



Comparison of Liquid Product Characteristics of PFAD Metal Soap Decarboxylation by Batch and Continuous Process

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Highlights:

- The yield from the batch process was relatively similar to that from the continuous process.
- The amount of paraffin produced by the batch process was higher than by its continuous counterpart.
- The decomposition of metal base soap with a continuous process is highly developable due to its potential to save time and cost of bio-hydrocarbon production.

Abstract. Well-run continuous processes will benefit the industrial world in the future. This paper investigated the effect of batch and continuous processes on metal basic soap decarboxylation in terms of the liquid product characteristics. The metal soap used in the process was made from palm fatty acid distillate (PFAD) reacted with mixed metal oxides of Zn, Mg, and Ca. While the batch decarboxylation was carried out in a batch reactor at 400 °C for 5 hours, the continuous decarboxylation was conducted at 400 °C with a feed flow rate of 3.75 gr/minutes. Theoretically, the yield of batch decarboxylation is 76.6 wt% while the yield of continuous decarboxylation is 73.37 wt%. The liquid product was fractionated to separate short-chain hydrocarbon of C7-C10 (gasoline fractions)

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from medium- to long-chain hydrocarbons, or greater than C11 (green diesel fraction). The result showed that the alkane content from the batch process was higher than from the continuous process, whereas the continuous process produced more ketone products compared to the batch process. Furthermore, the GC-FID analysis showed a similar amount of total hydrocarbon (alkane, iso-alkane, and alkene) in both the batch and the continuous process.

Keywords: *batch decarboxylation; continuous decarboxylation; metal basic soap; green diesel; bio-hydrocarbon.*

1 Introduction

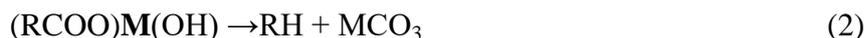
One of the biggest challenges in the use of oil-fat resources as diesel fuel substitute is the presence of oxygen content; it raises the affinity of fatty acid fuel molecules for water. Since water is a polar compound (one end is positively charged while the other is negatively charged) it is not compatible with nonpolar oil molecules [1]. Recently, biofuel without oxygen content, or drop-in biofuel, has been developed to address this issue. This renewable fuel in the form of non-oxygenated diesel fuel is called green diesel. It can be formed from fatty acids by conventional hydroprocessing technology.

This process takes place at temperatures ranging from 600 to 700 F, pressure ranging between 40 and 100 atm, reaction times ranging from 10 to 60 min, and it uses catalysts. The oil-fat can be processed via hydrogenation/hydro process or co-processing to obtain diesel fuel. It will be converted into a propane molecule and hydrocarbon molecules in the C12 to C18 range. It does not contain sulfur and the cetane number range is 90 to 100 [2]. The hydroprocessing technology is an expensive method because it consumes a large amount of hydrogen [3] and uses noble metals as catalysts [4].

Fatty acid deoxygenation is a method to obtain renewable bio-hydrocarbon. Decarboxylation is one pathway of deoxygenation. As an example, the decarboxylation reaction of palmitic acid is shown in Eq. (1):



Basic-soap decarboxylation is a very promising route to be developed as the basis for a commercial decarboxylation process [5]. This is particularly true for the decarboxylation of the basic-soap reaction shown in Eq. (2). Soap stock as the feed of decarboxylation is the main by-product from vegetable oil refining and it has low commercial value [6]. Besides, soaps from pyrolysis have high yields and can be operated at lower temperature [7].



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M in Eq. (2) stands for alkali metal or alkaline earth metal. This reaction (Eq. (2)) can take place under atmospheric pressure. For example, the basic-soap decarboxylation of palm kernel oils was carried out at 370 °C and atmospheric pressure for 3 hours in a semi-batch reactor [8]. Meanwhile, calcium-based soap decarboxylation was carried out at temperatures up to 370 °C for 5 hours in [9]. In this study, decarboxylation occurred at a temperature around 400 °C to obtain green diesel. This is very interesting because the operating temperature is lower than the pyrolysis temperature. For example, green diesel obtained by the pyrolysis of brown grease soap occurred at 450 °C in [10].

The use of metal catalysts, with or without support, is one of the competitive edges influencing the performance of thermal cracking, deoxygenation, and decarboxylation. Thermal cracking of palm oil held in a pilot-scale batch reactor of 143 L at 450 °C, atmospheric pressure, 15% (w/w) Na₂CO₃ catalyst yielded around 60% (wt.) of organic liquid products (OLP) with long-chain lengths between C₉ and C₁₉ hydrocarbon content at 92.84% (wt.). The hydrocarbon consisted of 27.53% paraffin, 54.78% olefin and 10.53% naphthenic [11]. Meanwhile, the catalytic cracking of soap phase residue in the neutralization process of palm oil was carried out in a batch reactor of 143 L at atmospheric pressure, 440 °C, with 15% (wt.) Na₂CO₃ catalyst. It yielded 71.34% (wt.) of organic liquid product (OLP), which comprised 6.69% (wt.) gasoline, 12.77% (wt.) kerosene, 15.52% (wt.) light diesel, and 38.02% heavy diesel-like hydrocarbons fuels according to the boiling range temperature range of fossil fuels. The chemical compounds of OLP by GC-MS are alkenes 51.43% (wt.), alkanes 29.94% (wt.), ketones 5.34% (wt.), etc. [6].

Deoxygenation of PFAD under reaction conditions of 3% (wt.) of cobalt/activated carbon catalyst, 350 °C under inert N₂ flow with a stirring rate of 400 rpm yielded 71% hydrocarbon (C₈-C₂₀) [12]. Catalytic deoxygenation of oleic acid carried out with 10% (wt.) 4Pt-8WO_x/Al₂O₃ catalyst, n-heptane solvent, 20 bar H₂ pressure, 320 °C for 5 hours gave oleic acid conversion 100% (mol). Product selectivity consisted of C₁₈ 67.1% (wt.), C₁₇ 31.6% (wt.) and C₁₀-16 1.3% (wt.) [13]. Decarboxylation of pelargonic (C₉ monocarboxylic acid) and azelaic acids (C₉ dicarboxylic acid) from oxidative cleavage of oleic acid gave 98.2 mol% n-octane and 73.1 mol% n-heptane was held at 300 °C/10 MPa and 300 °C/5 MPa (N₂ pressure) with 6 mol% Pd/C for 2-3 h [14]. The use of an alkali metal, which is better than noble or precious metals, is favorable in decarboxylation. Zhong, *et al.* used nickel and zinc metal for the deoxygenation of palmitic acid and obtained 90% pentadecane when operated at 300 °C and for 16 hours [15].

Commercialization of mixed metal oxide basic-soap decarboxylation is highly potential because it produces a true 'drop-in' replacement fuel, it can use a wide

variety of feedstocks, and it minimizes infrastructure incompatibilities [16]. Various researches have been conducted in a batch or semi-batch reactor [6,8,10-15]. Continuous hydrothermal decarboxylation of oleic acid in the presence of activated carbon catalyst gave a conversion rate of 91% of oleic acid, 89.3% selectivity to heptadecane when operated at 400 °C, 2 hours of space-time, water-to-oleic acid ratio of 4:1, and pressure < 500 psi. The activated carbon was deactivated at 45 hours time on stream [17]. Thus, the innovation of continuous decarboxylation of metal basic soap at atmospheric pressure and without replacement of fresh catalyst from the deactivated catalyst in this study is very interesting. Therefore, the purpose of this study was to investigate liquid product hydrocarbon characteristics, especially for green diesel from batch and continuous metal basic-soap decarboxylation.

2 Experimental Research

2.1 Material

Metal mix (Ca-Mg-Zn) basic soap was used as the feedstock for decarboxylation in both batch and continuous processes. The commercial metal mix comprising CaO, MgO, and ZnO was of technical grade from a local product. Palm fatty acid distillate (PFAD) was gifted by PT Tunas Baru Lampung.

2.2 Experiment

Metal basic soaps were made by fusion saponification of PFAD and mixed metal oxides of CaO, MgO, and ZnO with a mol ratio 0.25; 0.25; 0.5, respectively. Saponification occurred at 60-65 °C for 15 minutes. The batch decarboxylation reaction occurred in a stainless steel reactor for 5 hours at 400 °C with 1000 gr metal basic soaps as feedstock. Meanwhile, continuous decarboxylation occurred in a stainless steel reactor in which metal basic soaps were fed via a screw conveyor at constant flow rate (3.75 gr/minutes) and temperature 400 °C. Metal basic soaps entered the reactor vertically from the top. Liquid products from both batch and continuous decarboxylation were separated through fractional distillation. A flowchart of the preparation and measurement method is presented in Figure 1.

2.3 Analysis Measurement

The compositions of the PFAD and green diesel were measured using a GC-MS Shimadzu 2010 equipped with an RTX-5 MS column with dimensions of 30 m x 0.25 mm x 0.25 µm and an AOC-20i auto-injector. The GC-MS measurement method was as follows: one microliter of the sample was injected into the GC with a split ratio of 1:100. The injector temperature was set to 340 °C. The

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temperature of the GC oven was set as follows: the initial temperature was 40 °C, then the temperature was raised at a rate of 5°C/min to 300 °C.

The metal basic-soap decomposition was measured by a TGA analyzer [18] (Linseis STA Platinum Series – Simultaneous Thermal Analysis) using an alumina crucible. The method of the TGA analyzer was as follows: the initial temperature was 40 °C, then the temperature was raised at a rate of 20K/min to 1000 °C. This TGA analyzer could measure mass (TG) and energy (DTA/DSC) changes simultaneously in a temperature range from 150 to 1750 °C.

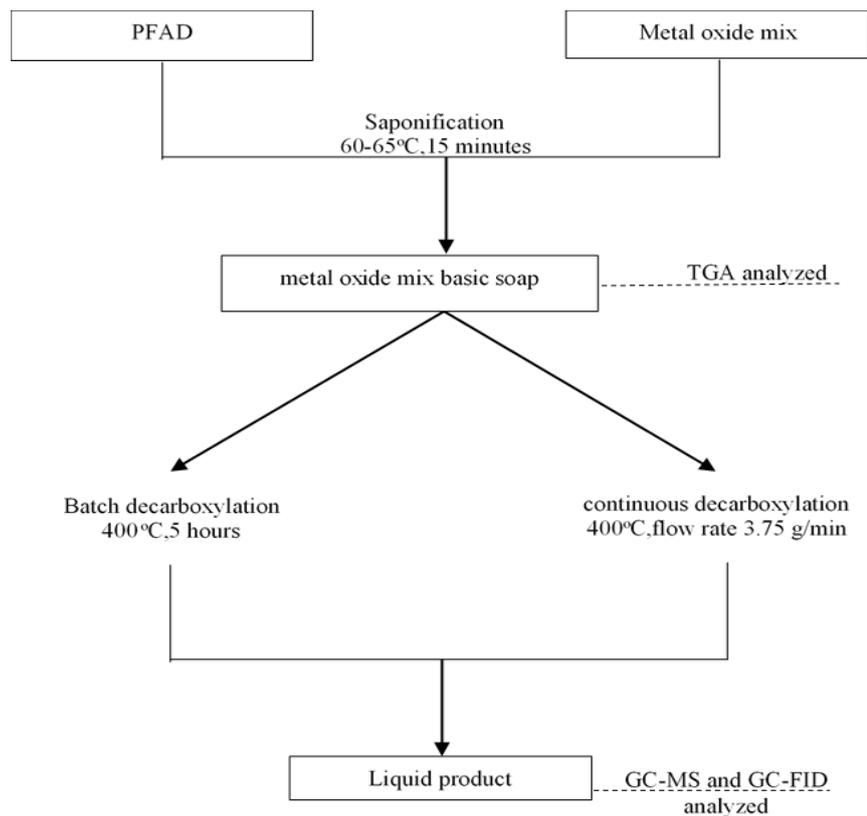


Figure 1 Block diagram of the preparation and measurement methods.

Hydrocarbons of green diesel were also measured using a Shimadzu GC-FID apparatus equipped with an RTX-1 FID column. The GC-FID measurement was conducted as follows: one microliter of the sample was injected into the GC with a split ratio of 1:100. The injector and detector temperature were set to 340 °C.

First, the temperature of the GC oven was set to an initial temperature of 40 °C. Subsequently, the temperature was raised at a rate of 5 °C/min to 300 °C. Finally, the temperature was raised to 315 °C at a rate of 1 °C/min.

3 Result and Discussion

3.1 Palm Fatty Acid Distillate (PFAD)

The PFAD composition was analyzed by GC-MS Shimadzu 2010, as shown in Table 1. Table 1 shows that the PFAD comprised of both saturated and unsaturated fatty acids. Palmitic acid (40.15 %-area) and oleic acid (40.32 %-area) were the main fatty acids of the PFAD.

Table 1 PFAD composition.

Fatty acid	%-area
Myristic acid (C14:0)	1.68
Palmitic acid (C16:0)	40.15
Linoleate acid (C18:2)	5.16
Oleic acid (C18:1)	40.32
Stearic acid (C18:0)	7.82
Methyl 18-methylnonadecanoate	1.32
Others	3.55
Total	100

3.2 Metal Basic Soap

Table 1 shows that the PFAD comprised of both saturated and unsaturated fatty acids. The main composition of PFAD was palmitic acid (40.15 %-area) and oleic acid (40.32 %-area). Metal basic soap was the feed for batch and continuous decarboxylation. It was made by a fusion process of metal oxide mix of Mg, Ca, and Zn with a ratio of 0.25, 0.25, and 0.5 respectively. The metal basic soaps were analyzed using thermal gravimetric analysis (TGA) to investigate the decomposition temperature. The TGA analysis result of the metal basic soaps is shown in Figure 2.

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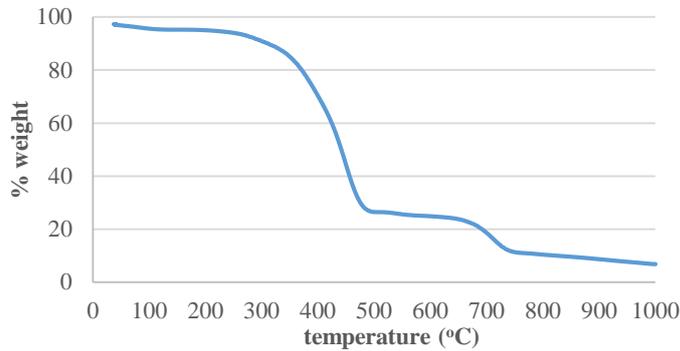


Figure 2 TGA analysis of the metal basic soaps.

The TGA analysis showed that the decomposition temperature range was approximately 275 to 450 °C. This indicates that 400 °C was an appropriate temperature for decarboxylation in this study.

3.3 Decarboxylation

While the batch decarboxylation was carried out at 400 °C for 5 hours, the continuous decarboxylation was carried out at the same temperature with a feed flow rate of 3.75 gram/minute. The yield of the decarboxylation process is shown in Table 2, while the calculation is presented in Eq. (3).

$$\text{yield of decarboxylation} = \frac{\text{actual weight of liquid product}}{\text{theoretical weight of liquid product}} \times 100\% \quad (3)$$

Table 2 Decarboxylation yield.

Yield (%-Wt.)	
Batch	Continuous
79.68	74.31
74.05	64.38
73.53	66.23
83.77	78.09
72.00	83.83
76.60 ± 4.95	73.37 ± 8.13

The theoretical weight of the liquid product is the maximum weight of the liquid product (RH) calculated based on the stoichiometry of the decarboxylation reaction equation (Eq. (2)).

The yield of metal basic-soap decarboxylation, both batch and continuous, was quite similar and higher than the thermal cracking of palm oil [11], the thermal cracking of soap phase residue of neutralization process of palm oil [6], and the deoxygenation of PFAD [12]. However, it was lower than hydro-processed rapeseed oil (83% (wt.)) [8]. Although the yield is not as high, the metal basic-soap decarboxylation process does not consume hydrogen and can be conducted under atmospheric pressure.

Metal basic-soap decarboxylation generated a liquid product consisting of kerosene, diesel, and heavy fuel fraction. To separate these three components, they were treated using fractional distillation. The kerosene fraction was obtained at a temperature of 180 to 200 °C, while the diesel fraction was obtained at a temperature 270 to 350 °C. The rest of the liquid products were heavy fractions. The diesel fraction or green diesel was analyzed by GC-FID Shimadzu 2010. The GC-FID chromatogram is shown in Figure 3.

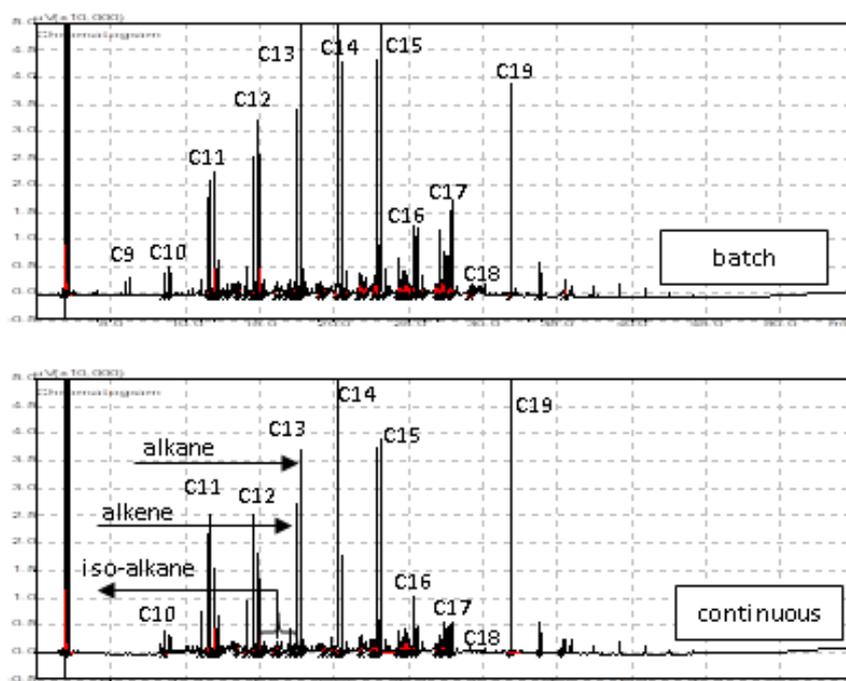


Figure 3 GC-FID chromatogram of green diesel from batch and continuous decarboxylation.

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The peak of the GC-FID chromatogram in Figure 3 indicates alkane, alkene, and iso alkane. Figure 4 shows the coincident long carbon chain range (C9 to C19) from batch and continuous decarboxylation.

The variety of carbon chain lengths produced in this process was between C10 and C20. This is because the metal not only selective forms C15 (as main decarboxylation product of palmitic acid) but also generates cracking to form shorter carbon chain lengths (<C15). In addition, there is a tendency for polymerization after decarboxylation of oleic acid. When C18 has formed C17 (decarboxylation product of oleic acid), soon after the C17 captures shorter molecules (from the cracking process) to form C19 molecules. The difference in liquid product quantity (wt%) from the batch and the continuous decarboxylation can be seen in the C15 and C19 carbon chains.

Figure 4 illustrates that the amount of C15 carbon chains obtained from the batch process was higher compared to the continuous process. However, the amount of C19 carbon chains obtained from the continuous process was higher than from the batch one. Figure 4 also shows that C15 was the main product of green diesel. This is because the main fatty acid of PFAD is palmitic acid.

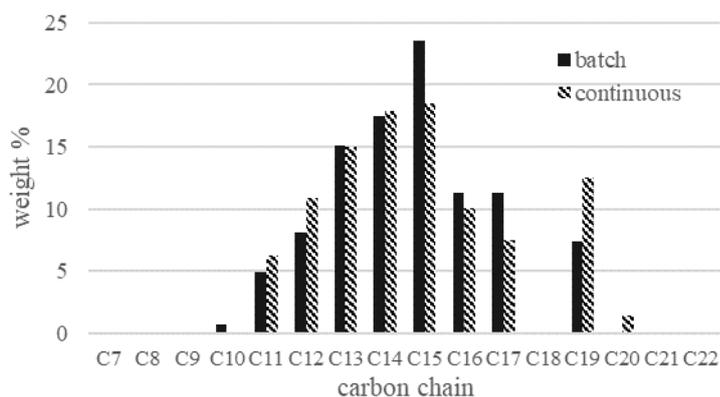


Figure 4 Carbon chain distribution of green diesel from batch and continuous decarboxylation.

As expressed in Eq. (2), palmitic basic soap generates pentadecane through decarboxylation. The other main fatty acid of PFAD is oleic acid. Oleic basic soap produces various short and long carbon chains since it is an unsaturated fatty acid.

The composition of green diesel was also analyzed in more detail by GC-MS. The results are shown in Figure 5 and Tables 3 to 4.

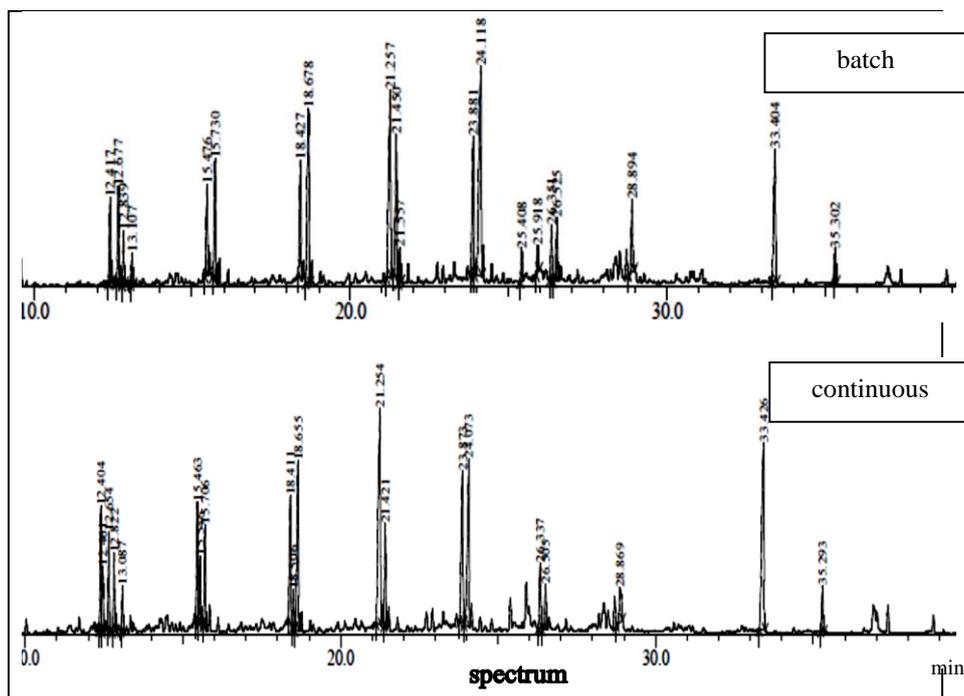


Figure 5 GC-MS chromatogram of green diesel.

Table 3 Hydrocarbon components of green diesel from batch decarboxylation.

Carbon chain	Compounds	% Area	Compounds	% Area
	Alkane		Alkenes	
C11	Undecane	3.84	1-undecene	3.53
C12	Dodecane	5.25	2-dodecene	3.94
C13	Tridecane	10.24	1-tridecene	5.43
C14	Tetradecane	7.04	1-tetradecene	12.2
C15	Pentadecane	15.87	1-pentadecene	7.14
C16	Hexadecane	3.03	1-hexadecene	2.53
C17	Heptadecane	3.26		
	Ketone		Cyclic	
C11			Octyl-cyclopropane	2
C12			Nonyl-cyclopropane	1.09
C14			Cyclotetradecane	1.37
C15			Nonyl cyclohexane	1.37
C16			Cyclohexene, 1-nonyl	1.24
C17	2-Heptadecanone	8.2		
C18	4-Octadecanone	1.43		

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Table 4 Hydrocarbon components of green diesel from continuous decarboxylation.

Carbon chain	Alkane	% Area	Alkene	% Area
	Alkane		Alkene	
C11	Undecane	3.52	1-undecene	5.38
C12	Dodecane	3.96	1-dodecene	5.05
C13	Tridecane	8.44	1-tridecene	5.66
C14	Tetradecane	4.11	1-tetradecene	14.14
C15	Pentadecane	9.32	1-pentadecene	8.16
C16	Hexadecane	1.89	1-hexadecene	2.83
C17	Heptadecane	1.96		
	Ketone		Cyclic	
C8	2-Octanone	2.04		
C10	2-Decanone	2.53		
C11	2-Undecanone	1.37	Octyl-cyclopropane	2.81
C12			Nonyl-cyclopropane	1.60
	2-			
C17	Heptadecanone	13.38		
C18	4-Octadecanone	1.87		

Tables 3 and 4 show that the green diesel from both batch and continuous decarboxylation contained alkane, alkene, ketone, and cyclic compounds. Pentadecane (15.87 %-area) and 1-tetradecane (12.2 %-area) were the main compounds of green diesel from batch decarboxylation. For the green diesel from the continuous process, 1-tetradecane (14.14 %-area) and pentadecane (9.32 %-area) were also the main compounds. The main liquid products from both GC-FID and GC-MS analyses were similar.

Figure 6 offers a specific comparison of the green diesel resulted from batch and continuous decarboxylation. The amount of green diesel paraffin (alkane) from the batch process was higher than from the continuous one. Meanwhile, the amount of olefin (alkene) in the green diesel from the continuous process was higher compared to its batch counterpart.

Reactions occurring in Ca soap pyrolysis from vegetable oil are decarboxylation, cracking, dehydrogenation, cyclization, hydrogenation, and olefin polymerization [19]. Therefore, the reaction pathway in the batch reactor perhaps started with decarboxylation, followed by cracking into a shorter olefin compound. Afterward, the olefin compound turned into paraffin through hydrogenation.

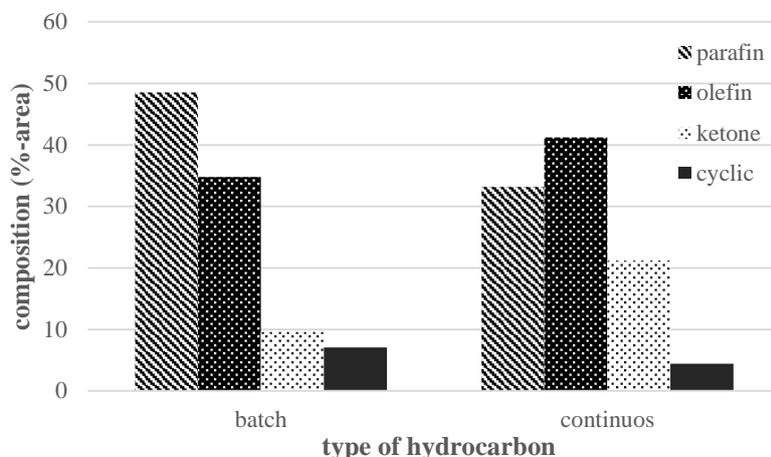


Figure 6 Type of green diesel hydrocarbon from batch and continuous decarboxylation.

Similarly, the reaction pathway in the continuous reactor also started with decarboxylation and continued with cracking into olefin compounds. However, the reaction did not resume with hydrogenation. This only occurred because the resident time in the batch reactor was much longer (5 hours) than in the continuous reactor. Therefore, the reactions in the batch reactor took place simultaneously and were more complex than in the continuous reactor.

There are two reasons for the generation of ketone products. Firstly, free fatty acids in basic soaps are catalyzed by MgO to form ketones at temperatures over 340 °C [20]. Secondly, ketones are formed by stoichiometric soap decarboxylation. As decarboxylation feedstock, metal basic soaps still contain stoichiometric soaps. The reaction is presented in Eq. (4):



The amount of ketone from the continuous process was higher than from the batch decarboxylation. This is because the batch process was carried out in a closed system, whereas continuous decarboxylation was carried out in an open system. This continuous reactor allows for air contamination since the feeding system is open.

The presence of olefins and ketones is unstable in fuel drops. Olefin does not contribute to the cetane number and ketones are oxygenated fuel. Hence, further investigation of continuous decarboxylation is necessary due to its potential use in the commercialization of liquid bio-hydrocarbon production. Also, further research to reduce the content of ketones and olefins in drop-in fuels is necessary.

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It is recommended that the research should focus on modifying the base-soap feed system into a continuous reactor by equipping the reactor with a hot melt extruder. The presence of the hot melt extruder can prevent the entry of oxygen from the surrounding air into the continuous process feed, which can trigger the formation of ketone and olefin compounds.

4 Conclusion

Theoretically, the yield from the batch process (76.6 wt%) was relatively similar to that from the continuous process (73.37 wt%). The amount of C15 carbon chains in the batch process was higher compared to the continuous process. In contrast, the quantity of C19 carbon chains produced by the continuous process was higher than the batch one. Also, the amount of paraffin generated by the batch process was higher than its continuous counterpart. Furthermore, the amount of ketones from the continuous process was higher than from the batch decarboxylation. In fact, the reactions in a batch reactor occur simultaneously and are more complex than in a continuous reactor.

The decomposition of metal base soap with a continuous process is highly developable due to its potential to save time and cost in bio-hydrocarbon production. Modification of the continuous reactor by adding a hot melt extruder is recommended to reduce ketones and olefins in the drop-in fuel product. The development of process automation as well as more detailed mass and energy balance calculations for the continuous decarboxylation process are also necessary to improve the effectiveness and efficiency of the decarboxylation process.

Acknowledgement

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