



Research article

The effect of Ca/Mg/Zn mixing ratio on the research octane number of bio-gasoline during basic soap pyrolysis



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ABSTRACT

Pyrolysis is one of the available technologies to convert oleic basic soap into gasoline-compatible fuel. In this research, the process mentioned was applied using the mixture of Ca, Mg, Zn in the production of oleic basic soap. The reactions were carried out in a batch glass reactor at atmospheric pressure at the temperature of 450 °C. Meanwhile, the basic soaps were made by reacting oleic acid mixed with metal hydroxides. The parameters observed were the Research Octane Number (RON) of bio-gasoline and the hydrocarbon content in the liquid product. The higher the octane number is, the better gasoline resists detonation and the smoother the engine runs. As observed, pyrolysis of oleic basic soap produced gasoline range hydrocarbon. GC-DHA results indicated that the highest RON (89.6) was achieved with Ca/Mg/Zn ratio of 0.15:0.85:1 (Ca-metal ratio of 0.15 mol). The products of the pyrolysis process comprised bio-hydrocarbon, solid residue, water, and gas. The bio-hydrocarbon contents were paraffin (5.9 wt%), iso-paraffin (31.3 wt%), olefin (18.5 wt%), naphthene (25.3 wt%), and aromatic compounds (15.3 wt%).

1. Introduction

At present, many researchers are interested in investigating the production of bio-hydrocarbon through the deoxygenation of vegetable oils/fats or fatty acids. Bio-hydrocarbon or liquid hydrocarbon biofuel is a renewable fuel derived from any material originating from biological matters [1]. The method is based on the similarity of the structural formula of fatty acids and hydrocarbon, in which there is a carboxyl group attached to fatty acids.

Currently, the main processes to obtain biofuels from vegetable oils are transesterification and thermal cracking (pyrolysis) or thermal-catalytic cracking (catalytic pyrolysis) [2]. Cracking is a thermal degradation of vegetable oils through the heat in almost no oxygen (air) called pyrolysis. The obtained products include alkanes, alkenes, alkadienes, carboxylic acids, aromatics, and a few gaseous products by Demirbaş in [3].

references on hydrocarbon production by pyrolysis of fatty acid or triglyceride have been widely reported. Several studies of pyrolysis with

fatty acid raw materials include; octanoic acid [4], oleic acid [5, 6], linoleic and linolenic acids [7]. On the other hand, studies involving triglyceride includes sun flower oil [8], rubber seed oil [9], plant acidified oil [10], and mustard oil [11]. The resulting hydrocarbon product depends on the feed and the pyrolysis operating conditions.

Based on the previous research, Some researchers have revealed specific weaknesses in the pyrolysis of fatty acids and triglycerides. Fortunately, technological innovations proceed, and metal soap pyrolysis, an alternative method to address these weaknesses, has been found. This method encourage the release of all carboxyl groups on fatty acids, and it is promising as it does not require H₂ (the soap comes from saturated fatty acids) and less H₂ (the soap comes from unsaturated fatty acids).

According to [12], metal soaps are a suitable soap type for raw material in making hydrocarbon via pyrolysis. The basic is prepared with metals from the alkaline earth and transitional groups. Several researchers reported comparing the yield of liquid products on the pyrolysis of fatty acids/triglyceride and the soap pyrolysis. The results

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discovered that the weaknesses detected in the fatty acid pyrolysis product were not found in the liquid soap pyrolysis product. These weaknesses include; high acid value [13], tendency to undergo isomerization to form much sludge and high viscosity [14], unstable and more wax formed [15], lower yield, and more oxygenate compounds produced [16].

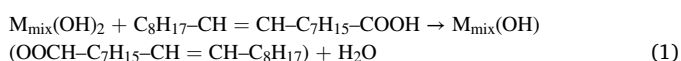
Previous researchers also have carried out investigations on metal types including sodium [17, 18, 19], calcium [20, 21], magnesium [20], and potassium [9]. In addition, our previous studies have shown that basic soap derived from oleic acids can be converted into renewable fuel. For instance, Ca, Mg, Zn basic soap have successfully converted gasoline-like hydrocarbon fuels (biogasoline) by pyrolysis, respectively [22].

Nevertheless, research involving the combination of several metals in the pyrolysis metal soaps is still limited. This study aimed to obtain hydrocarbons via pyrolysis of mixed metal soap and investigate the further effects of metal ratio (Ca, Mg, Zn) in Research Octane Number (RON) of bio-gasoline and terms of the hydrocarbon content in liquid product parameters. The selection of the metal used in this study was based on: the Mg metal known as decarboxylation catalyst and the low decomposition temperature of magnesium carbonate [23]. The temperature provides an advantage in the recycling process of metal carbonate. Whereas the selection of Ca metal was based on the high dehydration temperature of calcium hydroxide. This temperature was necessary to keep the basicity of soap in the pyrolysis temperature. Meanwhile, the selection of Zn metal was based on its catalytic ability to isomerize hydrocarbon [24]. In fact, the selection of alkaline and transition metals in the synthesis of metal soap aimed to form the soap basic in nature. Basic soap pyrolysis produces the only hydrocarbon, but stoichiometric soap is a hydrocarbon, ketone, and aldehyde compounds [25]. These components are not expected to exist. This study was carried out through several steps, including mixed metal hydroxides synthesized, saponification, and pyrolysis of basic soaps. The novelty of this study was the combination of 3 metals (Ca, Mg, Zn) as feed for making basic soap.

2. Material and methods

The raw material for making metal soap was oleic acid (78.8%) obtained from Energi Sejahtera Mas Inc, one of the oleochemical industries in Dumai. The oleic saponification and iodine values were 198.9 and 93.05 mg KOH/100 g samples, respectively. The mixed-hydroxide was obtained via a co-precipitation process of sodium hydroxide solution with high metal chloride base solution [22]. Calcium nitrate $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$, magnesium nitrate $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, zinc nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ and sodium hydroxide $[\text{NaOH}]$ were utilized from Merck with 99 % purity. The ratio of Ca metal compounds to Ca/Mg/Zn mixture determined for the effect of hydrocarbon content and RON value, respectively, are 0.15; 0.50, 0.65, and 0.85 mol.

The oleic mixed-metal basic soap was prepared through the modified fusion method. The saponification was carried out in a stirred reactor equipped with a heating jacket and a thermocouple. The procedure was as follows [22]: the mixed-metal hydroxide 40g and 140g oleic acids were mixed in a saponification reactor. The mixture is heated to 40–45 °C, and added 0.18 ml of formic acid, 98–100%, and 4 ml of water were added. After that, it was mixed for at least 30 min. The basic soap formed was dried at 60 °C for 12 h. The saponification reaction produced mixed metal basic soap as Eq. (1):



The soap variables observed were Total Alkali Content (TAC) and conversion of oleic acid to soap. According to [26], TAC consists of alkali bases combined as soap with fatty acids. The analysis was conducted to determine whether the soap was basic soap. The parameter was

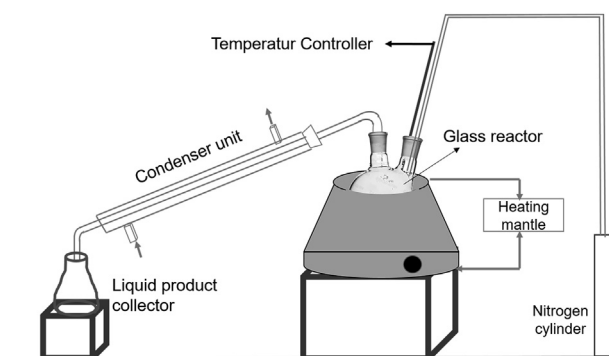


Figure 1. Schematic of pyrolysis setup apparatus.

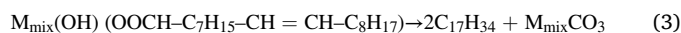
Table 1. Total alkali content and reaction conversion of basic soap.

Ca metal, mole	The ratio of Ca: Mg: Zn, mole	Total Alkali Content, %	Reaction Conversion, %
0.15	0.15: 0.85: 1	39.74	95.44
0.50	0.50: 0.50: 1	38.40	97.91
0.65	0.65: 0.35: 1	46.01	93.03
0.85	0.85: 0.15: 1	44.46	94.39

determined by the titration method based on ISO 685-1975, whereas the conversion of oleic acid to soap was determined by Eq. (2).

$$\text{Conversion} = ((\text{initial acid value} - \text{final acid value}) / \text{initial acid value}) \times 100 \% \quad (2)$$

The pyrolysis was carried out in 100 ml a glass batch reactor at atmospheric pressure. The reactor unit was equipped with a glass thermocouple, an air condenser, and a liquid collector. Before the basic soap was introduced, the reactor was fed with nitrogen gas to expel oxygen during the pyrolysis process. The process started with 10g basic soap feeding, and then it was heated to 450 °C for 2 h. The gas product formed condensed and was collected in a liquid product collector. The reaction of basic soap pyrolysis produced hydrocarbon and mixed-metal carbonate as Eq. (3). The schematic of the pyrolysis reactor is presented in Figure 1.



The liquid product was analyzed by gas chromatograph of Detailed Hydrocarbon Analyzed (DHA). An Agilent 7890B GC equipped with an Agilent 7693B autosampler was coupled with an FID for detection purposes. The instrument settings were as follows. The column is AC 21073.038 (40 m × 100 μm × 0.2 μm) purchased from Agilent Technologies. Then, the injection is 0.1 μL/min and it used helium as the carrier gas in constant pressure mode at 78 psi. The oven program is from 0 °C (11 min) – 4 °C/min – 35 °C – 4 °C/min – 45 °C – 4 °C/min – 60 °C – 7 °C/min – 200 °C (0 min), which corresponds to a 33 min run time.

3. Result and discussion

3.1. Saponification reaction

The basic soap has been successfully prepared at 40–45 °C. The physical character of basic soap was solid and difficult to separate, so it could not be formed as a powder. This appearance is caused by the characteristic of oleic acids as a reactant of the saponification reaction. The successful parameters of making basic soap were total alkali content and reaction conversion, as shown in Table 1.

The soap was truly basic when it obtained a TAC value ≤ 50 % [12]. The data in Table 1 show proves that the total alkali content in the soap

Table 2. Composition of product made by basic soap pyrolysis.

Types of product	Yields (wt%)			
	0.15	0.50	0.65	0.85
Liquid bio-hydrocarbon	43.1	48.7	39.6	37.9
Solid residues	21.3	22.8	25.7	26.3
Water	2.2	5.2	1.7	1.5
Others (including the gases)	33.4	23.3	33.0	34.3

for all of Ca metal ratio reached ≤ 50 %. The average value of TAC analysis results for soap was 42.15 %. This value indicated that the soap was basic and ready for pyrolysis feed. Furthermore, the success of the saponification reaction could be seen from the conversion of oleic acid into basic soap. Table 1 showed that saponification conversion of oleic acid into basic soap reached an average of 95.19 %. This conversion meant that the saponification reaction had been carried out successfully.

3.2. Product yield and selectivity

Pyrolysis of basic soap in a glass batch reactor produced liquid bio-hydrocarbon, solid residues, water, and others (including the gases). Table 2 shows the various product yields of the basic soaps pyrolysis with Ca metal ratio variation. The highest yield of liquid bio-hydrocarbon reached (48.7 wt.%) in Ca metal ratio 0.50 mol. Then the yield decreased until 37.9 wt.% in Ca metal ratio 0.85. It could be explained that Ca metal in the ratio 0.15 mol–0.50 mol provided sufficient basicity to keep the presence of the hydroxide (-OH) group. It encouraged the

pyrolysis of basic soap to obtain more hydrocarbons. Moreover, in the higher ratio of 0.65 mol–0.85 mol, Ca metal was converted to mixed metal carbonate, resulting in fewer bio-hydrocarbon products. The phenomenon was supported by the data of solid residues yield (Table 2). The data showed that the yield of solid residues increased in Ca metal ratio 0.15 mol–0.85 mol. In addition, it was supported by our previous research which investigated decarboxylation of stearic basic soap with mixed-metal ratio variation was equal with this study. The result discovered that decarboxylation of stearic basic soap in Ca metal ratio 0.50 mol produced the highest yield of biohydrocarbon (49.36 %wt) [27].

According to reaction 3, the residue of basic soap pyrolysis was a mix of metal carbonates. However, the resulting residue was, in fact, black and indicated that carbon was deposited in the mixed metal carbonate. The presence of carbon in the residue was most likely due to an alkene decomposition to form carbon and hydrogen. At the same time, alkene compounds were present due to the decomposition of alkanes [13]. Calcination of the pyrolysis residue of basic soap was carried out to prove the presence of mixed metal carbonates. The process was carried out at 550 °C for 2 h. The appearance of the calcined residue is shown in Figure 2. The figure shows the color change from black to grey in pyrolysis residue of metal soap after calcination. This change indicates that the residue contains true mixed metal carbonates.

The gas product yield of basic soap pyrolysis (Table 2) reached an average of 31 wt%. This yield could be explained that the cracking of basic soap at 450 °C produced a significant amount of uncondensable short-chain hydrocarbons (C_1 – C_4). Contrary to previous research, Neonufa [28] experimented on the pyrolysis of palm stearin soap using

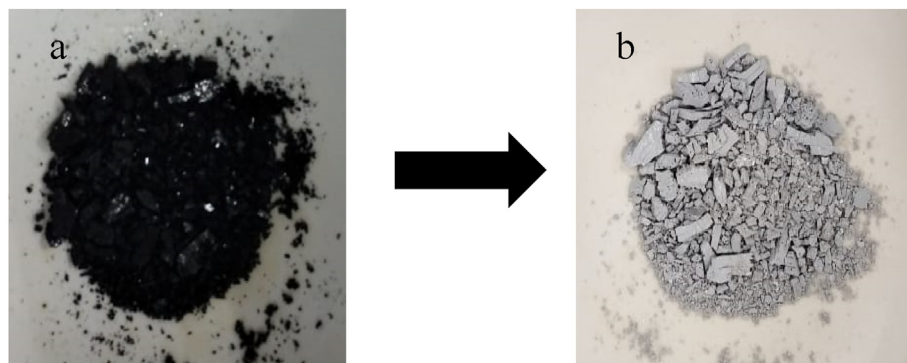
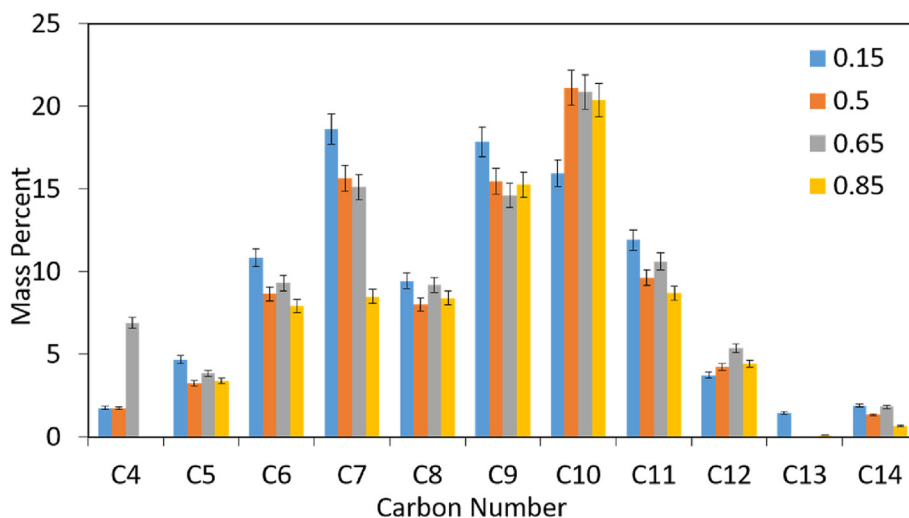
**Figure 2.** Metal soap pyrolysis residue: (a) before calcination; (b) after calcination.**Figure 3.** Typical carbon number distribution for liquid biohydrocarbon fraction.

Table 3. Classification of liquid products fraction from basic soap pyrolysis.

Parameters	Ca metal ratio, mole			
	0.15	0.50	0.65	0.85
Octane Number	89.6	83.8	87.7	83.6
P (wt% Paraffinic Content)	5.9	4.5	10.9	4.8
I (wt% Iso-paraffinic Content)	31.3	21.0	21.1	20
O (wt% Olefin Content)	18.5	31.6	33.6	25.9
N (wt% Naphthenic Content)	25.3	12.6	10.8	0.2
A (wt% Aromatic Content)	15.3	19.4	21.2	26.4

Mg and Fe metals. The yield of gaseous products reached 7.5 wt%. Meanwhile, Pratiwi [29], with the same feed, obtained a gas product of 22.8 wt%. This difference was possible due to the difference in pyrolysis temperature used. Neonufa carried out pyrolysis at 350 °C while Pratiwi at 370 °C. This phenomenon indicates that temperature was one of the factors that affect the production of pyrolysis gas products.

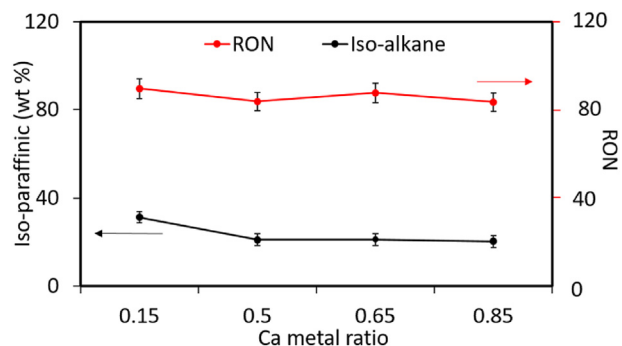
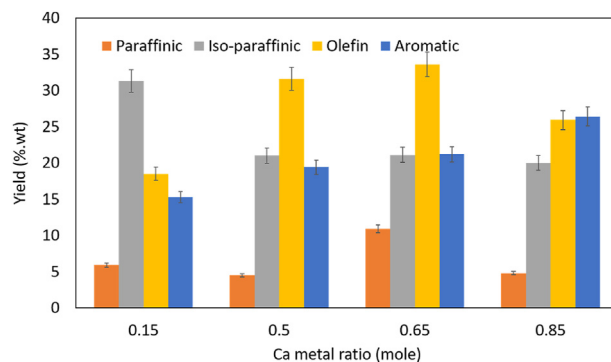
Table 2 shows that the quantity of water as a pyrolysis product is relatively low (average 2.7 wt%). This quantity also occurred in several previous soap pyrolysis studies [29, 30]. According to Eq. (3), the pyrolysis of basic soap should be a hydrocarbon and mixed metal carbonate. The presence of a small amount of water was considered to come from a small number of oxygen atoms in the hydroxyl group (-COO) of fatty acids that were not bound by metal. At the same time, the hydrogen atom was obtained from dehydrogenation of the C-C atomic bond, which leads to more double bonds and further forms aromatic compounds [31].

It is significantly essential to determine carbon distribution to know the type of liquid bio hydrocarbon. The DHA analysis obtained distribution of carbon of liquid bio-hydrocarbon fraction from pyrolysis of mixed metal basic soap for all of Ca metal ratio to 450 °C, depicted in Figure 3. It was shown that there was a similar pattern in carbon number distribution for liquid bio-hydrocarbon fractions. In all runs, C₆–C₁₁ was the prior product in the liquid fraction. According to [32], the carbon number range indicated that the product was biogasoline. Almost all variations of Ca metal ratio produced C₁₀ as the dominant product, except for Ca metal ratio of 0.15. The ratio obtained C₇ as the chief product in liquid bio-hydrocarbon fraction. It could be explained that the basic soap with a Ca metal ratio of 0.15 was more accessible to crack into shorter hydrocarbon than other soaps.

Furthermore, C₁₄ products only existed in small quantities. It showed that the cracking in basic soap pyrolysis had been carried out well. Previous oleic acid pyrolysis experiments showed similar results. The pyrolysis of oleic acid at 450 °C for 8 h produced a liquid product dominated by the gasoline fraction [33].

3.3. The effect of Ca metal ratio on distribution and RON of liquid biogasoline

Based on the carbon number distribution of liquid bio hydrocarbon, it proved that it is biogasoline. The content of the hydrocarbon components determines gasoline quality. Table 3 shows the classification of liquid products fraction (biogasoline) from basic soap pyrolysis of different Ca metal ratios. There were five types of hydrocarbons detected: paraffinic, olefin, naphthenic, iso-paraffinic, and aromatic. In all variations of Ca metal ratio, the liquid product of basic soap pyrolysis obtained higher saturated hydrocarbons than unsaturated hydrocarbons. It occurred as a result of the saturation reaction. The phenomenon was also found in the pyrolysis of unsaturated fatty acids [7] and other researchers when carrying out pyrolysis using different oils or fatty acids [4, 34, 35, 36]. It showed that the pyrolysis of fatty acids or triglycerides produces saturated hydrocarbons with or without saponification. The formation of hydrogen required in the saturation process was associated with the dehydrogenation reactions in the formation of cyclic alkenes and aromatic compounds and polymerization reactions [37, 38].

**Figure 4.** Effect of Ca metal ratio on the octane number and yield of iso-paraffinic.**Figure 5.** The effect of Ca metal ratio on liquid product composition.

In all variations of Ca metal ratio, both olefin and iso-paraffinic were the most significant hydrocarbons in biogasoline. The high amount of iso-paraffinic in biogasoline is probably due to the effect of the three metals used. It was supported by previous research that reports on the impact of metal type on basic soap pyrolysis to produce biogasoline. The report explained that basic soap Ca, Mg, Zn-oleate pyrolysis produced bio-hydrocarbon containing iso-paraffinic as a dominant product [22]. In addition, the five variations of the Ca metal ratio have the same metal composition of Zn, while Zn was a hydrocarbon catalyst.

The quantity of iso-paraffinic was one variable that affected the octane number of gasoline. Octane number was a method to measure the ability of the gasoline to resist knocking (reflect a gasoline's antiknock quality) when it is burned in an engine. The higher the octane number, the better gasoline resisted detonation, and the smoother the engine runs [39]. Table 3 shows that the highest octane number (89.6) of biogasoline was presented in Ca metal ratio 0.15 mol. Besides, a similar trend of both values (iso-paraffinic and octane number) was depicted in Figure 4. The figure reveals that the direction of octane and iso-paraffin numbers decreased with increasing Ca metal ratio, but it occurred quantitatively and was less significant. It probably happened because of the low variation range of Ca metal ratio. Furthermore, Table 3 described that Naphthenic content contributed the same trend as both. It meant that Naphthenic in liquid bio-hydrocarbon also affected octane number. The highest octane number provided the highest naphthenic range. It could be explained that the naphthenic was probably cyclopentane. According to [40], cyclopentane was Naphthenic which had a higher octane number of about 100.

The research in bio-gasoline synthesis through waste cooking oil pyrolysis at (450 °C–550 °C) had also been carried out [41]. The report showed that the highest RON of biogasoline reached 76. It indicated that the achievement of the biogasoline octane number from this study was very promising. The effect of the metal Ca ratio on the composition of the liquid product of basic soap pyrolysis was more clearly depicted in

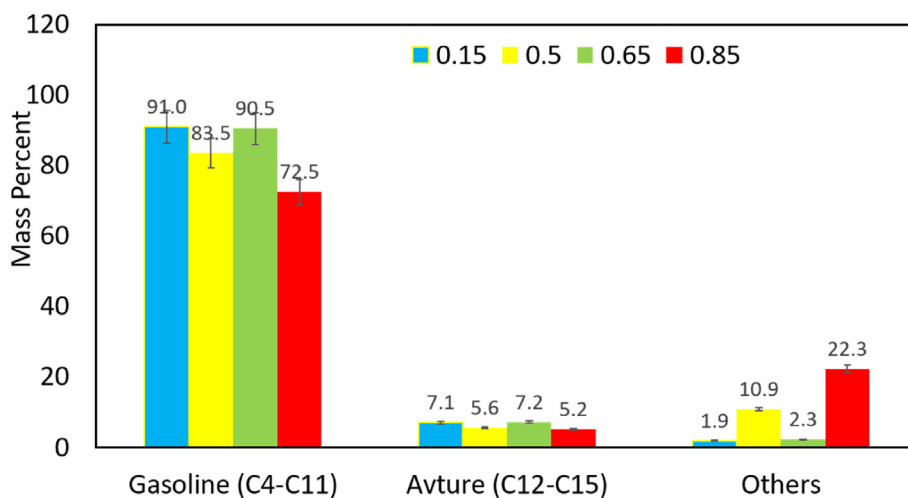


Figure 6. Fuel fraction composition in liquid bio-hydrocarbon.

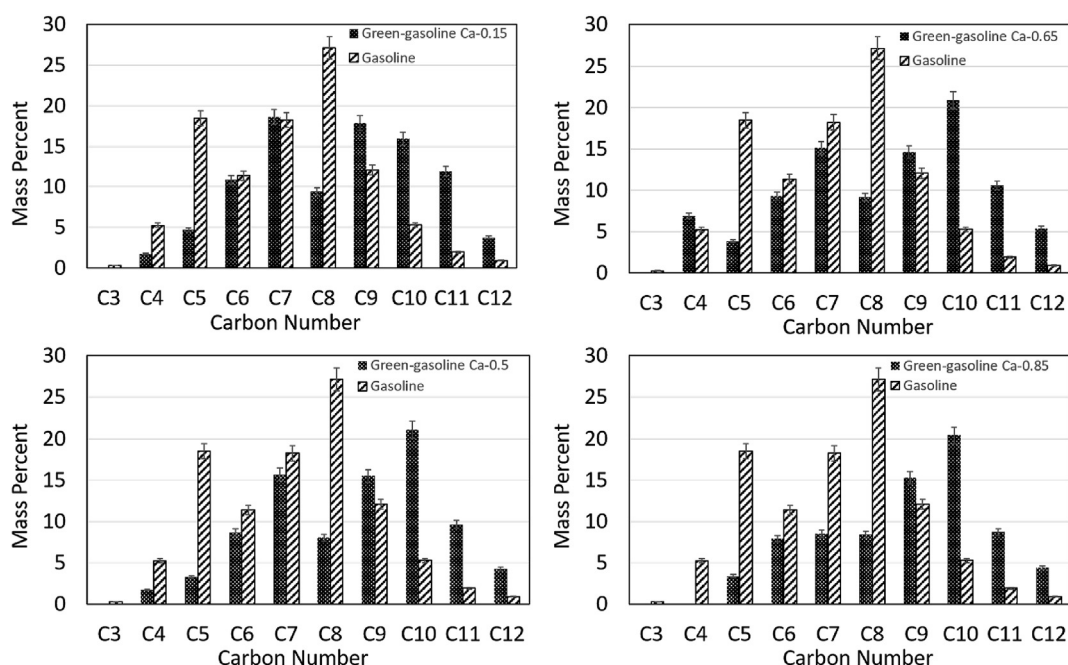


Figure 7. Typical carbon number distribution for gasoline and bio-gasoline.

Figure 5. The figure shows an irregular trend in the recovery of all hydrocarbon components (paraffinic, iso-paraffinic, and olefin). This trend indicated that the effect of the metal Ca ratio with μ value did not significantly affect the composition of the pyrolysis liquid product.

According to World Wide Fuel Charter, the gasoline requirements stated that the maximum olefin was 10 %v/v for gasoline 3-5 Euro category. In all runs, the high olefin was found in biogasoline from basic soap pyrolysis with an average of 27.4 wt% (Table 3). It is highly likely that a batch reactor in this work encouraged decarboxylation of basic soap for a long time. According to [42], the phenomenon caused a dehydration reaction of basic soap to partially dehydrated basic soap and water. Then, decarboxylation of this basic soap produces a mixture of paraffinic and olefin. It depended on the degree of basic soap dehydration. This phenomenon was supported by several previous researchers who discovered high olefins in the liquid product of soap pyrolysis [21, 29]. In addition, both studies carried out soap pyrolysis in a batch reactor.

The classification was based on fuel fraction carried out to find clear fractions contained in bio-hydrocarbons. The category includes gasoline and avture range hydrocarbon [43]. The fuel fraction composition in the liquid bio-hydrocarbon was obtained from basic soap pyrolysis at Ca-metal ratio variation, shown in Figure 6. The figure shows that three fractions were detected in liquid bio-hydrocarbon. These were gasoline, avture, and other unknown fractions. The fraction was probably the heavy fraction (diesel) that GC-DHA could not detect. It was supported by our previous study investigating the effect of temperature pyrolysis on bio-hydrocarbon products that used the same reactor. The result showed that for all temperature variations, the heavy fraction (diesel) was also detected. Figure 3 shows that gasoline was the dominant fraction in liquid biohydrocarbon in all runs, while the other fractions were much less. Basic soap pyrolysis with Ca metal ratio of 0.15 mol produced the highest gasoline fraction (91 %mass). This achievement was almost similar to the previous research. The research studied gasoline hydrocarbons from catalytic pyrolysis [29] of soapstock over corn cob-derived

activated carbons. The yield of gasoline range hydrocarbon could reach up to 91.03%-mass [44].

Subsequently, a comparison distribution of carbon between gasoline fuel and bio-gasoline of basic soap pyrolysis was done. Figure 7 indicated that the distribution of carbon of gasoline fuel [45] and bio-gasoline resulted from oleic basic soap pyrolysis. The Ca metal ratio of basic soap gave an almost similar carbon distribution effect in liquid bio-gasoline. It was also supported by Figure 1. The content of C₃–C₈ in bio-gasoline from all variations of Ca metal basic soap was lower than gasoline fuel. However, the biogasoline from basic soap pyrolysis with Ca ratio of 0.15 obtained almost the same C₇ value as gasoline fuel. In addition, Figure 4 shows that the catalytic thermal pyrolysis of oleic basic soap with Ca metal ratio 0.15 mol to bio-gasoline presented a carbon number distribution pattern which was the most similar to gasoline fuel. This supported the highest-octane number obtained in pyrolysis oleic basic soap with a Ca-metal ratio of 0.15 mol. However, C₉–C₁₂ in bio-gasoline were still higher than gasoline fuel.

4. Conclusion

Pyrolysis of oleic basic soap with mixed metal Ca, Mg, and Zn succeeds in obtaining a gasoline fraction hydrocarbon product. By comparing classification and typical carbon number distribution of liquid bio-hydrocarbon or biogasoline, the Ca-metal ratio in this experiment showed a less significant effect on the composition and Research Octane Number (RON) of the pyrolysis liquid product of basic soap. However, some important information was obtained in this study. The highest liquid bio-hydrocarbon yield (48.7 wt%) was achieved from the pyrolysis of basic soap in Ca-metal ratio of 0.50 mol. The combination of Ca-metal ratio of 0.15 mol in oleic basic soap pyrolysis proved to have a high catalytic ability because it produced bio-gasoline products (91%-mass). In addition, the Ca-metal ratio of 0.15 mol in oleic basic soap pyrolysis obtained the highest RON (89.6). This pyrolysis produced bio-hydrocarbon, solid residue, water, and gas. The bio-hydrocarbon contents were paraffin (5.9 wt%), iso-paraffin (31.3 wt%), olefin (18.5 wt%), naphthene (25.3 wt%), and aromatic compounds (15.3 wt%).

Declarations

Author contribution statement

Endar Puspawiningtiyas: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Meiti Pratiwi & Astri N Istiyami: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Ronny Purwadi, Subagio & Tatang Hernas Soerawidjaja: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Lidya Elizabeth: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Tirto Prakoso: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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