Effect of temperature and Mg-Zn catalyst ratio on decarboxylation reaction to produce green diesel from kapok oil with saponification pretreatment using NaOH

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Abstract. Green diesel is an emerging option to solve the increasing consumption of diesel (fossil based fuel). It involves converting readily available vegetable oils and animal fats to alkane hydrocarbons that can be considered to be drop-in replacements for petroleum-based fuel component. This review journal investigate the results of diesel-like hydrocarbon fuel by catalytic thermal decarboxylation of Mg-Zn basic soap by saponification using NaOH from kapok oil. Specifically, it outlines a comparative assessment of the operating parameters of the temperature and mole ratio of Mg-Zn catalyst to select the appropriate path based on the desired conversion, yield and selectivity. The results of the literature study show that kapok oil can produce diesel equivalent biohydrocarbon products by reviewing the main composition of the kapok oil which containing linoleic acid. An increase in the temperature of the decarboxylation reaction can increase the conversion to green diesel products, n-heptadecane. The result from previous experiment showed that the highest conversion of decarboxylation of castor oil is 65% at 475°C. However, high temperatures can cause decreased selectivity due to the production of undesirable products like in the decarboxylation experiment of soybean oil which showed that the yield at 400°C is decreased to 25%. The mole ratio of Mg-Zn used in the decarboxylation reaction does not have a significant effect on the yield of green diesel products.

1. Introduction
Currently, the world's population is increasing which in turn has resulted rapid increase for the need of petroleum as fuel for transportation. Due to increased demand of petroleum fuels, there is a rapid depletion in world’s petroleum reserves. In addition, the environmental impact of petroleum fuels on global climate change and air quality continues to increase. The various problems above motivate researchers to seek alternative fuels from renewable sources. Biodiesel is a type of biofuel that has been established as a renewable fuel. However, biodiesel is a type of oxygenated fuel [1], therefore its use is very limited (about 15-20% by volume) as a blending agent for petroleum fuels. For example, a blended fuel consisting of 20% biodiesel and 80% petrodiesel is called B20 [2]. Whereas green diesel refers to liquid hydrocarbon fuels that do not contain oxygen in their molecular structure. Therefore, the nature of green diesel is similar to petroleum fuel which can be used in larger quantities, even up to 100% by volume [3]. The advantages of green diesel compared to biodiesel are that it produces a high heating value, a cetane number between 80-90 and has lower NOx emissions. According to Asikin Mijan, et al
green diesel has good fuel properties compared to biodiesel, such as lower viscosity and better fuel stability.

Choosing kapok seed oil as raw material for green diesel is a wise step. This is because the oil is non-edible oil. Using edible oil as a raw material for making green diesel will cause problems, which are a food crisis in the future, an increase in the need for edible oil in the market, which will eventually increase the price of edible oil, and it is possible that many forests will be converted into edible oil field. So, it must use raw materials that can’t be consumed and it is a waste, one of the example is waste palm cooking oil. Kapok seed oil contains about 71.95% unsaturated fatty acids which causes kapok seed oil to go rancid easily, so it is not good to be developed as oil for cooking [5]. Hence, kapok seed oil is used as feed in green diesel production.

Green Diesel can be produced through several methods. The methods often used are thermal cracking, catalytic cracking and deoxygenation. Thermal cracking or pyrolysis and catalytic cracking are methods of breaking down triglyceride molecules with high molecular masses into lower molecular masses [6]. The difference between these two methods is the presence of a catalyst and the operating temperature used. The catalytic cracking method uses a catalyst and an operating temperature of 400-450°C [7]. The catalysts that are often used in this method are zeolite and mesoporous [8]. Meanwhile, the pyrolysis method does not use a catalyst and the temperature used is higher than the catalytic cracking method, which is 850°C [9]. The product of this cracking method is called bio-oil which cannot be used directly as a fuel due to the high level of oxygenated compounds (compounds with oxygen atoms in their molecular formula) in the form of phenols and their derivatives, such as esters, carboxylic acids, ethers, ketones and aldehydes. They are derived from the thermal degradation of cellulose, hemicellulose and lignin in biomass. This causes bio-oil to have undesirable properties, including: corrosive properties, low combustion efficiency and fuel instability which results in re-polymerization during storage [10,11].

Deoxygenation method is believed to be able to remove oxygenated compounds and convert them as carbon dioxide (CO₂) or carbon monoxide (CO) and water (H₂O). However, this method requires an external hydrogen gas source (H₂) to remove oxygenated compounds [12]. Deoxygenation can be done through different routes, namely hydrodeoxygenation, decarboxylation and decarbonylation [13]. The reaction steps that occur in hydrodeoxygenation, decarboxylation, and decarbonylation for saturated fatty acids in general can be illustrated as shown figure 1 below:

![Figure 1. Deoxygenation reactions on saturated fatty acids in general.](image)

According to Sari [14], hydrodeoxygenation is a reaction between triglycerides and FFA with hydrogen which can eliminate oxygen which then forms water and n-paraffin which is often referred to as n-alkanes. Direct hydrodeoxygenation of vegetable oils and animal fats is a method that is frequently used and has been studied in detail.

However, the hydrodeoxygenation method is an expensive method because it requires a large amount of H₂ gas. Based on Cheah [15], in the hydrodeoxygenation method 1 mole of fatty acids requires 3 moles of H₂ molecules. In addition, this method reacts at high temperatures and pressures [16]. The involvement of H₂ gas under high pressure to suppress O₂ bound to oil and fat feed molecules or fatty acids to be released from its bonds and produce liquid biohydrocarbons as fuel. Based on the explanation
above, it can be concluded that the hydrodeoxygenation method is considered less effective for the manufacture of green diesel.

Decarbonylation and decarboxylation methods are alternative methods for making green diesel. The decarboxylation method produces a by-product in the form of CO \(_2\), while for decarbonylation it produces CO and water as a by-product [17]. Decarbonylation can take place well if you use a metal-based catalyst such as Ni/ZrO\(_2\) and with the addition of H\(_2\) gas, which for decarbonylation of one fatty acid requires one mole of H\(_2\). Meanwhile, decarboxylation can take place well under inert conditions when the catalysts used are Pd and Pt. This is because the Pd and Pt catalysts are able to produce hydrogen in situ. However, currently researchers have conducted research so that green diesel can be produced through the decarboxylation process of metal soap using catalysts in the form of alkaline-earth metals and transition metals so that this method can be more affordable [13]. Therefore, the decarboxylation method is considered as an effective method for producing green diesel.

Decarboxylation of basic soaps (e.g., magnesium soap) into drop-in fuels, illustrated by the equation of reaction (1)

\[(\text{R-COO})\text{Mg(OH)} \rightarrow \text{RH} + \text{MgCO}_3\]  

(1)

2. Methodology

The general method to produce metal soaps derived from vegetable oil is metathesis process. The kapok seed oil is first mixed with hot ethanol in a glass batch reactor with a stirrer to get a uniform mixture. Then an aqueous solution of sodium hydroxide at 20% by weight is added to the mixture under continued stirring. Once the mixture has reached a firm consistency, a solution consist of magnesium–zinc acetate combination in distilled water is added to the mixture while stirring. The Mg–Zn basic soap produced by ion exchange is insoluble in water and can be easily separated from its soluble sodium counterparts. The saponification process usually takes about 1 hour. The produced basic soap from this process is filtered, washed with hot water and then dried in an oven at 70\(^\circ\)C for at least 48 hours. The dried basic soap is subsequently used as the material for the decarboxylation process.

Mg–Zn basic soap decarboxylation was performed, i.e. destructive distillation at 350\(^\circ\)C and atmospheric pressure in a glass batch reactor for 5 hours, without catalysts. The heat was supplied and maintained in the reactor by using an automatic system with thermocouples and electronic controls. Nitrogen was flushed into the reactor to remove the remaining air. When the temperature was reached, the reactant evaporated into gaseous phase products. These products were cooled in a condenser tube to get the liquid products, after which they were stored in a glass beaker. This liquid product is called green diesel and then the product is analysed with GC [13].

3. Result and discussion

3.1. Effect of temperature on conversion and yield of green diesel

The deoxygenation studies of triglycerides, fatty acids, and fatty esters are preferably carried out at temperatures ranging from 250 to 360\(^\circ\)C. It has been reported by many researchers that the reaction temperature has a considerable effect on the deoxygenation process and the product selectivity [19]. Research conducted by Setiadi and Susanto [20] shows a decarboxylation reaction through saponification with Ca(OH)\(_2\) to produce hydrocarbons equivalent to diesel. The temperature variation of the decarboxylation reaction was carried out from 400\(^\circ\)C - 475\(^\circ\)C. Based on Table 1, it is known that an increase in reaction temperature can increase the conversion of n-heptadecane. N-heptadecane is the major hydrocarbons in diesel fuel. The largest conversion was obtained at a temperature of 475\(^\circ\)C with the conversion of 65%.

In addition, research on the decarboxylation reaction with saponification pretreatment was also carried out by Setiadi and Rosul [21]. Cooking oil waste is reacted with Ca(OH)\(_2\) to form a soap with an oil to base ratio of 1: 4.5 and a reaction time of 90 minutes. Temperature variations carried out at
400°C-460°C. Based on Table 1, the conversion increases with increasing temperature, but at 460°C the conversion decreases. The largest conversion was obtained for a temperature of 440°C with the conversion of 32%.

The main composition of kapok oil is linoleic acid. The approach that can be used in this decarboxylation reaction is to use a similar material which has a large linoleic acid content as well. Soybean oil is one of the vegetable oils with a high linoleic acid content with 52%. Research on the decarboxylation of soybean oil has been carried out by Pimenta et al. [22], based on the results of this study, it was found that the higher the temperature, the yield of n-heptadecane products decreased. The high temperature causes the formation of short chain hydrocarbons (C₈-C₁₃). In addition, the production of aromatic and saturated hydrocarbons increases with a higher reaction temperature, whereas the production of unsaturated, but non-aromatic compounds, decreases with increasing reaction temperature. This shows that the hydrogenation reaction, which is responsible for the formation of more saturated compounds and the aromatization reaction is favored by the higher temperature. According to Yang et al [23], an increase in temperature leads to an increase in the α/β cutting rate of carbon, which could explain the larger concentration of the smaller compound produced at 400 °C.

| No | Feed | Catalyst | Type of Reaction & Reactor | Time (hr) | Temp. (°C) | Result | Reference |
|----|------|----------|--------------------------|----------|-----------|--------|-----------|
| 1  | Castor Oil | Ca(OH)₂ | Soap Decarboxylation & Batch reactor | 1.5 | 400 | C₁₇ Conversion = 17% | [20] |
|    |       |         |                          |          | 425       | C₁₇ Conversion = 42% |   |
|    |       |         |                          |          | 450       | C₁₇ Conversion = 56% |   |
|    |       |         |                          |          | 475       | C₁₇ Conversion = 65% |   |
|    |       |         |                          |          | 400       | C₁₇ Conversion = 17% |   |
| 2  | Waste Palm Cooking Oil | Ca(OH)₂ | Soap Decarboxylation & Batch reactor | 1.5 | 420 | C₁₇ Conversion = 21% | [21] |
|    |       |         |                          |          | 440       | C₁₇ Conversion = 32% |   |
|    |       |         |                          |          | 460       | C₁₇ Conversion = 20% |   |
|    |       |         |                          |          | 360       | Yield C₁₇ = 72% |   |
| 3  | Soybean Oil | NiMo | Decarboxylation & Autoclave reactor | 1.5 | 380       | Yield C₁₇ = 56% | [22] |
|    |       |         |                          |          | 400       | Yield C₁₇ = 25% |   |

3.2. Effect of Mg-Zn catalyst ratio on conversion and yield of green diesel

The amount of the catalyst used can affect a large percentage of the yield composition of the fraction hydrocarbon. Magnesium (Mg) catalyst is a catalyst for the decarboxylation process [24]. Meanwhile, Zinc (Zn) catalyst is a hydrocarbon isomerization catalyst [25]. The effect of the addition of Zn catalyst on the decarboxylation process can affect the order of hydrocarbons of the i-paraffin type. This is because Zn is known as a hydrogenation catalyst for unsaturated compounds [26] which can change the name of iso-alkanes as well [27]. i-paraffin group is a desired hydrocarbon in fuel because it has a lower cetane number than n-paraffin (between 10-80) which is very much needed in fuel. However, I-paraffin has a lower freezing point. The use of a lower amount of catalyst in the DO reaction leads to polymerization, which consequently increases the formation of aromatics and other unwanted products. Therefore, the optimal amount of catalyst plays an important role in determining the highest yield and selectivity of the desired hydrocarbon products [19].

Neonufa [13] has been researching using an Mg-Zn Catalyst (9:1 ratio) with palm stearin (saturated fatty acid, was approximately 63% by weight, while unsaturated fatty acid, was only approximately 26% by weight) at 350 °C and atmospheric pressure for 5 hours. In this study, the result were shown in Figure 1 shows that approximately 41.08 %-mole of liquid bio-hydrocarbons obtained from Mg-Zn basic soap decarboxylation were various 1-alkene molecules. The amount of Mg-Zn used will increase the formation of 1-alkene. That shows that there was a dehydrogenation reaction during the Mg-Zn basic soap decarboxylation or decomposition of long chain paraffin.
In addition, Neonufa [28] has been researching using an Mg-Zn catalyst (4: 1 ratio) with Pongamia pinnata seed oil (unsaturated fatty acid 47.45% mole, saturated fatty acid 25.42% mole) at 370 °C and atmospheric pressure for five hours. In this study, the results were shown in Figure 2 with the% yield of n-paraffin of 29.87%, while for i-paraffin of 50.78% and olefins of 19.35% mole. The amount of olefins formed proves that the more Mg-Zn mole ratio used will affect the formation of olefins in the decarboxylation reaction. The number of olefins formed at a 4:1 mole ratio is less than the formation of olefins in the nenoufa, 2017 which used the Mg-Zn 9: 1 mole ratio.

Based on the two studies that have been done, it is known that the Mg-Zn ratio can affect the hydrocarbons produced. In addition, the raw materials used also play an important role in determining the hydrocarbons produced. Kapok oil contains more unsaturated fatty acids, according to Neonufa et al. [2] it is necessary to hydrogenate palm oil in the biohydrocarbon (renewable fuel) production process (Green diesel), because otherwise it will produce n-heptadecene hydrocarbons and will produce more unwanted products such as alkenes. In addition, the Mg-Zn mole ratio does not really affect the yield of
hydrocarbons because the raw materials used have a high content of unsaturated fatty acids. According to Fu et al. [29], polyunsaturated fatty acids can pass through the decarboxylation reaction pathway as shown in Figure 4 to produce n-heptadecane, a hydrocarbon equivalent to diesel.

![Figure 4. Reaction pathways for linoleic acid.](image)

4. Conclusion
An increase in the temperature of the decarboxylation reaction can increase the conversion of green diesel products, n-heptadecane and the Mg-Zn catalyst ratio used in the decarboxylation reaction does not have a significant effect on the yield of green diesel products.

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