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RENEWABLE FUEL PRODUCTION BY THERMAL CATALYTIC DECARBOXYLATION OF BASIC SOAP FROM STEARIC ACID

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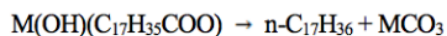
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1. Introduction

Nowadays, many countries have shown great interest in alternative fuel and sustainable technology dealing with the increasing hydrocarbon liquid fuel demand and environmental awareness. Biohydrocarbon or liquid hydrocarbon biofuel are renewable fuel derived from any material that originated from biological matters. Generally, they can be converted from vegetable oils and fats and their hydrolysis and fractionated product such as the stearic acid. Decarboxylation, that is, elimination of the -COOH group to be CO₂, is a known process. Decarboxylation is a decomposition of triglyceride molecules present in oils and fats leading to the formation of a mixture of chemical compound with properties very similar to fossil fuels and it can be used directly in conventional engines [1]. Fatty acid can be converted directly into alkanes by decarboxylated [2]. A number of researches conducted experiment on catalytic decarboxylation of fatty acids to generate hydrocarbons, in which clays were used mostly as the catalysts [3,4]. Fatty acids can be also converted to basic soap and then it decarboxylated by heating to produce green diesel, that is, a diesel-like hydrocarbon fuel. Green diesel possesses good fuel properties such as lower viscosity, better fuel stability and higher energy density than biodiesel [5, 6]. The presence of the properties mentioned above, green diesel is considered to be a drop-in replacements for fossil-based diesel.

Decarboxylation of basic soaps of the higher fatty acids generally gives better yields of hydrocarbon than that of obtained by direct decarboxylation of the corresponding fatty acids or fats [7]. Basic soap decarboxylation as illustrated in the reaction equation below with stearic acid, has not been studied intensively to be developed on an industrial scale.



Accordingly, the objective of the present invention to provide a better alternative process for producing green diesel from natural fats and oils and their derivatives. Generally, the invention is directed to the production green diesel from thermal catalytic decarboxylation of basic soap derived from stearic acid with combination magnesium and zinc metals. In particular, the present invention to investigate the decarboxylation of the basic soap at mild operating conditions without external supply of hydrogen.

2. Experimental

The Mg-basic soap were obtained via metathesis process. The process started by mixing stearic acid and hot ethanol. Then, stirred the mixture with an aqueous solution of sodium hydroxide at 20% (w/w) until it has reached a firm consistency. While continually stirring, to this mixture is then added slowly a solution of magnesium acetate tetrahydrate in distilled water. The resulting basic soaps were filtered, washed (by hot water) and dried for use in subsequent experiments.

Saponification reactions were carried out in a glass batch reactors. Decarboxylation reaction were performed in a glass batch reactor at atmospheric pressure with a water-cooled condenser. Heat was supplied by a high temperature heating mantle and both liquid (the melted soap) and vapor temperatures were measured with thermocouple. Mg-basic soap from acid stearic used as a reactant model compound and the reactions were performed without the aid of other catalysts. Decarboxylation proceeded at temperatures until 375°C for 3 hours. The liquid products were collected in a beaker and then 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 enabling product identification and calibration. Determination of the freezing point have been tested with ASTM D-2500 procedures.

3. Results and Discussion

3.1 Product yields from decarboxylation

Table 1 shows various products that obtained from Mg-basic soap decarboxylation to 375°C for 3 hours and at atmospheric pressure. These result showing that liquid bio- hydrocarbon yields to 65.87%-weight. It is prove that liquid bio-hydrocarbons could be synthesized from basic soap as a reactants. It also shows that the Mg metal have good catalytic activity for converting the reactants (Mg-basic soap) into hydrocarbons via decarboxylation reaction.

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

Types of product	Yields [%-wt]
liquid bio-hydrocarbons	65.87
water	8.43
solid residues	21.52
others (include the gas)	4.18

3.2 Physicochemical properties of bio- hydrocarbon product

Table 2 shows some selected physicochemical properties of liquid bio-hydrocarbons product of Mg-basic soap to 375oC for 3 hours. Acid value in liquid bio-hydrocarbon product is very small (0.8 mg KOH / g sample). It is shows that all about of the stearic acid has been converted into basic soap and subsequent to converted by decarboxylation reaction into bio- hydrocarbon. For the freezing point, Table 2 shows that liquid bio-hydrocarbon product were obtained of Mg-basic soap just not dominated by n-heptadecane (their freezing point is 22,0°C) as which are expected from stearic acid, but also consisted of mixture of bio-hydrocarbon with various of

carbon chain length ranges, particularly short chain molecule bio-hydrocarbons that has a lower freezing point.

Table 2. Some of physicochemical properties

Components	value
acid value [mg KOH/gr sample]	0.8
Freezing point (°C)	<5
Ketones/aldehydes group (-/+)	-

3.3 Distribution of bio-hydrocarbon products.

GC-FID chromatograms patterns associated to distribution of liquid bio-hydrocarbon fraction were obtained from decarboxylation of Mg-basic soap of stearic acid to 375°C for 3 hours, shown in Fig. 1.

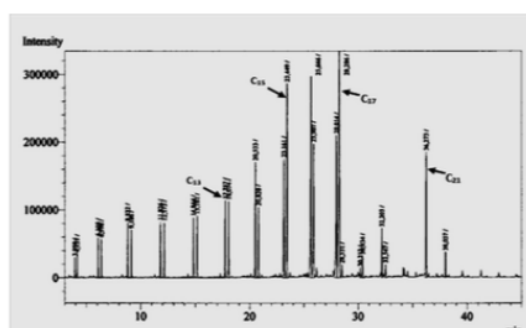


Fig. 1. GC-FID chromatograms patterns for liquid bio- hydrocarbon fractions

Fig. 1 shows that decarboxylation of Mg-basic soap was produced liquid bio-hydrocarbons in very diverse boiling range that is C9 to C21. It is also shows that, normal heptadecane (n-C17) observed as the dominant component in the liquid bio-hydrocarbon product at retention time around 28 minutes.

The results of GC-FID chromatogram analysis shows that the liquid bio-hydrocarbons comprises of C17 (27.15 %-mole) is the highest, the next is C16 (17.88%-mole) and C15 (15.32%-mole), respectively. These fractions are most expected from decarboxylation of Mg-basic soap of stearic acid, because included in diesel fuel ranges. The rest fractions is dominated by lower biohydrocarbon chain length molecules.

Table 3 shows the composition group of n- paraffin, olefins and i-paraffin in the liquid bio-hydrocarbon were obtained from Mg-basic soap decarboxylation of stearic acid.

Table 3 Liquid bio-hydrocarbon types Mg-Zn basic soap decarboxylation

compounds	Product yields (mole-%)
n-paraffins	56.70
Olefins	40.52
iso-paraffin	2.78

Table 3 shows that, approximately 40.518 %- mole of liquid bio-hydrocarbon were obtained from Mg-basic soap decarboxylation are various olefin molecules. The presence of olefins in

large amount shows that there has been a hydrogen consumption during the decarboxylation reaction by a specific element or residual oxygen in the reactor.

4. Conclusions

Biohydrocarbons in diesel boiling range, can be synthesized via basic soap decarboxylation, without the aid of hydrogen from the outside and the using not of commercial catalyst. The Mg-basic soap was derived from stearic acids and decarboxylated for 3 hours at atmospheric pressure and temperatures to 375oC, effectively yielding a diesel-type bio-hydrocarbons, with a liquid product yield of 65,87%-weight. The resulting hydrocarbon product is a complex mixture consisting of normal paraffins in the range of carbon chain length C8 - C21, iso-paraffins and the various olefin products.

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