The Effect of Activated Carbon Pellet on Hydrothermal Decarboxylation of Palm Olein into Renewable Diesel

Septriana, Desy
National Research and Innovation Agency, Indonesia

Priyanto, Unggul
National Research and Innovation Agency, Indonesia

Valentino, Novio
National Research and Innovation Agency, Indonesia

Sekar Kumala Desi
National Research and Innovation Agency, Indonesia

他

https://doi.org/10.5109/7151737

出版情報：Evergreen. 10 (3), pp.1868-1876, 2023-09. 九州大学グリーンテクノロジー研究教育センター
バージョン：

The Effect of Activated Carbon Pellet on Hydrothermal Decarboxylation of Palm Olein into Renewable Diesel

Desy Septriana[1,*], Unggul Priyanto[1], Novio Valentino[1], Sekar Kumala Desi[1], Restu Siti Nursaadah[1], Intan Machiya[1], Nesha Adelia[1], Bralin Dwiratna[1], Ali Nurdin[1], Ilhamsyah Noor[1]

[1]National Research and Innovation Agency, Indonesia

*E-mail: desy002@brin.go.id

(Received April 29, 2023; Revised August 10, 2023; accepted September 17, 2023).

Abstract: Renewable diesel from hydrogenated palm olein can substitute fossil diesel. This study used an activated carbon pellets catalyst in a 500-ml autoclave to decarboxylate palm olein hydrothermally. The experiment was conducted at 330-400 °C, the catalyst-feed ratio was 0.7, and the water-palm olein (palm cooking oil) weight ratio was 4 to 1. GC-MS and standard alkane and alkene characterized liquid products, while GC-TCD identified gas products. Renewable diesel's highest yields are 13.24% and 3.15% for samples with and without activated carbon pellets catalysts at 370 °C. In conclusion, activated carbon pellets increase renewable diesel recovery in hydrothermal decarboxylation.

Keywords: activated carbon pellet, decarboxylation, renewable diesel, hydrothermal, palm olein

1. Introduction

Renewable diesel or bio-hydrogenated diesel, purposely–to alternate diesel usage. It is predominantly n-paraffin, typically a C_{12} to C_{18} mixture of linear or branched in different portions. The n-paraffins are the constituents of gasoline, jet fuel, and diesel. Meanwhile, a report states biofuel would be more suitable for long-haul aviation and highly specialized uses such as industrial heat and power systems[1)]. Accordingly, diesel oil-like hydrocarbons could be cracked into more applicable fuels. Renewable diesel, the second-generation biofuel, is preferable to the more common biodiesel because of its superior heating value, more significant cetane number, lower corrosiveness, and more excellent oxidative stability due to its zero-oxygen content advantages[2,3)].

In addition, carbon deposits of combustion products in the combustion chamber might hinder engine performance when biodiesel is used as the alternative, especially at high concentrations[2,3,4)]. It differs from renewable diesel, which has molecules similar to fossil diesel fuel[5)]. The newer diesel oil generation techniques, mainly from algae, still face a high capital expenditure from its harvest method alone[2,5,6)].

Initially, The renewable diesel from popular hydrodeoxygenation vegetable oil consumes a high amount of hydrogen, which is not feasible economically on a large scale[7,8)]. Thus, a free-H_2 process is developed today, known as deoxygenation. The deoxygenation (DO) process can be summarized by initial hydrogenation, subsequently followed by reactions that comprise three possible routes, namely hydrodeoxygenation (HDO), decarbonylation (DCO), and decarboxylation (DCO_2)[9)]. HDO eliminates oxygen from Triglycerides (TG) with the help of hydrogen to form water and n-paraffin; in contrast, DCO/DCO_2 takes oxygen without the addition of hydrogen, resulting in carbon dioxide (CO_2), carbon monoxide (CO), and n-paraffin (n-paraffin).

DCO/DCO_2 is widely investigated among the three DO routes, especially DCO_2 since the H_2 consumption is the lowest[10)]. In addition, both DCO/CO_2 can be run under milder operating conditions than HDO, which reduces hydrogen usage, longer catalyst life, and lower moisture content[11)].

Various studies use TG-based feedstock such as oils and fats, fatty acids, or its derivatives (alkyl esters) to produce diesel-like hydrocarbons. Considering palm oil is Indonesia's most abundant oil resource, it is expected to be used as a potential biofuel resource. On that account, this study uses palm olein as the raw material. On the other hand, catalyst and operating conditions are well-known as determining keys to reaching high-rate conversion and selectivity.

Noble metal catalysts, typically palladium (Pd) and platinum (Pt) are widely studied[5,12)]. Nevertheless, it is expensive and limited in quantity, leading to finding alternatives to reach cost-effective production, that is, non-noble metal catalysts. Among the non-noble metal sources, activated carbon is majorly used as support since it has a high surface area, performs as a reinforcing site for the active metal sites, and can chemically absorb the reactants due to consisting of various functional groups on its surface, either having acidic or basic characteristics[5,13,14]. Activated carbon has also been successfully made into composites as a gasoline absorbent agent[15]. Nevertheless, there were only a few examinations on it as a primary catalyst for deoxygenation.

Adding a co-reactant as the hydrogen donor has also been investigated by many in the particular organic solvent, water, and compared under inert conditions (nitrogen gas only). Some studies mentioned that the co-reactant addition increased oil conversion in the following sequence: N_2 < N_2 with H_2O < N_2 in aqueous glycerol < H_2[10]. Still, glycerol or any organic solvent has the foremost drawbacks regarding cost and environmental aspects and thus making water an attractive co-reactant choice to explore. Aside from H_2 donor potential, water at high temperature and pressure will lose its hydrogen bonding ability to have similar properties to the non-polar solvent, which then aids in hydrolyzing the TG[16]. Moreover, under such conditions, the water's ionization constant will increase to be more acidic (more H^+ concentration, intensifying the hydrolysis.

The postulated hydrothermal decarboxylation for palm oil near supercritical water was initially dissolved in water into glycerol, linoleic acid, oleic acid, and palmitic acid. Then, hydrogen is generated internally through hydrothermal decarboxylation of triglycerides via gasification of fatty acids, carbon reforming in that order: Aqueous Phase Reforming (APR), glycerol decomposition, water gas shift reaction, and thermal cracking, which can be seen in eq. 1 – 9.[5,17,18,19])

Hydrolysis: $TG + 3H_2O \rightarrow Glycerol + Fatty\ Acid$ (1)

Gasification: $Fatty\ Acid \rightarrow CO_2 + CO$ (2)

WGS: $CO + H_2O \rightarrow H_2 + CO_2$ (3)

Carbon Reforming: $C + H_2O \rightarrow CO + H_2$ (4)

AQR: $Glycerol \rightarrow H_2 + CO_2$ (5a)
$Glycerol \rightarrow H_2 + CO_2 + CO$ (5b)

Thermal Cracking: $C_{17}H_{35}COOH \rightarrow CO + CO_2 + H_2 + CxHy$ (6)

Hydrogenation: $C_{17}H_{31}COOH + H_2 \rightarrow C_{17}H_{36}COOH$ (7a)
$C_{17}H_{33}COOH$ (7b)

Decarboxylation: $CH_3(CH_2)_{14}COOH \rightarrow C_{15}H_{32} + CO_2$ (8a)
$CH_3(CH_2)_{16}COOH \rightarrow C_{15}H_{32} + CO + H_2O$ (8b)

Decarbonylation: $CH_3(CH_2)_{14}COOH \rightarrow C_{15}H_{32} + CO + H_2O$ (9a)
$CH_3(CH_2)_{16}COOH \rightarrow C_{17}H_{36} + CO + H_2O$ (9b)

Since H_2 was not added to this study, the products are primarily saturated hydrocarbons. It means that H_2 must be obtained during the decarboxylation reaction. During hydrothermal decarboxylation of oleic acid, in-situ H_2 was generated while oleic acid was turned into gas simultaneously. Palm oil's hydrolysis produces fatty acids, while fatty acids' gasification may generate in-situ H_2 mentioned by several reports.

An efficient way to generate hydrogen gas locally is through glycerol's aqueous phase reforming (APR). Based on our findings, the best reaction temperature for glycerol degradation in the hydrothermal environment using activated carbon as a catalyst is 260°C, with the main byproducts being hydrogen, carbon monoxide, and carbon dioxide, and only trace amounts of shorter-chain hydrocarbon. Given the parallel nature of DCO_2 and DCO, CO may contribute to the water gas shift reaction to generate hydrogen gas. The generated hydrogen can be used in hydrogenating unsaturated linoleic and oleic acids to stearic acid. Meanwhile, saturated heptadecane and pentadecane are the byproducts of the reaction of stearic acid and palmitic acid with DCO and DCO_2, respectively. Longer-chain hydrocarbons can decompose into smaller-chain hydrocarbons or combine to generate more significant fractions, arenes, or ring compounds.

Several studies reported the utilization of activated carbon catalysts and water under supercritical conditions for gasification and oxidation reactions. Hossain studied powder-activated carbon that could be applied for producing renewable diesel with 100% oleic acid conversions, yielding 100% heptadecane after 5 hours of reactions under sub-critical water conditions at 40 bar and 250 °C[12]. While another report mentioned that 97% conversions of oleic acid were obtained with 81% pentadecane selectivity under 400 °C for 2 hours by applying water as the external hydrogen source to accommodate the deoxygenation process[8].

Fatty acid decarboxylation using activated carbon pellets in hydrothermal media has yet to be reported in the literature. Furthermore, no published research has proposed utilizing activated carbon pellets for hydrothermal decarboxylation of long-chain carboxylic acids (fatty acids). If the catalyst has excellent catalytic properties, it could serve as an appealing, cost-effective catalyst. Hence, this study hydrothermally investigates the impact of activated carbon pellets in decarboxylate palm olein. It is known that DCO_2 can be executed under inert gas and atmospheric conditions, while DCO can be carried out by utilizing hydrogen on-site. Localized hydrogen can be obtained amid diesel-like oil generation, such as water gas shift, thermal cracking, and Boudouard reactions[5].

2. Material and Method

This study's raw materials are palm oil (specifically palm olein oil), nitrogen gas, deionized water, activated carbon, and n-Hexane. Palm olein oil was purchased from retail stores, while n-hexane was from online shops. As a triglyceride, palm olein was hydrothermally decarboxylated either by utilizing activated carbon pellets or in the absence of it. Table 1 represents the detailed breakdown of palm olein.

Table 1. Palm Olein's Component.

Compounds	Average Percentages (%)
Terephthalic Acid	0.515
Myristic Acid	0.732
Palmitic Acid	38.637
Oleic Acid	23.748
Stearic Acid	2.791
Glycerol	21.486
Squalane	10.933
Vitamin E	1.158

Activated carbon pellets as catalysts in hydrothermal decarboxylation were obtained from the retail store—characterization of Activated Carbon Pellets as seen in Table 2. The BET surface area, pore size, and pore volume of the catalyst were determined via Anton Paar Novatouch (1x2 surface area) and a pore size analyzer. The N_2 adsorption isotherms in liquid N_2 medium at 77 k were measured using a Quantachrome Novawin instrument. All samples were vacuumed at 300 °C for 4 hours before measurement. Specific surface area (s_{BET}) and total pore volume (v_p) were calculated by employing BET (Branauer–Emmet–Teller) method and the point $p/p_o \approx 0.99$, respectively.

Meanwhile, both Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halen (BJH) methods were used to analyze pore size distributions of fresh and spent catalysts. Before measurements, at least 80 mg of the sample was heated at 150 °C for 12 hours to eliminate the water content and other gases on the catalyst surface. The experiment was conducted at 193 °C with 99.995% pure N_2 gas.

Table 2. Characterization Activated Carbon Pellets.

Parameter	Value
Surface Area (m^2/g) BET	833
Pore Volume (cc/g) BJH	0.49
Average Pore Radius (A)	11.865

In an autoclave with a 500 mL volume, palm olein was deoxygenated hydrothermally at various temperatures of 330 - 400 °C) with pressure range from 52-230 bar. Reactants are palm olein oil (30 grams), deionized water (120 grams), and activated carbon pellets (21 grams) were loaded for a typical reaction[19).]After purging and filling with N_2 gas under static conditions, the autoclave's temperature was adjusted to the reaction condition. After stabilizing the temperature, the reaction began by magnetic stirring (100 rpm) and was sustained for four hours. After four hours of reaction, the reactor was immediately cooled to a temperature below 60 ℃ over was performed as soon as cooling down was completed.

The solid, liquid, and gaseous products were subsequently obtained and split. Product recovery started with collecting into a gas sampling bag for Gas Chromatography Thermal Conductivity Detector (GC-TCD) analysis. Solids (catalysts) and liquid products were removed from the reactor and separated by the filter. Catalysts detached from the liquid product were washed twice with hexane to the liquid product left. The catalyst was then put in an oven at 90 °C with a vacuum for a whole night. To get a pure product, we evaporated the mixture of hexane, liquid product, and water using a rotary evaporator. Then, the product purified by the rotary evaporator was blended with the liquid product separated by the filter before calculating the liquid's yield.

The gaseous product was identified using a Gas Chromatograph Bruker Scion 456-GC installed with a TCD detector and chromatographic column Shincarbon ST to determine the gas mixture, such as H_2, N_2, O_2, CO_2, CO, and CH_4. The column was initially adjusted to 50 °C (held for 7 minutes), then elevated to 100 °C at a rate of 20 °C/minute for 10 minutes, and raised again to 200 Celsius at a rate of 20 °C/minute for 12 minutes. The injector and detector temperatures were set at 100 and 220 degrees Celsius.

Gas chromatography-mass spectrometry (GCMS) was used to analyze the liquid products qualitatively GCMS spectrometer, and 5977 (MSD) DB-5 Capillary Column was set to 40 degrees Celsius for 1 min, then elevated to 300 degrees Celsius at the rate of 5 °C/minute for 5 mins. The column's dimensions are 30 m x 0.32 mm x 0.25 m. Additionally, the temperature of the sample injector and the detector was regulated at 250 degrees Celsius.

The obtained data from the experiment were calculated to determine conversion, the selectivity and yield of renewable diesel. The conversion, selectivity and yield of renewable diesel were calculated based on the results of the GCMS analysis. Conversion was calculated by dividing the difference of the initial and final total area of free fatty acid in palm olein with initial total area of free fatty acid[21)] The renewable diesel yield and selectivity were determined by comparing the retention time of standard hydrocarbons (C_{12}–C_{18}) with experimental-based products. In the present study, the catalytic performance of the catalysts was studied by determining the yield of saturated and unsaturated straight-chain hydrocarbons (X) (eq. (10).[22)]

$$X = \frac{\sum n_D}{\sum n_P} \times 100 \qquad (10)$$

where, n_D = total area of alkene (C_{12}–C_{18}) and total area of alkane (C_{12}–C_{18}) in product, n_P = total area of the product. Thus, The renewable diesel selectivity (S_D) was determined by eq. (11)[22)].

$$S_D = \frac{\sum n_D}{\sum n_U} \times 100 \qquad (11)$$

where, n_D = total area of alkene (C_{12}–C_{18}) and total area of alkane (C_{12}–C_{18}) in product, n_U = total area of undesired product.

3. Result and Discussions

The gas product of hydrothermal decarboxylation was analyzed with GC-TCD. The analysis results are displayed as percent moles of gas, as shown in Figure 1 below. Most gas outcomes from the hydrothermal decarboxylation process are byproducts, namely CO_2 and CO. Furthermore, hydrogen gas is an intermediate and a hydrogen donor in the reaction.

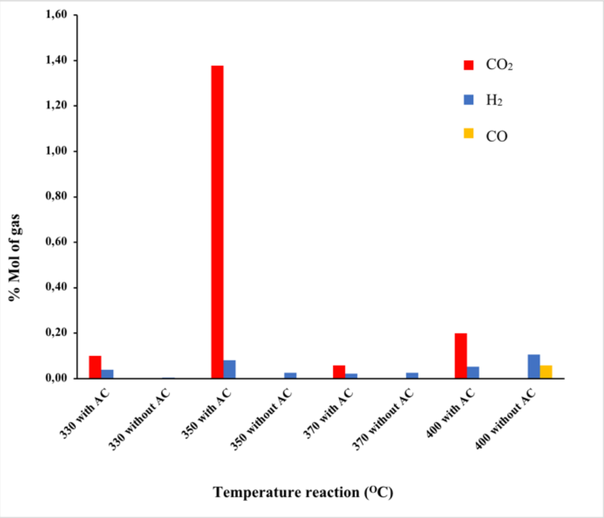

Fig. 1: Percentage of gas in decarboxylated products

Figure 1 shows that the highest number of moles of carbon dioxide is generated at 350 °C with activated carbon pellets catalyst. In this case, stearic acid's decarboxylation reaction to heptadecane has occurred. In the reaction of a higher reaction temperature of 350 °C and with activated carbon, CO_2 gas is formed with very high levels (up to 1.4% mole of gas). In addition, hydrogen gas is also included. At this temperature, the reaction is concluded as optimum. The reaction utilizing activated carbon also generates CO_2 gas when the temperature is raised to 370 °C. The decarboxylation reaction also occurs at 400 °C, which uses activated carbon, yielding a smaller amount of CO_2 gas. The increasing temperature until 400 °C happened a thermal cracking reaction, which produced more extensive hydrogen gas to hydrogenate without the activated carbon.

Furthermore, a study by Jin and Choi proved that 7 mol of H_2 can be made from 1 mol of glycerol. Decarboxylation does not need H_2; decarbonylation needs one H_2 molecule to be a saturated hydrocarbon. Then, Carbon monoxide from decarbonylation can be converted to H_2 with a water gas shift (WGS) reaction. Because of that, CO was invisible at 330, 350 and 370 °C[22]. Decarbonylation occurs simultaneously with decarboxylation, and CO can contribute to the water gas shift reaction, which generates H_2. Unsaturated linoleic and oleic acids can subsequently be hydrogenated into stearic acid with the help of the created H_2. Saturated heptadecane and pentadecane are created via the decarboxylation and decarbonylation of stearic acid and palmitic acid, respectively. The bigger hydrocarbon molecules may further join to form aromatic and cyclic compounds, or they may fragment to form smaller hydrocarbon molecules.[20]

In the reaction temperatures of 330, 350, 370, and 400 °C with the help of activated carbon pellets, the gas product contains CO_2 gas. On the other hand, reactions that do not use activated carbon pellets do not produce CO_2 gas. The gas output produced during the reaction determines the resulting liquid product, as seen in Fig. 2, tables 3 and 4, and Fig. 3, namely the conversion, selectivity, and yield calculation in liquid products.

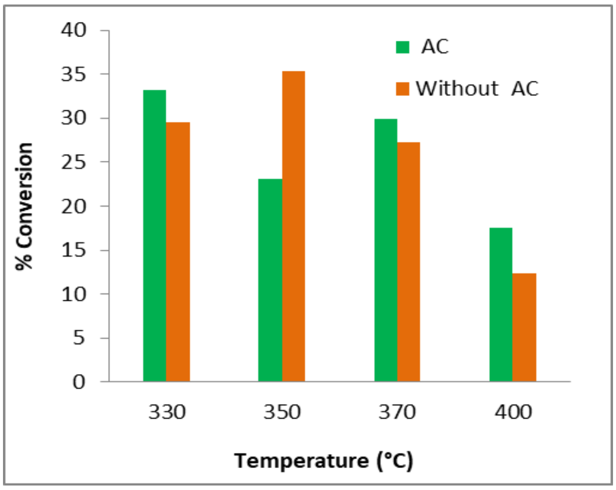

Fig. 2: Conversion of Palm olein after 4 h at different reaction temperatures

The highest conversion of palm olein, as seen in Figure 2 by hydrothermal decarboxylation using an activated carbon catalyst, was 33.25% at 330 °C, while the lowest conversion was only 17.52% (400 °C). The highest conversion of palm olein without activated carbon was 29.55% at 350 °C, and the lowest was 12.35% at 400 °C. The temperature of conversion of triglycerides into hydrocarbons in the absence of hydrogen generally occurs between 300°C to 450°C. These reactions are hydrodeoxygenation, decarboxylation, and decarbonylation, which generally produce the byproducts H_2O, CO_2, and CO, respectively. Hydrogenation and decarboxylation reactions are exothermic, while decarbonylation and cracking reactions are endothermic. Therefore, using an activated carbon catalyst, the reaction conditions that provide the highest conversion occur at 330 ^{0}C after cracking. At higher temperatures of

400 ^{0}C and above, the conversion will generally be low because dehydrogenation and decarboxylation reactions are dominant, which due to their exothermic nature, will decrease with increasing temperature. In the reaction conditions without a catalyst, the reaction conditions that produce the highest conversion temperature are higher because, without a catalyst, a higher temperature is needed to meet the higher activation energy requirements[24)].

Most of the transformation of palm olein into oxygenated compounds, namely carboxylic acids, and the remaining desired product is renewable diesel (C_{12}-C_{18}). Several studies indicate that decarboxylating oleic acid under supercritical conditions hydrothermally with no presence of a catalyst results in only 4.7% conversion. In comparison, with 80 % oleic acid conversion after 3 hours over activated carbon at 370 °C, the selectivity of heptadecane was only 7%, and the yield of heptadecane was only 6 %[12)].

A 30-33% oleic acid conversion was also observed after 4 hours under similar conditions (decarboxylation in supercritical water) with an Al-SBA-15-based catalyst. Unsaturated C_{17}, resulting from decarboxylation and decarbonylation reactions, was the primary product of the reaction for all catalysts. Furthermore, after 4 hours of reaction in supercritical water over NiWC/Al-SBA-15 catalyst, the hydrothermal decarboxylation of oleic acid achieved 30.7% conversion with only 0.72% selectivity for C_{17} and 53.6% selectivity for unsaturated C_{17}[23)].

Generally, temperature (350-400 °C), water/oleic acid ratio, catalyst-to-total feed ratio, and residence time all affected oxygen expulsion from oleic acid. The carboxylic group was eliminated after 2 hours at 400 °C with a water / oleic acid ratio of 4:1 (v/v), according to FTIR and 13C NMR data[17)]. The difference between this study and Hossain's study was the form of an activated carbon catalyst. Hossain used powder-activated carbon, while this study used activated carbon pellets with a larger pore size than powder form. The Hossain research's optimum conditions were adopted in this work: the water to oleic acid ratio of 4:1 (w/w), the catalyst to total feed ratio (0.7), and the residence time of 4 h[19)].

Hossain employed activated fresh carbon, which has an 857 m^2/g surface area, 0.63 cm^3/g pore volume, and pore radius of 17.5 A. The highest CO_2 gas was obtained at a temperature of 400 °C. It was comparable to the highest yield of heptadecane. However, compared with temperatures of 300 °C and 330 °C, there is a decrease in CO_2 [19)]. It is consistent with this study's findings that there is an increase and decrease in CO_2 gas production. However, the most significant yield of renewable diesel was not produced at 350 °C but at 370 °C. As a result, the outcome of this study differs from that reported by Hossain et al. Despite employing the same activated carbon, the catalyst's form is different.

Table 3 indicates that the product selectivity from hydrothermal decarboxylation using activated carbon pellets tends to produce renewable diesel (C_{12}- C_{18}). The highest renewable diesel selectivity was obtained at 370 °C with the help of activated carbon pellets. It follows research from other researchers who stated that the optimum temperature for decarboxylation is 370 °C. Therefore, at 400 °C, the selectivity for forming renewable diesel products is no longer available. At temperatures of 330°C and 350°C with a catalyst, only heavy fractions such as C_{16} and C_{17} are formed. This is probably due to the fact that the temperature for cracking(endotherm) is still too low, so light fractions such as C_{13}-C_{15} have not been formed. Whereas at 400 ^{0}C, the reaction conditions were too high for the decarboxylation and hydrodeoxygenation reactions (exothermic reactions), so the conversion to form liquid products was suspected to be low. Pressure in the reactor increases as the temperature rises. Increasing temperature will help reaction gain more energy to overcome the activation energy required. During our experiments, the pressure rose from 52 to 230 bar. The higher pressure will influence the reaction inside the reactor, which leads to a cracking reaction. Cracking reaction will happen in temperature of 400 °C and above, which generates more lighter hydrocarbon (C_{12} and shorter)[31)]. A similar explanation for the reaction without a catalyst (see Table 4), but it is the lower product because the temperature condition requirement is probably higher.

Table 3. Palm olein's product selectivity after decarboxylated hydrothermally for four h with activated carbon pellet[25)]

Temperature (°C)	**AC**							
	Selectivity (%)							
	C_{13}	**C_{14}**	**C_{15}**	**Unsaturated C_{15}**	**C_{16}**	**Unsaturated C_{16}**	**C_{17}**	**Unsaturated C_{17}**
330	0	-	-	-	1.324	-	-	1.373
350	0	-	0.592	-	1.822	-	-	2.132
370	0.084	0.688	2.564	0.615	0.670	-	3.908	6.735
400	-	-	-	-	-	-	-	-

Table 4. Palm olein's product selectivity after decarboxylated hydrothermally for four h without activated carbon pellets[25].

Temperature (°C)	AC							
	Selectivity (%)							
	C_{13}	C_{14}	C_{15}	Unsaturated C_{15}	C_{16}	Unsaturated C_{16}	C_{17}	Unsaturated C_{17}
330	-	-	-	-	2.376	-	-	-
350	-	-	-	-	0.514	-	-	-
370	-	-	1.122	-	-	-	1.139	0.986
400	-	-	-	-	-	0.158	-	0.255

Table 4 describes the selectivity of renewable diesel in the hydrothermal decarboxylation process without using activated carbon pellets. The selectivity and yield of renewable diesel produced in this study using activated carbon pellets differed from the results from Hossain. It is due to the shape of the catalyst used and reactor performance. Another report mentioned that 97% conversions of oleic acid were obtained with 81% pentadecane selectivity under 400 °C for two hours[17]. With no additional catalyst, this research demonstrated that heptadecane and heptadecene increased with increasing temperature.

Table 4 shows that the renewable diesel produced is mostly alkene (C_{15}-C_{17}). It indicates that the reaction is mostly decarbonylation, producing CO gas as a byproduct. It has been proven in Figure 1 above. In Hossain's hydrothermal decarboxylation of maize distiller oil, heptadecane's selectivity was 10% in a catalyst-free condition and 48.9% using a catalyst at 400 °C. Selectivity for heptadecene in the non-catalyzed process at 400 °C was only 3.1%, and it was reduced to 0.4% using the catalyst. We found that the selectivity for heptadecane without activated carbon was only 1.139%, while the selectivity for heptadecane with activated carbon at the optimal temperature (370 °C) was 3.908%. The selectivity of heptadecene from this study was only 0.986 % (without activated carbon), which was further increased to 6.735% with activated carbon at 370 °C. Figure 2 depicts the renewable diesel yield value.

In Figure 3, we can see a decrease in the yield value of renewable diesel when hydrothermal decarboxylation is carried out without using activated carbon pellets. The optimum yield of renewable diesel occurs at 370 °C with 13.24 % and 3.15 % by employing activated carbon and without any of it. Fu and his colleagues used powdered activated charcoal washed with phosphoric acid[12]. They found that using activated carbon, decarboxylating oleic acid in sub/supercritical water at 370 °C for 3 hours generated a (5.8±1.1) % heptadecane and a (24±1%) stearic acid yield. Thus, according to study of Elvan sari who used free fatty acid as feedstock, it is likely that Brown Grease FFAs undergo decarbonylation (Reaction II) and paraffins undergo dehydrogenation (Reaction I) in order to form olefins. The n-monoolefins can be further hydrogenated in the presence of H_2, whether they were created through dehydrogenation or decarbonylation[25]

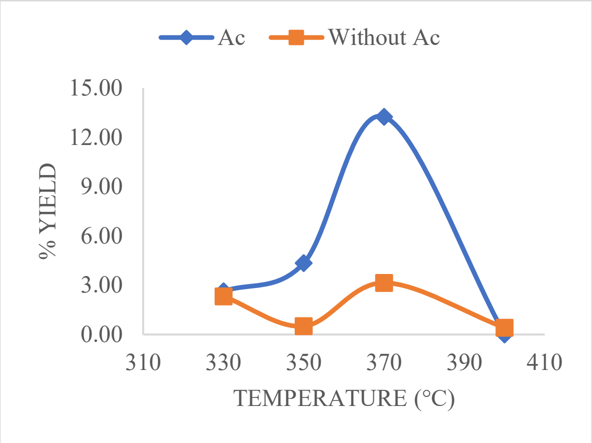

Fig. 3: Renewable diesel yields after four h at different reaction temperatures

This optimum temperature is the same as the study of Popov and Kumar by using granulated activated carbon with a BET surface area of 600 ± 20 m^2/g, pore volume of 0.95 ± 0.05 cm^3/g, and pore size diameter was 60 ± 5 nm. In addition to the maximum selectivity of 80.6% and heptadecane yields of 67.1 wt.% being recorded at 370 °C, heptadecane yields 69.7 wt.% at 380 °C. Meanwhile, the reaction at 400 ºC produced the lowest yield of heptadecane (9.7%), compared to other lower temperatures in the experiments[20]. Another is using catalytic hydrothermal reforming from jatropha oil with Pd/ Carbon, which had a yield of heptadecane was 6.2 % at 350 °C [26]. Edeh et al. give a low yield on Pd/C. At 300 C and 290 °C, pentadcane's selectivity was 4.1% and 3.2%, respectively. Meanwhile, heptadecane's yields at 330 and 290 ° C were 16.9 and 14.7 %, accordingly[27]. Active sites are essential in the formation of alkanes. A study on ZrO_2 support in Hydrothermal decarboxylation (0.5 g Palmitic acid, 0.5 g ZrO_2, and 4.5 ml water at 300 °C, 6 hours, 7 bar initial pressure H_2) obtained 6.6 C % of Palmitic Acid and paraffin yields less than 0.1 C %[28]. Additionally, Chen et al proved that the acidity of the catalyst affects its performance of the catalyst. The yield of heptadecane increased over dried Pt/C after adsorbing 20 wt% H_2O and 30 wt% H_2O from 60% to 65% and 70%, respectively. Hydrothermal decarboxylation over dried Pt/C at 350 °C for 2 hours and H_2O addition as a solvent only gave a 35 % yield of heptadecane[29].

According to Hossain's research, the -COO group from CDO could be thoroughly eliminated at 400 °C within 4 hours and water to CDO ratio of 4:1. The main products were C_8 to C_{16} (49.7% selectivity) and heptadecane (48.9%) saturated hydrocarbons[19]. So, this work used optimum conditions based on Hossain's study. Comparing our results to the literature as mentioned earlier data, we were able to produce 13.24% renewable diesel at 370 °C for 4 hours without the use of any external hydrogen or hydrogen-donor solvent sources with palm olein oil/water ratio of 1:4. This ratio is by a study by Miao et al. (2018), which demonstrated that the yield of paraffin raised from 2.8% at a water-to-stearic acid ratio of 0:1 to 64% at a water-to-stearic acid ratio of 4:1, while an increase in the water-to-stearic acid ratio more than 4:1, demonstrated a reduction in both conversion and paraffin yield[30].

Several factors, including catalyst choice, operating temperature, and reaction time, may account for different writers' discrepancies in results. For decarboxylation, the reaction temperature is an essential determinant of success. At higher temperatures, gasification predominates, while at lower temperatures, saponification takes over. Saponification prevails at temperatures below 350 °C, while decarboxylation plays a significant role at higher temperatures (T's > 350 °C)[31]. Furthermore, reaction time is directly proportional to the product yield or selectivity in the decarboxylation route. Improving hydrocarbon yields requires adjusting reaction time and catalyst choices. Hydrogen was created on-site during hydrothermal decarboxylation and gasification at the selected temperature, proving the suitability of the suggested reaction mechanism for this investigation[12].

Decarbonylation occurs concurrently with decarboxylation. Additionally, via a water-gas shift reaction, carbon monoxide can react with water to produce hydrogen gas. High-temperature thermal cracking of oleic acid releases hydrogen as well. The best temperature for palm olein decarboxylation utilizing activated carbon pellets to make renewable diesel fuel is 370°C, with a product yield of 13.24%. Activated carbon pellets affect the product of hydrothermal decarboxylation because of an increase in the yield of renewable diesel by using activated carbon pellets. The product yields for renewable diesel remained low at 13.24% because the deoxygenation was carried out under hydrothermal conditions, in which no extra hydrogen was needed, and no active metal was present in the catalyst. However, the technique might provide an economic advantage.

In the future, the hydrothermal deoxygenation process should be optimized utilizing response surface methods, and alternative catalysts should be researched to provide a larger yield of hydrocarbon products. It demonstrated that hydrogen produced by catalytic glycerol gasification may have contributed to increased yield by partial hydrogenation of unsaturated fatty acids. Based on the cost analysis, the process should be further optimized.

4. Conclusion

To get the highest output of renewable diesel by decarboxylating palm olein with activated carbon pellets, we should set the temperature at 370°C, producing a yield of 13.24%. Activated carbon pellets affect the product of hydrothermal decarboxylation because of an increase in the yield of renewable diesel. Given that the deoxygenation was carried out under hydrothermal circumstances without the addition of hydrogen and the use of active metal in the catalyst, the product yields of 13.24% for renewable diesel remain low. The hydrothermal deoxygenation process might be optimized using response surface methods, and new catalysts supported by active carbon could be tested to increase hydrocarbon product yields in future research. Partial hydrogenation of unsaturated fatty acids was shown to increase yield, proving that hydrogen produced by catalytic gasification of glycerol was responsible for this improvement. For this reason, future research should focus on finding ways to prevent the formation of such massive products.

Acknowledgments

This study was conducted in building no: 625, Manufacturing and Process Industry Research Center, Energy Research and Manufacturing Organization, BRIN. Furthermore, DIPA RP EBT, the National Research and Innovation Agency, supported this study financially. Analysis was provided by the National Research and Innovation Agency via E-Layanan Sains, which the authors gratefully acknowledge.

References

1) "EU Biomass Use in a Net-Zero Economy A Course Correction for EU Biomass" https://www.energy-transitions.org/material-economics-launch-eu-biomass-report/ (accessed February 9, 2022).
2) V. Palany et al., "Biodiesel and Green diesel generation: An Overview," *Oil & Gas Science and Technology,* **76,** (6), p. 1-10, (2021). doi: 10.1007/s11244-010-9456-1
3) E. Rafael et al., "Biodiesel is Dead: Long Life to Advanced Biofuels – a Comprehensive Critical Review," *Energies*, **15,** (3173), p. 1-39, (2022). doi: 10.3390/en15093173
4) J.A. Hidayat, S. Bambang, "Characteristic, Structure, and Morphology of Carbon Deposit from Biodiesel," *Evergreen*, **7**(4), p.609-613, (2020). doi: 10.5109/4150514
5) N. Hongloi, P. Prapainainar, T. Muadmai, J. Namboonlue, A. Seubsai, and C. Prapainainar, "Green Diesel Production from Oleic Acid

Deoxygenation Using Subcritical Water under Hydrogen-Free Condition.” *Engineering Journal 25*, 115–122 (2021). doi:10.4186/ej.2021.25.10.115

6) A. Rahman, N.B. Prihantini, Nasrudin, “Biomass Production and Synthesis of Biodiesel from Microalgae Synechococus HS-9 Cultivated using Bubble Column Photobioreactors”, *Evergreen*, **7**(4), p.564-568, (2020). doi: 10.5109/4150507

7) K.D. Nugrahaningtyas et al., “Metal Phase, Electron Density, Textural Properties, and catalytic activity of CoMo Based Catalyst Applied in Hydrodeoxygenation of Oleic Acid,” *Evergreen,* **9**(2), p.283-289, (2022). doi: 10.5109/4793665

8) F. Takaya, “Evaluation of Green Paradox: Case Study of Japan,” *Evergreen,* **5**(4), p.26-30, (2018). doi: 10.5109/2174855

9) K.N. Papageridis, N.D. Charisiou, S. Douvartzides, V. Sebastian, S.J. Hinder, M.A. Baker, A.A. AlKhoori, S.I. AlKhoori, K. Polychronopoulou, and M.A. Goula. “Continuous selective deoxygenation of palm oil for renewable diesel production over Ni catalysts supported on Al_2O_3 and La_2O_3-Al_2O_3.” *RSC Adv 11*, 8569–8584 (2021). doi:10.1039/d0ra08541c

10) R. Kaewmeesri, J. Nonkumwong, T. Witoon, N. Laosiripojana, and K. Faungnawakij. “Effect of Water and Glycerol in Deoxygenation of Coconut Oil over Bimetallic NiCo/SAPO-11 Nanocatalyst under N2 Atmosphere.” *Nanomaterials 10*. https://doi.org/10.3390/nano10122548

11) N. Krobkrong, V. Itthibenchapong, P. Khongpracha, and K. Faungnawakij, “Deoxygenation of oleic acid under an inert atmosphere using molybdenum oxide-based catalysts.” *Energy Convers Manag 167*, 1–8 (2018). doi:10.1016/j.enconman.2018.04.079

12) J. Fu, X. Lu, and P.E. Savage, “Hydrothermal decarboxylation and hydrogenation of fatty acids over Pt/C.” *ChemSusChem 4*, 481–486 (2011). doi: 10.1002/cssc.201000370

13) U. Priyanto, K. Sakanishi, O. Okuma, and I. Mochida, The catalytic activity of FeMoNi ternary sulfide supported on a nanoparticulate carbon in the liquefaction of Indonesian coals”. *Industrial & engineering chemistry research*, *40*(3), 774-780 (2001). doi : 10.1021/ie000432i

14) U. Priyanto, K. Sakanishi, O. Okuma, and I. Mochida, “Liquefaction of Tanito Harum coal with Bottom recycle using FeNi and FeMoNi catalysts supported on carbon nanoparticles”. *Fuel processing technology*, *79*(1), 51-62 (2002). doi: 10.1016 / S0378 – 3820 (02) 00101 -7

15) M. Niken A., B. Rusdiarso, and W. Trisunaryanti . “Synthesis of Activated Carbon-Fe3O4 Composite a Gasoline Adsorbent in Gasoline-Water Mixture and Its Adsorption Kinetics Study,” *Evergreen*, **7**(4), p.701-710, (2022). doi: 10.5109/4843101

16) N. Galamba, A. Paiva, S. Barreiros, and P. Simões, “Solubility of Polar and Non-polar Aromatic Molecules in Subcritical Water: The Role of the Dielectric Constant" *Journal of Chemical Theory and Computation 15*(11), 6277–6293 (2019). Doi: 10.1021/acs.jctc.9b00505

17) M.Z. Hossain, A.K. Jhawar, M.B.I. Chowdhury, W.Z. Xu, Wu, W., D.V. Hiscott, and P.A. Charpentier, “Using Subcritical Water for Decarboxylation of Oleic Acid into Fuel-Range Hydrocarbons.” *Energy and Fuels 31*, 4013–4023 (2017). doi: 10.1021/acs.energy fuels.6b03418

18) J. Mingyu Jin and C. Minkee Choi, “Hydrothermal deoxygenation of triglycerides over carbon-supported bimetallic PtRe catalysts without an external hydrogen.” *Molecular Catalysis 474*, 110419 (2019). doi:10.1016/j.mcat.2019.110419

19) M.Z. Hossain, A.K. Jhawar, M.B.I. Chowdhury, Xu, W.Z., and P.A. Charpentier, “Hydrothermal Decarboxylation of Corn Distillers Oil for Fuel-Grade Hydrocarbons.” *Energy Technology 6*, 1261–1274 (2018). doi: /10.1002/ente.201700957

20) S. Popov, and S. Kumar, “Rapid hydrothermal deoxygenation of oleic acid over activated carbon in a continuous flow process.” *Energy and Fuels 29*, 3377–3384 (2015). doi: 10.1021/acs.energy fuels.5b00308

21) L. Chen, H. Li, J. Fu, C. Miao, P. Lv, and Z. Yuan, “Catalytic hydroprocessing of fatty acid methyl esters to renewable alkane fuels over Ni/HZSM-5 catalyst” Catalysis today 259 p. 266-276 (2016) doi: 10.1016/j.cattod.2015.08.023

22) N.A. Mijan, H.V. Lee, J.C. Juan, A.R. Noorsaadah, and Y.H. Taufiq-Yap “Catalytic Deoxygenation of Triglicerides to Green Diesel Over Modified CaO-based catalyst”. *RSC Advances* 7, 46455. (2017) doi: 10.1039/c7ra08061a

23) Al Alwan and A. Al. Basem "Biofuels Production Via Catalytic Hydrocracking Of Ddgs Corn Oil And Hydrothermal Decarboxylation Of Oleic Acid Over Transition Metal Carbides Supported On Al-SBA-15” *Graduate School of Wayne State University, Detroit* (2014)

24) Estevez, R., Aguado-Deblas, L., López-Tenllado, F. J., Luna, C., Calero, J., Romero, et al. (2022). “Biodiesel is dead: Long life to advanced biofuels A comprehensive critical review. *Energies*, *15*(9)”, *Energies 15 (9)*, 3173 (2022). doi: 10.3390 / en15093173 3173.

25) “Green Diesel Production Via Catalytic hydrogenation/Decarboxylation of Triglycerides and Fatty Acids of Vegetable Oil and Brown Grease”, n.d. https://digitalcommons.wayne.edu/cgi/viewcontent.cgi?article=1793&context=oa_dissertations (accessed August 4, 2023)

26) S. Idesh, S. Kudo, K. Norinaga, and J.I. Hayashi, “Catalytic hydrothermal reforming of jatropha oil in subcritical water for the production of green fuels:

Characteristics of reactions over Pt and Ni catalysts," in Energy and Fuels. pp. 4796–4803 (2013). doi: 10.1021/ef4011065

27) I. Edeh., T. Overton, and S. Bowra, "Catalytic hydrothermal deoxygenation of fatty acids over palladium on activated carbon catalyst (Pd/C) for renewable diesel production." *Biofuels 12*, 1075–1082 (2021). doi: 10.1080/17597269.2019.1580971
28) C. Miao, O.M. Flores, S.D. Davidson, T. Li, T. Dong, D. Gao, Y. Wang, M.G Perez, and S. Chen, "Hydrothermal Catalytic Deoxygenation of Palmitic Acid Over Nickel Catalyst" *Fuel 166*, 302-308 (2016). doi: 10.1016/j.fuel.2015.10.120
29) H. Chen, K. Chen, J. Fu, X. Lu, H. Huang, P. Ouyang, "Water-mediated promotion of the catalytic conversion of oleic acid to produce an alternative fuel using Pt/C without an H_2 source" Catalysts Communication 98, 26-29 (2017). doi: 10.1016/j.catcom.2017.04.044
30) C. Miao, O.M. Flores, T Dong, D. Gao, Y. Wang, M.. Perez, S. Chen, "Hydrothermal Catalytic Deoxygenation of Fatty Acid and Bio-oil with In Situ H_2" ACS Sustainable Chem. Eng. 6, 4521-4530 (2018). doi: 10.1016/j.catcom.2017.04.044
31) J.G. Na, B.E. Yi, Kim, Ju Nam, Yi, K.B., S.Y. Park, J.H. Park, Kim, Jong Nam, and Ko, C.H, "Hydrocarbon production from decarboxylation of fatty acid without hydrogen." *Catal Today 156*, 44–48 (2010). doi 10.1016/j.cattod.2009.11.008