

CrossMark

Available online at www.sciencedirect.com



Procedia Chemistry

Procedia Chemistry 9 (2014) 139 - 150

International Conference and Workshop on Chemical Engineering UNPAR 2013, ICCE UNPAR 2013

Synthesis of Renewable Diesel Through Hydrodeoxygenation Using

Pd/zeolite Catalysts

Bambang Heru Susanto^a*, Mohammad Nasikin^a, Sukirno^a, Andri Wiyo^a

^aChemical Engineering Department-Universitas Indonesia, Kampus Baru Universitas Indonesia, Depok 16424, Indonesia

Abstract

Hydrodeoxygenation of oleic acid as model compound of vegetable oils over Pd/zeolite catalysts was investigated under conditions of 375–400°C and 15 bar in a semi batch stirred autoclave reactor. Pd/zeolite-1 and Pd/zeolite-2 catalysts were prepared using microwave polyol method with different treatment conditions. The liquid hydrocarbon products named Renewable Diesel have suitable density and viscosity, and quite high cetane index in accordance with standard commercial diesel and ASTM D-975. The IR spectrum of Renewable Diesel products have similarities with commercial diesel. The oxygenation removal pathway of oleic acid over Pd/zeolite 1 catalyst was primarily compiled through decarboxylation at 375°C.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/). Peer-review under responsibility of the Organizing Committee of ICCE UNPAR 2013

Keywords: Hydrodeoxygenation ; oleic acid; Pd/zeolite ; Renewable Diesel

* Corresponding author. Tel.: +6285624202530 ; fax: +62217863515. *E-mail address:* bambanghs@che.ui.ac.id

1. Introduction

Biodiesel production from trans-esterification of vegetable oils is currently the primary route for production of biofuels from vegetable oils. Biodiesel as a type of oxygenated fuels is renewable fuel, biodegradable and non-toxic, and has a higher flash point than petroleum diesel [2]. Furthermore, it has lower sulfur and aromatic content, higher combustion efficiency, and higher lubricity than petroleum diesel [6]. However, biodiesel also has higher viscosity, higher cloud point and pour point, higher nitrogen oxides (NO_x) emissions, lower energy density, and higher injector/engine wear [7]. With the inherent disadvantages of Biodiesel, it would be advantageous to make a renewable fuel with the benefits of a biofuel (i.e., renewable, low sulfur, low aromaticity) but exhibiting petroleum Diesel-like properties (lower cloud and pour points, lower NO_x emissions, higher energy density, lower engine wear). To avoid the disadvantageous physical properties of oxygenated fuels, hyrodeoxygenation of vegetable oil has been investigated as an alternative pathway of biofuel production.

Hydrogeoxygenation belongs to a group of hydrotreating reactions and it means removal of oxygen from an oxygen- containing compound under hydrogen pressure at high temperatures with the help of catalyst. Hydrodeoxygenation includes a number of other reactions such as hydrogenation, cracking, decarbonylation and decarboxylation. Hydrodeoxygenation can be a very expensive process due to the temperature and pressure requirements to deoxygenate of 300-400°C with hydrogen pressure up to 200 bar. However, aromatic structures can be preserved which yields a high octane fuel [10]. In hydrogenation process, C-O bond will be cut using H₂ gas, the carboxylic functional group is disconnected into form of CO_2 compound by decarboxylation process, and CO and H₂O compounds were released through decarbonylation process. Metal in catalyst and pressure hydrogen is useful for saturation process of unsaturated carbon chains in triglycerides.

Forming reaction of Renewable Diesel involves catalyst to decrease the activation energy of the reaction and increase its selectivity. The type of catalyst used in this study is Pd/zeolites catalyst which synthesized through microwave polyol method. In recent time, microwave polyol method has been successfully used to produce nano-sized catalysts for Pd/C and Pt/C catalysts. Several studies using microwave polyol method are: Boyas et al. [12] synthesizing Pt/zeolite catalysts for the production of Renewable Diesel, He Li et al. [4] synthesizing Pd/C catalysts for methanol electro-oxidation reaction, Amin et al. [1] synthesizing Pt/C catalysts for Fuel Cell applications, and Feng Wu et al. [3] who observe the effect of the use of ethylene glycol in synthesizing nano-catalysts using microwave polyol method. Studies above were using the same method but with different treatments. This study will use the treatment performed by Jie Zhao et al. [5] and He Li et al. [4] to obtain the Pd/zeolite catalyst which will be named as the Pd/zeolite-1 and Pd/zeolite-2 catalysts. Both of these catalysts will be observed and tested its activity in hydrodeoxygenation reaction to produce Renewable Diesel.

2. Methodology

2.1. Materials

The following chemicals were commercially available and used as received : oleic acid (Bratachem Indonesia) as a model compound of triglyceride, PdCl2 salt (Merck) and zeolite-Lampung (clinoptilolite type), HCl (Merck), KBr (Merck), NaOH (Merck), KOH (Merck), ethylene glycol or EG (Merck) and glycerol (Bratachem Idonesia).

2.2. Catalyst Preparation (Treatment 1)

Pd/zeolite-1catalysts with the Pd loading of 5% were prepared by microwave polyol method in the solution of EG polyols with PdCl₂ as a precursor salt. 0.05 M H₂PdCl₄ at 50 ml was prepared by dissolving 0.2 M PdCl₂ 25 ml with 25 ml of 0.4 M HCl. The solution was then added to 50 ml of ethylene glycol. The mixture was added with 10 grams of zeolite- Lampung (activated with 3 M HCl) and 0.8 M KOH. These mixture were then dispersed with ultrasonic for 45 minutes. After ultrasonic treatment, the solution was put into a household microwave oven and then heated at a temperature of 200°C for 3 hours.

2.3. Catalyst Preparation (Treatment 2)

Pd/zeolite-2 catalysts with the Pd loading of 5% were prepared by microwave polyol method in the solution of EG polyols and glycerol. Zeolite-Lampung was impregnated with 25 ml of 0.196 M PdCl2 and added with 1.6648 M KBr 25 ml. After ultrasonic treatment for 1 hour, the mixture was added with 0.2 M NaOH at 25 ml. The mixture was put into a household microwave oven and then heated for 2 minutes at 800W. Finally, the mixture was filtered, washed with distilled water and ethanol and dried in oven for 12 hours at 60 °C.

2.4. Catalyst Characterization

The catalysts were characterized by XRD to determine the nature and type of crystal catalyst, Autosorb-6B BET to determine area, pore size and pore volume of catalyst and SEM-EDX (JED-2300 Analysis Station JEOL) to determine the morphology and composition of the catalyst.

2.5. Hydrodeoxygenation of Oleic Acid

The Hydrodeoxygenation of oleic acid was carried out in a 330 mL semi batch stirred reactor. The ratio of oleic acid as model compound of vegetable oils and Pd/zeolite as catalyst was 100:1 The reactions were performed at temperature between 375° C and 400° C and H₂ pressure of 15 bar in batch stirred autoclave reactor. Every 15 minutes, the resulting gas was analyzed online by GC-TCD with adsorption column 6' x 1/8' SS packed with molecular sieve to identify the carbon dioxide, carbon monoxide and methane. The bottom product was distillated using Koehler Model K 45090 and characterized its physical properties such as : density (ASTM D86 using Stadbinger Densitometer), viscosity (ASTM D7042-04 using Viscometer SVM 3000) and cetane index. FT-IR (Shimadzu) and GC-MS (Agilent) were used to identify functional groups and components in the hydrodeoxygenation products respectively.

3. Result and Discussion

3.1. Results of Catalysts Characterizations

X-ray diffraction (XRD) pattern of Pd/zeolite-1 and Pd /zeolite-2 catalyts synthesized by microwave polyol method is shown in Figure 1. The peaks that appear in both catalyst is in the same 2θ values. The peak which first appears is the top constituent zeolite components such as SiO2 and Na(AlSi3O8) at a value of 2 θ =21.66 deg and 2 θ =22.42 deg of cristobalite and albite structures.

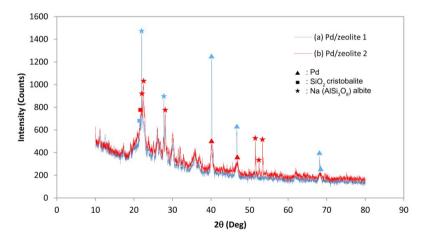


Fig. 1. Diffractogram of (a) Pd/zeolite-2 and (b) Pd/zeolite-1.

The XRD shows that Pd/zeolite formed are crystalline. Crystal diffractograms which construct Pd/zeolite-1 has a narrow peak and a high intensity compared with the diffractogram peak of Pd/zeolite-2. It shows that a well-formed crystals of zeolite-metal crystals and Pd-metal crystal in the catalyst Pd/zeolite-1 are much more crystalline than Pd/zeolite-2. This is caused by the low heating temperature of the Pd/zeolite-2 catalyst (60°C for 12 hours) so that the rate of solvent evaporation occurs only on the surface. This can allow the solvent trapped in the pores of the zeolite, it is not entrained perfectly and imperfect crystals formed. The size of Pd nanoparticle supported on zeolite (Pd/zeolite-1 and Pd/zeolite-2) estimated from the Debye–Scherrer formula are 23.40 nm and 90.94 nm.

	Surface Area (m ² /g)	Pore Size (Å)	Pore Volume (cc/g)	
Zeolite-Lampung	51.9	10.53	0.0045	
Pd/zeolite-1	27.26	9.91	0.0139	
Pd/zeolite-2	20.45	9.64	0.0098	

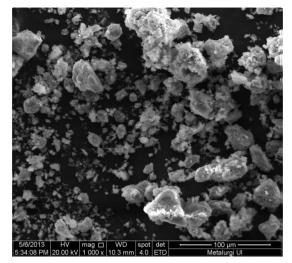
Table 1. Testing Result of Catalyst Using BET

BET shows that pore volume of the catalyst (Pd/zeolite-1 and Pd/zeolite-2) is greater than the unactivated natural zeolite-Lampung. This result shows that the activation process on the physical and chemical pre-treatment of zeolite successfully removed salts and alkaly-metal impurities which trapped in the pores of the catalyst. In catalysis reaction, large volume is needed to achieve the complete reaction, as the pore volume is the site of the reaction medium and can be regarded as a mini reactor. Furthermore, Table 1 shows the differences in the area of zeolite before Pd metal embedded and zeolite after Pd metal embedded. zeolite had a very large area before embedded by Pd metal, and slowly decreased after Pd metal entered into zeolite pores. This result is similar to the research performed by Therdthianwong et al. [9].

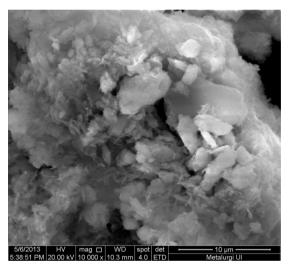
Pd/zeolite-1 catalyst at heating temperature 200°C for 2 hours, had a surface area, pore size and pore volume larger than Pd/zeolite-2 catalyst given heat treatment at a temperature of 60°C for 12 hours. This indicates that the heating at low temperatures can not vaporize impurities and polyols solvent which were still trapped in the pores of the zeolite. The obtained surface area of the catalyst was able to produce a fraction of collisions needed for the hydrodeoxygenation reaction. This is confirmed later through several physical test of Renewable Diesel product which show that the product was almost similar to the diesel specification.

From Figure 2, it can be seen that the Pd/zeolite-1 catalyst is still forming clots formed from a number of single particles. Number of single particles dispersed on the surface was very little. This shows that the catalyst obtained had a difference size. In general, the morphology of the resulting zeolite support in this study is similar to that produced by the morphologic Maroufi et al. [11] with the same type of zeolite (clinoptilolite type).

For confirming the core content of the active Pd and other metals in the catalyst, it was identified using EDX. The test result shows that the average yield active core Pd content in the catalyst was 4.09 wt%. This number is almost close to the number of active nuclei were added during preparation. The test results can be seen in Table 2.



(a)



(b)

Fig. 2. Catalyst Morphology of Pd/zeolite-1 (a) 1000xMagnification and (b) 10000xMagnification

Table 2.	Measuring	Result of	of Pd/zeolite-1	Catalyst	Using EDX.

Element	Wt (%)	Wt (%) Average		
	Particle A	Particle B	Particle C	
Pd	3.90	6.14	2.25	4.09
0	47.83	38.68	50.51	45.67
Al	9.10	7.82	7.87	8.26
Si	39.17	47.35	39.37	41.96

3.2. Renewable Diesel Synthesis With Hydrodeoxygenation Process

Activity catalyst test with hydrodeoxygenation process of oleic acid consisted of two main phases, namely activation of the catalyst and hydrodeoxygenation reaction stages. The activation of catalysts was carried out in order to provide selectivity performance during the reaction. Hydrodeoxygenation reactions were carried out after the catalyst activation completed and the reactor temperature reaches 100°C. In this study, there were produced 4 different liquid hydrocarbon products of Renewable Diesel, respectively are RD 1 (Pd/zeolite-2 at 375°C), RD 2 (Pd/zeolite-2 at 400°C), RD 3 (Pd/zeolite-1 at 375°C) and RD 4 (Pd/zeolite-1 at 400°C). The resulting products can be seen in Table 3.

Table 3. Hydrodeoxygenation Reaction Products.

Product	Bottom Pro	duct t	Condensate			
	Color	Viscocity	Color	Viscocity		
RD 1	Black	Liquid	Colorless	Liquid		
RD 2	Black	Liquid	Yellow	Liquid		
RD 3	Black	Liquid	Colorless	Liquid		
RD 4	Black	Liquid	Yellow	Liquid		

The bottom product of hydrodeoxygenation of oleic acid was still in mixture and had to be purified through distillation process. Distillation was carried out at a temperature in a range of 200°C Initial Boiling Point (IBP 200), 200-300°C and 300°C End Point (EP 300). Distillation products at temperature 300 EP were carried out to determine the physical and chemical properties of Renewable Diesel product.

3.2.1. Density of Renewable Diesel

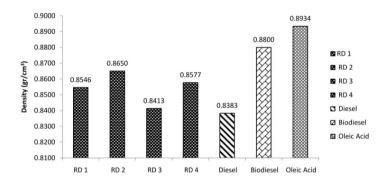


Fig. 3. Comparation of Density (Renewable Diesel, Diesel, Biodiesel and Oleic Acid)

From Figure 3 it can be seen that the density of Renewable Diesel is less than density of general biodiesel standard [13] and slightly higher than the density of commercial diesel. Density of oleic acid decreased due to oleic acid converted into Renewable Diesel. It shows that the cracking and hydrodeoxygenation reaction over Pd/zeolite catalysts occurred. Renewable Diesel produced using Pd/zeolite-1 at 375°C (RD 3) has better density quality than biodiesel and almost meet the specification of commercial diesel. This means that the oxygenation removal pathway of oleic acid over Pd/zeolite 1 catalyst was primarily compiled through decarboxylation at 375°C.

3.2.2. Viscosity of Renewable Diesel

Oleic acid used as a reactant in the synthesis of Renewable Diesel has a very high viscosity before hydrodeoxygenation. In Figure 4 it can be seen that the viscosity of oleic acid decreased after hydrodeoxygenation occured to convert oleic acid into Renewable Diesel. It was caused by the carboxylate bonding termination of oleic acid containing a carbonyl group (CO) and hydroxyl (-OH). Hydroxyl group in the carboxylic bond can form hydrogen bonds with the carbonyl group (CO) which lead to stronger bonds between the molecules and the higher viscosity.

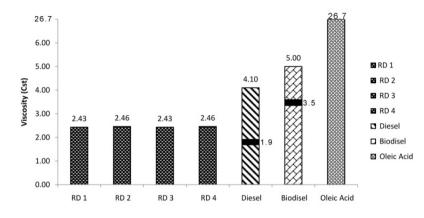


Fig. 4. Comparation of Viscosity (Renewable Diesel, Diesel, Biodiesel and Oleic Acid)

The viscosity of the Renewable Diesel products (RD 1 to RD 4) have already met the standards which refer to ASTM D- 975. The average viscosity obtained was 2.4 Cst which is on the range of standard viscosity ASTM D- 975 (1.9 to 4.1 Cst). In addition, the viscosity values generated by the Renewable Diesel product is much better comparing with the standard viscosity of biodiesel based on Standard EN 14214 with a minimum viscosity 3.5 Cst. Similar to the density analysis above, the use of catalysts Pd/zeolite 1 at 375oC is the optimum condition to obtain Renewable Diesel product with a viscosity approaching commercial diesel density.

3.2.3. Cetane Index of Renewable Diesel

Cetane index measurements performed to estimate the cetane number in the fuel. The cetane index value will not change if there is an addition some additive of cetane number into the fuel. Cetane index value is determined to find out the quality of combustion, emissions and the ability of the fuel to combust at the low temperature. The result of cetane index measurement can be seen in Table 4.

Table 4. Cetane Number of R	Renewable Diesel Products
-----------------------------	---------------------------

Product	Cetane Index				
	Renewable Diesel	Diesel			
RD 1	44.41	Minimum 40			
RD 2	46.63	Based on ASTM D-975			
RD 3	44.69				
RD 4	40.19				

Table 4 shows that the cetane index values of Renewable Diesel produced meet the minimum cetane index of diesel fuel (ASTM-D975). In general, the products of both types of catalysts at reaction temperatures 375oC and 400oC have a very suitable cetane index value, even better than diesel. The cetane index value was strongly influenced by the density and vapor temperature of Renewable Diesel read at the thermocouple.

3.2.4. Identification of Functional Groups Using FTIR

The FTIR shows that Renewable Diesel, diesel and oleic acid have the same great absorption on the wavelength 2924 cm-1 and 2854 cm-1. Absorption at a wavelength of 2924 cm-1 indicates the presence of C-H and C-C bonds. While, the absorption at 2854 cm-1 shows a typical absorption bands of aliphatic hydrocarbons, such as stretching vibration asymmetry and symmetry of C-H. Based on the IR spectra, it can be indicated that those three ingredients have a dominant hydrocarbon straight-chain compounds containing atoms C and H. Renewable Diesel, diesel and oleic acid have the same absorption at wavelength 1458 cm-1. The Absorption occur due to the stretching vibration of functional group-C = C-which shows the presence of an aromatic ring [14].

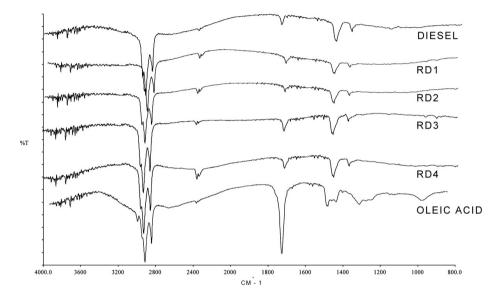
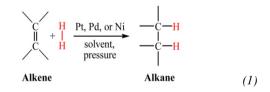


Fig. 5. Diesel, Renewable Diesel and Oleic Acid Spectrum.

Significant absorption at wavelength 3300 cm-1 occurs in oleic acid and does not occur in commercial diesel and Renewable Diesel. Absorption at this wavelength indicates the presence of alkene group in oleic acid which was not found in the Renewable Diesel product. This result shows that the catalytic hydrogenation reaction of oleic acid achieved and produced Renewable Diesel which have saturated hydrocarbons. This reaction is described on the following equation (1) [14].



IR absorption spectra in the wave number 1700 cm-1 occured in Renewable Diesel product, diesel and oleic acid. It shows the stretching vibration absorption of carbonyl groups such as ketones, aldehydes and carboxylic acids. Figure 5 shows that oleic acid has a wide IR absorption at these wave numbers which was indicated by the low transmission percentage (%T = 20%). It shows that oleic acid used as a raw material still has a carbonyl group (carboxylate group) which should be eliminated through hydrodeoxygenation. The IR absorption showed in small quantities with high percentage transmission (%T = 50-55%) was detected in the measurements, indicated as an aldehyde group resulting from the reduction reaction of carboxylic acids. This reaction is described in the equation (2) [14].

$$\begin{array}{c} \mathbf{O} \\ \mathbf{R} - \mathbf{C} - \mathbf{OH} \end{array} \xrightarrow[\text{H}]{} \begin{array}{c} [\mathrm{H}] \\ \text{reduction} \end{array} \xrightarrow{} \begin{array}{c} \mathbf{O} \\ \mathbf{R} - \mathbf{C} - \mathrm{H} \end{array}$$
(2)

In general, the result using FTIR shows that oleic acid used as a raw material was successfully converted into Renewable Diesel and its IR spectra had similarities with IR diesel spectrum that was used as a standard.

3.2.5. Identification of Bottom Product Using GCMS

From Table 5, it can be seen that the liquid bottom products consist of hydrocarbon fractions (C1-C25) and oxygenates such as acetone, alcohol, aldehyde, carboxylic acid, etc. The average mass percentage hydrocarbon fraction was more dominant than the oxygenate fraction which was above 50%. C13-C19 fraction was the primary hydrocarbons fraction contained in the bottom product suspected all as Renewable Diesel. The remaining oxygenate fraction in the product could be used as an indicator in determining hydrodeoxygenation reaction. In this study, hydrodeoxygenation of oleic acid produced the percentage of oxygenate contained in the product less than 50%

Table 5. Total Conversion, Total Hydrocarbon, Total Oxygenate and Total Percentage of Hydrocarbon Fraction (Selectivity and Yield).

Product	Conversion (%)	Selectivity (%)				Yield (%)				Total Hydrocarbon	Total Oxygenate
		C5- C11	C11- C13	C13- C19	C19- C25	C5- C11	C11- C13	C13- C19	C19- C25	(%)	(%)
RD 1	91.44	9.71	11.50	40.27	6.79	8.28	9.81	34.35	5.79	56.34	43.66
RD 2	87.82	5.01	8.43	33.12	2.28	3.45	5.80	22.81	1.57	42.76	57.23
RD 3	90.23	14.88	10.78	42.70	1.03	12.15	8.80	34.87	0.84	60.81	39.19
RD 4	93.34	8.31	12.19	40.11	3.07	6.87	10.09	33.185	2.54	53.33	46.67

Sample 3 reacted at 375°C over Pd/zeolite-1 was a sample that produced the largest mass percentage of hydrocarbon (60.81%) and smallest percentage of oxygenate (39.19%). Based on this result, it can be seen that the operating conditions at 375°C using Pd/zeolite-1 were the appropriate conditions to produce Renewable Diesel with the largest hydrocarbon content.

Hydrodeoxygenation produced bottom liquid product, condensate and gas. From Table 5 it can be seen that the largest conversion of reactants occurred at RD 4 products. However, it did not guarantee that RD 4 has the largest selectivity and yield of C13-C19 Fraction. It can be seen from Table 4 that RD 3 has the largest selectivity and yield of C13-C19 fraction, which is 42.72 % and 34.87 %.

3.3. Effect of Temperature and Catalyst on Distribution Product

To test the dependence of the hydrodeoxygenation on temperature and catalyst, a number of reaction runs were conducted at temperatures at 375° C and 400° C. The batch stirred autoclave reactor was charged with H₂ so that the pressure at the reaction temperature was 15 bar. The results of oleic acid hydrodeoxygenation are gathered in Figure 6 and 7, where RD 1 (Pd/zeolite-2 at 375° C), RD 2 (Pd/zeolite-2 at 400° C), RD 3 (Pd/zeolite-1 at 375° C) and RD 4 (Pd/zeolite-1 at 400° C).

From Figure 6 shows that with increasing temperature at the constant H_2 pressure, the rate of CO_2 formations (decarbocylation reaction) were more dominant than the rate of formation of CO (decarbonylation reaction) and methane gas (side reaction/methanation). It means that in the parameter range analyzed, decarboxylation was predominant and Pd/zeolite catalysts were selective to be used for hydrodeoxygenation of oleic acid. The temperature of 375°C was the optimum reaction temperature to break carboxylic groups on the reactants compared to the reaction temperature at 400 °C. It can be seen on the curve 6(a) and 6(c) where the percentage of volume generated at the optimum temperature of 375°C is \pm 60% (v/v) which is ten percent higher than the percent volume produced at a temperature of 400°C.

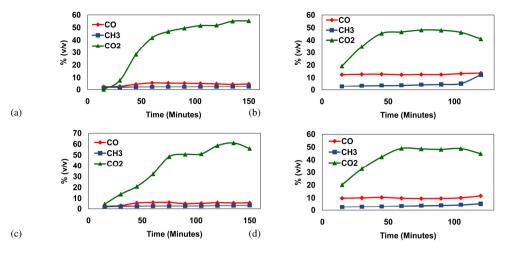


Fig. 6. Gas Rate Formation Curve (a) RD 1, (b) RD 2, (c) RD 3, (d) RD 4

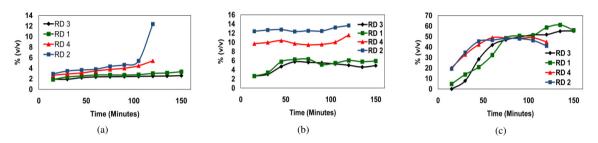


Fig. 7. Gas Rate Formation Curve (a) Methane, (b) Carbon Monoxide and (c) Carbon Dioxide

From figure 7 shows that utilization of Pd/zeolite-1 and Pd/zeolite-2 as catalyst in the hydrodeoxygenation of oleic acid at temperature of 375°C and 400°C had almost the same capabilities in directing path of reaction to decarboxylation. The difference between the two catalysts at the same temperature condition was the ability to control the side reaction such as water gas shift and methanation. From figure 7a, it can be seen that the catalyst Pd/zeolite-1 was able to suppress the rate of methane formation greater than Pd/zeolite-2. Similarly, the catalyst Pd/zeolite-1 was able to control the formation rate of CO gas greater than Pd/zeolite-2 either at temperature of 375°C or 400°C (figure 7.b). This result shows that the Pd/zeolite-1 catalyst has some characteristics that better than Pd/zeolite-2 catalyst and has a great influence in directing the reaction path to decarboxylation during the hydrodeoxygenation process.

The effect of temperature in the product distribution can be seen in figure 8. The results confirm that at constant pressure (15 bar) an increase temperature, from 375° C to 400° C, favors the production of condensate rather than bottom liquid product. It means that product of renewable diesel at temperature of 400° C could be lower than that at temperature of 375° C.

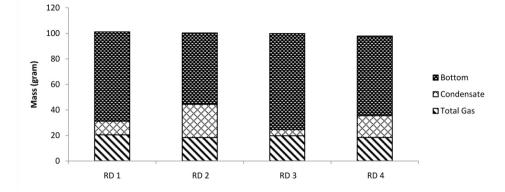


Fig. 8. Comparation of Gas, Condensate and Bottom For Each Product

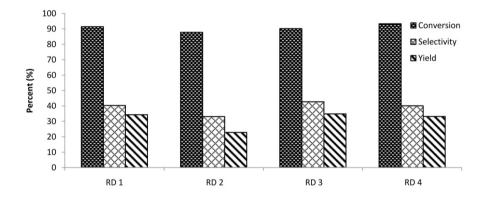


Fig. 9. Comparation of Conversion, Selectivity and yield For Each Product

Figure 9 summarizes the effect of temperature and catalyst on the conversion, selectivity and yield of renewable diesel. In general, the variation of the catalyst and the operating temperature produced high conversion even though the selectivity and yield was still low. Selectivity and yield of the four samples were strongly influenced by the reaction temperature. The yield and selectivity has been observed to rise at an optimum temperature of 375°C but with the increase in temperature yield reduces either using Pd/zeolite-1 or Pd/zeolite-2.

4. Conclusion

The Synthesis of Catalysts Pd/zeolite using treatment 1 was suitable in synthesizing Pd/zeolite catalysts through microwave polyol method. Catalyst Pd/zeolite-1 produced from treatment 1 had a high crystalline with Pd crystallite size 23.40 nm and has a surface area of 27.26 m²/g, pore size and pore volume 9.91 Å and 0.0139 cc/g.

FTIR shows that oleic acid used as a raw material successfully converted into the Renewable Diesel and its IR spectra of Renewable Diesel products have similarities with IR diesel spectrum used as the standard in this study. The average mass percentage of oxygenate in the product was less than 50%, the density and viscosity were below the value of biodiesel standard (EN-14214) and on the range of values of commercial diesel standard (ASTM D-975) and also, the cetane index obtained is above the lower limitation of commercial diesel cetane index (ASTM D-975). It means the oxygenation removal pathway of oleic acid over especially Pd/zeolite-1catalyst was primarily compiled through decarboxylation

Hydrodeoxygenation of oleic acid for synthesizing Renewable Diesel was performed on two Pd/zeolite catalysts. The main conclusions derived from this work are the following: Both Pd/zeolite-1 and Pd/zeolite-2 catalysts show quite good performance at temperatur of 375 $^{\circ}$ C and H₂ pressure of 15 bar : significantly they have suitable density and viscosity and quite high cetane index.

Acknowledgements

Directorate General of Higher Education- Indonesia Ministry of Education and Culture through Riset Madya UI 2012 is acknowledged for the financial support to carry out the present study.

References

- Amin R., Elzatahry A., El-Khatib K., Youssef M. Nanocatalyst Prepared by Microwave and Impregnation Methods for Fuel Cell Application. Int. J. Electrochem. Sci 2011;6:4572-4579.
- [2] Demirbas A. Importance of biodiesel as transportation fuel. Energy Policy 2007; 9: 4661-4670
- [3] Feng W., Yanhong L., Chuan W. Preparation of Pt/C Nanocatalyst by Ethylene Glycol Method in Weakly Acidic Solution. J. Mater. Sci. Technol 2010;26(8):705-710.
- [4] He Li., Shichao Z., Shaohui Y., Ye L., Yanbiao R. Pd/C Catalyst Synthesized by Microwave Assisted Polyol Method for Methanol Electro-Oxidation. International Journal of Electrochemical Science 2013;8:2996-3009.
- [5] Jie Z., Weixiang C., Yifan Z., Xiang L., Zhude X. Microwave polyol synthesis of Pt/C catalysts with size-controlled. J Mater Sci 2006;41:5514-5518.
- [6] Knothe G, Sharp CA, and Ryan TW. Exhaust Emissions of Biodiesel, Petrodiesel, Neat Methyl Esters, and Alkanes in a New Technology Engine. Energy & Fuels 2006;20:403-408.
- [7] Knothe G. Designer Biodiesel: Optimizing Fatty Ester Composition to Improve Fuel Properties. Energy and Fuels 2008; 22 (2): 1358-1364
- [8] Lestari S., Palvi MA., Kari E., Beltramini J., Max L., Dmitry YM. Diesel-Like Hydrocarbons from Catalytic Deoxygenation of Stearic Acid Over Support Pd Nanoparticles on SBA-15 Catalyst. Catalyst Letter 2010;134:250-257.
- [9] Therdthianwong S., Chairut S., Apichai T. Improvement of Coke Resistance of Ni/Al2O3 Catalyst in CH4/CO2 Reforming by ZrO2 Addition. Fuel Processing Technology 2008;89(2):160-168.
- [10] Boyás R. S., Yanyong L., Tomoaki, M. Production of Green Diesel By Hydrocracking of Canola Oil On Ni-Mo/γ- Al2O3 And Pt-Zeolitic Based Catalysts. Instituto Politécnico Nacional 2008:2-7.
- [11] Maroufi, N. G., Khatamian M., Salari D., Niaei A. Effect of Ultrasound on Modified Nano Catalyst of Transition Metal-Zeolite in VOC Catalytic Oxidation. Proceedings of the 4th International Conference on Nanostructures 2012:1-3.
- [12] Boyas RS., Zarraga FT., Loyo FD. Hydroconversion of Triglycerides into Green Liquid Fuels. ISBN 978-953-51-0785-9;2012
- [13] Drapcho CM., Nhuan NP., Walker TH. Biofuels engineering Process Technology. United State: McGraw-Hill;2008.
- [14] Solomon TG. Fundamental of Organic Chemistry. 5th Edition ed. New York: John Wiley and Sons. 1997.