



Catalytic and Thermal Decarboxylation of Mg-Zn Basic Soap to Produce Drop-in Fuel in Diesel Boiling Ranges

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Abstract. Fatty acid deoxygenation is a method for producing renewable hydrocarbon fuels such as green diesel, jet biofuel and biogasoline. In the present commercial method, deoxygenation is directly applied to vegetable oils through liquid phase hydrotreatment. This method is expensive because it consumes a large amount of hydrogen and requires severe operating conditions. The objective of this study was the production of a diesel-like hydrocarbon fuel that can be considered as drop-in replacement for petroleum-based diesel fuels, by catalytic thermal decarboxylation of Mg-Zn basic soap. In particular, this study investigated the decarboxylation of Mg-Zn basic soap at low temperature and pressure, without external supply of hydrogen. The Mg-Zn basic soap (9/1 mole ratio of Mg/Zn) was derived from palm stearin and decarboxylated at 350 °C and atmospheric pressure for 5 hours. The basic soap effectively decarboxylated, yielding a diesel-like hydrocarbon fuel with a liquid product yield of 62%-weight. The resulting hydrocarbon product is a complex mixture consisting of normal paraffins in the range of carbon chain length C₈-C₁₉, iso-paraffins and various olefin products.

Keywords: *basic soap; decarboxylation; deoxygenation; drop-in fuel; green diesel; hydrocarbon.*

1 Introduction

Nowadays, increasing fossil-based liquid fuel demand and environmental awareness encourage interest in obtaining alternative fuels from biological sources. Oils and fats are feedstock candidates that have high potential in producing renewable fuels [1,2]. Approximately 201.1 million tons of oils and fats were produced worldwide in 2014 from animal and vegetable feedstocks [3]. In the same period, the production of biodiesel (fatty acid methyl esters, FAME) was nevertheless relatively low, i.e. 1.4 million tons [4]. The production of renewable diesel fuels is an emerging option to increase the availability of liquid fuels and achieve the goal set by the Indonesia government of replacing 20% of the nation's petroleum consumption with renewable alternatives by 2020 [5,6].

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Renewable diesel, also called green diesel, is a diesel-like hydrocarbon fuel. It possesses good fuel properties compared to biodiesel, such as lower viscosity, better fuel stability and higher energy density [7,8]. Because of the presence of the abovementioned properties, green diesel is considered to be a drop-in replacement for fossil-based diesel. Fatty acid deoxygenation is a method to generate renewable hydrocarbon fuels such as green diesel, bio-jet fuel and biogasoline. Deoxygenation can proceed through different routes, namely hydrodeoxygenation, decarboxylation and decarbonylation, as illustrated below for stearic acid (See Eqs. (1) to (3)).

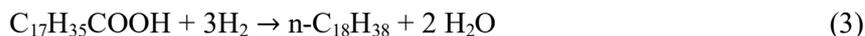
Decarboxylation yields CO₂ and n-heptadecane:



Decarbonylation yields CO, water and heptadecenes:



Hydrodeoxygenation yields H₂O and n-octadecane:



Direct hydrodeoxygenation of vegetable oils and animal fats is a commercial method [9] that has been studied extensively. However, little work has been done on basic soaps containing more than 1 metal, particularly without noble metals as catalysts, and the experiments were carried out at low temperature and atmospheric pressure. Although already commercial, hydrodeoxygenation is an expensive method because it consumes a large amount of hydrogen [10], requires noble metals as catalysts [11], and is conducted at severe operating conditions [12-13]. Therefore, basic soap decarboxylation has emerged as a very promising route to be developed as the basis of a commercial decarboxylation process.

Basic soap decarboxylation is the deoxygenation process used in producing diesel-like hydrocarbon fuels by the removal of oxygen as carbon dioxide at 350 °C and atmospheric pressure [14]. The metal in the basic soap acts directly as catalyst [15]. Other literature [16] also reports that soaps derived from vegetable oils and animal fats can be processed into liquid hydrocarbon fuels at high yields by pyrolysis at low temperature. Decomposition of alkaline and alkaline earth metal soaps of higher fatty acids generally provides better yields of alkane hydrocarbons than decomposition of the corresponding fatty acids [17].

Chang and Wan have studied the formation of a hydrocarbon that corresponds to its oil fraction by pyrolysis of calcium soap derived from rapeseed oil, peanut oil and Tung oil [18]. The calcium soap of the fatty acids was found to

decompose more slowly and at higher temperature than the corresponding magnesium soap. Decomposition of the calcium soap begins at 350-400 °C and becomes rapid at 450-500 °C, whereas decomposition of magnesium soaps begins at about 300 °C and becomes very rapid between 350 and 400 °C [19]. However, green diesel resulted from magnesium soap decarboxylation contains a large amount of olefin compounds (> 18%-mole) [20]. Zinc is known as a hydrogenation catalyst of unsaturated compounds [21] that can promote the formation of iso-alkanes as well [22].

In the present study, a magnesium-zinc combination to prepare the basic soap was designed to study the effects of the transition/alkaline earth metal combination, especially considering that the metals have two valences, on the decarboxylation of basic soap. The combination of magnesium-zinc in the basic soap for decarboxylation may produce a lower olefin compound than long chain alkane, as expected for green diesel.

The objective of this study was the production of a diesel-like hydrocarbon fuel that can be considered as a drop-in replacement for petroleum-based diesel fuels, by catalytic thermal decarboxylation of magnesium-zinc (Mg-Zn) basic soap. In particular, this study investigated the decarboxylation of Mg-Zn basic soap at low temperature and pressure, without external supply of hydrogen.

2 Experimental Setup

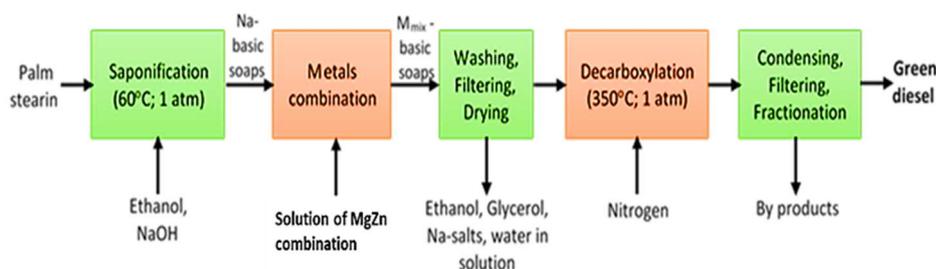
Magnesium acetate tetrahydrate [$\text{Mg}(\text{OOC}_2\text{H}_5)_2 \cdot 4\text{H}_2\text{O}$] and zinc acetate dihydrate [$\text{Zn}(\text{OOC}_2\text{H}_5)_2 \cdot 2\text{H}_2\text{O}$] were supplied by Merck (analytical grade) and used to prepare the soap. Palm stearin was purchased from PT. Ecogreen Batam-Indonesia. The composition of palm stearin was identified by fragmentation patterns with a Shimadzu 2010 Plus Mass Spectrometric (MS) detector and by matching gas chromatograph retention times with known standards. Product separation was achieved using a Restek RT-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 temperature was programmed from 150 to 200 °C at a rate of 5 °C/min and then raised to 290 °C at a rate of 10 °C/min and kept at that temperature until no more peaks appeared. The fatty acid composition of the palm stearin is shown in Table 1. The content of palmitic acid (saturated fatty acid, C16: 0) was approximately 63% by weight, while oleic acid (unsaturated fatty acid, C18: 1) was only approximately 26% by weight. Palm stearin was chosen as feedstock to prepare basic soap because it is easily obtained at a low price.

Table 1 Fatty acid composition of palm stearin.

| Fatty acid carbon chair | C _{12:0} | C _{14:0} | C _{16:0} | C _{18:0} | C _{18:1} | C _{18:2} | C _{18:3} | C _{20:0} |
|-------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Composition (wt.%) | 0.6 | 1.2 | 62.8 | 5.7 | 26.4 | 2.8 | 0.2 | 0.3 |

Green diesel production was performed by basic soap that resulted from saponification. Furthermore, by catalytic thermal decarboxylation it was transformed into green diesel. The general order of each step included in green diesel production is shown in Figure 1. The palm stearin is first mixed with hot ethanol in a glass batch reactor with a stirrer to get a uniform mixture. Then an aqueous solution of sodium hydroxide at 20% by weight is added to the mixture under continued 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 is added to the mixture while stirring. The Mg-Zn basic soap produced by ion exchange is insoluble in water and can be easily separated from its soluble sodium counterparts. The saponification process usually takes about 1 hour. The produced basic soap from this process is filtered, washed with hot water and then dried in an oven at 70 °C for at least 48 hours. The dried basic soap is subsequently used as the material for the decarboxylation process.

**Figure 1** Flowchart diagram of soap-derived green diesel production.

Mg-Zn basic soap decarboxylation was performed, i.e. destructive distillation at 350 °C and atmospheric pressure in a glass batch reactor for 5 hours, without catalysts. The heat was supplied and maintained in the reactor by using an automatic system with thermocouples and electronic controls. Nitrogen was flushed into the reactor to remove the remaining air. When the temperature was reached, the reactant evaporated into gaseous phase products. These products were cooled in a condenser tube to get the liquid products, after which they were stored in a glass beaker.

The catalytic activities of the Mg-Zn combination in the basic soap were evaluated by determining the yield of liquid bio-hydrocarbon and its fraction distribution. The fraction distribution was analyzed by a Shimadzu 2010 gas chromatograph equipped with a flame ion detector (FID) and a Restek-1 capillary column, using helium as carrier gas. The injection port temperature and the temperature program were the same as those used with the GC-MS. Standard alkanes, i.e. n-C₁₂, n-C₁₆ and n-C₁₈, were used for identification of retention times and calibration of response. The gas product (CO₂, CO, H₂, CH₄, etc.) were identified by a GC-8A Shimadzu gas chromatograph equipped with a thermal conductivity detector (TCD) and a porapak Q and molsive-5 capillary column combination, using helium as the carrier gas as well. Determination of the freezing point was tested with ASTM D-2500 procedures.

3 Results and Discussion

This section presents information about the product observed from the decarboxylation reactions of Mg-Zn basic soap of palm stearin. At 350 °C and atmospheric pressure for 5 hours, the conversion of Mg-Zn basic soap was about 73%.

3.1 Product Yields from Decarboxylation

Table 2 shows various products that resulted from Mg-Zn basic soap decarboxylation at 350 °C for 5 hours and atmospheric pressure.

Table 2 Results of Mg-Zn basic soap decarboxylation.

| Type of product | Yield [%-wt] |
|-------------------------|--------------|
| Liquid bio-hydrocarbons | 62.00 |
| Water | 10.53 |
| Solid residues | 19.39 |
| Gas | Undetermined |

This result shows that 62%.wt of liquid bio-hydrocarbons were produced via decarboxylation of Mg-Zn basic soap from palm stearin. This proves that liquid bio-hydrocarbons can be synthesized with basic soap as reactant. It also shows that the Mg-Zn combination has good catalytic activity for converting the reactant (Mg-Zn basic soap) into liquid bio-hydrocarbons via decarboxylation at 350 °C for 5 hours. This result shows that renewable hydrocarbon synthesis via basic soap decarboxylation does not depend on the presence of Pt and Pd (noble metals) catalysts and high pressure operation, as reported by previous researchers [9,23,24]. Evaporation of the water molecules of the basic soap was found to begin at about 120 °C, very rapidly proceeding to completion between 160 and 180 °C. After that, melting of the basic soap began at about 250 °C and became very rapid between 300 and 310 °C. Subsequently, the candidate

product in the form of steam started to be observed at about 325 °C. Most of the candidate products will be condensed into liquid bio-hydrocarbon (or green diesel) products, whereas the uncondensable part comes out as gas.

The percent weight of the gas cannot be determined, but the composition of the gas fraction was analyzed by GC-TCD. Comparison of the peak retention times from standards (CH₄, CO₂, CO and H₂) showed that the gaseous fraction contained CO₂, H₂ and CH₄. The presence of CO₂ proves that there had been a decarboxylation reaction, whereas the presence of H₂ indicates that there had been a dehydrogenation reaction. In addition, the CH₄ shows that there had been a dehydrocarbonation reaction.

The solid residue, namely Mg-ZnCO₃, was calcinated at 500 °C and atmospheric pressure for 3 hours. The calcination result indicates that about 33%-weight of carbon could be removed from the Mg-ZnO. Thereafter, the Mg-ZnO was converted to Mg-Zn(OH) through hydration and could be used again for preparing subsequent basic soaps. Therefore, the Mg-ZnCO₃ can be recycled.

3.2 Physicochemical Properties of Liquid Bio-hydrocarbon Product

Table 3 shows some selected physicochemical properties of the liquid bio-hydrocarbon product of Mg-Zn basic soap from palm stearin produced at a temperature of 350 °C for 5 hours.

Table 3 Physicochemical properties of liquid bio-hydrocarbon products.

| Components | Value |
|-------------------------------|-------|
| Acid value [mg KOH/gr sample] | 0.4 |
| Freezing point (°C) | <5 |
| Ketone/aldehyde group (-/+) | - |

The acid value of the liquid bio-hydrocarbon product was very small (0.4 mg KOH/g sample). This shows that about all of the free fatty acids (from palm stearin) were converted into basic soap and subsequently converted by the decarboxylation reaction into liquid bio-hydrocarbons. As for the freezing point, Table 3 shows that liquid bio-hydrocarbon products resulted from the Mg-Zn basic soap were not only dominated by n-heptadecane (its freezing point is 22.0 °C), as expected from palm stearin (C₁₈ predominantly contains fatty acids), but also consisted of a mixture of liquid bio-hydrocarbons with various carbon chain lengths, particularly short chain molecule bio-hydrocarbons, which have a lower freezing point.

3.3 Distribution of Liquid Bio-hydrocarbon Products

Figure 2 shows the chromatogram patterns of the liquid bio-hydrocarbon fraction from the reaction conducted at 350 °C and atmospheric pressure for 5 hours.

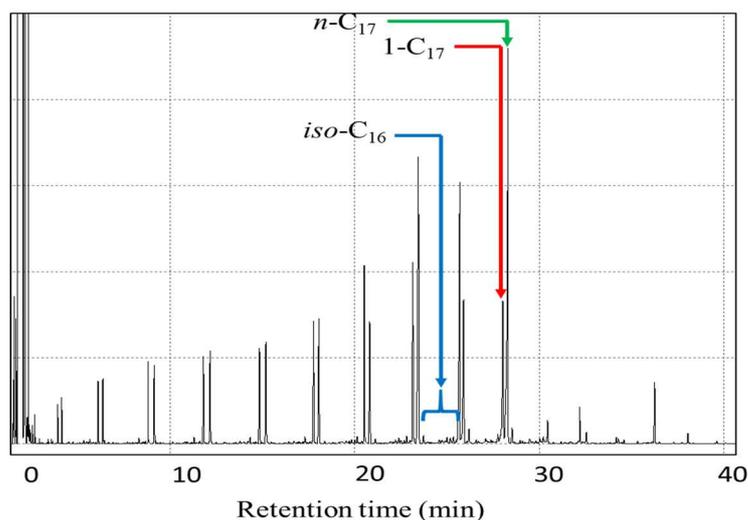


Figure 2 GC-FID chromatogram patterns for liquid bio-hydrocarbon fractions.

Figure 2 shows that decarboxylation of Mg-Zn basic soap produced liquid bio-hydrocarbons in very diverse boiling ranges, i.e. C₉ to C₂₁. It is indicated that, under the conditions of the experiment, not only decarboxylation took place but there may also have been a catalytic thermal cracking reaction of the liquid bio-hydrocarbons obtained, breaking them into smaller molecules, more like in jet fuel and bio-gasoline. In Figure 2 it can be seen that normal heptadecane (n-C₁₇) was observed as the dominant component in the liquid bio-hydrocarbon products at a retention time of around 28 minutes. However, bio-hydrocarbons with C₈ to C₁₆ fractions were also observed at a retention time of around 4 to 26 minutes with significant intensity. Note that the area represented by the C₈ to C₁₇ iso-alkanes in the chromatogram appears to be much smaller than the area for the corresponding carbon number in the n-alkanes and 1-alkenes.

The liquid product (between C₈ and C₂₀) was subjected to a detailed and careful analysis by gas chromatography, of which the results are shown in Table 4. The percentage of compounds above C₁₉ could not be carefully identified so that they were combined into a single unit. Table 4 shows that the main product of liquid bio-hydrocarbons was about 18.9%-mole, i.e. n-heptadecane fractions. This corresponds to the expected liquid bio-hydrocarbon products of the

decarboxylation of Mg-Zn basic soap derived from palm stearin. This experiment also produced significant amounts of n-pentadecane fractions (about 11%-mole). As for the 1-alkene fraction, more resulted from the carbon C₁₆ than from the other carbons. The remaining fractions were dominated by lower n-paraffin molecules besides olefin and iso-paraffin molecules.

Table 4 Distribution of liquid bio-hydrocarbons.

| Bio-hydrocarbon compounds | Formula | Product yield (%-mole) |
|------------------------------------|---------------------------------|------------------------|
| n-octane | C ₈ H ₁₈ | 0.84 |
| 1-octenes | C ₈ H ₁₆ | 0.70 |
| n-nonane | C ₉ H ₂₀ | 1.32 |
| 1-nonenes | C ₉ H ₁₈ | 1.32 |
| n-decane | C ₁₀ H ₂₂ | 1.80 |
| 1-decenes | C ₁₀ H ₂₀ | 1.90 |
| n-undecane | C ₁₁ H ₂₄ | 2.77 |
| 1-undecenes | C ₁₁ H ₂₂ | 2.23 |
| n-dodecane | C ₁₂ H ₂₆ | 3.28 |
| 1-dodecenes | C ₁₂ H ₂₄ | 2.53 |
| n-tridecane | C ₁₃ H ₂₈ | 3.60 |
| 1-tridecenes | C ₁₃ H ₂₆ | 3.45 |
| n-tetradecane | C ₁₄ H ₃₀ | 3.82 |
| 1-tetradecenes | C ₁₄ H ₂₈ | 5.04 |
| n-pentadecane | C ₁₅ H ₃₂ | 10.99 |
| 1-pentadecenes | C ₁₅ H ₃₀ | 5.15 |
| n-hexadecane | C ₁₆ H ₃₄ | 5.49 |
| 1-hexadecenes | C ₁₆ H ₃₂ | 7.95 |
| n-heptadecane | C ₁₇ H ₃₆ | 18.90 |
| 1-heptadecenes | C ₁₇ H ₃₄ | 4.63 |
| n-octadecane | C ₁₈ H ₃₈ | 0.97 |
| 1-octadecenes | C ₁₈ H ₃₆ | 0.29 |
| n-nonadecane | C ₁₉ H ₄₀ | 0.42 |
| 1-nonadecenes | C ₁₉ H ₃₈ | 1.10 |
| unidentified as individual species | > C ₁₉ | 1.80 |
| <i>i</i> -paraffins | | 7.44 |

In general, the alkane content was higher than the 1-alkene in C₈-C₁₉, except for C₁₄, C₁₆ and C₁₉. Equimolar fractions of n-alkanes and 1-alkenes were observed at lower carbon numbers than C₁₅. The ratio of alkane to its pair alkene in C₈-C₁₄ was smaller than 2 or close to 1. The proportion of n-heptadecane and n-

pentadecane was higher than its pair in 1-alkene. Therefore, the ratios between alkane and its pair alkene in C_{15} and C_{17} were 2.13 and 4.08 respectively. This shows that the combination of Mg-Zn has a significant selectivity toward the formation of green diesel bio-hydrocarbons. The formation of small alkanes and alkenes ($< C_{15}$) was probably due to the further decomposition of the long-chain bio-hydrocarbons that were generated previously. According to Rice [25], when an organic compound (e.g. hydrocarbon) decomposes, it is broken up into two or more radicals depending on the number of bonds in the molecule. Such a radical may either decompose into an olefin and a smaller free radical or it may react with the surrounding molecules to form hydrocarbons and generate a new free radical.

The composition group of n-paraffin, olefins and i-paraffin in the liquid bio-hydrocarbons was obtained from Mg-Zn basic soap decarboxylation of palm stearin, as shown in Figure 3. Figure 3 shows that approximately 41.08 %-mole of liquid bio-hydrocarbons obtained from Mg-Zn basic soap decarboxylation were various 1-alkene molecules. The presence of 1-alkene in a large amount shows that there was a dehydrogenation reaction during the Mg-Zn basic soap decarboxylation or decomposition of long chain paraffin. According to Rice [26], larger radicals (derived from decomposition of long chain hydrocarbons) apparently decompose to yield one or more molecules of an olefin and either a methyl group, an ethyl group or atomic hydrogen.

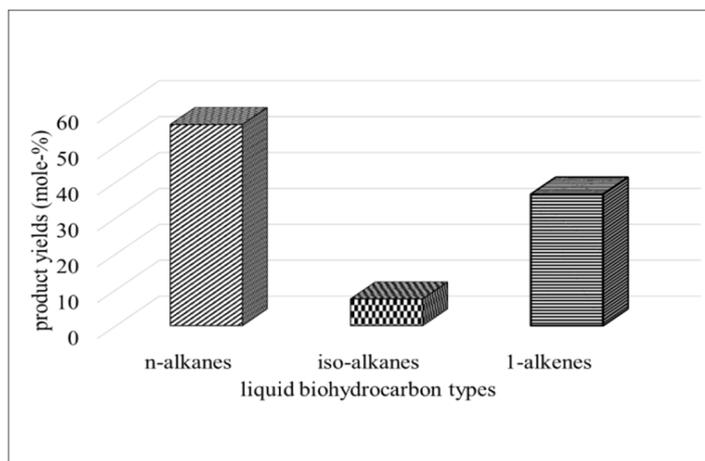


Figure 3 Liquid bio-hydrocarbon types of Mg-Zn basic soap decarboxylation.

Figure 4 shows the carbon chain length distribution of n-paraffin type in liquid bio-hydrocarbons produced from Mg-Zn basic soap of palm stearin at 350 °C for 5 hours. It shows that bio-hydrocarbon with carbon chain length C_{17} (n-heptadecane) was most dominant (18.90 %-mole) in the liquid product of Mg-

Zn basic soap decarboxylation at 350 °C for 5 hours. The bio-hydrocarbons with further carbon chain length were C₁₅ (n-pentadecane, 10.99 %-mole), C₁₆ (n-hexadecane, 5.49 %-mole), and other n-paraffin molecules lower than C₁₆, respectively.

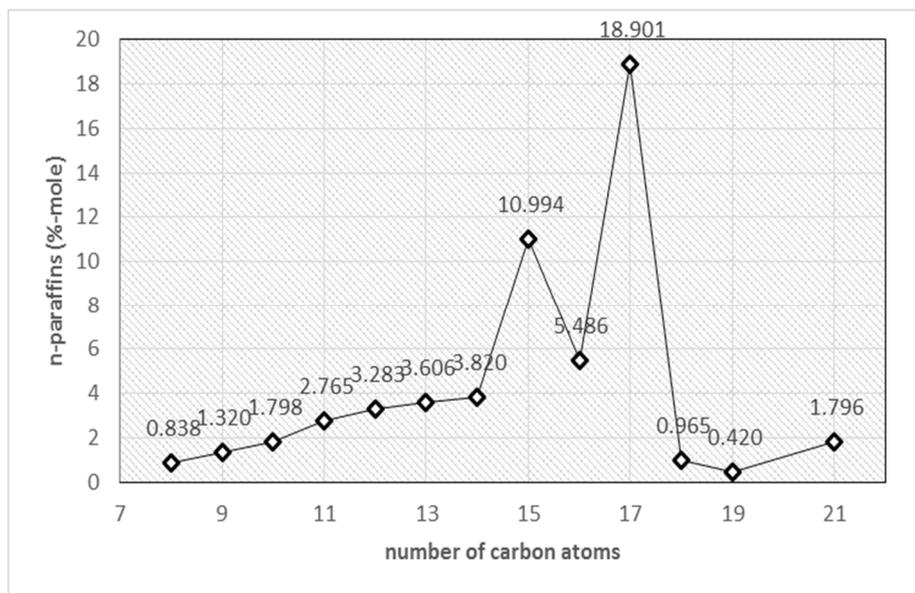


Figure 4 Formation of paraffins during decarboxylation of Mg-Zn basic soap.

4 Conclusion

Drop-in fuel (liquid bio-hydrocarbons) in the boiling range of diesel can be synthesized via basic soap decarboxylation without the aid of hydrogen from the outside and without using commercial catalyst. Mg-Zn basic soap (9/1 mol ratio of Mg/Zn) was derived from palm stearin and decarboxylated for 5 hours at atmospheric pressure and temperature between 250 to 350 °C, effectively yielding a diesel-type bio-hydrocarbon fuel, with a liquid product yield of 62%-weight. The resulting hydrocarbon product was a complex mixture consisting of normal paraffins in the range of carbon chain length C₈–C₁₉, iso-paraffins and various olefin products.

Acknowledgements

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