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Effect of metal type on basic soap pyrolysis produce bio-gasoline

E Puspawiningtiyas^{1,2}, M Pratiwi¹, G F Neonufa³, R Purwadi¹, A N Isyami¹, L Elizabeth¹, T H Soerawidjaja¹, Subagjo¹, and T Prakoso¹

¹Department of Chemical Engineering, Institut Teknologi Bandung, Ganesha Street No 10, Bandung, West Java, Indonesia

²Department of Chemical Engineering, University Muhammadiyah of Purwokerto, Purwokerto 53182, Center Java, Indonesia.

³Department of Agriculture Product Technology, Universitas Kristen Artha Wacana, Kupang 85000, Indonesia

E-mail: endartiyas@yahoo.com

Abstract. The basic metal soap from oleic acid submitted to pyrolysis to produce gasoline-like hydrocarbon fuels (biogasoline). The pyrolysis was carried out in a semi-batch reactor at 450°C and a feeding rate of 5 g/ 15 min. The influences of various metal (Ca, Mg, Zn) hydroxides, which are used to made basic soap, have been examined. The bio hydrocarbon of basic metal soap was characterized by GC-FID and FT-IR, showing the formation of paraffin, iso-paraffin, olefin, ketone, and aromatics. The liquid fraction derived from the pyrolysis of basic metal soap was dominated by gasoline (C7-C11) fraction hydrocarbon. The maximum yield of light C7-C11 hydrocarbon was 82.3 %-mol fraction of basic Ca soap and the highest yield of biohydrocarbon reached 34.77 wt.% from pyrolysis of basic Mg soap.

1. Introduction

The conversion of biomass, vegetable or animal oils, and fat to obtain renewable fuels has been studied. There are many potential biohydrocarbon production methods [1] which products having compatible characteristics to be used as renewable fuels. Pyrolysis is one of the most extensive methods to convert vegetable oil or fatty acids to hydrocarbon. Pyrolysis of various oils to produce hydrocarbon has been investigated, including bio-oil [2], macauba fruit oil [3], waste cooking oil [4], cooking oils [5], waste oil [6], palm mesocarp fiber oil [7]. Asomaning et al. [8], Billaud et al. [9], and Wan and Chang [10] have pyrolyzed fatty acids into hydrocarbon. However, these processes have disadvantages, which are the yield of biohydrocarbon still low relatively and contains many oxygenated compounds [11], high acid value [10], undergo polymerization, much form sludge and high viscosity [12]. Furthermore, it was not stable and formed abundant wax [13]. In their study, they compared biohydrocarbon from triglycerides or fatty acid pyrolysis and its metal soap pyrolysis. The results of these investigations showed that metal soap pyrolysis could overcome the weaknesses of biohydrocarbon from triglycerides or fatty acids pyrolysis.



According to Kaisha (1923) [14], a good metal soap for use as raw material for making bio hydrocarbons via pyrolysis is basic soap. The report showed that stoichiometric soap produces not only short-chain hydrocarbon but also ketone and aldehyde, while on basic soap, the liquid product of pyrolysis contains just hydrocarbon. This statement was supported by Hites and Biemann (1972) [15] who found there was always ketone and carbonyl group presented in the liquid product of stoichiometric soap pyrolysis and it disappeared at a temperature more than 500 °C.

Types of triglyceride or fatty acids affect the hydrocarbon chain in liquid product pyrolysis. Mahera and Bressler in [16] pyrolyzed stearic acid into hydrocarbon that the biohydrocarbons are comprised mainly of a homologous series of hydrocarbons from carbon numbers C1 to C4, while least of alkane-alkene \geq C8 (5 %). However, pyrolysis of oleic acid and linoleic acid produce biohydrocarbon contains much more hydrocarbon from carbon number C6 – C10. These showed that the pyrolysis of unsaturated fatty acids produces much more gasoline fraction hydrocarbon than saturated fatty acids pyrolysis [17].

For this study, we proposed to generate gasoline-like hydrocarbon fuels via pyrolysis of basic metal soap from oleic acid and to further investigate the effect of metal types (Ca, Mg, Zn) in the liquid product of oleic metal basic soap pyrolysis.

2. Method

The oleic acids, 78 %, were obtained from PT Energi Sejahtera Mas. Calcium chloride dihydrate [$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$], zinc chloride tetrahydrate [$\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$], and magnesium chloride hexahydrate [$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$] were supplied by Merck, used to prepare metal hydroxide by co-precipitation with sodium hydroxide [18]. The Ca, Mg, and Zn soap was obtained by the saponification reaction of oleic acids with metal hydroxide that refers to [19], [20] and [21]. Pyrolysis of the basic soap was performed in a semi-batch reactor at 450 °C, atmospheric pressure and feeding rate 5 g/ 15 minutes. The pyrolysis liquid products were analyzed by GC-FID that following [22].

2.1. Preparation of metal hydroxide

Metals (Ca, Mg, Zn) hydroxide were prepared by the co-precipitation method. The first burette filled with 50 ml of 0.2 mol sodium hydroxide [NaOH] and the second burette with 50 ml of 0,1 mol solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ severally. The process was controlled by the droplet rate of A burette to keep the pH of the solution in 9.6. When the co-precipitation was finished, the suspension was kept stirred for 30 minutes. The metal hydroxide which formed was separated by filtering; then, it was washed with water. Thereafter, the metal hydroxide was dried at 105 °C for 1 hour.

2.2. Preparation of basic soap

The metals hydroxide 0.05 mol and 0.1 mol oleic acids were mix in saponification reactor. The mixture was heated to 40 – 45 °C, added 0.18 of formic acid 98- 100 % and 4 ml of water. The mixture was mixed at least 30 minutes, basic soap that formed was dried at 60 °C for 12 hours.

2.3. Pyrolysis experiments

The Pyrolysis of basic soap was conducted in a stainless steel reactor unit equipped with a vessel (ID: 8 cm, L: 36 cm), two thermocouples for the liquid and vapor phases, feeder, an air condenser, and liquid collector. The reactor was heated to 450 °C, then N_2 gas was passed into the reactor for about 10 minutes to drive out O_2 from the reactor. 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. Afterward, reactor heating continued for 2 h. The pyrolytic vapor was condensed and collected as pyrolytic oil in liquid collector for GC-FID and FTIR analysis.

2.4. Variable analysis

The variables observed were yield of biohydrocarbon, identify hydrocarbon fraction distribution and various functional groups and compounds contained in pyrolysis liquid product. The yield hydrocarbon was calculated by comparing the weight of the actual liquid product to the theoretical product. Analysis of biohydrocarbon composition used a Shimadzu GC-FID 2010 instrument. The GC-FID is equipped with a capillary column (RTX-1) with a dimension of 30 m x 0.25 x 0.25 μm with a flame ionization detector. The sample (one microliter) was injected into GC with a split ratio of 1:50 with a carrier gas flow rate (Helium) of 42.9 ml/minute. The injector and detector temperature of 430°C. The GC-FID temperature program used for analysis was initially of 40°C, 5°C/minute to 300°C, then 1 °C/ minute until 340°C. The Fourier Transform Infra-Red (FT-IR) analysis was carried out with the Bruker FT-IR instrument, ALPHA-Platinum FT-IR spectrometer with Platinum Diamond sampling.

3. Result and Discussion

The effect of metal type on yield and composition hydrocarbon by pyrolysis of oleic basic soap has been investigated. The pyrolysis temperature 450 °C with tolerance ± 5 °C. In the previous studies, pyrolysis of palm stearin soap was carried out at the temperature 400 – 500 °C [23] while the pyrolysis of stearic, oleic and linoleic sodium soap was carried out at the temperature 450 – 750 °C. The composition of oleic acids used as renewable material on the saponification reaction, as shown in table 1. The Table shows that oleic acids as material content, total unsaturated fatty acid 92.9 %-wt (oleic acid 80.6 %-wt).

Table 1. The composition of oleic acids

Fatty acids	%-wt
\leq C18	6.4
Oleic acids (C18:1)	80.6
Linoleic acids (C18:2)	12.3
Others	0.7

To ensure that Ca, Mg, Zn-Oleic soap were basic soap, Ft-IR analyses have to be done. The peak intensity of the hydroxyl group (-OH) usually appears in the range of wavenumber regions between 3200-3570 cm^{-1} . Figure 1 shows that at all of metal oleic detected a hydroxyl (-OH) group. The detection of the -OH group implies that the soap produced by the three metals is basic soap.

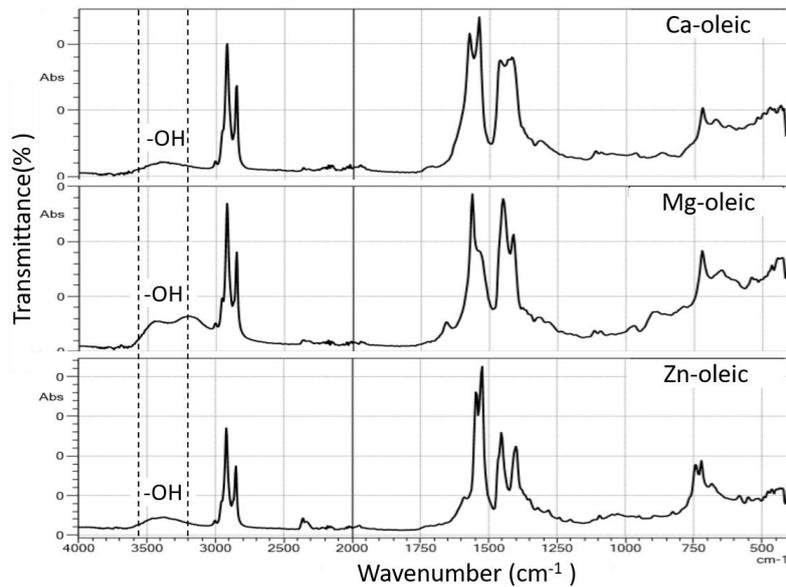


Figure 1. FT-IR spectra of the basic soaps on Ca, Mg, and Zn-oleic

3.1. Yield of biohydrocarbon

Mass percentage yields were calculated based on bio hydrocarbon theoretical yields, as depicted in Figure 2. The mass percent yield of bio hydrocarbon from Mg-oleic soap is 34.78 %, higher than Ca-oleic soap (23.23 %). The observed could be explained decomposition temperature of $Mg(OH)_2$ (285 - 380 °C) is lower than $Ca(OH)_2$ (325 - 415 °C), which results in earlier on formed bio hydrocarbons. The mass percent yield of bio hydrocarbon from Zn-oleic soap is 8.4 %, lower than Mg-oleic and Ca-oleic soap, although decomposition temperature of $Zn(OH)_2$ is the lowest among the others. This fact also was not supported by the previous researcher that reported Zn affects increasing hydrocarbon yield on decarboxylation of stearin MgZnCuFe soap [24]. The possible explanation for the observed difference could be in temperature reaction. The temperature in this study was higher (450 °C) than Neonufa, in [24]

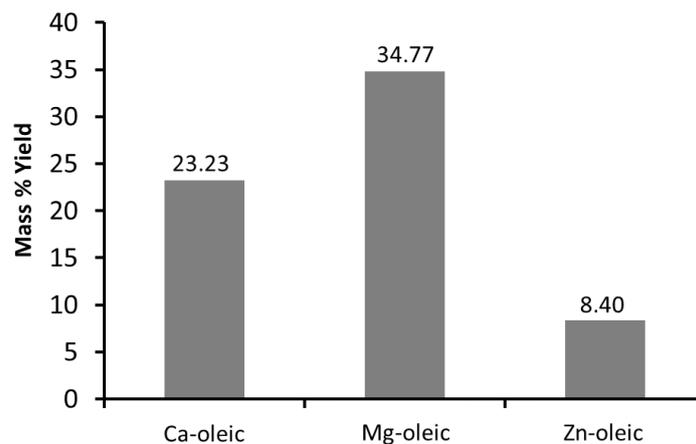


Figure 2. Mass percentage yields of different basic soap

3.2. Characteristic of biohydrocarbon distribution

The pyrolysis of oleic basic soap resulted in a series of products observed as periodic sets of peak when analyzed by GC-FID. Figures 3 and 4 show the results of GC-FID analysis of biohydrocarbon in the liquid fraction product of oleic basic soap pyrolysis and composition as a function of carbon number at various metal. The results indicated the presence of hydrocarbon molecules ranging from C7 (heptane) to C19 (nonadecane) in the pyrolysis liquid product. All of the metal soap variation, the most abundant hydrocarbon product of in the pyrolysis liquid fraction, were C7 to C11 alkane and alkene, suggesting that the cracking process has been going well. Figure 4 shows that the liquid fraction product of Mg-oleic soap and Ca-oleic soap were dominated C10 (decane), while Zn-oleic soap was C11 (undecane).

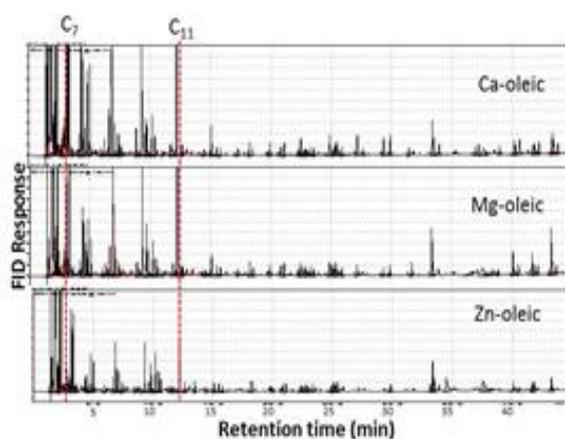


Figure 3. GC-FID chromatogram of hydrocarbon in the liquid fraction product of oleic basic soap pyrolysis at 450 °C

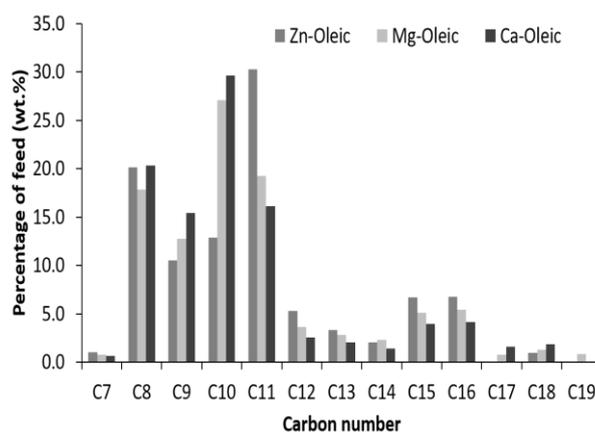
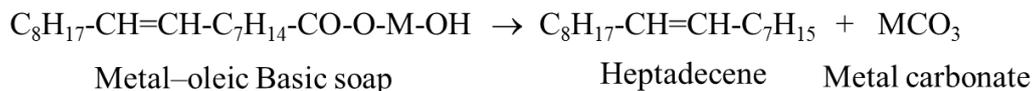


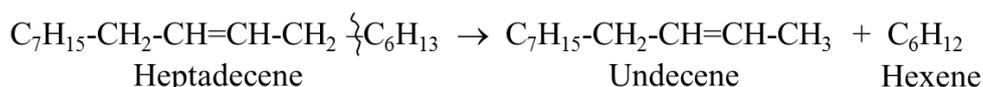
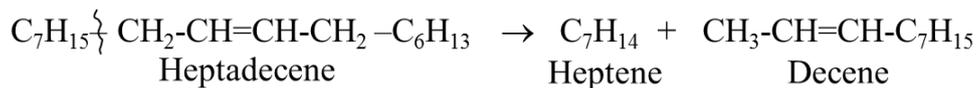
Figure 4. Composition as a function of carbon number at various metal.

The mechanism of cracking reactions in metal oleic basic soap pyrolysis start with decarboxylation basic soap :

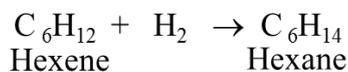
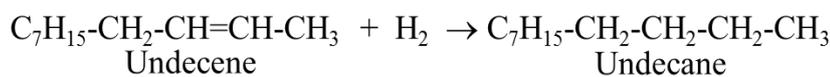
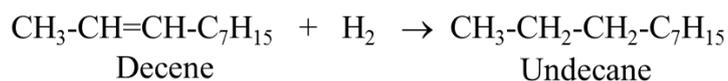
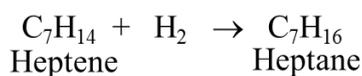


Then, the following types of reactions are possible :

Cracking of heptadecene



Then, hydrogenation of alkene



3.3. Quantitative analysis

The identification and quantification of chemical compounds contained in bio hydrocarbon reported in Figure 5. The classification of bio hydrocarbon in Fig.5 based on hydrocarbon fraction type and chemical species depicted in Fig.6. Figure 5 showed the most abundant hydrocarbons fraction were light fraction (C7-C11) in all of the oleic metal soap. The light fraction Ca-oleic (82.3 wt. %) is higher than Mg-oleic (77.7 wt.%) and Zn-oleic (74.9 wt.%).

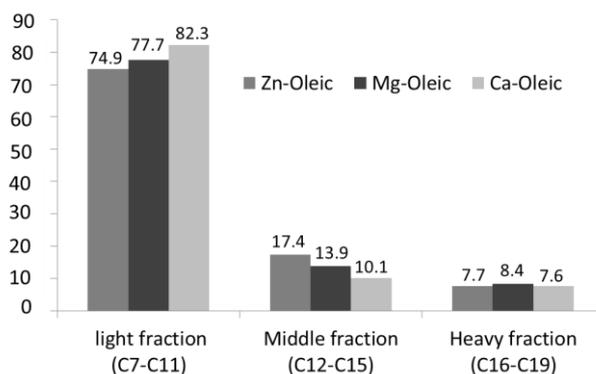


Figure 5. Fraction composition of hydrocarbon in the liquid fraction of oleic soap pyrolysis at 450 °C for various

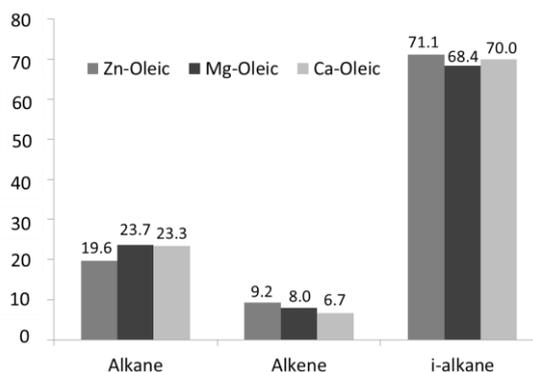


Figure 6. Alkane, alkene, and i-alkane composition as a function of carbon number at various metal.

According to [10], generally, decomposition of oleic acid into short alkane begins decarboxylation to reduce CO_2 and formed a long alkene chain, afterward cracking to formed two shorter alkenes and finally hydrogenation to obtained short alkane. Lappi and Alén in [25] reported that radicals formed in these reactions then undergo various other reactions such as disproportionation, β -scission, isomerization, hydrogen abstraction, and aromatization. Figure 6 illustrates product distribution and selectivities of alkane, alkene, and iso-alkane (i-alkane) in bio hydrocarbon. All of metal oleic soaps produce i-alkane were higher than alkane and alkene. This could be explained isomerization rate was higher than the hydrogenation rate. Zn-oleic soap obtained the highest i-alkane (71.1%) among others due to that Zn is a transition metal that could be isomerized hydrocarbon [26].

3.4. Oxygenate compound analysis

The presence of oxygenate compounds in hydrocarbons is not expected because these cause an auto-oxidation/ thermal oxidation reaction that forms a polymer that could be damage the engine. Analysis to detect the presence of oxygenate compounds in bio hydrocarbon carried out used FT-IR. The results of FT-IR analysis bio hydrocarbons that obtained pyrolysis of oleic basic soap is shown in Fig.7

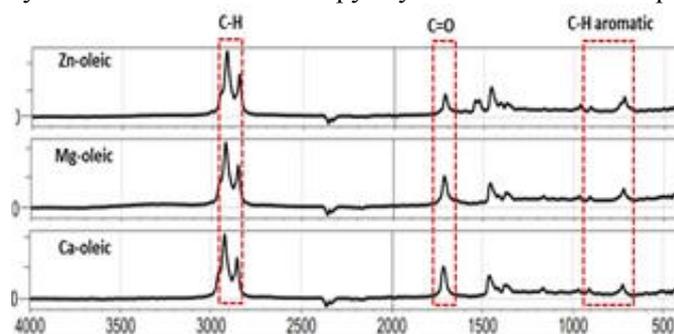


Figure 7. FT-IR of biohydrocarbon of oleic basic soap pyrolysis

Figure 7 shows the functional group that detected in bio hydrocarbon were alkane group (C-H) appear in the range of wavenumber regions between $2845 - 2935 \text{ cm}^{-1}$, ketone group (R-CO-R) in $1705 - 1725 \text{ cm}^{-1}$ and aromatic ring group (aryl) in $670 - 900 \text{ cm}^{-1}$ [27]. The alkanes group that has been detected supported the result of GC-FID analysis that presences of alkane and i-alkane, while the ketone group indicated still detected oxygenate in bio hydrocarbon. The presence of ketones was caused by the persistence of fatty acids in the oleic basic soap or the soap that was made still stoichiometry. The aromatic ring group in biohydrocarbon showed aromatization reaction occurred during pyrolysis.

4. Conclusions

The oleic basic soap can be converted to liquid biohydrocarbon, especially gasoline (C7-C11) fraction hydrocarbon. The maximum of light C7-C11 hydrocarbon fraction 82.3 %-mol from Ca basic soap and the highest yield of biohydrocarbon reached 34.77 wt.% from pyrolysis of Mg basic soap.

5. Acknowledgments

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References

- [1] Demirbaş A 2002 Diesel fuel from vegetable oil via transesterification and soap pyrolysis *Energy Sources* **24**(9) 835-42
- [2] Adjaye J D and Bakhshi N N 1995 Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil, Part I: Conversion over various catalysts *Fuel Processing Technology* **45**(3) 161-83
- [3] Fortes I C P and Bough P J 2004 Pyrolysis-GC/MS studies of vegetable oils from Macauba fruit *Journal of Analytical and Applied Pyrolysis* **72**(1) 103-11
- [4] Wang J, Zhong Z, Zhang B, Ding K, Xue Z, Deng A and Ruan R 2016 Upgraded bio-oil production via catalytic fast co-pyrolysis of waste cooking oil and tea residual *Waste Management*
- [5] Chiamonti D, Buffi M, Rizzo A M, Prussi M and Martelli F 2015 Bio-hydrocarbons through catalytic pyrolysis of used cooking oils: Towards sustainable jet and road fuels *70th Conference of the Italian Thermal Machines Engineering Association ATI 2015* (Elsevier Ltd)
- [6] Lam S S, Liew R K, Jusoh A, Chong C T, Ani F N and Chase H A 2016 Progress in waste oil to sustainable energy with emphasis on pyrolysis techniques *Renewable and Sustainable Energy Reviews* **53** 741-53
- [7] Khanday W A, Kabir G and Hameed B H 2016 Catalytic pyrolysis of oil palm mesocarp fibre on a zeolite derived from low-cost oil palm ash *Energy Conversion and Management* **127** 265-72
- [8] Asomaning J, Mussone P and Bressler D C 2014 (a) Pyrolysis of polyunsaturated fatty acids *Fuel Processing Technology* **120** 89-95
- [9] Billaud F, Guitard Y, Tran Minh A K, Zahraa O, Lozano P and Pioch D 2003 Kinetic studies of catalytic cracking of octanoic acid *Journal of Molecular Catalysis A: Chemical* **192**(1-2) 281-88
- [10] Wan S W and Chang C C 1947 China's Motor Fuels from Tung oil *Industrial and Engineering Chemistry* **39** 1543-8
- [11] Lappi H and Alén R 2009 Production of vegetable oil-based biofuels-thermochemical behavior of fatty acid sodium salts during pyrolysis *Journal of Analytical and Applied Pyrolysis* **86**(2) 274-80
- [12] Hiebert D R 1985 Decarboxylation and hydrogenation of safflower and rapeseed oils and soaps to produce diesel fuels *Master Thesis* (Montana: Montana State University)
- [13] Joonwchien S A D A 2006 The study of preparation of biodiesel from pyrolysis of palm stearin and soap of palm stearin over catalyst *International Conf. on Green and Sustainable Innovation*
- [14] Kaisha N G K K 1923 A Method of Manuacfturing Hydrocarbon oils from oils, fats or fatty acids *US Patent* No GB175974
- [15] Hites R A and Biemann K 1972 On the mechanism of ketonic decarboxylation Pyrolysis of calcium decanoate *Journal of the American Chemical Society* **94**(16) 5772-7
- [16] Maher K D and Bressler D C 2007 Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals *Bioresource Technology* **98**(12) 2351-68

- [17] Asomaning J, Mussone P and Bressler D C 2014 (b) Thermal deoxygenation and pyrolysis of oleic acid *Journal of Analytical and Applied Pyrolysis* **105** 1-7
- [18] Zhao R., Yin C, Zhao H and Liu C 2003 Synthesis, characterization, and application of hydrotalcites in hydrodesulfurization of FCC gasoline *Fuel Processing Technology* **81**(3) 201-9
- [19] Hirsch A and Fleischer E 1990 Process for The Production of Basic Soaps of Divalent Metals in Powder Form *US Patent* No 4.927.548
- [20] McAskie W 1989 Ruminant Feedstuffs, Their Production and Apparatus for Use There *US Patent* No 4.826.694
- [21] Rogers R H and Blew W R 1956 Manufacture of Metal Soaps *US Patent* No 2.890.232 31 Serial No 588.265
- [22] Neonufa G F, Pratiwi M, Soerawidjaja T H and Prakoso T 2017 High Selectivity of Alkanes Production by Calcium Basic Soap Thermal Decarboxylation *24th Regional Symposium on Chemical Engineering (RSCE)* (Semarang Indonesia: C-62)
- [23] Joonwichien S 2007 Bio oils From Palm Stearin by Pyrolysis Over Catalysts *Thesis*
- [24] Neonufa G F 2018 Drop-in Fuel Production Technology of Diesel and Bioavtur Type via Catalytic Thermal Decarboxylation Basic Soap Base on Magnesium and Transition Metal Combination *Ph.D Thesis* (Institut Teknologi Bandung)
- [25] Lappi H and R Alén 2011 Pyrolysis of vegetable oil soaps - Palm, olive, rapeseed and castor oils *Journal of Analytical and Applied Pyrolysis* **91**(1) 154-8
- [26] Fontaine M F, Fishkill M, Riordan D, Beacon N Y, Ryer J and New Brunswick N J 1961 Treatment of Reformed Hydrocarbons with A Zinc Oxide-Zinc Chromite Catalyst *US Patent* No 2.967.143
- [27] Coates J 2000 *Interpretation of Infrared Spectra A Practical Approach* (New Jersey: John Wiley & Sons Ltd) pp 10815-37