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December 3, 2021

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

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Abstract. There has been large interest to convert palm oil to green diesel. Green diesel is a hydrocarbon compound that is similar to the components in conventional diesel fuel, hence it is expected as a substitute for conventional diesel fuel in diesel vehicle engines. The process to produce green diesel is also called the deoxygenation process, namely: the process to remove oxygenate components in oil or fat. The current study evaluated 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 the present work is to investigate palm oil decarboxylation under sub critical water condition. The scope of this research includes: catalyst activity test 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 hydrocarbon yield of 28.22% with a selectivity of heptadecane ($C_{17}H_{36}$) of 10.28% at 330 °C. However, the highest selectivity of green diesel was 75.39% which was obtained at 320°C. It can be conclude that pellets of Ni-CaO/AC can give selectivity and yield of green diesel in decarboxylation under sub critical water.

1. Introduction

Green diesel is a hydrocarbon fuel derived from renewable source which has similar characteristic with conventional diesel fuels because the oxygenate component has been removed by the deoxygenation process. The deoxygenation process is the process of removing the oxygenate component in fatty acids or fatty oils from biomass. All plants containing oil or fatty acids have the potential to be converted to green diesel. Oil palm is the most abundant crop in Indonesia and hence provide large potential to produce oil / fatty acids. Palm oil is made up of mostly fatty acids. The highest fatty acid composition in palm oil is oleic acid as much as 55%. Oleic acid is a long-chain unsaturated fatty acid composed of 18 C atoms with one double bond between the 9th and 10th C atoms. Green Diesel is a drop-in/non-oxygenate biofuel which has a hydrocarbon range of C12 – C18.[1] The deoxygenation process can be carried out in 3 types of reactions: hydrodeoxygenation, decarboxylation, and decarbonylation. [2] Hydrodeoxygenation (HDO) reactions can remove oxygen by reacting triglycerides and free fatty acids with hydrogen to form water and n-paraffin. While the decarboxylation or decarbonylation reaction removes oxygen by forming carbon dioxide or carbon monoxide and n-paraffin. Among these three reactions, there has been large interest to improve the decarboxylation reaction with appropriate catalyst. The decarboxylation reaction does not require external hydrogen gas to saturate the double bonds in the oil. 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 (C12-C18).

A decarboxylation reaction is a chemical reaction that removes a carboxyl group (-COOH) into a CO_2 molecule. While the carbonylation reaction is a reaction to separate the carbonyl group (C=O).[2] Hydrodeoxygenation reactions and decarboxylation reactions can produce green diesel, but there are several advantages of decarboxylation reactions over hydrodeoxygenation. The decarboxylation reaction can take place at a lower pressure than the hydrodeoxygenation and the CO_2 produced from the decarboxylation reaction can be captured in a pure state, furthermore the decarboxylation reaction requires hydrogen only to saturate the olefins, whereas the hydrodeoxygenation reaction requires hydrogen to saturate the olefins and removes oxygen by producing water. These decarboxylation and hydrodeoxygenation reactions both produce CO_2, the CO_2 products from decarboxylation can be captured in a pure state. Therefore, the decarboxylation and decarbonylation reactions are more practical because they can be carried out under moderate conditions, i.e. less hydrogen consumption, longer catalyst life, and less water content. [2] Thus, among the three fatty oil deoxygenation reactions, the decarboxylation reaction is the most favorable for the production of Green Diesel.

The hydrothermal conditions in the decarboxylation reaction affect the yield and selectivity of the decarboxylation reaction. Our previous work showed that non-hydrothermal decarboxylation using Ni-CaO/AC catalyst in the form of pellets did not provide sufficient yield and selectivity for green diesel as expected.[3] Therefore, in this study, sub-critical water or hydrothermal conditions are used for decarboxylation of palm oil. Hydrothermal treatment is a thermochemical process that can decompose organic compounds with the help of water at high temperatures and pressures. Some literatures stated that water as a solvent in oleic acid decarboxylation is more advantageous than hydrocarbon solvents as it is a more environmentally friendly solvent. Hydrothermal decarboxylation of oleic acid with Pt/SAPO-11 catalyst after 2 hours increased the conversion from 20% to 90% with temperatures from 200 to 325°C, as well as the selectivity increased 4 times .[4] Increasing the reaction time will increase cracking and reduce selectivity, so that increasing the spece velocity will decrease conversion .[5] For this reason, the reaction time that is often used is between 1 to 6 hours. The hydrothermal treatment process carried out in this study is a hydrothermal process with a pressure range between 13 to 70 bar and a temperature between 150-350°C .[6] In the hydrothermal treatment process, the palm oil can be converted to green diesel by decarboxylation reactions.[7] The water used in the hydrothermal process can be in a subcritical or supercritical state. In the hydrothermal process, water will be ionized into H and O_2 ions so that they can react with organic compounds. According to Singh, et al. (2013) the higher the temperature, the value of the dielectric constant of water will decrease.[8] This is due to a reduction in the electronegativity of the water molecule, thus turning the previously polar water molecule into a fairly non-polar one. Under these conditions, water can function as a solvent as well as a reactant for organic compounds.[8] Thus, the solubility of fat in water increases, because most fats include non-polar compounds.[4] In addition, at a temperature of 220-300°C, water molecules are more easily dissociated into H^+ and OH^-, so the value of the ionization constant will increase. As the ionization constant increases, water will become more acidic (high H^+ concentration) and could facilitate hydrolysis reactions .[9]

Triglycerides are neutral fats that can be hydrolyzed in hydrothermal media to produce saturated and unsaturated free fatty acids and glycerol. The process used to hydrolyze triglycerides to produce free fatty acids and glycerol in a hydrothermal medium is usually called fat-splitting. The resulting glycerol undergoes hydrothermal catalytic reforming, which is commonly called aqueous phase reforming (APR) to produce hydrogen. Utilization of APR glycerol in hydrogen production in situ can promote the hydrogenation of unsaturated fatty acids. This hydrolysis reaction is a very important reaction in hydrothermal, because various organic compounds that are formed are further products of the monomers formed from the hydrolysis reaction. In the hydrolysis reaction, an acid catalyst is needed so that more water molecules are dissociated into H^+ and OH^-. The cations and anions will attack the bonds (triglycerides), so that they are broken and release the monomers. Water in subcritical water conditions has a much higher pKW value than water in ambient conditions.[10] The greater the pKW value, the more H^+ and OH^- are formed in the water, so as to facilitate the hydrolysis reaction into monomers which then undergo reactions, namely dehydration, dehydrogenation, deoxygenation, decarboxylation and cracking. Therefore, by using an acid-base catalyst, the hydrogenation of unsaturated fatty acids can encourage selectivity for decarboxylation reactions to produce green diesel.

The basic theory for the catalytic process in hydrocracking of palm oil consists of two sites: an alkaline site and an acid site. Base sites are required for hydrogenation, decarboxylation, decarbonylation and hydrodeoxygenation reactions. Base sites of metal oxides can attract hydrogen in carbonyl compounds, then the C-O bond is broken to form hydrocarbon compounds .[11] While 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 selectivity, activity and resistance of the catalyst can be obtained optimally.[4] Because the decarboxylation and decarbonylation reactions occur overlapping, the catalyst used should be the same and have a dual function, so it is also called an acid-base catalyst. [11]

Incorporation of acid-base metals to give acid-base properties can promote decarboxylation reactions with low coke formation. Acid-base properties can enhance oxygenate transfer by decarboxylation and decarbonylation reactions. The use of a single active site that is alkaline without an acidic site is not favored by deoxygenation reactions because of the breakdown of carbon bonds with carbon which will reduce the diesel fraction of range hydrocarbons.[12] Furthermore, studies have proven acid-base catalysts such as: CaO-SiO_2-Al_2O_3 and NiO SiO_2-Al_2O_3 have high stability and produce products that do not change until used for 4 reaction cycles, and low coke formation compared to acid catalysts derived from Ni- Cu/Al_2O_3 and Ni-Sn/Al_2O_3.[13] Modification of metal catalyst Ni with CaO can increase the catalytic activity compared to Ni-Al_2O_3 without modification.[14] Catalysts with acid-base sites can hydrolyze triglycerides to carboxylic acids and carboxylic acids are dehydrated and cracked.[11] More hydrogen is needed for the decarbonylation reaction than for the decarboxylation. Therefore, palm oil can be turned into the desired green diesel product, it needs a catalyst that can carry out dual functions in the reaction, namely an acid-base catalyst. Thus, in this study, the pelleted Ni-CaO/AC catalyst was selected which was made in the previous study to test its performance by decarboxylation of palm oil in subcritical water.

Activated carbon was chosen as catalyst support because it has many advantages. Support (catalyst carrier) is an inert material that is used as a support for the active site so that it is well distributed. One of the suitable supports in acid base catalyst for decarboxylation of oil is activated carbon. Carbon has good properties as a support because it is inert, stable, has good mechanical properties, surface area, and porosity .[15] In addition, activated carbon also has many acidic sites so that it can encourage decarboxylation reactions .[16] Activated carbon is also resistant to coke formation during the reaction and has a high surface area .[16,17] In addition, the oxygen group on the carbon surface determines the hydrophilic / hydrophobic nature of the carbon support thereby making the base, acidity or neutrality of the catalyst surface. The oxygen group affects the acidity of the carbon surface, thereby reducing the hydrophobicity of the carbon. This surface group plays an important role in the dispersion of the active phase, and the catalytic activity.[16] Furthermore, carbon is also neutral because the electronegativity of activated carbon is neutral, so activated carbon can be used as a substitute for noble metal catalysts in converting unsaturated fatty acids into alkanes to produce more diesel range hydrocarbons.[12] Another study has carried out hydrothermal decarboxylation of oleic acid using an activated carbon catalyst at optimum conditions, namely a temperature of 400 ^oC, without the addition of hydrogen from the outside for 2 hours, with a volume ratio of oleic acid and water is 1:4 with a catalyst of 5 grams of activated carbon (AC). The results gave 97% oleic acid conversion and 81% heptadecane selectivity in the batch reactor. Meanwhile, in a continuous fixed bed reactor, the conversion was 91% and the heptadekane selectivity was 89.3%. The activity of activated carbon catalyst has also been tested by comparing it with activated carbon catalyst that has been regenerated, the selectivity drops to 8.1 %. Thus, activated carbon catalysts are resistant to coke formation. [18] So activated carbon is suitable as a support in decarboxylation of palm oil in sub critical water.

The choice of nickel as an acid site is preferable, besides being cheaper than noble metals, it has good performance in deoxygenation. The order of deoxygenation activity of the catalyst with an active core base with activated carbon support is Pd > Pt > Ni > Rh > Ir > Ru > Os. Catalysts with high nickel content can compete with the activity of catalysts with Pd and Pt metal bases.[19] Ni supported on activated carbon has the highest number of acid sites, the smallest particle size and the highest surface area compared to the ZrO_2 support, H-ZSM-5.[16] Ni/C conversion by decarboxylation reaction is not as good as Pt/C, but the selectivity of Ni/C and Pt/C is close to the same at longer reaction times and higher temperatures than operating conditions with Pt/C catalysts .[5] In addition, nickel can increase the active surface area of the catalyst, for example nickel metal impregnated with activated carbon on a 10%Ni/AC catalyst has the largest BET surface area of 807.264 cm^2/g, followed by 10% Ni/ZrO_2 of 19.797 cm^2/g , and 10% Ni/H-ZSM-5 of 321.211 cm^2/g. [16] Furthermore, the choice of calcium oxide as the base active site for the decarboxylation reaction is very appropriate. Because calcium oxide (CaO) can increase the dispersion of Ni nanoparticles and can stabilize the catalyst with an active nickel core .[20] In addition, CaO can suppress carbon deposits (coke) on the surface of the catalyst because CaO can form $CaCO_3$.[14] Then, calcium oxide can transfer oxygen because it can absorb CO_2 gas in the gas phase. [11] So, Ni-CaO/AC catalyst can be used in decarboxylation of palm oil in sub critical water.

The objective of the present work was to evaluate performance pellets of Ni-CaO/AC catalyst in decarboxylation of commercial cooking oil (oil palm based) under sub critical water. The resulting products were analyzed using GC-MS to evaluate the change of chromatogram area before and after treatment.

Proposed Reaction Mechanism

Palm oil is reacted under subcritical water condition with the help of Ni-CaO/AC catalyst to produce green diesel through several reaction stages. At first, the triglyceride compounds in cooking oil undergo a hydrolysis reaction to produce glycerol and fatty acids. Furthermore, glycerol is hydrolyzed to produce hydrogen and carbon dioxide. The hydrogen and carbon dioxide produced can undergo a water gas shift (WGS) reaction. In this case, hydrogen can be formed in situ to be able to hydrogenate the oleic acid to stearic acid.[4] Furthermore, this stearic acid undergoes several deoxygenation reactions to produce green diesel, including: decarboxylation, decarbonylation, and cracking as seen as eq. (8,9,10,11). During reaction, acidic sites facilitated hrdrolysis and cracking, while basic sites promoted decarboxylation and partially removing oxygen from the triolein simultaneously .[11]

Hydrolysis of triglyceride

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

Hydrolisis of glycerol (Aqueous Phase Reforming)

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

Water Gas Shift Reaction

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \tag{6}$$

Hydrogenation of oleic acid

$$3C_{18}H_{34}O_2 \ + 3H_2 \longrightarrow 3C_{18}H_{36}O_2 \tag{7}$$

Deoxygenation of stearic Acid:

- Decarboxylation of stearic Acid

$$C_{18}H_{36}O_2 \ \longrightarrow C_{17}H_{36} + CO_2 \tag{8}$$

- Decarbonylation of stearic Acid

$$C_{18}H_{36}O_2 \ \longrightarrow C_{17}H_{34} + CO \ + H_2O \tag{9}$$

- Cracking

$$C_{18}H_{36}O_2 \ \longrightarrow CO \ + CO_2 + H_2 + lighterC_xH_y \tag{10}$$

$$C_{18}H_{36}O_2 \ \longrightarrow C_{17}H_{32}O_2 + CH_4 \tag{11}$$

2. Experimental Section

2.1. Materials.

The Ni-CaO/AC Catalyst powder with the size of 0.9 cm OD and height of 0.8 cm was obtained from previous research.[3] Deionized water was purchased from CV. Progo Mulyo, N_2 gas (99,9% pure) was supplied by Samator gas industri, Acetone (technic standard) from Merck, n-Hexane (GC grade) > 98% were obtained from Merck was used for dilution. The feedstock of this work, commercial palm oil-cooking oil that was obtained from mini market with the brand of Bimoli. Commercial cooking oil was used as the No. longer contains gum, impurities and odors. In addition, the main compound which was analyzed as a 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 the commercial cooking oil. Before the cooking oil sample was analyzed, a transesterification reaction must be carried out on the cooking oil. After transesterification, the cooking oil was analyzed using gas chromatography mass spectrometer (GCMS) to determine its composition as shown in table 1 below. Table 1 shows that oleic acid is the most abundant composition in cooking oil based palm oil.

Table 1. Fatty Acid Composition of Cooking Oil

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

2.2. Reaction Procedure

The first hydrothermal decarboxylation procedure was carried out by weighing 31.5 grams of cooking oil and 2.625 grams of pelleted Ni-CaO/AC catalyst. Aquadest added as much as 126 grams, with the ratio of oil and water is 1:4 (w/w). The mixture was put into the autoclave. The series of autoclave tools are closed completely tightly. N2 gas is then put into the autoclave until the pressure indicator shows the number 5 bar gauge. After reaching the 5 bar gauge pressure, the valve leading to the N_2 tank was closed, while the purge valve is opened until the pressure indicator shows 0 bar gauge. Then the purge valve is closed and the autoclave is again filled with N_2 gas. The purging gas cycle in the autoclave using N_2 was carried out 3 times. After 3 purgings, N_2 gas is put back into the autoclave until the pressure indicator shows 10 bar gauge. Then the heater is turned on by setting the heating rate at 10^oC/minute until the operating temperature is obtained at 300^oC. At the same time, the stirrer is also turned on. After reaching the desired temperature, the hydrothermal process is maintained for 120 minutes. After the process is complete, the heater and stirrer motor are turned off. The heating process was repeated for temperatures of 310, 320 and 330 ^oC on different samples. After 2 hours, the autoclave reached ambient temperature, the product was taken from the autoclave. Subsequently, the product was dissolved with hexane to facilitate the separation of catalyst, water and product. Next, the solution was separated by filter paper with the help of a vacuum pump. The resulting filtrate forms a boundary layer, where the top layer was taken to separate water, product and hexane by distillation to obtain a pure product that can be analyzed by Gas chromatography mass spectrometer (GC-MS).

2.3. Product analysis

Product distribution of the deoxygenized liquid product were qualitatively characterized using Gas chromatography mass spectrometer (GC-MS) (model SHIMADZU QP2010S) equipped 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 prior to the yield analysis. The injection temperature was at 300^oC. Helium gas was served as the carrier gas. The initial temperature of the oven was at 70^oC and held for 5 min, then ramped up to 300^oC .

The conversion of the reactants under consideration are oleic acid, palmitic acid and stearic acid. The conversion of these reactants is equivalent to determining the change in the loss of the carboxyl group in the carboxylic acid. percentage removal of carboxylic acid (C) can be computed with comparing the reactants that react to the reactants before reacting can be seen in equation (1).

$$C = \frac{\sum n_i - \sum n_p}{\sum n_i} \times 100 \qquad (1)$$

Where C represents percentage removal of carboxylic acid, n_i = initial peak area of –COOH group in Cooking Oil, n_p = peak area of –COOH group in the liquid product

The catalytic performances of the catalysts was studied by determining the percentage yield of saturated and unsaturated straight-chain hydrocarbon as seen in equation (2). The compound identification was based on a probability match equal to. Total product include hydrocarbon fractions, carboxylic acid, alcohol, aldehid etc, exclude carboxylic acid in palm oil.

$$X = \frac{\sum n_x}{\sum n_z} \times 100 \qquad (2)$$

Where, X denotes percentage yield of saturated and unsaturated straight-chain hydrocarbon (C_5-C_{18}) , n_x = area of hydrocarbon (C_5-C_{18}), n_z = area of the product.

The selectivity of greendiesel can be obtained by comparing the area of the green diesel produced to the total area in the product according to equation (3). [13]

$$S_D = \frac{\sum n_D}{\sum n_x} \times 100 \qquad (3)$$

Here, S_D refers to percentage selectivity of green diesel, n_x represents area of hydrocarbon (C_5-C_{18}), n_D represents area of green diesel (C_{12}-C_{18}).

3.Results and Discussion

3.1. Effect of temperature on degree of decarboxylation

Hydrothermal decarboxylation of palm oil was carried out to evaluate the effect of water on the performance of the Ni-Cao/AC catalyst. The hydrothermal decarboxylation product of palm oil after filtering can be seen in Figure 1.

FIGURE 1. Palm Oil Hydrothermal Decarboxylation Products using pellets of Ni-CaO/AC Catalyst

In Figure 1 it can be seen that there is a color change from left to right, that the higher the reaction temperature used, the higher the turbidity level of the decarboxylation product. The higher the temperature, the more the product sample will turn to be blackish brown and the form will be more liquid and less viscous. The viscosity of the product is due to the long carbon chain. The length of the carbon chain makes the London force stronger. This force is a nonpolar interaction force that gets stronger when the number of atoms increases or in this case is longer. The viscosity of the carboxylic oil was caused by the reaction temperature used was too low, which did not reach the boiling point of the oleic acid of 363°C, so that the termination of the carboxyl and carbonyl bonds did not occur effectively. The higher the temperature, the higher deoxygenation will occur. This is because the decarboxylation, decarbonylation and hydrogen reactions run effectively. The effectiveness of this reaction causes the more compact the molecules in the deoxygenated oil. The compactness of this molecule will cause the London force to become weaker because there is less space to form the London force. The result of the deoxygenation process is black, due to the presence of carbon deposits in the deoxygenation reaction which are difficult to separate. Carbon deposits are clearly visible in the deoxygenation reaction products so that the color of the product is blackish brown.[1] Only some of the carbon settles, but most of the carbon is in a floating position due to the viscosity of the oil. Carbon deposits, also known as coke, are intermediate products of cation intermediates that are more stable and accumulate during the reaction. The results of the activity test for the Ni-CaO/AC pellet catalyst in hydrothermal decarboxylation can be seen in Table 2 and Figure 3.

TABLE 2. Conversion of Oleic Acid and Stearic Acid from Hydrothermal Decarboxylation Products Using pellets of Ni-CaO/AC Catalyst

Temperature (°C)	Conversion of Oleic Acid	Conversion of Stearic Acid
300	100	100

310	100	99,69
320	100	100
330	99,82	100

In table 2 above, we can see that the conversion of oleic acid and stearic acid is almost 100% converted at various temperatures from 300 °C to 330 °C. The decrease in conversion of about 1% at a temperature of 310 °C for stearic acid and a temperature of 330 °C for oleic acid does not have a significant effect on the yield and selectivity of green diesel. Temperature variations taken close together due to the limited resistance of the reactor used are usually reached maximum at 330°C after the addition of water. Thus, it can be concluded in table 2 that there is an increase in conversion along with an increase in temperature, but the optimum temperature cannot be determined because the range of temperature variations is small. In Figure 3, it can be seen the yield of hydrocarbons and selectivity of green diesel produced from hydrothermal decarboxylation using pellets of Ni-CaO/AC catalyst. Before calculating the yield and selectivity of the decarboxylation product, the chromatogram data as shown in Figure 3 was compiled and grouped the compounds formed based on their functional groups or groups of compounds as shown in table 3 below.

3.2. Liquid products quantification

The composition of the product can be seen from the results of the GCMS analysis. GCMS results display chromatogram data based on retention time and area. As an illustration, the chromatogram data on the decarboxylation product at a temperature of 330 C can be seen in Figure 2 below.

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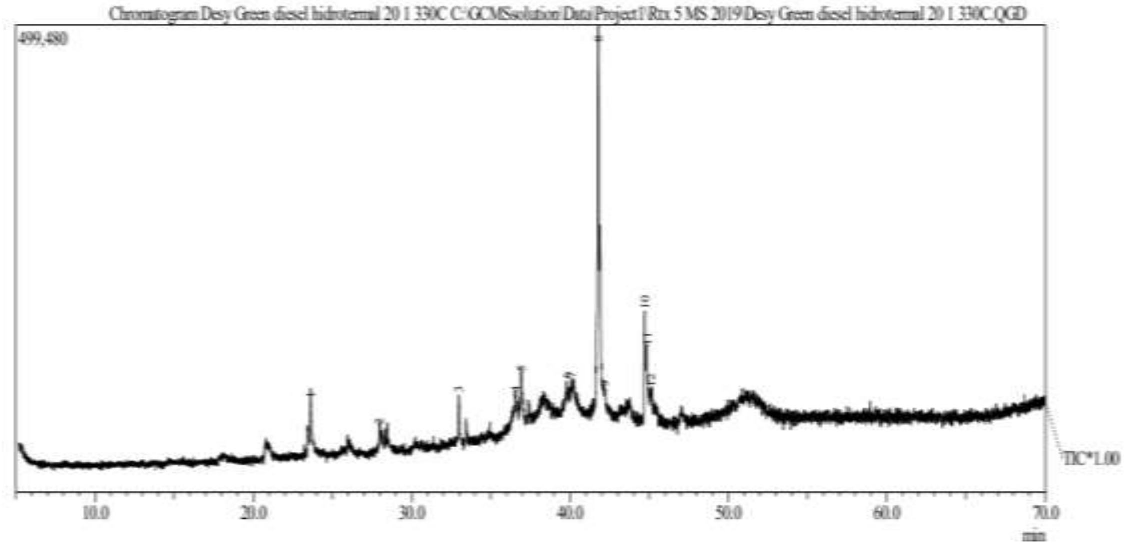

FIGURE 2. GCMS Chromatogram of Hydrothermal Decarboxylation Products at 330 °C with pellets of Ni-CaO/AC Catalyst

In Figure 2, it displays a chromatogram or two-dimensional graph that has peaks. In Figure 2 there are 12 detected peaks that represent the components or compounds contained in the decarboxylation product. Each peak of each component has a different area according to different retention times, which is usually called the peak area. The peak area of each component can be seen in table 3 below.

TABLE 3. 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	Biokerosine
2	$C_{11}H_{22}$	257336	3,09	Biokerosine
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	Aldehid
12	$C_{10}H_{16}O_2$	253077	3,04	Carboxylic Acid

Table 3 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 that have different peak areas are grouped according to their group of compounds or functional groups as shown in table 3. 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 3.

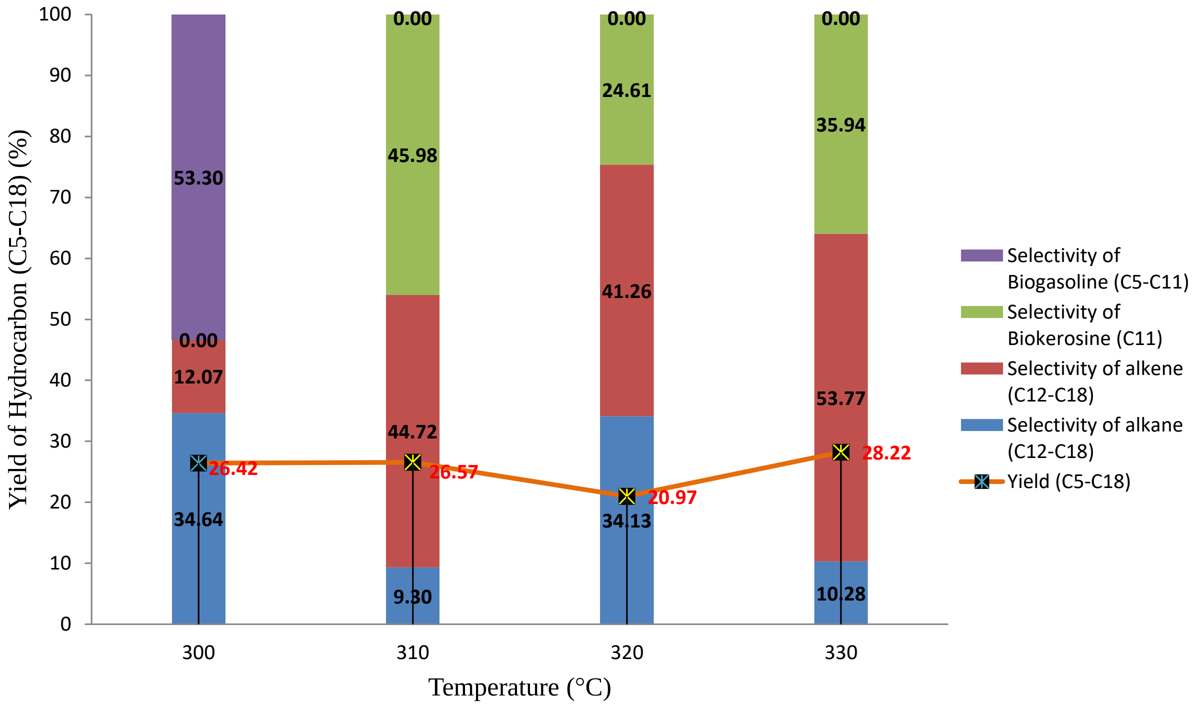

FIGURE 3. Hydrocarbon Yield of Hydrocarbon and Selectivity in Decarboxylation with pellets of Ni-CaO/AC Catalyst under Subcritical Water

In Figure 3, it can be seen that the yield of hydrocarbons increases with increasing temperature used in hydrothermal decarboxylation. The increase in yield is not too large, because the temperature range used in this study is small. Although at 320^{o}C there was a slight decrease in hydrocarbon yield, there was an increase in the selectivity of alkane compounds forming green diesel, namely C_{12}-C_{18}. Furthermore, alkane and alkene compounds forming green diesel (C_{12}-C_{18}) also increased with increasing temperature. The highest hydrocarbon yield was obtained at the highest temperature of 330°C at 28.22%. However, the highest green diesel selectivity of 75.39% was obtained at 320°C. Furthermore, at a temperature of 330°C it can give a selectivity of heptadecane ($C_{17}H_{36}$) of 10.28%, the rest is olefins (C_{14} and C_{18}) with a total selectivity of green diesel of 64.05%. The selectivity of green diesel at a temperature of 330°C is not much different from the selectivity of green diesel at a temperature of 320°C.

In addition to the compounds that form green diesel, there are also other hydrocarbon compounds, such as biogasolin (C_5-C_{10}) and biokerosin (C_{11}). Biogasoline is formed only at a temperature of 300°C, while at this temperature no biokerosene is formed and biokerosene is formed at temperatures of 310, 320, and 330 °C. Biokerosin and biogasolin are formed due to the cracking reaction. This is because the Ni catalyst has a high C-O bond cutting activity (decarboxylation and decarbonylation), but Ni has a drawback, namely the C-C bond cracking activity is also high. This causes the main product of decarboxylation with Ni catalyst to tend to be light hydrocarbons. The selectivity of alkene compounds (C_{12}-C_{18}) that make up green diesel fuel is marked with a red bar which is greater than the selectivity of alkane compounds (C_{12}-C_{18}) that make up diesel fuel as well. The difference between alkanes (C_{12}-C_{18}) and alkenes (C_{12}-C_{18}) lies in the presence of double bonds or not. Alkane compounds (C_{12}-C_{18}) do not have double bonds, meaning these compounds are the result of decarboxylation of saturated carboxylic acids, such as stearic acid, palmitic acid and myristic. Alkene compounds (C_{12}-C_{18}) have double bonds, meaning these compounds are the result of decarbonylation of saturated carboxylic acids as well. The composition of alkane compounds formed at 330 °C is 2.72%, while the alkene compounds formed due to decarbonylation are only 7.04%, the rest occurs because the cracking reaction has occurred at 330 °C.

All by all, it can be concluded that the tendency of the reaction that occurs with the Ni-CaO/AC pellet catalyst under hydrothermal conditions in the temperature range of 300 °C to 330 °C is decarbonylation compared to decarboxylation. This is because the major thing that occurs before decarboxylation is the breakdown of the double bond in the carboxylic acid through hydrogenation. Further decarboxylation allows CO_2 to be separated. 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. So there is an increase in CO concentration. The increase in H_2 pressure in the reactor increases the hydrogenation reaction in the form of breaking the double bonds in the alkene structure produced by the decarbonylation reaction and the triglyceride cracking reaction.

Increasing the pressure will increase the decarbonylation reaction. This is in accordance with Le Chatelier's principle of equilibrium, namely in an equilibrium reaction, an increase in reaction pressure causes the reaction to move towards the substance that has a smaller number of coefficients. The higher pressure of H_2 appeared to inhibit FFA decarboxylation reaction and can increase the concentration of FFA undergoing decarbonylation reaction. More olefin compounds are formed as the main product compared to n-alkanes, 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 compounds, the hydrogenation reaction will not occur so that the main product of the FFA decarbonylation reaction is an alkene compound (olefin). However, in another study it showed the tendency of decarboxylation compared to decarbonylation with increasing temperature, as has been done by Hossain, 2017.[18]

According to Hossain, 2017 with a powder AC catalyst from DARCO G-60 which has a surface area of 851 m^2/g, a pore volume of 0.56, and a pore diameter of 2.6 nm as much as 5 grams, the reaction was carried out in an Autoclave of 300 ml, for 2 hours., at a temperature of 400 °C (optimum), with a ratio of subcritical water and oleic acid is 4:1, stirring speed of 800 rpm, has resulted in 97% oleic acid conversion, 81% heptadecane selectivity, and no heptadekene selectivity. [18]Thus, at 350 °C, the conversion of oleic acid was below 80% and the selectivity of heptadekane was about 50% and heptadekene was about 5%.

Furthermore, according to a literature study conducted by (Zhang et al., 2019) that 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 can produce alkanes yields of C_{17} about 35% and C_{15} about 23%.[21] Ru/C catalyst has a surface area of 735.3 m^2/g with a metal dispersion of 47%. Hydrothermal deoxygenation occurs due to the formation of hydrogen in situ during aqueous phase reforming (APR) of glycerol formed from the hydrolysis of oil, in addition hydrogen is produced from the water gas shift (WGS) reaction. The hydrogen produced from each mole of glycerol has been proven by Jin and Choi, 2019 that there is an increase of 1 mole of hydrogen for every 1 mole of glycerol hydrolyzed with water, so that the amount 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.[22] Hydroprocessing palm oil with external hydrogen requires 5.3 moles of hydrogen per 1 mole of palm oil.

Jin and Choi, 2019 carried out hydrothermal decarboxylation using Pt/CNT catalyst for 20 grams of palm oil, 80 grams of deionized water, 0.92 grams of Pt/CNT catalyst, 10 bar N_2 gas pressure, temperature 285°C for 24 hours to produce paraffin yield < 20 wt %, while the PtRe/CNT catalyst yielded 72 wt% paraffin. Hydrothermal decarboxylation with Ni-CaO/AC catalyst has been carried out with operating conditions that are close to those carried out by Jin and Choi, can produce paraffin yields of 28.22%, but the yields obtained are not close to yields as with PtRe/CNT catalysts. [22]This is because the reaction time used is different and the surface area of the PtRe/CNT 171 m^2/g catalyst is much larger than that of the pelletized Ni-CaO/AC catalyst namely 19.129 m^2/g. [3] Super-critical water promotes hydrogenation reaction until decarboxylation of oleic acid because the reactivity of water increases at super-critical temperature. Water under supercritical conditions becomes more reactive with lower dielectric constant and higher dissociation constant. It can be concluded that the Ni-CaO/AC pellet catalyst can be increased paraffin yield and heptadecane selectivity by increasing the temperature used, so that the condition of subcritical water or supercritical water also increases and the catalyst is made using a stronger binder but does not cover much of the active surface area.

4. Conclusion

The influence of temperature to the hydrothermal decarboxylation of commercial cooking oil (oil palm based) over NiCaO/AC catalyst hace been invetigated. The green diesel product appeared to be darker with increasing operating temperature. This might be due to carbon deposition in the product. In general, the NiCaO/AC catalyst gave high conversion based on the peak area changed in GC-MS. The highest hydrocarbon yield was obtained at 330°C which gave yield of 28.22%. However, the highest green diesel selectivity of 75.39% was obtained at 320°C. Furthermore, at a temperature of 330°C it can give a selectivity of heptadecane ($C_{17}H_{36}$) of 10.28%, the rest is olefins (C_{14} and C_{18}) with a total selectivity of green diesel of 64.05%. The selectivity of green diesel at a temperature of 330°C is not much different from the selectivity of green diesel at a temperature of 320°C. It can be conclude that pellets of Ni-CaO/AC catalyst can give selectivity and yield for green diesel production.

ACKNOWLEDGEMENT

This study has been conducted at the Coal Gas and Petroleum Technology Lab at the Department of Chemical Engineering, Faculty of Engineering, UGM. We are thankful to the support of Mr Suhardi for the practical help in the lab.

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