

An innovative method to produce drop-in fuel by alkaline earth-transition metals basic soap decarboxylation

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Abstract. Decarboxylation of metal soap is an emerging method to produce drop-in fuels as an alternative to the expensive hydrotreatment process. In this study, the Mg-Fe basic soap produced from palm kernel fatty acid had been successfully decarboxylated into jet-fuel type biohydrocarbons. The Mg-Fe basic soap with ratio of 8:2 mol was decarboxylated for 5 hours at atmospheric pressure and temperature varied up to 370°C; it produced a liquid product whose yield was around 60 %-weight. The resulting hydrocarbon product was a complex mixture consisted of normal paraffins in the range of carbon chain length C₈ – C₁₇, iso- and cyclo-paraffins, and various olefin products.

1 Introduction

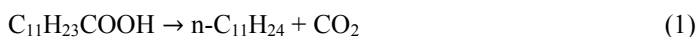
Interest in renewable fuels has been encouraged in recent years due to environmental, economic and geopolitical considerations, including global warming, dwindling petroleum deposits, rising crude oil prices and a desire for energy independence. Biofuels have been proposed as a renewable alternative to fossil fuels. Renewable hydrocarbon biofuels (also called drop-in biofuels) are fuels produced from biomass resources through a variety of biological and thermochemical processes. Biomass such as vegetable oils and fats are the feedstock candidates that are very potential and promises to produce renewable fuels [1-2]. Approximately 201.1 million tons of oils and fats were produced worldwide in 2014, from animal and vegetable feedstocks [3].

The production of renewable fuel become important nowadays due to the achievement of the goal set by the Indonesian government, i.e. replacing 20% of the nation's petroleum consumption with renewable alternatives by 2020 [4-5]. Drop-in biofuels are liquid transportation fuels made from oils and fats which are expected to replace FAME biodiesel. These fuels can be used as whole fuel as well as additive to the current petroleum gasoline, diesel, or jet fuel, thus they are considered as fully infrastructure-compatible fuels i.e. they can be used in vehicles without engine modifications and can utilize existing petroleum distribution systems [6]. Jet biofuel meets or exceeds the most rigorous jet fuel standards for

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performance. For example, blending the jet biofuel in a 50/50 ratio with petroleum-based jet fuel offers significant advantages over petroleum jet fuel, such as reducing greenhouse gas emission by 65-85% compared to petroleum-based fuels. Moreover, it has shown higher energy density in flight, which allows aircraft to fly farther on less fuel. Furthermore, it meets or exceeds critical jet fuel specifications, such as flash point, freeze point, stability and heat of combustion [7]. Fatty acids and their derivatives such as fatty acid methyl esters of palm kernel oil can be converted to renewable and carbon-neutral fuel-like hydrocarbons (e.g. jet biofuels) that are entirely fungible with fossil fuels by deoxygenation methods. This method can be conducted via decarboxylation, decarbonylation and hydrodeoxygenation pathways, as illustrated below for lauric acid.

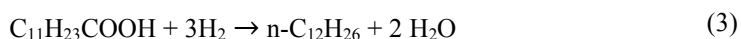
Decarboxylation yields CO₂ and n-undecane:



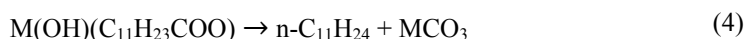
Decarbonylation yields CO, water and undecenes:



Hydrodeoxygenation yields H₂O and n-dodecane:



In the present commercial method, hydrodeoxygenation is directly applied to vegetable oils through liquid phase hydrotreatment. This method is expensive because it requires the use of problematic sulfide catalysts and high pressure of hydrogen; it also requires severe operating conditions. In view of this, an alternative has been sought in the deoxygenations of triglycerides and fatty acids or their derivatives via basic soap decarboxylation. The literatures report that soaps made from vegetable oils or fats can be processed into products that are rich in hydrocarbons by pyrolysis reaction with high yields and temperatures not so high as expected [8]. Decomposition of the alkali and alkaline earth metals soaps of the higher fatty acids generally gives better yields of hydrocarbons than that of obtained by decomposition of the corresponding fatty acids or fats [9]. Chang and Wan have been studied the formation of hydrocarbons which correspond to its oil fraction. The products are obtained from catalytic and thermal cracking of vegetable oils and soaps. Pyrolysis calcium soaps derived from rapeseed oil, peanut oil and Tung oil [10] was conducted and appears to be effective to produce hydrocarbons whose physical-chemical properties similar to the specifications of fossil oil fractions. Basic soap decarboxylation as illustrated below, has not been studied intensively to be developed on an industrial scale.



When compared with hydrodeoxygenation via hydrotreating and hydro-decarboxylation of the fatty acids or their derivatives, basic soap decarboxylation permits the use of simpler catalysts and requires less hydrogen, which makes deoxygenation via basic soap decarboxylation appealing from an economic standpoint [11]. Therefore, basic soaps decarboxylation has emerged as a route that is very promising to be developed as the basis of a commercial decarboxylation process.

The objective of this study was to produce alkane that can be considered to be drop-in replacements for petroleum-based jet fuels, by catalytic thermal decarboxylation of Mg-Fe basic soap. In particular, this study investigated the decarboxylation of the basic soap at mild operating conditions without external supply of H₂.

2 Experiments

Mg(OOC₂H₅)₂·4H₂O and Fe(OOC₂H₅)₃·2H₂O supplied by Merck (analytical grade), were used to make the soap. The palm kernel oil was obtained from PT. Ecogreen, Batam. Mg-Fe basic soap was obtained by metathesis process and it was used as a reactant model compound. Decarboxylation reaction was performed in a glass batch reactor at temperatures up to 370°C and atmospheric pressure for 5 hours. The liquid reaction products were analyzed by gas chromatograph (Shimadzu 2010) equipped with a capillary column (rtx-1) with dimensions of 30 m x 0.25 mm x 0.25 μm and flame ionization detector. One microliter of sample was injected into the GC with a split ratio 1:50 and the carrier gas (helium) flow rate was 42.9 ml/min. The injector and detector temperature were 340°C and 340°C, respectively. The following chromatographic temperature program was used for analysis: 40°C (at first) – 300°C (5°C/min) – 340°C (1°C/min, constant 45 min). A number of chemical standards were purchased to enable product identification and calibration. Determination of the freezing point had been tested with ASTM D-2500 procedures.

3 Results and Discussion

This section presents information about the product observed from the decarboxylation reactions of Mg-Fe basic soap from palm kernel oils.

3.1 Product Yield from Decarboxylation

Table 1 shows various products that arise from Mg-Fe basic soap decarboxylation at 370°C for 5 hours and at atmospheric pressure.

Table 1. The results of Mg-Fe basic soap decarboxylation.

Types of product	Yields [%-wt]
liquid bio-hydrocarbons	59.98
water	2.31
solid residues	25.12
others (including the gas)	15.59

These result shows that liquid bio-hydrocarbons yield to 59.98 %-weight were produced via decarboxylation of Mg-Fe basic soap from palm kernel oils. It proved that liquid bio-hydrocarbons could be synthesized from basic soap as a reactants. It also shows that the combination of Mg-Fe metals had good catalytic activity for converting the reactants into hydrocarbons via decarboxylation reaction at 370°C for 5 hours. This result shows that the renewable hydrocarbon synthesis via basic soap decarboxylation did not depend on the presence of Pt and Pd catalysts and high pressure operation, as reported by previous researchers [11-13].

3.2 Physicochemical Properties of Liquid Bio-hydrocarbons Product

Table 2 shows some selected physicochemical properties of liquid bio-hydrocarbons product of Mg-Fe basic soap from palm kernel oils at 370°C for 5 hours. Acid value in liquid bio-hydrocarbons product was very small (0.4 mg KOH / g sample). It shows that all free fatty acid (from palm kernel oils) had been converted into basic soap which then was subsequently converted by decarboxylation reaction into bio-hydrocarbons. For the freezing point, Table 2 shows that liquid bio-hydrocarbons product obtained from Mg-Fe basic soap were not just

dominated by n-undecane (whose freezing point is 21.0 °C) as expected from palm kernel oils (C₁₂ predominantly fatty acids).

Table 2. Physicochemical properties of liquid biohydrocarbons.

Components	Value
Acid value (mg KOH/gr sample)	0.5
Freezing point (°C)	< 11
Ketones/aldehydes group (-/+)	-

It also consisted of a mixture of bio-hydrocarbons with various range of carbon chain length, particularly short chain molecule bio-hydrocarbons with lower freezing point.

3.3 Distribution of Liquid Bio-hydrocarbons Product

GC-FID chromatogram patterns associated to distribution of liquid bio-hydrocarbons fraction were obtained from decarboxylation of Mg-Fe basic soap from palm kernel oils at 370°C for 5 hours; they are shown in Figure 1.

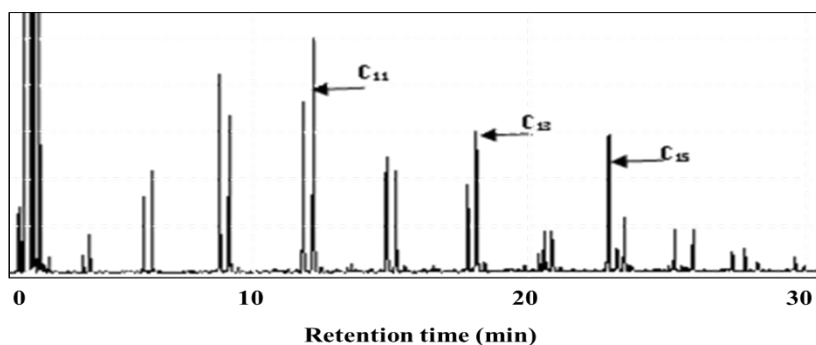


Fig 1. GC-FID chromatograms patterns for liquid bio-hydrocarbons fraction.

Figure 1 shows that decarboxylation of Mg-Fe basic soap produced liquid bio-hydrocarbons with the boiling point ranging from C₈ to C₁₇. The normal undecane (n-C₁₁) was suspected as the dominant component in the liquid bio-hydrocarbons product with retention time around 13 minutes, followed by normal decane (n-C₁₀) with retention time around 9 minutes. It indicated that the basic soap decarboxylation reaction had perfectly occurred, because it had produces higher component of normal undecane (n-C₁₁). The palm kernel oil has more fatty acids with C₁₂ (lauric acids) that is around 66.57%-wt and 23.56%-wt of myristic acid/C₁₄ and 7.34%-wt of palmitic acid/C₁₆ as well. Therefore, when the basic soap decarboxylation is normal, it would produce a high amount of n-undecane.

The result of GC-FID chromatogram analysis related to the distribution of the liquid bio-hydrocarbons fraction obtained from Mg-Fe basic soap decarboxylation is summarized in Table 3. Table 3 shows that approximately 12.37 %-mole of n-undecane were obtained from decarboxylation of Mg-Fe basic soap of palm kernel oil. The rest of the fraction was dominated by n-decane and lower n-paraffin molecules, including olefin and iso-paraffin molecules.

The composition group of n-paraffin, olefins and iso-paraffin in the liquid bio-hydrocarbons obtained from Mg-Fe basic soap decarboxylation of Mg-Fe basic soap of palm kernel oil is shown in Figure 2. Figure 2 shows that, approximately 73%-mole of liquid bio-

hydrocarbons obtained from Mg-Fe basic soap decarboxylation were paraffin molecules which are expected in jet fuel. The rest (around 27%-mole) were various 1-alkenes molecules.

Table 3. The results of GC-FID chromatogram analysis of liquid bio-hydrocarbons.

Bio-hydrocarbon compounds	formulas	Product Yields (%-mole)
n-octane	C ₈ H ₁₈	0.94
1-octenes	C ₈ H ₁₆	0.00
n-nonane	C ₉ H ₂₀	2.67
1-nonenes	C ₉ H ₁₈	1.81
n-decane	C ₁₀ H ₂₂	6.58
1-decenes	C ₁₀ H ₂₀	2.82
n-undecane	C ₁₁ H ₂₄	12.37
1-undecenes	C ₁₁ H ₂₂	7.58
n-dodecane	C ₁₂ H ₂₆	3.30
1-dodecenes	C ₁₂ H ₂₄	3.29
n-tridecane	C ₁₃ H ₂₈	6.54
1-tridecenes	C ₁₃ H ₂₆	4.06
n-tetradecane	C ₁₄ H ₃₀	1.46
1-tetradecenes	C ₁₄ H ₂₈	1.46
n-pentadecane	C ₁₅ H ₃₂	3.50
1-pentadecenes	C ₁₅ H ₃₀	3.49
n-heptadecane	C ₁₇ H ₃₆	0.22
Total i-paraffins		21.78

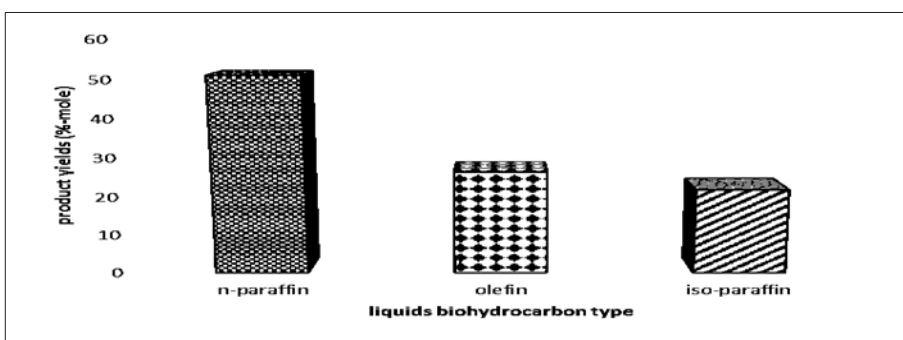


Fig. 2. Liquid bio-hydrocarbon types Mg-Fe basic soap decarboxylation.

The presence of 1-alkene in significant amount shows that there had been a dehydrogenation reaction during the basic soap decarboxylation in the batch reactor. In particular, Figure 3 shows the carbon chain length distribution of n-paraffin type in liquid bio-hydrocarbons was produced from Mg-Fe basic soap of palm kernel oil at 370°C for 5 hours. Figure 3 shows that bio-hydrocarbon with carbon chain length C₁₁ (n-undecane) was most dominant (around 12 %-mole) in the liquid product of Mg-Fe basic soap decarboxylation up to 370°C for 5 hours. The bio-hydrocarbons with further carbon chain length were C₁₀ (n-decane, 6.5%-mole) and C₁₃ (n-tridecane, 6.1%-mole).

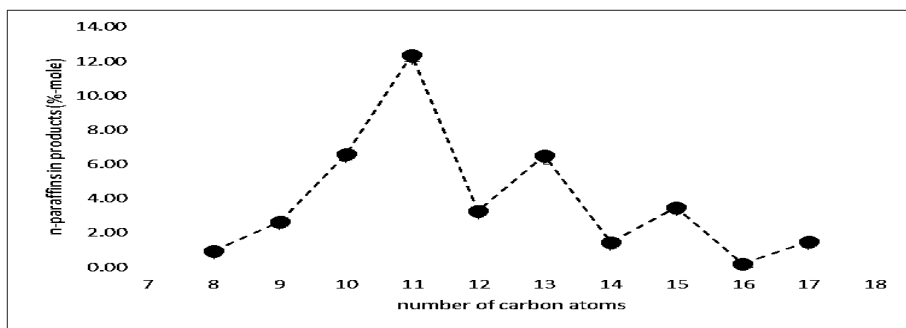


Fig. 3. Distribution of liquid n-paraffin plot according to carbon chain length.

4 Conclusion

The drop-in fuels in jet fuel type can be synthesized via basic soap decarboxylation, without the aid of hydrogen from the outside and without the using of commercial catalyst. The Mg-Fe basic soap was derived from palm kernel oil and decarboxylated for 5 hours at atmospheric pressure and temperatures up to 370°C; it effectively produced a jet fuel-type biohydrocarbons with a liquid product yield around 60 %-weight. The resulting hydrocarbon product was a complex mixture consisting of normal paraffins in the range of carbon chain length C₈ – C₁₇, iso-paraffins and various olefin products.

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