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Catalytic Decarboxylation of Palm Oil to Green Diesel over Pellets of Ni-CaO/Activated Carbon (AC) Catalyst Under Subcritical Water

Desy Septriana,1,2*
***Muhammad Mufti Azis**1*
***Joko Wintoko**1*
1Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, 55281 Indonesia
2Research Organization for Energy and Manufacture, National Research and Innovation Agency, Indonesia
*e-mail: desy002@brin.go.id

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Abstract. There has been a considerable in converting palm oil to green diesel. Green diesel is a hydrocarbon compound similar to conventional diesel fuel's components. It is expected to substitute conventional diesel fuel in diesel vehicle engines. The process of producing diesel is also called the deoxygenation process. One of the deoxygenation processes is decarboxylation. The current study evaluates the performance of Ni-CaO/AC catalyst in the form of pellets by mixing a powder Ni-CaO/AC catalyst and phenolic resin. The aim of this study namely to evaluate the performance pellets of Ni-CaO/AC catalyst in the decarboxylation of palm oil under sub-critical water. This research includes catalyst activity carried out by decarboxylation in subcritical water with temperature variations: 300, 310, 320, and 330 °C using pellets of Ni-CaO/AC catalyst. The decarboxylation products obtained were analyzed with Gas Chromatography-Mass Spectroscopy (GC-MS). The results obtained in this study showed that the highest percentage composition and selectivity of green diesel were obtained at a temperature of 330 °C, with values of 18.08 and 22.07, respectively. These results suggest that higher temperature promotes the hydrogenation-decarboxylation reaction of palm oil. Pellets of Ni-CaO/AC catalyst can increase the selectivity of green diesel if the phenolic resin is replaced with a binder that can provide physical strength to the catalyst but does not damage the function and cover much of the active surface area of the catalyst. We can conclude that pellets of Ni-CaO/AC catalysts have the potential to do hydrothermal decarboxylation if the increased operating condition.

Keywords: Catalyst, Decarboxylation, Green Diesel, Phenolic Resin, Subcritical Water

INTRODUCTION

All plants containing oil or fatty acids have the potential to produce green diesel. Green diesel is a drop-in/non-oxygenate biofuel with a hydrocarbon range of $C_{12} – C_{18}$ (Rosmelina, 2012). Green diesel is similar to conventional diesel because deoxygenation has removed the oxygenate component. The deoxygenation process can be carried out in 3 types of reactions: hydrodeoxygenation, decarboxylation, and decarbonylation (Krobkong et al., 2018). Hydrodeoxygenation (HDO) reactions can remove oxygen by

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reacting triglycerides and free fatty acids with hydrogen to form water and n-paraffin. At the same time, the decarboxylation or decarbonylation reaction removes oxygen by forming carbon dioxide or carbon monoxide and n-paraffin. The decarboxylation reaction does not require external hydrogen gas to saturate the double bonds in the oil—three types of reactions as seen in Eq. (1)-(3) (Hossain, 2017).

$$C_{18}H_{34}O_2 + 4H_2 \longrightarrow nC_{18}H_{38} + 2H_2O \quad (1)$$

$$C_{18}H_{34}O_2 + 2H_2 \longrightarrow nC_{17}H_{36} + CO + H_2O \quad (2)$$

$$C_{18}H_{34}O_2 + H_2 \longrightarrow nC_{17}H_{36} + CO_2 \quad (3)$$

Removal of oxygen via decarboxylation or decarbonylation represents an alternative and direct pathway to produce hydrocarbon fractions almost identical to commercial fuels without alteration (Hossain, 2017). Decarboxylation only requires 1 mole of hydrogen per mole of oxygen removed. Hence, the catalyst in the decarboxylation reaction is the determining factor for the success of green diesel production, especially its selectivity to form paraffin compounds (C_{12}-C_{18}).

This study uses pellets of Ni-CaO/Activated Carbon catalyst for decarboxylation of degummed palm oil because it has an acid and alkaline site. Base sites are required for hydrogenation, decarboxylation, decarbonylation, and hydrodeoxygenation reactions. Base sites of metal oxides can attract hydrogen in carbonyl compounds, and then the C-O bond is broken to form hydrocarbon compounds (Asikin et al., 2017). In comparison, the acid site is needed for isomerization and cracking reactions. For this reason, the balance between alkaline and acid sites is very important in the catalyst so that the catalyst's selectivity, activity, and resistance can be obtained optimally. Because the decarboxylation and decarbonylation occur overlapping, the catalyst used should be the same and have a dual function, so it is also called an acid-base catalyst (Al-Alwan, 2014). Our previous work showed that non-hydrothermal decarboxylation using Ni-CaO/AC catalyst in pellets did not provide sufficient yield and selectivity for green diesel as expected (Septriana et al., 2021). Therefore, in this study, sub-critical water or hydrothermal conditions are used for the decarboxylation of palm oil over pellets of Ni-CaO/AC Catalyst. Because water can easily hydrolyze triglycerides to provide an aqueous stream of fatty acids, and water properties are tunable by changing temperature and pressure.

Proposed Reaction Mechanism

Palm oil is reacted under subcritical water over pellets of Ni-CaO/AC catalyst to produce green diesel through several reaction stages (Eq. (4)-(11)). At first, the triglycerides in palm oil to produce free fatty acids and glycerol in hydrothermal media is commonly called fat–splitting. Furthermore, liberated glycerol can undergo catalytic Aqueous Phase Reforming (APR) to produce H_2 and carbon dioxide. Then, the hydrogen and carbon dioxide produced can undergo a water gas shift (WGS) reaction. Hydrogenation of oleic acid to be stearic acid was accomplished by in situ hydrogens from APR reaction and thermal cracking. Then, dehydration of unsaturated fatty acid produces alcohol compounds and water.

Furthermore, this stearic acid undergoes several deoxygenation reactions to produce green diesel, including decarboxylation and decarbonylation in parallel and cracking, as seen as Eq. (9)-(11). During the reaction, acidic sites facilitated hydrolysis and cracking, while basic sites promoted decarboxylation and partially removed oxygen from the triolein simultaneously (Asikin et al., 2017)

Hydrolysis of triglyceride

$$C_{57}H_{104}O_6 + 3H_2O \xrightarrow{Ni-CaO/AC} C_3H_8O_3 + 3C_{18}H_{34}O_2 \quad (4)$$

Hydrolysis of glycerol (Aqueous Phase Reforming)

$$C_3H_8O_3 + 3H_2O \xrightarrow{Ni-CaO/AC} 7H_2 + 3CO_2 \quad (5)$$

Water Gas Shift reaction

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad (6)$$

Hydrogenation of oleic acid

$$C_{18}H_{34}O_2 + H_2 \longrightarrow C_{18}H_{36}O_2 \quad (7)$$

Dehydration of oleic acid

$$C_{18}H_{34}O_2 \longrightarrow C_{18}H_{32}O + H_2O \quad (8)$$

Deoxygenation of stearic Acid:

- Decarboxylation of stearic Acid

$$C_{18}H_{36}O_2 \longrightarrow C_{17}H_{36} + CO_2 \quad (9)$$

- Decarbonylation of stearic Acid

$$C_{18}H_{36}O_2 \longrightarrow C_{17}H_{34} + CO + H_2O \quad (10)$$

- Cracking

$$C_{18}H_{36}O_2 \longrightarrow CO + CO_2 + H_2 + C_xH_y \quad (11)$$

$$C_{18}H_{36}O_2 \longrightarrow C_{17}H_{32}O_2 + CH_4 \quad (12)$$

The objective of the present work was to evaluate the performance pellets of Ni-CaO/AC catalyst in the decarboxylation of palm oil under subcritical water. The liquid products were analyzed using GCMS to evaluate the change in the chromatogram area before and after treatment.

METHOD

Materials

The pellets of Ni-CaO/AC Catalyst with a size of 0,9 cm OD and height of 0,8 cm were obtained from previous research (Septriana et al., 2021). The catalyst was prepared by the wet impregnation method. Two precursor solutions, 20% Ni $(NO_3)_2.6H_2O$ and 15% $Ca(NO_3)_2 \cdot 4H_2O$ were used. Furthermore, two of these solutions are impregnated into activated carbon continuously for 5 hours under vacuum pressure. Subsequently, the impregnation solution was left overnight, followed by evaporation, filtering, and drying at 105°C to obtain a dry powder. Later, the resulting dry impregnation solution is called Ni-CaO / AC powder which was calcined at 700°C for 4 hours with N_2 gas flowing at atmospheric pressure in a tubular furnace. Then, the powder of Ni-CaO/AC was modified into pellets with 40 wt% of phenolix resin and 6% of plasticizer (Septriana et al., 2021).

Deionized water was purchased from CV. Progo Mulyo, N_2 gas (99,9% pure) was supplied by the Senator gas industry, acetone (technic standard) was purchased from Merck, and n-Hexane (GC grade) > 98% was obtained from Merck was used for dilution. The feedstock of this work was degummed palm oil from Bimoli because no contains gum, impurities, and odors. In addition, the main compound which was analyzed as the main parameter of evaluation performance of the Ni-CaO/AC catalyst for the decarboxylation reaction was oleic acid. Oleic acid is the most abundant compound contained in degummed palm oil. Before the degummed palm oil was analyzed, a transesterification reaction must occur on the cooking oil. After transesterification, degummed palm oil was analyzed using a gas chromatography-mass spectrometer (GCMS) to determine its composition, as shown in Table 1. Table 1 shows that oleic acid is the most abundant component in oil-based palm oil.

Table 1. Fatty acid composition of degummed palm oil

Components	Values (%)
Myristic Acid	0,6294
Palmitic Acid	0.3175
Stearic Acid	41.1458
Oleic Acid	57.9073

Volume/size analysis of the catalyst was carried out with a NOVA 2000e surface area and pore size analyzer (Quantachrome Instruments) as in the previous study in Table 2 (Septriana et al., 2021)

Table 2. Characterization of pellets of Ni-CaO/AC catalyst

Parameter	Value
Surface area (m^2/g) by BET	19.13
Pore volume (cc/g) by BJH	5.61×10^{-2}
Average pore radius (Å)	26.61

Structural and Compositional Properties. The BET surface areas, pore volume, and average pore radius for Ni-CaO/AC Catalyst pellets were 19.13 m^2/g, 5.61×10^{-2} cc/g, and 26.61 A, respectively.

Characterizations

The actual metal loadings were confirmed by EDXRF analysis. EDXRF analysis using Xenemetrix with spectra method. The analysis time with X-Rays is about 300 seconds.

Reaction Procedure

The same experimental protocol as our previous experiment was followed in this study with the same autoclave (250 mL). First, degummed palm oil and deionized water were loaded into the autoclave with degummed palm oil, and the water ratio was 1:4 (w/w) (Hossain et al., 2017). Catalyst loading was 5% w/w of degummed palm oil (Jin et al., 2019). Subsequently, purging autoclave with 10 bar N_2 gas to ensure the inert condition in the entire reactor. Afterward, the autoclave was heated to the reaction temperature under static conditions. After temperature stabilization, the reaction was initiated by stirring (100 rpm) and continued for 2 h. After completing the process, the heater and stirrer motor was turned off. The running process was repeated for 310, 320, and 300 ^oC temperatures on different samples.

Furthermore, after the autoclave reached ambient temperature, the product was taken from the autoclave. Subsequently, the product was dissolved with hexane to separate the catalyst, water, and product. Before experiment use, the reactor was washed with hexane and water. Next, the product was separated by filter paper with the help of a vacuum pump. Filtrate formed a boundary layer, where the upper layer was taken to separate water, product, and hexane by distillation to obtain the pure product that can be analyzed by Gas chromatography-mass spectrometer (GCMS).

Product Analysis

Liquid products, which mainly consisted of n-paraffin, oxygenated intermediates (long-chain aldehydes, ketones, and alcohols), stearic acid, and oleic acid, were analyzed by a gas chromatography-mass spectrometry (model SHIMADZU QP2010S) with a non-polar Rtx 5 column (30 m x 0,25 mm x 0.25 µm) with split inlet flow. The liquid product was diluted with GC grade n-hexane before the yield analysis with a split ratio of 100. The injection temperature was at 300 °C, a detector temperature of 305 °C. Helium gas served as the carrier gas. The initial temperature of the oven was 70°C and held for 5 min, then ramped up to 300°C and held for 19 min.

The obtained data from the experiment were calculated to determine the selectivity and composition of green diesel and other by-products. The green diesel selectivity and composition percentage of green diesel were calculated based on the results of the GCMS analysis.

The percentage of green diesel composition is calculated by dividing the total area of the green diesel fraction by the total product produced according to Eq. (13) below. The composition percentage of other products can be determined by Eq. (13) and by dividing the total area by the total obtained product.

$$P = \frac{\sum n_D}{\sum n_P} \times 100 \qquad (13)$$

The selectivity of green diesel can be obtained by dividing the area of green diesel (desired area) by the total area of unwanted product (undesired area) according to Eq. (14) (Fogler, 2016).

$$S_D = \frac{\sum n_D}{\sum n_U} \times 100 \qquad (14)$$

Desired area (green diesel) includes alkane and alkene (C_{12}-C_{18}), while the undesired area includes total products except for alkane and alkene (C_{12}-C_{18}).

RESULTS AND DISCUSSION

This study obtained the elemental analysis of Ni-CaO/ Activated Carbon Catalyst pellets and liquid product analysis. We can see the result of the elemental analysis in Table 3.

Table 3. Elemental analysis from pellets of Ni-CaO/AC catalyst with Energy Dispersive X-ray Fluorescence (EDXRF)

Components	Composition (%)
K	0.330
Ca	26.076
Mn	0.059
Fe	0.646
Ni	72.815
Zn	0.020
As	0.002
Br	0.044
Sr	0.009

The results of the EDXRF analysis in Table 3 have proven correct that the largest content of pellets of Ni-CaO/AC catalyst is Nickel and calcium, with the Ni and Ca content of 72.815% and 26.076 %, respectively. In contrast, the Ni-CaO/AC catalyst support, namely carbon, cannot be detected with EDXRF. The results of EDXRF are almost the same as those of Energy Dispersive X-ray (EDX), according to the previous study. The EDX mapping of the catalyst said that before powder of Ni-CaO/AC mixed with 40 wt% of phenolic resin and 6% of plasticizer gave results with the actual Ni, and Ca content of 64.314 and 34.783 %, respectively (Septriana et al., 2021). Although, when the synthesis powder of Ni-CaO/AC, Ni and Ca loading was 15 wt% and 15 wt%, respectively, EDXRF results showed active metals in Ni-CaO/AC Catalyst.

Liquid products quantification

The gas chromatography-mass spectrometry (GCMS) results show composition of products. GCMS results display chromatogram data based on retention time and area. Typically, liquid products consist of n-paraffin, oxygenated intermediates (long-chain aldehydes, ketones, and alcohols), stearic acid, and oleic acid. The chromatogram data on the decarboxylation product at a temperature of 330 °C can be seen in Figure 1.

Figure 1 displays a chromatogram or two-dimensional graph that has peaks. In Figure 1, 12 detected peaks represent the components or compounds in the decarboxylation product. Each peak of each component has a different area according to different retention times, usually called the peak area. The peak area of each component can be seen in Table 4 below. Table 4 shows the results of the GCMS chromatogram reading, which detected 12 components in the hydrothermal decarboxylation of palm oil using a Ni-CaO/AC pellet catalyst.

Furthermore, the compounds with different peak areas are grouped according to their group of compounds or functional groups, as shown in Table 4. After grouping these compounds, it is easy to calculate the total product area, green diesel selectivity, and hydrocarbon yield. The calculation results can be shown in Figure 2.

Figure 2 shows the composition percentage of the product from hydrothermal decarboxylation over pellets of Ni-CaO/AC catalyst at various temperatures under subcritical water. Figure 2 shows the highest product, namely alcohol. Furthermore, the ester component dominates and is followed by other components in almost the same amount at various temperatures. The composition percentage of each component is calculated by Eq. (13). Biogasoline and biokerosene components are also formed due to this hydrothermal decarboxylation. Biokerosene and biogasoline are formed due to the cracking reaction. This is due to the Ni catalyst cutting the C-O bond (decarboxylation and decarbonylation). However, the Ni-based catalyst has a drawback. Namely, the C-C bond cracking activity is also high. Then, the result showed that the main product of decarboxylation with Ni catalyst tends to be a light hydrocarbon. The expected composition in this study is green diesel.

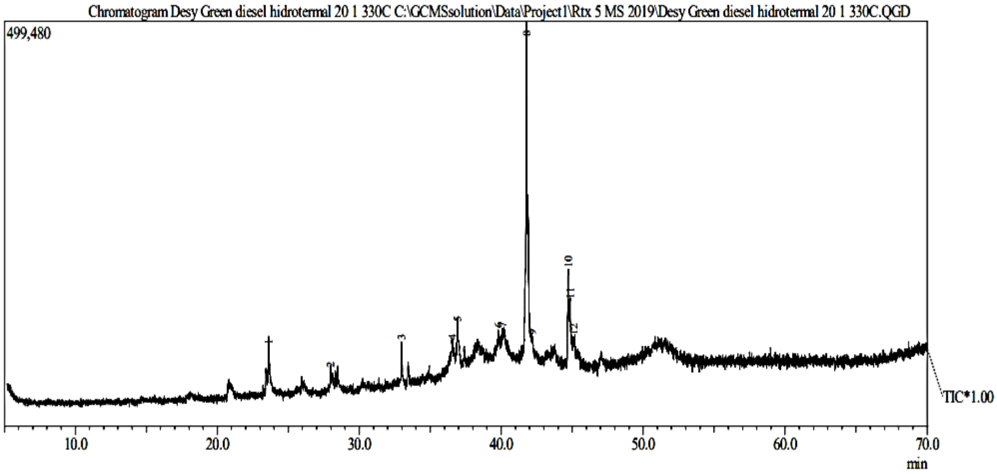

Fig. 1: GCMS spectrum of the product obtained from the hydrothermal decarboxylation of palm oil at 330°C over pellets of Ni-CaO/AC Catalyst

Table 4. GCMS chromatogram of hydrothermal decarboxylation products at 330 °c using pellets of Ni-CaO/AC catalyst

Hit	Chemical Formula	Peak Area	% Area	Compound Groups
1	$C_{11}H_{24}$	533251	6,41	Biokerosene
2	$C_{11}H_{22}$	257336	3,09	Biokerosene
3	$C_8H_{16}O$	207182	2,49	Ketone
4	$C_{24}H_{46}O_2$	346969	4,17	Carboxylic acid
5	$C_{19}H_{36}O_2$	531159	6,38	Oleic acid
6	$C_{18}H_{36}O$	360470	4,33	Alcohol
7	$C_{14}H_{28}$	596788	7,17	Alkene
8	$C_{26}H_{54}O$	3765695	45,24	Alcohol
9	$C_{17}H_{36}$	226219	2,72	Alkane
10	$C_{18}H_{34}$	585967	7,04	Alkene
11	$C_{18}H_{36}O$	660285	7,93	Aldehyde
12	$C_{10}H_{16}O_2$	253077	3,04	Carboxylic acid

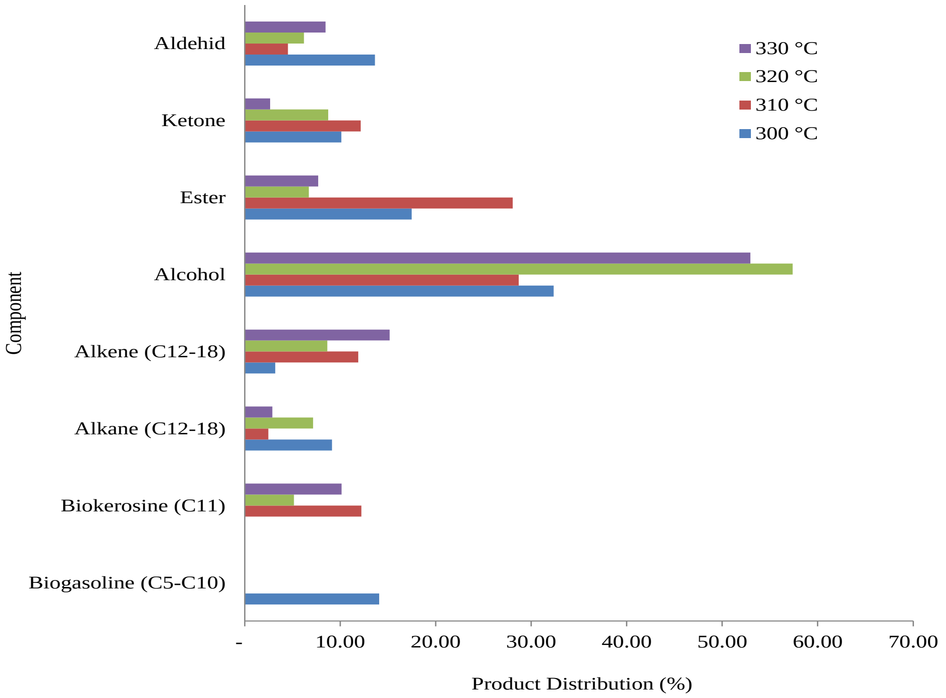

Fig. 2: Products distribution of hydrocarbon and selectivity in decarboxylation with pellets of Ni-CaO/AC catalyst under subcritical water

The composition percentage of alkane and alkene of C_{12}-C_{18}, a component of green diesel, was the most expected product in this study. The difference between alkane (C_{12}-C_{18}) and alkene (C_{12}-C_{18}) lies in the presence of double bonds. Alkane compounds (C_{12}-C_{18}) do not have double bonds, resulting from the decarboxylation of saturated carboxylic acids, such as stearic acid, palmitic acid, and myristic acid. Alkene compounds (C_{12}-C_{18}) have double bonds, resulting from the decarbonylation of saturated carboxylic acids. The tendency of the reaction that occurs with pellets of Ni-CaO/AC catalyst in subcritical water at a temperature range of 300 °C to 330 °C is decarbonylation compared to decarboxylation. The result in Figure 2 has proven it where more alkene than Alkana.

Decarboxylation happens breakdown of the double bond in the carboxylic acid through hydrogenation. Decarboxylation released CO_2 gas as a by-product. The decrease in CO_2 concentration caused by the increase in pressure causes the reaction in the reactor to be dominated by the decarbonylation reaction. Therefore, there is an increase in CO concentration. The increased H_2 pressure in the reactor increases the hydrogenation reaction by breaking the double bonds in the alkene structure produced by the decarbonylation and triglyceride cracking reaction. This follows Le Chatelier's equilibrium principle: In an equilibrium reaction, increasing pressure causes the reaction to move towards a substance with fewer coefficients. The higher H_2-inhibited free fatty acid (FFA) decarboxylation reaction can increase the concentration of FFA undergoing a decarbonylation reaction. Decarboxylation happens when the breakdown of the double bond in the carboxylic acid through hydrogenation (Al-alwan, 2014). As seen in Figure 2, more olefin (alkene C_{12}-C_{18}) compounds are formed than paraffin (alkane C_{12}-C_{18}). This is due to the lack of H_2 consumption to hydrogenate alkenes, so the reaction tends to move towards the right of equilibrium to form olefin compounds. However, if the H_2 given by the reaction is less than the minimum H_2 required for the hydrogenation reaction of alkene, the hydrogenation reaction will not occur, and the main product of the FFA decarbonylation reaction is an alkene compound (olefin) (Al-Alwan, 2014).

Most of the compounds produced in this study are alcohols or esters due to high temperature, high pressure, and water. The expected products in this study were mainly saturated alkanes rages from C_{12} to C_{18}. Nevertheless, the main product in this study was alcohol, as seen in Figure 2. The composition of the product at the highest temperature in this study (330 °C) is as follows: 10.145% of biokerosene, 2.902% of Alkane (C_{12} to C_{18}), 15.17 % of Alkene (C_{12} to C_{18}), 52.945%of alcohol, 7.699% of ester, 2.658 % of ketone, 8.473% of aldehyde. This result was almost identical to Al-alwan's (2014) NiWC/Al-SBA-15 catalyst study. His study can give selectivity of saturated C_{17} and unsaturated C_{17}, 0.01% and 35.8%, respectively, under subcritical water. Al-Alwan (2014) reported in his study that saponification is dominant at T's <350°C, and decarboxylation is the main reaction occurring at T's > 350°C. Some other authors also reported that the typical temperature range for decarboxylation of oleic acid into liquid hydrocarbons is 290-380°C (Al-Alwan, 2014).

Al-Alwan (2014) explained that one of the possible mechanisms of forming alcohols consists of two reactions: cracking and hydration. The long-saturated hydrocarbon chains are cracked in the presence of the catalyst and high temperature to form saturated and unsaturated hydrocarbon chains. Then, the unsaturated hydrocarbons are hydrated in water to produce alcohol. A free radical mechanism is another mechanism that could be responsible for converting hydrocarbons to alcohol. In that mechanism, the alkane produces a radical at the surface of active metal sites, which then reacts with the dissolved oxygen to make a peroxy radical species that leads to alcohol. So, happened mechanisms in this study have proven it.

The proposed mechanism in this study is the same as the study used by Al-Alwan, 2014: degummed palm oil was first hydrolyzed (hydrolysis reaction) into glycerol, linoleic acid, oleic acid, and palmitic acid in hydrothermal media. Hydrothermal catalytic reforming of glycerol, commonly referred to as aqueous phase reforming (APR), generates hydrogen. Utilizing glycerol APR for *in situ* hydrogen production can promote the hydrogenation of unsaturated fatty acids. In addition, hydrogen is produced from the water gas shift (WGS) reaction. Jin et al. (2019) have proved the hydrogen produced from each mole of glycerol. This hydrolysis reaction is important in hydrothermal, as seen in Eq. (4) and Eq. (5), An acid catalyst is needed in the hydrolysis reaction. Water in subcritical conditions has a much higher pK_W value than in ambient conditions. Kruse et al. (2015) said that the greater the pK_W value, the more H^+ and OH^- are formed in the water. These cations and anions will attack the bonds (triglycerides), so they are broken and release the monomers, so that facilitates hydrolysis reaction and then undergoes reactions, namely dehydration, dehydrogenation, deoxygenation, decarboxylation, and cracking. Therefore, using an acid-base catalyst was the main factor in the tendency of decarboxylation reactions to produce green diesel.

The presence of nickel metal in Ni-CaO/Activated Carbon (AC) catalysts is essential for providing sufficient hydrogen for the hydrocracking reactions and enhancing the metal dispersion. The decrease in green diesel selectivity can be attributed to the secondary reactions that convert the green diesel to alcohol. Since the products obtained in this study, as seen in Figure 2, are mainly alcohol without adding any external H_2. These products indicate that C-C bond cracking reactions occurred during this hydrothermal process. Figure 2 shows the percent composition of the product formed from hydrothermal decarboxylation using pellets of Ni-CaO/AC catalyst at various temperatures. Most composition in the liquid product is oxygenated intermediates, such as aldehydes, alcohols, carboxylic acid, and ketones. Figure 2 shows that alcohol is the biggest. Next, ester dominates and is followed by other compounds.

Many factors influence the degree of decarboxylation: the amount of catalyst, temperature, the ratio of water to boil, residence times, and others. Hossain et al. (2017) reported that increasing the catalyst-feed ratio from 0.15 to 0.75 resulted in the gradual decrease and eventual disappearance of the C=O, C-O, and OH. Higher catalyst loading has less tendency towards catalyst deactivation and better selectivity towards heptadecane as the main decarboxylated product. However, a low amount of catalysts sometimes helps with polymerization, subsequently increasing the formation of aromatics and other undesired products. Thus, a higher degree of decarboxylation and higher yield/selectivity of the products require an optimum amount of catalyst.

Nevertheless, this study used a ratio of catalyst to feed, namely 0.05. This same ratio was used by Jin et al. (2019) over Pt-Re/CNt with a yield of 72 wt% n-paraffin from palm oil. metal can give a higher yield of n-paraffin although a lower amount of catalyst.

However, this study over non-noble metal cannot yield a higher n-paraffin yield. Furthermore, a higher amount of catalyst over non-noble metal catalyst-like study used by Miao, 2018 concluded that complete conversion of stearic acid (SA) over 20% Ni/ZrO_2 with 63.59% liquid paraffin yield was achieved at 300 °C, 6 h, catalyst/substrate at 70% and stearic acid /water mass ratio at 1:4, with no external H_2 supply. Furthermore, the optimal amount of non-noble metal catalyst is needed in hydrothermal decarboxylation to get optimal green diesel.

Besides the amount of catalyst, the amount of water in decarboxylation needs so much. Increasing water to oil ratio can increase the degree of decarboxylation. Increasing the water to Corn Distilled Oil ratio is favorable for decarboxylation at shorter residence times which can significantly reduce the cost of the process. Then, the carboxylic acid peaks disappeared completely after a reaction at 400 °C for 4 h with a water to CDO ratio of 4:1, considered the optimum reaction condition (Hossain, 2017). The selectivity of pentadecane increased (from 7.2 to 24% and 9.2 to 24%) with an increasing ratio of water to feed from 2:1 to 5:1 and space-time from 0.5 to 4 hours, respectively. The selectivity of hexadecane slightly increased with increasing water-to-OA ratio and space-time. The selectivity of Heptadecane increased with increasing ratio and decreased with increasing space-time (Hossain, 2017). Pentadecane, Heptadecane, and hexadecane were the main and expected components in green diesel. Jin et al., 2019 also studied the decarboxylation of palm oil with water to palm oil ratio: 4:1(w/w). So, this study used a water-to-palm oil ratio, namely 4:1 (w/w).

Furthermore, in this current study, over pellets of Ni-CaO/AC catalyst at 330 °C, 2 hours of reaction time, palm oil /water mass ratio at 1:4 with no external H_2 only give 18.08 % green diesel yield and 22.07 % green diesel selectivity. We can conclude that although we used a non-noble metal catalyst with a lower amount of catalyst in the reaction did not give a higher yield and selectivity of green diesel. However, Increasing the temperature will increase the selectivity of green diesel, as can be seen in Figure 3.

The composition percentage and selectivity of green diesel can be seen in Figure 3. The selectivity of green diesel consists of alkane and alkene compounds (C_{12}-C_{18}). Selectivity is indicated by a red bar, and the composition percentage of green diesel is indicated by a blue bar. The composition percentage and selectivity of green diesel increase with increasing temperature. Temperature affects water conditions in an autoclave. The highest composition percentage and selectivity of green diesel were obtained at the highest temperature of 330^0 C, with values of 18.08 and 22.07, respectively. This study has been proven by Hossain (2017). His study concludes that the degree of decarboxylation increases with increasing temperature. Moreover, obtained optimum conditions at 400°C, water-to-Corn Distiller Oil (CDO) ratio of 4:1, 4 h of reaction time, and 800 rpm over activated carbon catalyst.

Furthermore, the Water to CDO ratio of 5:1, 2 h of reaction time, and 800 rpm over activated carbon also provides full removal of –COO groups and almost similar product distribution. His result indicates that the increasing water-to-CDO ratio is favorable for decarboxylation at shorter residence times, significantly reducing the process's cost (Hossain, 2017).

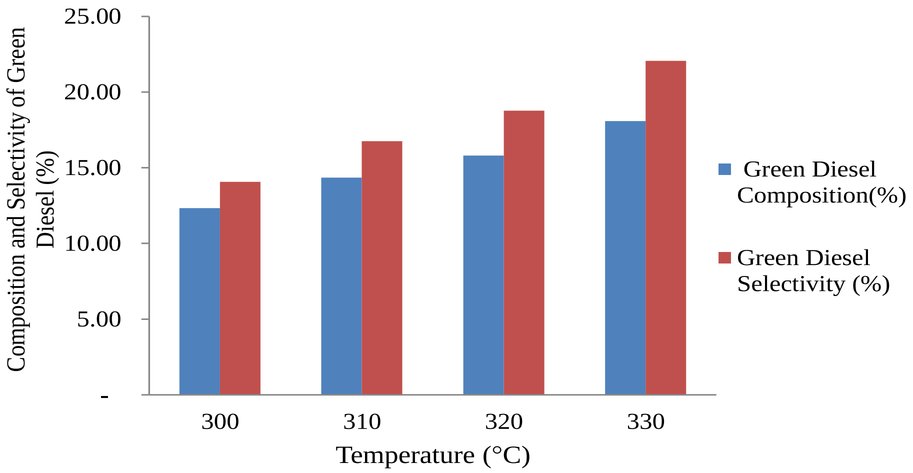

Fig. 3: Composition percentage or selectivity of green diesel from hydrothermal decarboxylation products over pellets of Ni-CaO/AC catalyst

The study by Hossain (2017) showed that decarboxylation tendency compared to decarbonylation as increasing temperature. Jin et al., 2019 said that an increase of 1 mole of hydrogen for every 1 mole of glycerol is hydrolyzed with water so that the number of hydrogen increases with the increase in reaction temperature from 175 °C to 285°C. The hydrogen needed to saturate the C=C bond in 1 mole of palm oil is 1.71 moles. Hydroprocessing palm oil with external hydrogen requires 5.3 moles of hydrogen per 1 mole of palm oil. This phenomenon can be explained by water conditions changing as temperatures increase.

Water conditions depend on the used temperature, which affects decarboxylation. This statement has been proven in this study. An increase in temperature can increase the selectivity of green diesel, as seen in Figure 3. An increase in the selectivity of green diesel at 300°C, 310°C, 320°C, and 330°C, namely 14.08 %, 16.76%, 18.78%, and 22.07%, respectively. This experiment used a maximum temperature of up to 330° C due to the limited ability of the used autoclave. So, the water condition in this study is still subcritical water. Furthermore, Hossain et al., 2017 reported 97% conversion of oleic acid and 81 % selectivity to Heptadecane and no heptadecene selectivity during decarboxylation of oleic acid using an oleic acid to water ratio of 1:4 and 5 g of activated carbon catalyst after 2 h of reaction time at 400°C in 300 ml stainless steel batch reactor. Activated Carbon (AC) catalyst from DARCO G-60 has a surface area of 851 m^2/g, a pore volume of 0.56, and a pore diameter of 2.6 nm. The same operating conditions but at a different temperature of 350 °C, so the conversion of oleic acid is below 80%, and selectivity of Heptadecane is about 50%, and heptadecene is about 5% (Hossain, 2017). Compared with the above literature data, we can conclude that supercritical water is preferable to subcritical water.

Subcritical water is not a physically defined since all water above the triple point and below the critical point is either liquid or gas. Subcritical water is in the range (200-374°C and 5-20 MPa) (Al-Alwan, 2014). Under these conditions, water's dielectric constant decreases, making water similar to non-polar solvents. Therefore, the solubility of lipids in water increases since most lipids are non-polar materials (Al-Alwan, 2014). The value of the dielectric constant decreases with increasing temperature, which indicates that the solubility of ionic molecules strongly decreases with temperature, whereas that of hydrophobic molecules such as fatty acids increase. The density of subcritical water lies between that ambient and supercritical conditions. The relatively high density and the high dissociation constant of subcritical water favors ionic reactions. All ionic reactions involving water molecules as reacting agents are generally enhanced in subcritical water. In supercritical conditions, water becomes a highly reactive medium due to the constant dielectric reduction and self-dissociation increase (Al-Alwan, 2014).

Furthermore, all ionic reactions are prompted due to the stabilization of the charged transition state (Hossain, 2017). Therefore, operating conditions affect yields and selectivities of green diesel in decarboxylation. Many studies have proven this statement.

Zhang et al. (2019) conducted hydrothermal decarboxylation of 5.5 grams of commercial lipids (glycerol and stearic acid) using a catalyst of 0.5 grams 5 wt% Ru/C, 80 grams of water, with a pressure of 20 bar (N_2) at a temperature of 330 °C for 2.5 hours, stirring above 1000 rpm which showed a yield of about 35% C_{17} alkane and about 23% C_{15}. Ru/C catalyst has a surface area of 735.3 m^2/g with a metal dispersion. The study by Zhang et al., 2019 can be compared using Ni-CaO/Activated Carbon with a surface area of 19.129 m^2/g. The result showed the highest composition percentage and selectivity of green diesel at 330°C, namely 18.08%, and 22.07, respectively. This study obtained a smaller yield and selectivity of green diesel than a conducted study by Zhang et al., 2019. This is due to the small surface area of Ni-CaO/AC Catalyst pellets. Ni-CaO/AC catalyst pellets have a small surface area because it uses phenolic resin as a binder to form pellets from the powder of Ni-CaO/Activated Carbon catalyst. Moreover, Jin and Choi (2019) carried out hydrothermal decarboxylation with 20 grams of palm oil, and 80 grams of deionized water, 0.92 grams of Pt/CNT catalyst, N_2 gas pressure of 10bar, the temperature of 285°C for 24 hours where this study produce paraffin yield < 20 wt %, while over PtRe/CNT catalyst yielded 72 wt% paraffin. In comparison with the above literature data, we can conclude that the lower temperature, smaller amount of catalyst, shorter time, and smaller surface area of catalyst will get a smaller composition percentage and selectivity of green diesel in hydrothermal decarboxylation than others.

CONCLUSION

The composition percentage and selectivity of green diesel over pellets of Ni-CaO/AC catalyst can be increased by increasing operating conditions, one of which is temperature. This study obtained the highest composition percentage and selectivity of green diesel at a maximum temperature of 330° C, with values of 18.08 and 22.07, respectively. Temperature affects water conditions due to subcritical water or supercritical water. Powder of Ni-CaO/AC catalyst with a mixture of phenolic resin in pellets can produce green diesel by hydrothermal decarboxylation of palm oil at lower operating conditions under subcritical water. However, the results still showed a little bit due to a decrease of the active surface area of the catalyst. These results suggest that higher temperature promotes hydrothermal decarboxylation of palm oil. We can conclude that pellets of Ni-CaO/AC catalysts can do hydrothermal decarboxylation with the increased operating condition and good binder.

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NOMENCLATURE

P	:	composition percentage of determined product
n_D	:	The total peak area of green diesel (C_{12}-C_{18}).
n_p	:	the total peak area of liquid product
S_D	:	selectivity percentage of green diesel
no	:	the total peak area of undesired product

REFERENCES

Al Alwan, Basem A. Al., 2014. Biofuels Production *via* Catalytic Hydrocracking of Dogs Corn Oil and Hydrothermal Decarboxylation of Oleic Acid Over Transition Metal Carbides Supported on Al-SBA-15. the Graduate School of Wayne State University, Detroit

Asikin-Mijan, N., Lee H.V, Juan J.C., Noorsaadah A.R., and Taufiq-Yap Y.H., 2017. "Catalytic deoxygenation of triglycerides to green diesel over modified CaO-based catalyst", *RSC Adv., 7,* 46445.

Fogler H.S., 2016. Elements of Chemical Reaction Engineering, Fifth Edition, Pearson Education, United States

Hossain, Z., 2017. Hydrothermal Decarboxylation of Fatty Acids and Their Derivatives for Liquid Transportation Fuels. PhD Thesis. Chemical and Biochemical Engineering, The University of Western Ontario

Hossain, Z., Jhawar, A.K., Chowdhury, M.B.I, W.Z., Wu, W., Hiscott, D. V., and Charpentier, P. A., 2017. "Using subcritical water for decarboxylation of oleic acid into fuel-range hydrocarbons." *Energy and Fuels*, *31(4),* 4013–4023.

Jin, M. and Choi, M., 2019. "Hydrothermal deoxygenation of triglycerides over carbon-supported bimetallic PtRe Catalysts without an external hydrogen source." *Molecular Catalysis, 474*, 110419.

Krobkrong, N., Itthibenchapong, V., Khongpracha, P., and Faungnawakij, K., 2018. "Deoxygenation of oleic acid under an inert atmosphere using molybdenum oxide-based catalysts." *Energy Conversion and Management*, *167*, 1–8.

Kruse, A. and Dahmen, N., 2015. "Water - a magic solvent for biomass conversion." *J. Supercrit. Fluid., 96,* 36–45.

Miao, C.. , Marin-Flores, O., Dong, T., Gao D., Wang Y., Garzia-Perez, M., Chen, S.. 2018. "Hydrothermal catalytic deoxygenation of fatty acid and bio-oil with *in situ* H_2." *ACS Sustainable Chemistry and Engineering*, *6(4),* 4521–4530

Rosalina, L., 2012. "Preparation and Characterization of $NiMo/Al_2O_3$ Nanoparticle Catalyst Using Simple Heating Method for Renewable Diesel Synthesis." Bachelor Thesis, Universitas Indonesia.

Septriana, D., Azis, M.M., and Wintoko, J.,

2021. "Synthesis of Ni-CaO/Activated Carbon (AC) catalyst for cooking oil conversion to green diesel." The 13th AUN/SEED-Net Regional Conference on Chemical Engineering 2020 (RCChE-2020), Institute of Technology of Cambodia, Phnom Penh, Cambodia

Zhang, J., Huo, X., Li, Y. and Strathmann, T.J., 2019. "Catalytic hydrothermal decarboxylation and cracking of fatty acids and lipids over Ru/C." *ACS Sustainable Chemistry and Engineering, 7(17),* 14400–14410.