of vegetable oils and animal fats or fatty acids are commercial methods [7] that have been extensively studied. Moreover, it is an expensive method that consumes a lot of hydrogen [8], requires noble metals (e.g. Pt and Pd) as catalysts [9], and generally it operates at severe conditions [10, 11]. On the other hand, there are other deoxygenation processes i.e. decarboxylation of metal soaps, that consume little hydrogen (for hydrogenation of double bonds), do not require precious metal catalysts (but alkaline earth and transition metals) and may operate in relatively lower conditions, that have not been widely studied to produce liquid bio-hydrocarbon fuel [12]. The objective of this study was to investigate the production of jets biofuel which can be considered to be drop-in replacements for

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petroleum-based jet fuels, by catalytic thermal decarboxylation. In particular, this study investigated the decarboxylation of Mg-Zn basic soaps derived from $C_{12/14}$ and $C_{12/16}$ methyl esters (ME $C_{12/14}$ and ME $C_{12/16}$) at 350ºC and atmospheric pressure, without external supply of hydrogen.

2 Materials and methods

2.1 Materials and reagents

Magnesium acetate tetrahydrate $[Mg(OOC_2H_5)_2.4H_2O]$ and zinc acetate dihydrate $[Zn(OOC_2H_5)_2.2H_2O]$ 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.

2.2 Experimental set-up

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 chromatograph retention times with known standards. Product separation was achieved using a restex-5 capillary column with a length of 30 m and inner diameter of 0.25 mm. The injector and detector port temperature was 300 °C. The column temperatures were programed from 150 to 200 °C at a rate of 5 °C/min and then raised to 290 °C at a rate 10 ºC/min and were kept at that temperature until no appearance of peak. The fatty acids composition of the methyl esters is shown in **Table 1**.

Table 1. Main fatty acids of model compounds

Model compounds	Fatty acids, (wt %)		
	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$
ME $C_{12/14}$	74.3	25.1	0.4
ME $C_{14/16}$	67.1	25.5	7.4

The jets biofuel 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 jets biofuel production is shown in **Fig. 2**. 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 continuing stirring. Once the mixture has reached a firm consistency, a solution consist 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.
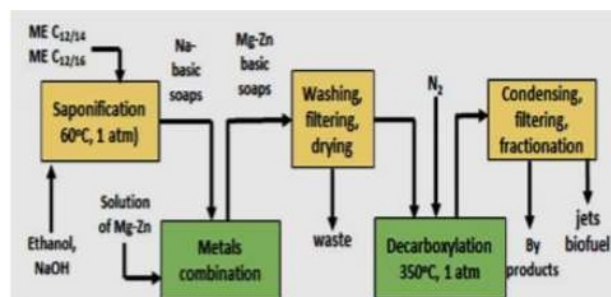

Figure 2. Flowchart diagram of soap-derived jets biofuel production.

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 were 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_{12}, n-C_{16} and nC_{18} were used for identification of retention times and calibration of response. The determination of the freezing point has been tested with ASTM D-2500 procedures.

3 Results and discussion

Table 1 shows that ME $C_{12/14}$ compound contained the main fatty acids consisting 74.3 wt% dodecanoate ($C_{12:0}$), 25.1 wt% tetradecanoate ($C_{14:0}$) and 0.4 wt% hexadecanoate ($C_{16:0}$), respectively. Meanwhile, ME C12/16 compound contained the main fatty acids composition of about 67.1 wt% dodecanoate, 25.5 wt% tetradecanoate and 7.4 wt% hexadecanoate, respectively. Both ME compounds with profiles as above had been converted to basic soaps Mg-Zn(OH)(ME $C_{12/14}$) and Mg-Zn(OH)(ME $C_{12/16}$) and were decomposed through a series of decarboxylation process to result in liquid bio-hydrocarbons (jets biofuel). Experiment result showed that there was a significant difference on the yield of liquid bio-hydrocarbons derived from decarboxylation of basic soap $C_{12/14}$ and $C_{12/16}$ (**Table 2**).

Table 2. Biohydrocarbon of basic soap decarboxylation

Model compounds	Yield (wt%)
ME $C_{12/14}$	40.06
ME $C_{14/16}$	62.17

The highest yield of liquid bio-hydrocarbon was generated by basic soap of Mg-Zn(OH)(ME $C_{12/16}$) (62.17 wt%) compared to Mg-Zn(OH)(ME $C_{12/14}$) (40.06 wt%). These difference is possibly due to the presence of significantly different content of dodecanoic fatty acids ($C_{12:0}$) and hexadecanoic ($C_{16:0}$) on both basic soaps. Chromatograms of the liquid bio-hydrocarbons

resulted by decarboxylation of basic soap Mg-Zn(OH)(ME $C_{12/14}$) and Mg-Zn(OH)(ME $C_{12/16}$) are shown in **Fig. 3**. The liquid bio-hydrocarbons that resulted by both basic soaps had a relatively wide range of carbon chain length, i.e. between C8 - C19. It showed that Mg-Zn, which was expected to act as a catalyst in decarboxylation process of the basic soaps, was relatively not selective to be resulted in the main product, i.e. n-undecane.
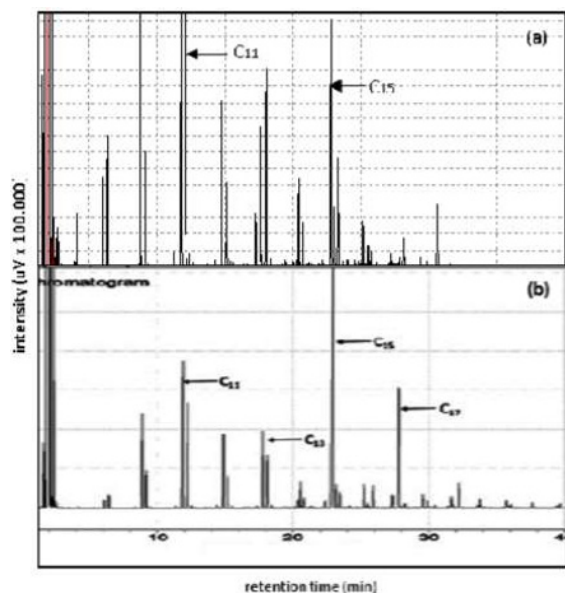

Figure 3. Chromatograms of biohydrocarbon were resulted in: (a) Mg-Zn(OH)(ME $C_{12/14}$), (b) Mg-Zn(OH)(ME $C_{12/16}$)

Variation of the carbon chain length in the liquid biohydrocarbon suggested that the conversion process of basic soaps Mg-Zn(OH)(ME $C_{12/14}$) and 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). The temperature of decarboxylation in the reactor was considered as an important factor contributing to the cracking process of long-chain alkane products as soon as the decarboxylation process occurs. In particular, reactants (e.g. basic soaps) for producing jet biofuels are better derived from methyl esters or dodecanoate fatty acids ($C_{12:0}$). By decarboxylation process, dodecanoate (its boiling point of 218.9 °C) will be converted to biohydrocarbon (mainly n-undecane) that has been known to have a boiling point about 195.8°C (Ralston, 1948). In the case of n-undecane formed in the reactor still being exposed to a high temperature around 350°C, then the cracking process must be experienced by the product. According to Cermak, (2012) methyl ester molecules have a low boiling point, therefore, they easily crack and require only a little energy to fractionation. Methyl ester compounds tend to boil at about 30°C below the counterpart fatty acids. Therefore, methylesters are sensitive to high temperature and highly potential to crack.

Table 3 presents a summary of the distribution composition of liquid bio-hydrocarbon products generated from decarboxylation of basic soaps of Mg-Zn(OH)(ME $C_{12/14}$) and Mg-Zn(OH)($C_{12/16}$). The analysis results showed that n-undecane (n-C_{11}) appeared as the most dominant liquid bio-hydrocarbon product (23.80 mol%) generated from basic soap decarboxylation of Mg-Zn(OH)(ME $C_{12/14}$). In contrast, n-pentadecane (n-C_{15}) appeared as the most dominant liquid bio-hydrocarbon product (32.12 mol%) generated from basic soap decarboxylation of MgZn(OH)(ME $C_{12/16}$). The analysis results also showed that the decarboxylation process with basic soap of MgZn(OH)(ME C_{12}/C_{14}) was better because it resulted more nundecane as the expected target product, whereas with MgZn (OH) (ME $C_{12/16}$) basic soap, the decarboxylation process was not selectively run to produce the expected main product. Moreover, the forming of long chain biohydrocarbons such as n-pentadecane (n-C_{15}) and n-heptadecane (n-C_{17}) was not expected. It seemed that the yield of n-C_{15} biohydrocarbon exceeded the potential of hexadecanoic ($C_{16:0}$) fatty acids contained in MgZn(OH)(ME $C_{12/16}$) basic soap. These phenomenon could possibly be explained like this; the presence of n-C_{15} biohydrocarbon is likely originated from the accumulation of n-C_{15} products from decarboxylation of all hexadecanoic fatty acids (about 7 mole%) and n-C_{15} products which was generated by polymerization of short biohydrocarbons already been formed due to the cracking of $C_{12:0}$ and C14:0 fatty acids in Mg-Zn(OH)(ME $C_{12/16}$) basic soap. However, a more accurate explanation of the phenomenon still needs to be studied further.

The liquid hydrocarbon yield profiles, especially n-paraffin fractions in the range of n-C_8 to n-C_{19}, are shown in **Fig. 4**.

Fig. 4 shows that the yield profiles of n-paraffin products contained 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 $C_{12/14}$) basic soap, the yield of n-C11 was found the highest followed by n-C_{15}. Whereas for the MgZn(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.
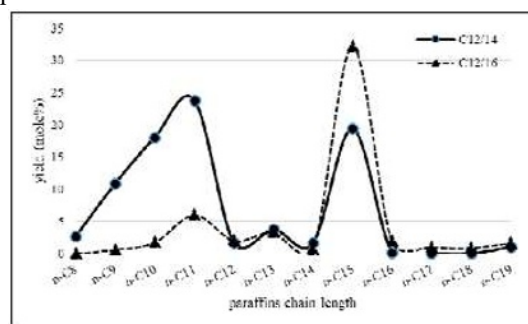

Fig. 4. Relationship between yield and chain length of the n-paraffin fraction.

Table 3. Liquid biohydrocarbon fraction (mole%) of basic soap decarboxylation base on C_{12}/C_{14} and C_{12}/C_{16} methyl esters.

Hydrocarbon compounds	Formulas	$C_{12/14}$	$C_{12/16}$
n-octane	C_8H_{18}	2,66	-
1-octene	C_8H_{16}	-	-
n-nonane	C_9H_{20}	10,87	0,57
1-nonene	C_9H_{18}	-	0,37
n-decane	$C_{10}H_{22}$	18,03	1,75
1-decene	$C_{10}H_{20}$	-	4,52
n-undecane	$C_{11}H_{24}$	23,80	5,99
1-undecene	$C_{11}H_{22}$	-	8,73
n-dodecane	$C_{12}H_{26}$	1,68	2,01
1-dodecene	$C_{12}H_{24}$	3,41	4,11
n-tridecane	$C_{13}H_{28}$	3,72	3,28
1-tridecene	$C_{13}H_{26}$	2,37	4,55
n-tetradecane	$C_{14}H_{30}$	1,63	0,76
1-tetradecene	$C_{14}H_{28}$	0,26	1,57
n-pentadecane	$C_{15}H_{32}$	19,37	32,12
1-pentadecene	$C_{15}H_{30}$	1,42	-
n-hexadecane	$C_{16}H_{34}$	0,18	1,92
1-hexadecene	$C_{16}H_{32}$	0,32	1,48
n-heptadecane	$C_{17}H_{36}$	4,22	9,66
1-heptadecene	$C_{17}H_{34}$	-	1,01
n-oktadecane	$C_{18}H_{38}$	-	0,86
1-oktadecene	$C_{18}H_{36}$	-	1,02
n-nonadecane	$C_{19}H_{40}$	1,00	1,60
1-nonadecene	$C_{19}H_{38}$	-	-
Other n-paraffin	$C_{24}H_{50}$	3,63	2,92
i-alkane (total)		2,66	5,91

The behavior of increasing the yield of n-C_8 to n-C_{11} and n-C_{15} paraffins chain length shown in **Fig. 4** can be explained as follows: Dodecanoate ($C_{12:0}$) is the main component of ME C12/14 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 paraffin 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. The impact of cracking reactions, resulted in light paraffin hydrocarbons such as n-C_1 to n-C_4 as well **[12]**. Therefore, n-C_8 to n-C_{10} hydrocarbons are more suitable to be called products from cracking than decarboxylation reactions. It seems that the cracking process is effective, so the products produced are relatively high compared to n-C_{11}. Meanwhile, n-C_{15} hydrocarbons are estimated as a result of polymerization of 1-C_{13} hydrocarbons, i.e. decarboxylation products from tetradecanoate ($C_{14:0}$) with 1-C_2 produced both dodecanate ($C_{12:0}$) and n-C_{11} hydrocarbons carcking **[13]**. In addition, n-C_{15} 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-paraffin (< n-C_8) was most likely to occur slowly, therefore, n-C_{10} were still found more than other short n-paraffins. 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 occured rapidly as soon as decarboxylation process began. As a result, n-C_{15} products were the most resulted (by polymerization) as well as the small and light nparaffin products under n-C_8 (by cracking); thus it reduced the yield of the n-C_{11} and n-C_{10}.

4 Conclusion

Mg-Zn(OH)(ME $C_{12/14}$) and Mg-Zn(OH)(ME $C_{12/16}$) basic soaps were both able to be used as decarboxylation feeds to produce liquid bio-hydrocarbons corresponding to the jets biofuel. 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. Also, basic soaps decarboxylation reaction was always accompanied by cracking and polymerization reactions. This study has proven that the production of drop-in fuel can take place without consuming hydrogen and operating at atmospheric pressure.

References

[1] Demirbas, A. Biofuels sources, biofuel policy, biofuel economy and global biofuel projections, Energy Conversion and Management 49, 2008, 2106-2116.

[2] Jahirul, M.I., Rasul, M.G., Chowdhury, N.A. and Aswath, N. Biofuels production through biomass pyrolysis-A technological review, Energies 5, 2012, 4952-5001.

[3] Balkose, D., Egbuchhunam, T.O. and Okieimen, F.E. Thermal behaviour of metal soaps from biodegradable rubber seed oil, J Therm Anal Calorim 101, 2010, 795-799.

[4] Available online at www.pubchem.ncbi.nlm.gov

[5] Neonufa, G.F., Soerawidjaja, T.H. and Prakoso, T. Thermal catalytic decarboxylation of Mg-Zn basic soap to produce drop-in fuels in jet fuel boiling ranges: Proceedings 2nd International Multidisciplinary Conference, Jakarta, 2016, pp. 332-338.

[6] Neonufa, G.F., Soerawidjaja, T.H. and Prakoso, T. Catalytic and thermal decarboxylation of Mg-Zn basic soaps to produce drop-in fuel in diesel boiling rang, J Eng. Techol. Sci. 49, 2017, 575-586.

[7] Fu, J., Lu, X. and Savage, P.E. Catalytic Hidrothermal Deoxygenation of Palmitic Acid, Journal of Energy and Environmental Science 3, 2010, 311-317.

[8] Gunawardena, D.A. and Fernando, S.D. Methods and Applications of Deoxygenation for the Conversion of Biomass to Petrochemical Products, Intech, 2013.

[9] Wang, Y., Fang, Y., He, T., Hu, H. and Wu, J. Hydrodeoxygenation of Dibenzofuran over Noble

Metal Supported on Mesoporous Zeolite, Catal. Communications, 12, 2011, 1201-1205.

[10] Kubicka, D., Future Refining Catalysis – Introduction of Biomass Feedstocks Collect Czech, Chemical Communications, 73, 2008, 1015-1024.

[11] Simacek, P., Kubicka D., Kubickova, I., Homola, F., Pospisil, M. & Chudoba J., Fuel Properties of Hydroprocessed Rapeseed Oil, Fuel, 89, 2010, 611615.

[12] Neonufa, G.F., Soerawidjaja, T.H., Indarto, A. and Prakoso, T. An innovative technique to suppress alkene-bond in green diesel by Mg–Fe basic soap thermal decarboxylation, International Journal of Ambien Energy, 2017, 1-7.

[13] Neonufa, G. F. Drop-in fuel production technology of green-diesel and bioavtur type via catalytic thermal decarboxylation of basic soap base on magnesium and transition metal combination, Doctoral Dissertation, Institut Teknologi Bandung, 2017.