Production of Biogasoline via Pyrolysis of Oleic Acid Basic Soaps

Endar Puspawiningtiyas[1,2], Tirto Prakoso[1,3,*], Meiti Pratiwi[3], Subagjo[1] & Tatang Hernas Soerawidjaja[3]

[1]Department of Chemical Engineering, Institut Teknologi Bandung,
Jalan Ganesa No. 10, Bandung 40132, West Java, Indonesia
[2] Department of Chemical Engineering, Universitas Muhammadiyah Purwokerto,
Jalan Ahmad Dahlan, Purwokerto 53182, Indonesia
[3]Department of Bioenergy and Chemurgy, Institut Teknologi Bandung,
Jalan Ganesa No. 10, Bandung 40132, West Java, Indonesia
*E-mail: tirto@che.itb.ac.id

Highlights:

- The development of bio-hydrocarbon synthesis without hydrogen consumption.
- Oleic acids were used to produce bio-hydrocarbon via saponification and pyrolysis of metal soap.
- The choice of metals for saponification is significant to obtain a basic soap that is an excellent raw material for bio-hydrocarbon synthesis through pyrolysis.

Abstract. In this study, an investigation on the effect of the Ca/Mg/Zn mixing ratio on gasoline-range hydrocarbon production by oleic basic soap pyrolysis was carried out. The ratios of calcium to magnesium used were 15%, 35%, 50%, 65%, and 85% with constant Zn. Oleic basic soap was obtained by saponification with the modified fusion method. Pyrolysis experiments were carried out at 450 °C using a semi-continuous reactor with a feed flow rate of 5 g/15 min. The process produced three fractions, i.e., gas, solid, and liquid (bio-hydrocarbon + water). The gas products were characterized by GC-TCD, and the results showed the presence of carbon dioxide, hydrogen, nitrogen, oxygen, and methane. Based on the GC-FID and FT-IR results, the bio-hydrocarbon comprised mainly homologous hydrocarbon from carbon number C_7 to C_{19} containing n-alkanes, alkenes, various iso-alkanes, and some oxygenated compounds. All calcium ratios in the oleic basic soap produced hydrocarbon in the range of gasoline (C_7-C_{11}) as the dominant product. The maximum yield of gasoline (74.86%) was achieved at 15% calcium.

Keywords: *bio-hydrocarbon; gasoline; metal soap; oleic acid; pyrolysis.*

1   Introduction

Increasing global concern about climate change has encouraged the use and development of renewable energy technology. Many studies have been conducted by researchers to find production methods and sources of raw materials that have
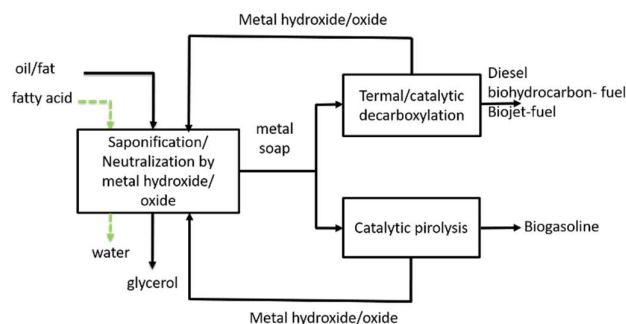
the potential to produce renewable fuels as alternatives for fossil fuels. Pyrolysis, one of those methods, is a thermal degradation process that can be used to treat materials in an oxygen-free atmosphere to produce liquid oil, gases, and char [1]. Previous studies have shown that some raw materials with the potential to produce bio-hydrocarbon equivalent to fossil fuels via pyrolysis are biomass, plastic, triglyceride/fatty acids, and metal soaps. Pyrolysis of various biomasses can pyrolyze plastic into hydrocarbon, as investigated in [2-7]. In [8-14], triglycerides/fatty acids were used as the raw material for pyrolysis. Moreover, investigations on bio-hydrocarbon production via pyrolysis of metal soaps have been carried out in [15-17].

Metal soap is a salt of fatty acids with non-alkali metals. It is generally made from metals with a valence of 2 or more. If M is a metal with a valence of 2 and R is an alkyl group, then $M(OOCR)_2$ is a metal stoichiometric soap and $M(OH)(OOCR)$ is a metal basic soap. According to [18], metal soaps that are good to use as raw material for making bio-hydrocarbon via pyrolysis are basic. The report shows that a significant difference between the pyrolysis of basic soaps and stoichiometric soaps lies in the obtained product. While the former produces only hydrocarbons, the latter produces not only hydrocarbons but also ketones and aldehydes. This is supported by Hsu [19] who proposed the mechanism of stoichiometric soap pyrolysis, similar to Kaisha [18]. The first step is stoichiometric soap reduction into metal carbonates and long-chain ketones and the second step is breakdown of the long-chain ketones into hydrocarbons, shorter ketones, and aldehydes. Although almost all research on metal soap pyrolysis only involved a single metal, there are also some works in the literature that report the use of two metals [15].

This research investigated the production of gasoline-range hydrocarbon via pyrolysis of oleic basic soap. The purpose of this research was to study the effect of the Ca/Mg/Zn mixing ratio on gasoline-range hydrocarbon production by oleic basic soap pyrolysis. The choice for calcium was based on the decomposition temperature of calcium carbonate, which is higher than 400 °C. This keeps the basicity of the soap at pyrolysis temperature. Magnesium is known as a decarboxylating compound, while zinc is an alkane isomerization catalyst. The technology used to achieve the research goal is shown in Figure 1.

The fatty acids used in this study were oleic acids. Mechanisms for the thermal decomposition of fatty acids are likely to be complex. Figure 2 outlines a schematic that explains the formation of alkanes, alkenes, alkadienes, aromatics, and carboxylic acids from the pyrolysis of oleic acids [20].

Figure 1 Flow diagram of bio-hydrocarbon fuel production from vegetable oil/fatty acids.
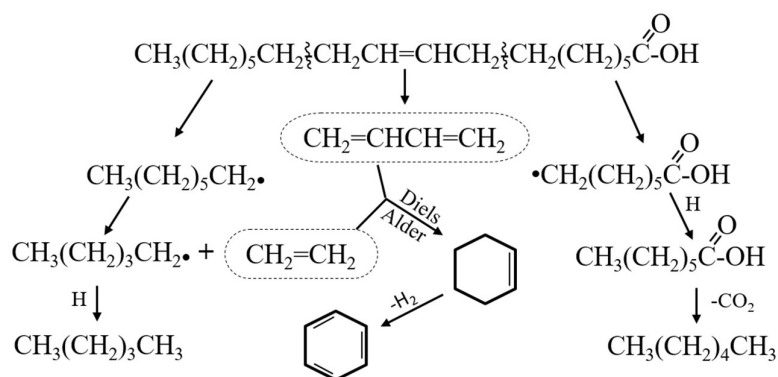
Figure 2 Decomposition mechanisms of an oleic acid into its hydrocarbons.

2   Experiments

The oleic acids that were used as raw material for saponification were taken from PT Energi Sejahtera Mas, an oleochemical manufacturer in Dumai, Riau, Indonesia. The saponification and iodine values of the oleic acids were 198.9 and 93.05 mg KOH/100 g sample. There was no pre-treatment of the acid. The composition is shown in Table 1. Mixing the metal hydroxide was done by co-precipitation of the mixed metal (Ca, Mg, Zn) chloride with sodium hydroxide. Calcium chloride dihydrate [$CaCl_2.2H_2O$], magnesium chloride hexahydrate [$MgCl_2.6H_2O$], zinc chloride tetrahydrate [$ZnCl_2.4H_2O$], and sodium hydroxide [NaOH] with 99 % purity were purchased from Merck.

Table 1   Composition of commercial oleic acids, % of total.

Fatty acids	Composition (%)
Stearic acids (C18:0)	8
Oleic acids (C18:1)	79
Linoleic acids (C18:2)	11
Others	2

2.1   Preparation of Mixed Metal Hydroxide

The mixed divalent metal hydroxides were prepared using the co-precipitation method reacting sodium hydroxide solution with high carbonate chloride content in a base solution. The molar ratio of Ca compounds to Mg, denoted as μ, was varied in the range of 15% to 85%, as depicted in Table 2, while the molar ratio of Zn remained constant at 1. Consideration of the molar ratio of Zn was based on Zn being easier to form soap than the other two metals. According to [21-23], when a mixture of CaO or MgO with Zn is reacted with fatty acids, then Zn will bind to the fatty acids. In addition, the function of Zn as an isomerization catalyst is very beneficial for the quality of the liquid bio-hydrocarbon. The ratios of Ca and Mg were varied to determine the effect of Ca in maintaining the alkalinity of the soap. Besides that, to study the effect of Mg in removing the carboxyl groups from the fatty acids during pyrolysis. The first A burette contained 50 ml of 2 molar (Ca + Mg + Zn) chloride combination solution and the second B burette contained 50 ml of 4 molar NaOH solution. The co-precipitation was controlled by the drop rate of the B burette to keep the pH of the slurry at 9.6. After 30 minutes of stirring, the formed slurry precipitate was separated by filtering and washing with water. Then, the slurry was dried at 105 °C for 12 hours.

Table 2   Ca molar ratios.

Ca composition notation	Ca metal (μ)	Mg metal	Zn metal
15 μ	0.15	0.85	1
35 μ	0.35	0.65	1
50 μ	0.50	0.50	1
65 μ	0.65	0.35	1
85 μ	0.85	0.15	1

2.2   Saponification

The saponification procedure used a combined method based on previous researchers [21,24,25]. First, 0.1 mol oleic acids was mixed with 0.05 mol mixed metal hydroxide based on procedure 2.1. Subsequently, 4 ml distilled water and 0.18 formic acid 98-100% were added to the mixture. An exothermic reaction occurred in the basic soap formation. Thereafter, mixing was carried out for 30 minutes. Eventually, the metal basic soap was dried at 60 °C for 12 hours.

2.3 Pyrolysis of Basic Soap

The pyrolysis reactions were carried out in a stainless reactor unit equipped with a vessel (ID: 8 cm, L: 36 cm), two thermocouples for the liquid and vapor phases, a feeder, an air condenser, and a liquid collector (Figure 3). After the reactor was heated to 450 °C, N_2 gas was passed into it for about 10 minutes to drive out the oxygen. According to [26], the presence of oxygen in pyrolysis is a trigger for oxidation of the fatty acids; oleic acids as raw material of basic soap are unsaturated fatty acids that are not stable and are prone to oxidation. The reaction is not beneficial because it will produce 1-alkene.

Basic soap samples (50 mg) were fed to the reactor at a feeding rate of 5 g/15 min. The temperature was kept constant during the feeding process. Reactor heating was continued for 2 hours. Basically, oleic metal soap pyrolysis is the process of removing carboxyl groups and cracking oleic acids. The choice of the pyrolysis temperature of 450 °C was based on previous reports on the pyrolysis of oleic soap or oleic acids [27-29]. In these reports, the most optimum liquid bio-hydrocarbon product was produced at a temperature of 450 °C.
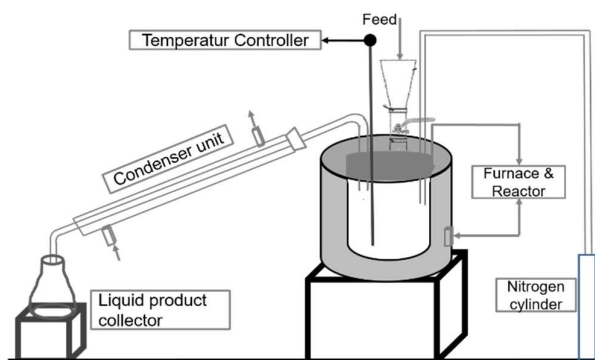

Figure 3 Schematic of the pyrolysis setup.

2.4 Analytical Method

2.4.1 Basic Soap Analysis

The successfulness of the saponification reaction can be seen from the acid value (AV) and the total alkali content (TAC). AV indicates the amount of free fatty acids used to calculate the reaction conversion, while TAC shows the basicity of the metal soap. These analyses are in accordance with AOCS CD 3D-63 (AV) and ISO 685-1975 (TAC). The conversion of saponification reaction (Cs) can be expressed as follows:

$$Cs = \left(\frac{Avi - Avs}{Avs} \right) x \ 100\%$$

(1)

where Avi and Avs denote the acid value of the saponification feed (oleic acids) and the reaction product (metal soap), respectively.

2.4.2   Product Analysis

The yield (Yp) of the liquid product can be expressed as follows:

$$Yp = \left(\frac{np}{nt} \right) x \ 100\%$$

(2)

where np and nt denote the actual and the theoretical weight, respectively. To identify the hydrocarbon fraction distribution, the liquid products were analyzed on a gas chromatograph-flame ionization detector (GC-FID) with the procedure from [30]. The GC-FID was equipped with an Rxi-5 column (5 % diphenyl 95% dimethyl polysiloxane, 30 m x 0.25 μm x 0.25 mm) and an MS detector. Helium was used as carrier gas at a flow rate of 1 ml/min. The following chromatograph temperature program was used for analysis: 40 °C (initially) – 300 °C (5 °C/min) – 340 °C (10 °C/min, constant 45 min). Identification of various functional groups and compounds contained in the basic soap was conducted with Fourier transform infra-red (FT-IR) analysis. The instrument, a Bruker Alpha-platinum FT-IR, is a spectrometer with platinum diamond sampling. The gas product of the basic soap pyrolysis was analyzed in a Shimadzu GC-TCD (thermal conductivity detector). The instrument was equipped with two columns: a capillary column (Porapak-Q, 30 m) and a molecular sieve column (5A, 30 m).

3   Result and Discussion

3.1   Saponification Reaction

Metal basic soap was synthesized by reacting oleic acids with mixed metal hydroxide. The analysis of the acid value and the TAC on the metal basic soap at various Ca ratios was carried out to discover the free fatty acids and the soap alkalinity. The results of the analysis are shown in Table 3. In addition, the acid value was used to calculate the conversion of the saponification reaction, which is a parameter of the successfulness of the reaction (column 3). This showed that the reaction conversion for all Ca ratio variations was more than 90%, which means that saponification occurred. The soap is declared alkaline when the TAC value reaches ≤50% [30]. Table 3 shows that the TAC value in all metal soaps showed basicity. This is also supported by the results of the FT-IR analysis of the metal basic soap in Figure 4. This shows that the results for all Ca ratios had a similar peak group identifier. The hydroxyl group (-OH) appeared in the range of

wave number 3200 to 3600 cm^{-1}. The C-H group was detected at wave numbers 2850 to 2970 cm^{-1}. This group reflects the bonding of C-H atoms in the long alkyl group on the basic soap. Another group detected by FT-IR analysis was the carboxyl group (COO) at wave numbers 1050 to 1760 cm^{-1}. The presence of this group may be the result of using oleic acids as raw material for making the metal basic soap.

Table 3 shows that the 15 μ and 50 μ Ca molar ratios had almost the same TAC. On the other hand, the acid values were quite different. According to [31], TAC is the sum of the alkali bases combined as soap with fatty and rosin acids. This is a parameter for the basicity of the soap. In comparison, the acid value indicates the amount of free fatty acids that are not saponified. These parameters cannot be directly related with each other because the acid value affects the conversion of the reaction more (Eq. (1)). The smaller the acid value, the larger the conversion. This is in line with the results of the reaction conversion at 50 μ, i.e., greater than 15 μ.

Table 3   Reaction conversion, acid and tac value of basic soap at various Ca metal ratios.

Ca composition	Total alkali content (%)	Acid value (mg KOH/g sample)	Reaction conversion (%)
15 μ	40	14	95
35 μ	51	15	91
50 μ	38	3.0	98
65 μ	46	10	93
85 μ	44	7	94

3.2   Phenomena in the Basic Soap Pyrolysis

Table 3 presents the response intensity diagram at a certain retention time. It shows that the pyrolysis product contained CO_2, H_2, N_2, O_2, and CH_4. The presence of CO_2 gas predicts that the production of bio-hydrocarbon via basic soap pyrolysis occurs through a decarboxylation reaction. Moreover, the existence of a low CO_2 gas content indicates that discharge of the CO_2 group by the metal mixture to form mixed metal carbonate occurred sufficiently. Besides the decarboxylation reaction, the hydrogen formation (65.59%-mol) was attributed to dehydrogenation reactions in the formation of alkenes and H_2 as well as decomposition of alkenes, which produces carbon and H_2. According to [32], these reactions can be represented by Eqs. (3) and (4).

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2 \qquad\qquad\qquad (3)$$

$$C_nH_{2n} \rightarrow nC + (n+1)H_2 \qquad\qquad\qquad (4)$$
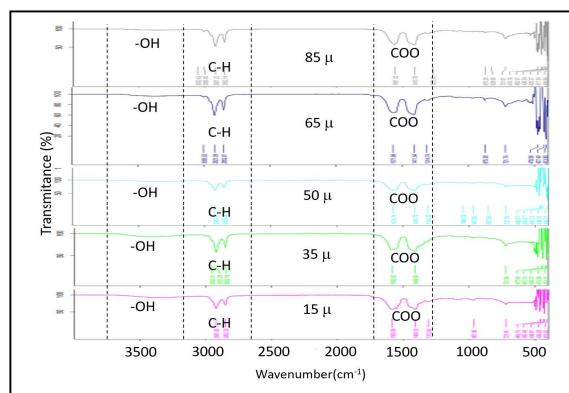
Figure 4 FT-IR of basic mixed metal soap from oleic acids.

Table 4 GC-TCD analysis of pyrolysis gas product pyrolysis.

Retention time (min)	Product	
	Gas	%-mol
2.83	CO_2	14
4.58	H_2	66
5.27	N_2	11
5.49	O_2	6
7.84	CH_4	4

As shown in Table 3, the presence of methane (CH_4) indicates the occurrence of hydrogen transfer based on [33] in Equation 5. Another possible mechanism for the formation of methane is alkane decomposition to produce alkenes and methane [34], as expressed in Eq. (6). The report explains that alkane decomposition involves displacement of the hydrogen position relatively far from carbon, from one end to the other. In addition, this type of reaction is rare so that the reaction that occurs in the pyrolysis of mixed metal oleic basic soaps due to the presence of methane is a hydrogen transfer reaction.

$$C_nH_{2n} \rightarrow C_nH_{2n+1} + CH_4 \tag{5}$$

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + CH_4 \tag{6}$$
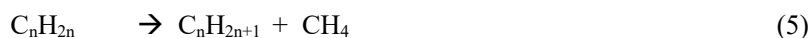
According to [32], the reaction that occurs after decarboxylation involves breaking the long chain alkenes into two shorter alkenes. These alkenes will undergo a hydrogen transfer reaction to form two free radicals, which will subsequently react with hydrogen as in Eq. (3) and (4) to form alkanes (bio-hydrocarbons).

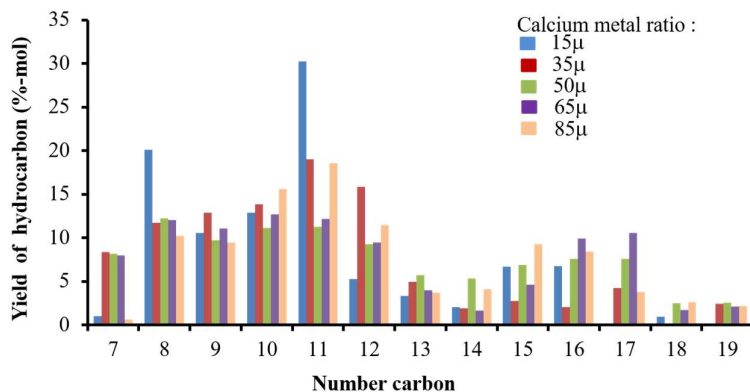### 3.3   Distribution of Product in the Liquid Fraction

The distribution of products in the liquid fraction can be observed from the result of GC-FID analysis on the liquid pyrolysis products. Chromatograms of the liquid product of the mixed metal basic soap from oleic acids conducted at various Ca ratios are shown in Figure 5. Only products with a molecular weight higher than hexane (C_6) were identified and quantified due to peak overlap between the solvent and low boiling compounds. Figure 5 shows that the identified bio-hydrocarbon series contained C_7 to C_{19} at all Ca ratio variations, including n-alkane series, 1-alkene series, and iso-alkanes. This means that the oleic acid was not completely cracked. Moreover, it shows that the reactions that occurred were not only decarboxylation and pyrolysis but also polymerization. Although the oleic acids were not cracked, Figure 6 shows that for almost all Ca ratio variations, the bio-hydrocarbons were dominated by C_7-C_{11}. This shows that the cracking reaction occurred adequately as expected.
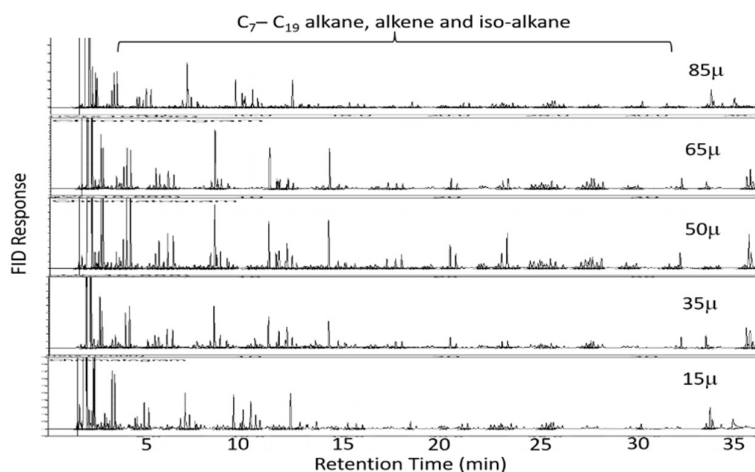
Figure 5 GC-FID chromatograms of liquid product pyrolysis of basic mixed metal soap from oleic acids for various Ca ratios.

Almost all Ca ratios showed a liquid bio-hydrocarbon composition dominated by C_{11}. This is supported by a previous study, which pyrolyzed Ca, Mg, Zn oleic soap, respectively [35]. The report showed that pyrolysis of Zn oleic soap produced C_{11} as the dominant product in liquid bio-hydrocarbon. Based on Table 2, the molar ratio of Zn was higher than that of the other two metals for all Ca ratio variations. It is very reasonable that the bio-hydrocarbon composition is dominated by C_{11}. Figure 6 shows that the composition with a Ca molar ratio of 15 μ had a higher molar amount of Mg than Ca. In addition, the decomposition

601

temperature of Mg hydroxide is lower than that of Ca hydroxide. This causes this soap to crack easily at a temperature of 450 °C.

Figure 6 Compositions of hydrocarbons from pyrolysis of various Ca ratios.

## 3.4   Distribution of Liquid Products Based on Fuel Fraction

As shown in Figure 7, the distribution of products based on fuel fraction was classified as follows: light fraction/gasoline (C_7-C_{11}), middle fraction (C_{12}-C_{15}), and heavy fraction (C_{16}-C_{19}). The figure shows that the most abundant bio-hydrocarbon content was light fraction with an average yield of approximately 60.76 %-mol. The predominance of light fraction at all µ variations (figure 7) indicates that cracking was carried out well. The highest light fraction (74.9%) was obtained at 15 µ.
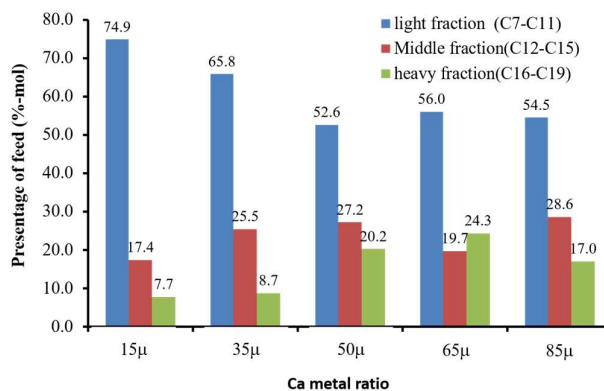
Figure 7 Light (C_7-C_{11}), (C_{12}-C_{15}) and heavy (C_{16}-C_{19}) fraction product composition after mixed metal basic soap pyrolysis for various Ca molar ratios.

3.5 Distribution of Liquid Products Based on Carbon Chain Groups

The content of carbon chain groups certainly affects the quality of the bio-hydrocarbon produced by basic soap pyrolysis. Distribution of the pyrolysis liquid products based on carbon chain groups is shown in Figure 8. This figure shows that alkanes did not change significantly from 15 μ to 65 μ (mean = 19.5% approximately) but decreased at 85 μ.
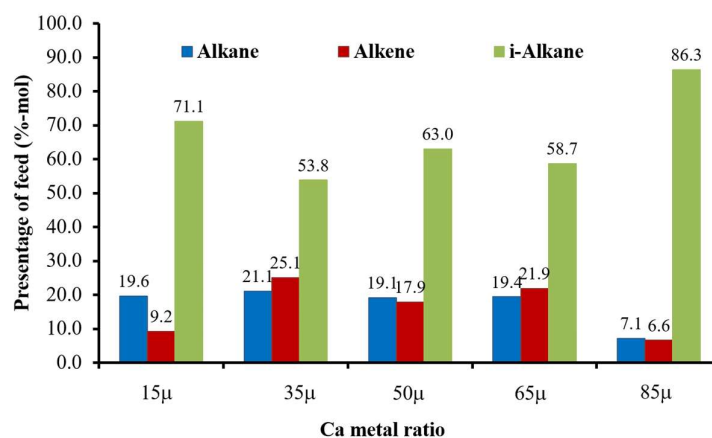
Figure 8 The n-alkane, 1-alkene and iso-alkane composition of liquid products from pyrolysis of mixed metal basic soap for various Ca molar ratios.

An alkene amount ≤10 % was reached with Ca 15 μ and 85 μ; however, at 35 μ, 50 μ, and 65μ, the amount showed fluctuation. Furthermore, all μ variations produced more i-alkanes than alkanes and alkenes. This could be explained by the fact that the isomerization rate was higher than the hydrogenation rate. Moreover, Zn was used in the hydroxide mixture, which is a transition metal that could isomerize hydrocarbons [36].

The bio hydrocarbon had a higher amount of saturated product compared to unsaturated product at all μ variations, possibly as a result of reaction saturation. A phenomenon that supports this hypothesis is the presence of hydrogen in gas fraction, as shown in Table 3. This is supported by previous research, which showed hydrogen in the pyrolysis product of different lipid feedstocks [37][38]. However, the result of the FT-IR analysis showed that the bio-hydrocarbon still contained ketone compounds.

603

Furthermore, the light fraction decreased from 15 μ to 50 μ, whereas the middle and heavy fraction showed an opposite trend. However, between 65 μ and 85 μ, there were no significant changes in the yield of light, middle and heavy fractions. These phenomena are opposite to the function of Ca. The aim of using Ca in oleic soaps is to keep the basic properties of the soap at a high pyrolysis temperature, because calcium hydroxide decomposition occurs above 400 °C. It is important to keep the basic properties of oleic soaps because soap pyrolysis produces only hydrocarbon, as reported by [18], while pyrolysis of stoichiometric soaps produces not only hydrocarbon but also ketone/aldehyde compounds so that the hydrocarbon yield will decrease. This means that the higher the Ca ratio in the basic soap, the higher the yield of light fraction hydrocarbon. Our previous research on the pyrolysis of Ca, Mg, and Zn oleic soaps separately showed that the highest light fraction yield was reached by Ca, followed by Mg and Zn oleic soap.

3.6 Distribution of Liquid Products based on the Length of the Carbon Chain in Product Types

The selectivity to the formation of alkane, alkene and iso-alkane components for every Ca ratio is shown in Figure 9. The figure shows that for all Ca ratios, bio-hydrocarbons with selectivity toward iso-alkanes were produced in significant amounts. The catalyst Zn was the largest component at all Ca metal ratios.
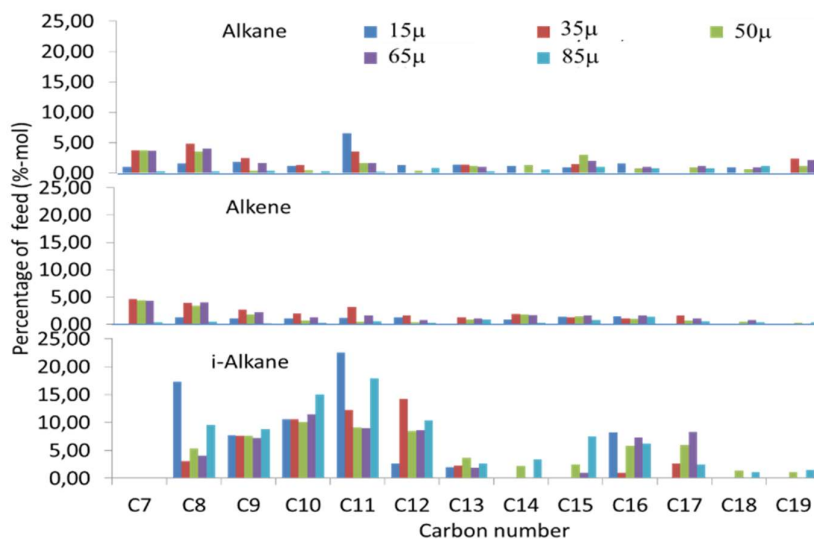

Figure 9 Composition of hydrocarbon from pyrolysis of mixed metal oleic basic soap at various Ca ratios.

It is a good result to have iso-alkane as the dominant product in this study, as it increases the octane number of gasoline. Figure 9 also shows that the selectivity of the products at a Ca ratio of 35 μ was towards dodecane (C_{12}) iso-alkane; at 15 μ and 85 μ it was towards undecane (C_{11}) iso-alkane; and at 50 μ and 65 μ it was toward iso-alkane C_{10}.

3.7   Phenomena in the Breakdown of Oleic Acid into Alkanes

Based on the results of this research, the breakdown steps of oleic acids into alkane could be predicted. The first step of oleic acid breakdown is carbon dioxide being released (decarboxylation) to form 8-heptadecene, as evidenced by the formation of heptadecane (C_{17}) in the bio-hydrocarbon (Figure 6). This was obtained by hydrogenation of 8-heptadecene (decarboxylation product). The next step is the cracking of 8-heptadecene into two shorter alkenes. There are two possible C-C bond locations for the breaking of 8-heptadecene. Both possibilities occurred [39]. The first possibility is the breaking of the C_6-C_7 bond to form undecene and hexene, while the second is the breaking of the C_{10}-C_{11} bond to form decene and heptene. Furthermore, the former will result in hydrogenation of alkene to form alkane, undecane, and hexane, while the latter will form decane and heptane. The mechanism of oleic acid breakdown is depicted in Figure 10.
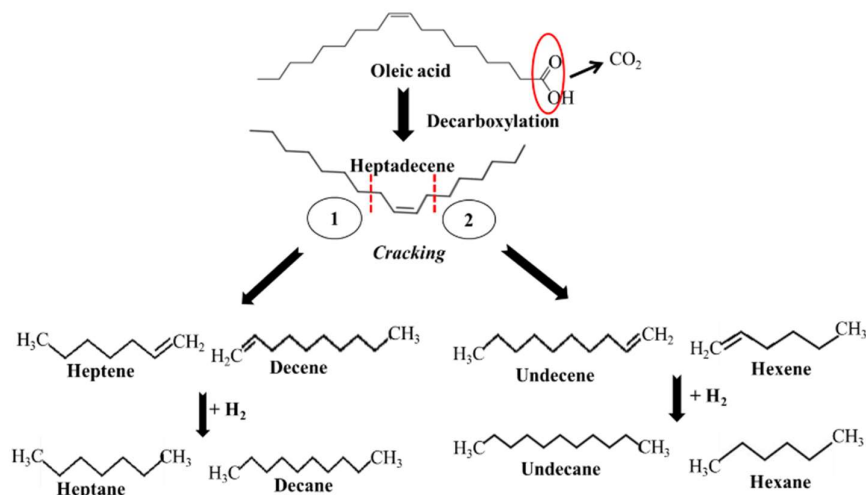
Figure 10   Mechanism of oleic acid pyrolysis.

The predominance of undecane (C_{11}) in bio-hydrocarbon (Figure 6) indicates that the first possibility of the C-C bond breaking was generally more dominant,

although the second possibility also occurred, as shown by the detected decane (C_{10}) at an amount below undecane (C_{11}).

This result is different from the previous research [40], which studied pyrolysis of polyunsaturated fatty acids at 350 to 450 °C. This report states that the presence of a double bond in oleic acids means that the breaking of the C-C bond was dominated by deoxygenation of short chain molecules. This may be due to the lower dissociation energy of the C-C allyl bond compared to the C-C bond next to a carboxyl group [41], which was evidenced by the formation of C_9 and C_{10} fatty acids as well as C_6 to C_9 alkane. The observed difference could be explained by differences in pyrolysis operation. While [40] conducted pyrolysis in a batch reactor whose feed was heated from room temperature to pyrolysis temperature, in this research pyrolysis was carried out in a semi batch reactor and the basic soap was fed at pyrolysis temperature.

4   Conclusion

Synthesis of bio-hydrocarbons in the gasoline range was successfully carried out via pyrolysis of metal basic soap from single unsaturated fatty acids, in this case oleic acids. Along with the pyrolysis process of oleic metal basic soap, both decarboxylation and cracking of the allylic C-C bonds occurred, simultaneously producing related hydrocarbons. The optimal metal molar ratio (μ) for producing gasoline-range hydrocarbon with the highest yield (±75%) was 15 μ. However, the bio-hydrocarbon product still contained oxygenated compounds such as ketones and aldehydes.

Acknowledgments

References

[1]   Lam, S.S., *Progress in Waste Oil to Sustainable Energy, with Emphasis on Pyrolysis Techniques*, Renewable and Sustainable Energy Reviews, **53**, pp. 741-753, 2016.

[2]   Scott, D.S., Plskorz, J. & Radleln, D., *Liquid Products from the Continuous Flash Pyrolysis of Biomass*, Industrial and Engineering Chemistry Process Design and Development, **24**(3), pp. 581-588, 1985.

[3]   Lede, J., *Flash Pyrolysis of Wood in a Cyclone Reactor*, Chemical Engineering and Processing, **20**(6), pp. 309-317, 1986.

[4]   Bridgwater, A.V., Meier, & Radlein, D., *An Overview of Fast Pyrolysis of Biomass*, Organic Geochemistry, **30**(12), pp. 1479-1493, 1999.

[5]   Anuar Sharuddin, S.D., *A Review on Pyrolysis of Plastic Wastes*, Energy Conversion and Management, 115, pp. 308-326, 2016.

[6]   Aramideh, S., *Numerical Simulation of Biomass Fast Pyrolysis in an Auger Reactor*, Fuel, **156**, pp. 234-242, 2015.

[7]   Kassargy, C., *Gasoline and Diesel-Like Fuel Production by Continuous Catalytic Pyrolysis of Waste Polyethylene and Polypropylene Mixtures Over USY Zeolite*, Fuel, **224**, p. 764-773, 2018.

[8]   Fortes, I.C.P. & Baugh, P.J., *Pyrolysis-GC/MS Studies of Vegetable Oils from Macauba Fruit*, Journal of Analytical and Applied Pyrolysis, **72**(1), pp. 103-111, 2004.

[9]   Buzetzki, E., *Effects of Oil Type on Products Obtained by Cracking of Oils and Fats*, Fuel Processing Technology, **92**(10), pp. 2041-2047, 2011.

[10]   Chiaramonti, D., *Bio-Hydrocarbons Through Catalytic Pyrolysis of Used Cooking Oils: Towards Sustainable Jet and Road Fuels*, in 70th Conference of the Italian Thermal Machines Engineering Association, ATI 2015, Elsevier Ltd., 2015.

[11]   Li, L., *Catalytic Hydrothermal Conversion of Triglycerides to Non-Ester Biofuels*, Energy and Fuels, **24**(2), pp. 1305-1315, 2010.

[12]   Herskowitz, M., *A Commercially-viable, One-Step Process for Production of Green Diesel from Soybean Oil on Pt/SAPO-11*, Fuel, **111**, pp. 157-164, 2013.

[13]   Asomaning, J., Mussone, P. & Bressler, D.C., *Thermal Cracking of Free Fatty Acids in Inert and Light Hydrocarbon Gas Atmospheres*, Fuel, **126**, pp. 250-255, 2014.

[14]   Dandik, L., Aksoy, H.A. & Erdem-Senatalar, A., *Catalytic Conversion of Used Oil to Hydrocarbon Fuels in a Fractionating Pyrolysis Reactor*, Energy and Fuels, **12**(6), pp. 1148-1152, 1998.

[15]   Kufeld, S.E., *Production of Diesel from Safflower Oil by a Soap-Pyrolysis Process*, Thesis, Master of Science in Chemical Engineering, Montana State University, United States, 1988.

[16]   Hilten, R., *Production of Aromatic Green Gasoline Additives Via Catalytic Pyrolysis of Acidulated Peanut Oil Soap Stock*, Bioresource Technology, **102**(17), pp. 8288-8294, 2011.

[17]   Santos, M.C., *Gasoline-Like Hydrocarbons by Catalytic Cracking of Soap Phase Residue of Neutralization Process of Palm Oil (Elaeis Guineensis Jacq)*, Journal of the Taiwan Institute of Chemical Engineers, 2016.

[18]   Kaisha, N.G.K.K., *A Method of Manucafturing Hydrocarbon Oils from Oils*, Fats or Fatty Acids, 1923.

[19]   Hsu, O.G., *Pyrolysis of the Calcium Salts of Fatty Acid*, Industrial and Engineering Chemistry, pp. 2141-2145, Oct.1950.

[20]   Schwab, A.W., *Diesel Fuel from Thermal Decomposition of Soybean Oil*, Journal of the American Oil Chemists' Society, **65**(11), pp. 1781-1786, 1988.

[21] Hirsch, A. & Fleischer, E., *Process for the Production of Basic Soaps of Divalent Metals in Powder Form*, US Patent No: 4.927.548, 1990, 22 May 1990.

[22] Worschech, K.W.P., Jaeckel, M. & Fleischer, E., *Basic Calcium/ Zinc Mixed Soaps*, Canadian Journal of Chemical Engineering, Canada Patent No CA2156929C, 1995.

[23] Worschech, K.F.E., *Basische Magonesium/Zinc- Seifan, Verfahren zur ihrer herstellung und ihre Verwendung als Stabilisatoren fur thermopastische Kunstoffe*, German Patent no DE4204866, 1993, 26 August 1993.

[24] Rogers, R.H. & Blew, W.R., *Manufacture of Metal Soaps*, *US Patent No: 2.890.232, 1956, Serial No. 588.265,* 31 May 1956.

[25] McAskie, W., *Ruminant Feedstuffs, Their Production and Apparatus for Use Therein, US Patent No: 4.826.694, 1989*, 2 May 1989.

[26] Neonufa, G.F., *Biohydrocarbon Production for Jet Fuel from Palm Oil Derivative Products*, IOP Conference Series: Materials Science and Engineering, **823**, pp. 012-029, 2020.

[27] Joonwichien, S.A.D., A., *The Study of Preparation of Biodiesel from Pyrolysis of Palm Stearin and Soap of Palm Stearin Over Catalyst*, 2006.

[28] Zheng, Y., *Efficient and Stable Ni-Cu Catalysts for Ex Situ Catalytic Pyrolysis Vapor Upgrading of Oleic Acid into Hydrocarbon: Effect of Catalyst Support, Process Parameters and Ni-To-Cu Mixed Ratio*, Renewable Energy, **154**, pp. 797-812, 2020.

[29] Wang, F., *Promoting Hydrocarbon Production from Fatty Acid Pyrolysis Using Transition Metal or Phosphorus Modified Al-MCM-41 Catalyst*, Journal of Analytical and Applied Pyrolysis, **156**, pp. 105-146, 2021.

[30] Pratiwi, M., *Metal Basic Soaps as Intermediate of Biohydrocarbon Production from Vegetable Oil/ Fats*, Doctoral Dissertation, Institut Teknologi Bandung, Indonesia, 2019.

[31] Neonufa, G.F., *Investigation of Ca/Mg/Zn Metals Mixing Ratio for Production of Soap with High Alkali Content*, International Journal of Chemical Engineering and Applications, **10**, pp. 149-153, 2019.

[32] Wan and Chang*, China's Motor Fuels from Tung Oil*, China Vegetable Oil Corporation, pp. 1543-1548, Dec. 1947.

[33] Avidan, A.A. & Shinnar, R., *Development of Catalytic Cracking Technology. A Lesson in Chemical Reactor Design*, Industrial and Engineering Chemistry Research, **29**(6), pp. 931-942, 1990.

[34] Rice, F.O., *The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. III. The Calculation of the Products Formed from Paraffin Hydrocarbons*, Journal of the American Chemical Society, **55**(7), pp. 3035-3040.1933.

[35] Puspawiningtiyas, E.*, Effect of Metal Type on Basic Soap Pyrolysis Produce Bio-gasoline*, IOP Conference Series: Materials Science and Engineering, **823**, pp. 012-027, 2020.

[36] Fontaine, M.F., *Treatment of Reformed Hydrocarbons with a Zinc Oxide-Zinc Chromite Catalyst*, US Patent No: 2.967.143, 1961.

[37] Luo, Y.*, The Thermal Cracking of Soybean/Canola Oils and Their Methyl Esters*, Fuel Processing Technology, **91**(6), pp. 613-617, 2010.

[38] Idem, R.O., Katikaneni, S.P.R. & Bakhshi, N.N., *Thermal Cracking of Canola Oil: Reaction Products in the Presence and Absence of Steam*, Energy and Fuels, **10**(6), pp. 1150-1162, 1996.

[39] Kubátová, A., *New Path in the Thermal Cracking of Triacylglycerols (Canola and Soybean Oil)*, Fuel, **90**(8), pp. 2598-2608, 2011.

[40] Asomaning, J., Mussone, P. & Bressler, D.C., *Pyrolysis of Polyunsaturated Fatty Acids*, Fuel Processing Technology, **120**, pp. 89-95, 2014.

[41] Melero, J.A., García, A. & Clavero, M., *15 - Production of Biofuels via Catalytic Cracking,* in Handbook of Biofuels Production, Luque, R. Campelo, J. & Clark, J. (Ed.), Woodhead Publishing. pp. 390-419. 2011.