Enzymatic pretreatment effect on product composition in biohydrocarbon synthesis via metal soap decarboxylation

A N Istyami¹, M Pratiwi¹, T Prakoso¹, and R Purwadi²

¹Department of Bioenergy Engineering and Chemurgy
Institut Teknologi Bandung, Kabupaten Sumedang 45363 Indonesia
²Department of Food Engineering
Institut Teknologi Bandung, Kabupaten Sumedang 45363 Indonesia

E-mail: anistyami@che.itb.ac.id

Abstract. The recent demand of green energy sources has driven technology development into production of renewable fuels. Among the types of renewable fuels, biobutanol is one of the most attractive forms. It can be applied onto current automotive machine without blending with fossil fuel. Biohydrocarbon can be produced from plant oils via decarboxylation of metal soap. Nevertheless, a hydrolysis step to convert plant oils into free fatty acids is required to synthesize metal soap. A low-cost technology to overcome this problem is hydrolysis reaction using lipase enzyme. In this paper, a study was established to determine the effect of enzymatic pretreatment on biobutanol product composition. Results show that enzymatic pretreatment increased selectivity towards diesel fuel fraction, although fractionation will enable utilization of shorter chain fractions.

1. Introduction
The impact of fossil fuel application on the environment has drawn the public’s attention in the last decades. Aside from being the source of carbon dioxide which contributes to the greenhouse effect, fossil fuel is considered as unsustainable source of energy on account of its limited reserves. Consequently, the technology of renewable energy sources developed rapidly, such as biodiesel (based on fatty acid methyl ester, FAME) and bioethanol as a mixture for diesel fuel and gasoline. Nevertheless, these types of biofuel cannot be applied without blending with fossil fuel, because both FAME and ethanol are oxygenated compounds. To imitate the conventional diesel fuel and gasoline, hydrocarbon-based biofuel (or biohydrocarbons) has been synthesized in many kinds of research methods [1, 2]. The product, which is also called drop-in biofuel, is readily applied into automotive engine without the necessity of blending with fossil fuel.

Biohydrocarbons can be synthesized via decarboxylation of metal soap, which is saponification product from triglyceride [3]. Triglyceride is abundant resource, especially because it is the main component of plant oils, but synthesis of metal soap from triglyceride requires high pressure [4]. Severity of process increases operation cost, and in the case of biofuel products, economic feasibility is a strong consideration. Alternatively, synthesis of metal soap can also be established from free fatty acid in mild operating conditions [5]. Triglycerides, consequently, need to be hydrolyzed into free fatty acids
prior to saponification. Hydrolysis of triglyceride can be established with noncatalytic thermal decomposition [6], which requires high temperature and high pressure (250 °C, 50 bar), nevertheless, mild process condition is preferable. Conversion of triglyceride into fatty acid can alternatively be done with enzymatic reaction, i.e., lipolysis. Using the lipase enzyme, the pretreatment step in biohydrocarbon synthesis is feasible to be established in atmospheric pressure and around room temperature.

Enzymatic synthesis biohydrocarbon from lipid has been reported before with Escherichia coli with yield of alkane under 0.5 g/L [7]. It requires active microorganism; thus oil in water emulsion is chosen for reaction medium. In this research, isolated enzyme was used instead of microorganisms, enabling the reaction to occur in oil-based medium and yields higher products.

This research aims to provide a comparison between biohydrocarbon product composition involving enzymatic pretreatment and without enzymatic pretreatment. Palm oil was selected as process feed, and crude plant lipase was selected as the lipolytic agent.

2. Material and Methods

2.1. Lipolysis of triglycerides
Lipolysis was conducted with crude plant latex lipase from frangipani (Plumeria rubra). Frangipani latex suspension was settled in 7°C and dried to obtain its dry, white powder precipitate. The latex lipase was mixed with palm oil and pH 8.25 buffer and stirred for 24 hours at room temperature. Lipolysis product, containing fatty acids and unreacted glycerides, was then converted into metal soap. In several experiments, sweet water was removed from lipolysis product prior to metal soap preparation. To separate sweet water, lipolysis product was heated until two layers were formed.

2.2. Preparation of metal soap
Metal hydroxide reagent was a mixture of calcium, magnesium, and zinc hydroxide, and was prepared using the procedure from reference [5]. In process without enzymatic pretreatment, palm fatty acid distillate (PFAD) was used as feed. In the process involving enzymatic pretreatment, lipolysis products were used as feed. Saponification products, which are in the form of dry, white powder, were then subjected to decarboxylation.

2.3. Decarboxylation of metal soap
Biohydrocarbon was produced via decarboxylation of metal soap in the previous step. Sample of 10 g metal soap was heated to 370°C and the temperature was held for 3 or 5 hours. The product obtained were clear yellow liquids, which was then analyzed using GC-FID.

2.4. Analysis of biohydrocarbon
The composition of biohydrocarbon was analyzed using gas chromatography Shimadzu 2010 (30 × 0.25 mm × 0.25 μm) equipped with an FID and a Restex-1 capillary column. Helium gas was used as a carrier. The temperature of injection was 340 °C. The column temperature was set from 40 to 300 °C with 5 °C/min rate, then raised to 315 °C at a rate of 1 °C/min and kept for 10 min. Alkane C8–C20 was used for calibration standards.

3. Results and Discussion
The objective of metal soap decarboxylation is the removal of carboxylate group from esters of fatty acids, leaving hydrocarbons as the product. Researches have been conducted to develop this technology, i.e., selection of metal oxide [8] and operating condition in saponification and decarboxylation [3].

Temperature rise in decarboxylation facilitates carbon chain cracking, which leads to various lengths of hydrocarbon products. The product is then fractionated so they can be applied based on their respective characteristics. Generally, a long carbon chain (C13-C17) to diesel engines, medium carbon chain (C10-C14) is dedicated to aviation jet engine, and a shorter carbon chain (C7-C10) is dedicated for Otto engine.
This research aims to identify the effect of enzymatic pretreatment on product composition in biohydrocarbon synthesis via metal soap decarboxylation. Figure 1 shows the GC-FID chromatogram of biohydrocarbon synthesized. Figure 2 and Figure 3 shows experimental results with no enzymatic pretreatment. Biohydrocarbon was synthesized from palm fatty oil distillate (PFAD), which mostly consists of fatty acids. Figure 4 and Figure 5 shows the experimental result with enzymatic pretreatment. Plant oils, which mostly consists of triglyceride, were hydrolyzed using crude plant lipase to increase its fatty acids content prior to saponification.

In process without enzymatic pretreatment, product distribution was spread into C11-C15 biohydrocarbons. Isoalkane content was high, indicating a high reaction rate of isomerization during the process. The product was roughly suitable for aviation jet engine, though higher alkane content is preferable to comply with jet fuel specification. There was no significant difference between 3rd and 5th hour decarboxylation products. The results also confirm the feasibility of biohydrocarbon synthesis in atmospheric pressure.

PFAD, which is a by-product from the palm oil industry, mainly consists of free fatty acids (mostly palmitic and oleic acids). It is the top product of steam distillation in fatty acid removal, thus considered to be oleochemical industrial waste. Utilization of PFAD into biofuels is an effective way of increasing value of palm oil, nevertheless, biofuel is commonly produced in huge-capacity. It is desired to provide technology of biohydrocarbon synthesis from the more abundant resources, such as the plant oil itself.

Fatty acids, which is good substrate for metal soap synthesis in mild operation condition, has been commercially produced from plant oils through thermal hydrolysis of triglyceride (Colgate-Emery) process. This process is very effective and results in high yield; nevertheless, it requires high temperature and high pressure. The severity of process tends to increase product cost, and in the biofuel industry, it is expected to reduce operating costs as low as possible. Alternative technology of converting plant oil into fatty acids is enzymatic hydrolysis, which is feasible in room temperature and atmospheric pressure. Triglycerides in plant oils are converted into fatty acids with the utilization of lipase enzyme (thus the reaction is also known as lipolysis) prior to saponification and decarboxylation.

Biohydrocarbon produced using enzymatic pretreatment, as shown in Figure 4, contains a longer chain compared to biohydrocarbon from PFAD (Figure 2). It might be an effect of monoglyceride presence, which is produced from lipolysis. Monoglyceride is an intermediate substance in the hydrolysis of triglyceride. It might be easier to be saponified than triglyceride, thus metal soap from monoglyceride might be formed. When decarboxylation was performed into monoglyceride metal soap, long chains of hydrocarbons may have been produced more compared to decarboxylation of fatty acid metal soap.

Prolonged decarboxylation into 5 hours yields in more alkane (and alkene), suggesting that isoalkane was polymerized into a longer chain. The product composition was dominated by diesel fuel fraction (C14-C15 alkane). The shorter carbon chain fraction, which also contains isoalkane, is a potential source of jet biofuel and green gasoline. Compared to biohydrocarbon synthesis from PFAD, the enzymatic pretreatment process is more selective towards C15-C17 alkane formation, which is the theoretical product of metal soap decarboxylation derived from palm oil. Monoglyceride appeared to decarboxylate in different mechanism from fatty acids, which promotes diesel fraction more than pure metal soap from fatty acids.

This product was then improved by removing lipolysis lower product, which consists of glycerine and water (also known as sweet water). Glycerine and water were considered to be contaminant in saponification. The results are shown in Figure 6 and Figure 7. Separation of glycerine product, as identified in Figure 7, yields in a higher content of C14 and C15 alkane.
Figure 1. GC-FID chromatogram of of biohydrocarbon synthesized (a) from PFAD and 3 hours decarboxylation, (b) from PFAD and 5 hours decarboxylation, (c) from lipolyzed oil and 3 hours decarboxylation, (d) from lipolyzed oil and 5 hours decarboxylation, (e) from upper layer of lipolyzed oil and 3 hours decarboxylation, (f) from upper layer of lipolyzed oil and 5 hours decarboxylation
Figure 2. Product composition of biohydrocarbon synthesized from PFAD and 3 hours decarboxylation

Figure 3. Product composition of biohydrocarbon synthesized from PFAD and 5 hours decarboxylation

Figure 4. Product composition of biohydrocarbon synthesized from lipolysis product and 3 hours decarboxylation
Figure 5. Product composition of biohydrocarbon synthesized from lipolysis product and 5 hours decarboxylation

Figure 6. Product composition of biohydrocarbon upper layer of lipolysis product and 3 hours decarboxylation

Figure 7. Product composition of biohydrocarbon upper layer of lipolysis product and 5 hours decarboxylation
4. Conclusion

In this research, an enzymatic approach was established to pretreat plant oils into an intermediate that enables metal soap synthesis in atmospheric pressure. The pretreatment appeared to increase the selectivity of biohydrocarbon product into a specific fraction, i.e., diesel fuel fraction. Monoglyceride presence was predicted to offer a different mechanism of saponification and decarboxylation. The decarboxylation period takes a role in deciding how far the reaction proceeds. Removal of sweet water in lipolysis product yields in higher selectivity towards diesel fuel fraction. Overall, biohydrocarbon production with enzymatic process in this research results in higher yield compared to previous references.

Reference

[1] Kubičková I, Snåre M, Eränen K, Mäki-Arvela P and Murzin D Y 2005 Hydrocarbons for diesel fuel via decarboxylation of vegetable oils Catal. Today 106 197–200
[2] Wang W C, Thapaliya N, Campos A, Stikeleather L F and Roberts W L 2012 Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation Fuel 95 622–9
[3] Pratiwi M, Neonufa G F, Prakoso T and Soerawidjaja T H 2018 The synthesis of magnesium soaps as feed for biohydrocarbon production MATEC Web Conf. 156
[4] Blachford J 1980 Manufacture of metallic soaps US4316852A
[5] Rogers J R H and Blew J W R 1956 Manufacture of metal soaps US2890232A
[6] Lascaray L 1952 Industrial fat splitting J. Am. Oil Chem. Soc. 29 362–6
[7] Rahman Z, Nawab J, Sung B and Kim S 2018 A critical analysis of bio-hydrocarbon production in bacteria: current challenges and future directions Energies 11
[8] Neonufa G F, Pratiwi M, Istyami A N, Elizabeth L, Dewi S S, Purwadi R, Prakoso T and Soerawidjaja T H 2018 An innovative method to produce drop-in fuel by alkaline earth-transition metals basic soap decarboxylation MATEC Web of Conferences 156
[9] Barnebey H L and Brown A C 1948 Continuous fat splitting plants using the colgate-emery process J. Am. Oil Chem. Soc. 25 95–9

Acknowledgment

The authors are thankful for support given by Institut Teknologi Bandung and BPDPKS (Indonesian Oil Palm Plantation Fund Management Agency) for the research fund awarded through P3MI 2019 and GRS 2018 program.