

PAPER • OPEN ACCESS

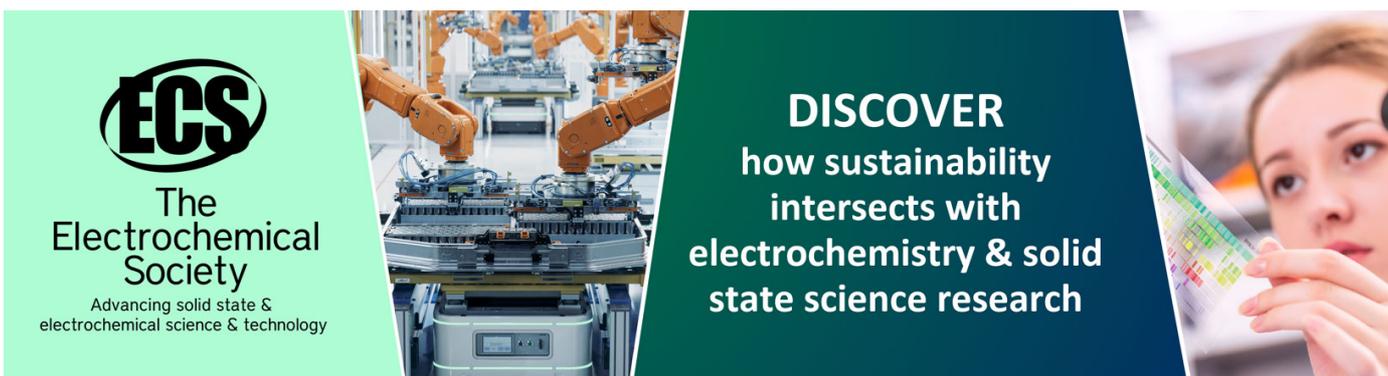
Synthesis of green diesel through hydrolysis and hydrodeoxygenation reaction from waste cooking oil using NiMo/Al₂O₃ catalyst

To cite this article: R U Putri *et al* 2018 *IOP Conf. Ser.: Earth Environ. Sci.* **105** 012051

View the [article online](#) for updates and enhancements.

You may also like

- [Effect of Support on the Hydrodeoxygenation of Phenol using Ni-based Metal Catalysts: Ni/SiO₂, Ni/ZrO₂, and Ni/Al₂O₃](#)
Arda Rista Lestari, Suratmo and Siti Mariyah Ulfa
- [Hydrodeoxygenation \(HDO\) of oleochemical waste oil into paraffins using iron molybdate \(Fe-Mo-O\) catalyst](#)
N A Mohamad, S P Foo, M Nagai *et al.*
- [Influence of Solvent on Liquid Phase Hydrodeoxygenation of Furfural-Acetone Condensation Adduct using Ni/Al₂O₃-ZrO₂ Catalysts](#)
S M Ulfa, A Mahfud, S Nabilah *et al.*



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Synthesis of green diesel through hydrolysis and hydrodeoxygenation reaction from waste cooking oil using NiMo/Al₂O₃ catalyst

R U Putri¹, B H Susanto¹, D F Pratama¹ and M B Prakasa¹

¹Chemical Engineering Department, Universitas Indonesia

Kampus Baru Universitas Indonesia, Depok 16424, Indonesia

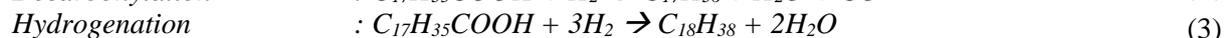
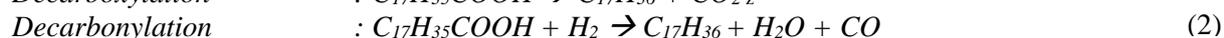
E-mail: bambanghs@che.ui.ac.id

Abstract. Green diesel is a second generation of biofuel that has a potential to answer the energy needs in Indonesia, also in the world. The reactions used to produce green diesel are hydrolysis and hydrodeoxygenation by using NiMo/Al₂O₃ catalyst. Hydrolysis will change the triglycerides in the raw material, which is waste cooking oil into free fatty acids (FFA) and then converted into green diesel through hydrodeoxygenation. Hydrolysis of waste cooking oil carried out at temperature of 200°C and pressure of 16 bar for 3 hours with water and oil volume ratio of 1:1. FFA product of hydrolysis is as much as 73.89%. For hydrodeoxygenation, variation in operating condition used are 375°C with pressure of 12 bar and 400°C with pressure of 15 bar. Characterizations of green diesel have shown that both of hydrodeoxygenation products have met the specifications of diesel, except the acid number with optimum operating condition at 400°C and pressure of 15 bar. These conditions with NiMo/Al₂O₃ activated led to dominant yield of 68.87% of diesel fraction, selectivity of 69.58%, and conversion of 82.15%.

1. Introduction

Due to depletion of crude reserves, shortage in petroleum supply, and increased demand for clean hydrocarbon fuels, the production of renewable fuels has emerged to solve this problem. As a result, nowadays more consumers are turning to biodiesel instead of petroleum-based diesel for transportation. Unfortunately, biodiesel has low oxidative stability, higher viscosity, higher cloud point and pour point, higher nitrogen oxides (NO_x) emissions, lower energy density, and higher injector or engine wear [1]. To avoid the disadvantageous physical properties of oxygenated fuels, hydrodeoxygenation has been investigated as an alternative pathway of biofuel production.

Hydrodeoxygenation is a series of reactions that convert the molecular structure of triglyceride in oil to linear hydrocarbon and it means removal of oxygen from an oxygen-containing compound under hydrogen pressure at high temperatures and pressure with heterogenous catalyst, which product known as green diesel [2]. The hydrodeoxygenation process consisted of decarboxylation, decarbonylation, and hydrogenation reactions [3]. The main drawback of this reactions seem to be large consumption of hydrogen during the process, which increase the production cost.

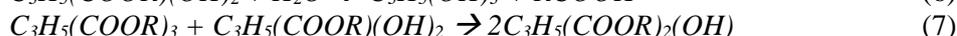
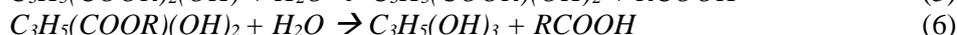
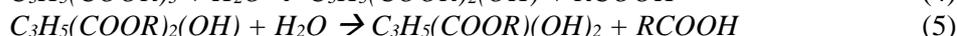
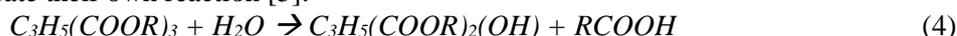


The green diesel that obtained directly by hydrodeoxygenation is mainly composed by C17 and C18 n-paraffins that have a high cetane number. To produce green diesel, the reaction needs catalyst, as the



acid sites of the catalyst promote the conversion of larger alkyl chains into smaller chains, so that the NiMo/Al₂O₃ is used. Besides, it has been observed that NiMo/Al₂O₃ catalyst promote hydrodeoxygenation to have high selectivity toward diesel range products [4]

The feeds of hydrodeoxygenation are free fatty acids, so they need hydrolysis as a pre-treatment to increase the free fatty acids which in the end will increase selectivity, yield, and conversion of green diesel product. When water is maintained at temperatures within the range of its boiling point (100°C) and its critical point (374°C) and kept in the liquid state, this is referred to as the subcritical water condition. For the hydrolysis of the oil, subcritical water presents higher solubility in the oil due to the modification of its properties, such as a reduction in its dielectric constant with increasing temperature. Thus, water in subcritical conditions in hydrolysis acts both as reactant and as a solvent for a reaction. Free fatty acids which are formed in the hydrolysis reaction of vegetable oils, they act as acid catalysts and are able to accelerate their own reaction [5].



In the reaction above, triglycerides are converted to diglycerides and FFA (RCOOH), then to monoglycerides and FFA, and ultimately into glycerol and FFA.

The aims of this experiment are to know the best operating condition of hydrolysis and hydrodeoxygenation reactions and also to produce green diesel in high conversion, selectivity, and yield from waste cooking oil.

2. Methodology

2.1. Materials

The materials needed in this experiment are: waste cooking oil (household waste), NiMo /Al₂O₃, ethanol (Merck), potassium hydroxide (Merck), phenolphthalein (Merck), Wijs solution (Merck), potassium iodide (Merck), chloroform (Merck), amylum (Merck), sodium thiosulfate (Merck), and aquadest (Merck).

2.2. Pre-treatment of Waste Cooking Oil Through Hydrolysis

Hydrolysis was performed in 330 mL batch stirred autoclave reactor integrated with a condenser and furnace. Extensive stirring of the oil and water in the reactor was achieved using a magnetically driven stirrer with a DC geared motor. Waste cooking oil and water was used as feed with ratio of 1:1 % wt. Temperature and pressure during the reaction was kept constant at 200°C and 16 bars, also the stirrer speed at 500 rpm. Nitrogen was used to give the reactor pressure [4]. Reaction time was varied from one to three hours. The best result of hydrolysis with optimum reaction time would be used as hydrodeoxygenation feed.

2.3. Hydrodeoxygenation of Waste Cooking Oil

The reaction was performed in the same reactor with same equipment as hydrolysis. Hydrolysis product and NiMo/Al₂O₃ catalyst was used as feed with ratio of 100:1 % wt. Nitrogen gas purged for 30 minutes. Stirrer speed during the reaction was kept constant at 800 rpm. The reaction has two different operating condition i.e. 375°C at 12 bar and 400°C at 15 bar. The reactions were performed at temperature of the reactor reached the target value and the hydrogen pressure was adjusted to desired value. From this time onwards, the reaction time was occurred. In this step, the double bonds that were present in the triglycerides were saturated with hydrogen gas. The gas products were condensed and collected as condensate. The bottom product was distilled according to the boiling range of petroleum products in three categories i.e. IBP-200°C, 200-300°C, and 300-EP [5].

2.4. Hydrolysis and Hydrodeoxygenation Product Characterization

Hydrolysis and hydrodeoxygenation products were characterized by GC-MS (Agilent) to identify fraction component of sample, FTIR (Termo Scientific) to know the functional groups of the product, and GC-TCD to know the gas consumption and formation. Chemical properties of green diesel were

investigated through iod number and acid number to know the amount of double bonds and free fatty acids in the products. Acid numbers were determined by titration with KOH whereas iod number with $\text{Na}_2\text{S}_2\text{O}_3$. Physical properties of green diesel were investigated through density, viscosity, and cetane index to know the quality of the products.

3. Result and Discussion

3.1. Pre-treatment of Waste Cooking Oil Through Hydrolysis

Waste cooking oil has a low free fatty acid content caused by the presence of triglyceride bonds in large quantities. Figure 1 shows that the longer the reaction time, the more triglycerides are changed to free fatty acids, so it can increase the feed for the hydrodeoxygenation process. The optimum reaction time for hydrolysis is at 3 hours.

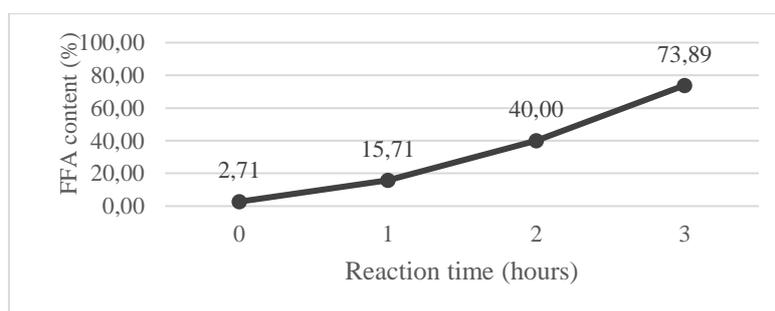


Figure 1. Effect of hydrolysis time on free fatty acid content.

The success of waste cooking oil pre-treatment through hydrolysis is indicated by the result of purer free fatty acids and the loss of glycerols. Table 1 shows an increase in the amount of fatty acids characterized by an increase in the percentage of palmitic acid, also the formation of lauric acid and myristic acid. This indicates the breakdown of triglycerides to free fatty acids and glycerol, but glycerol cannot be seen in GC-MS results because it has dissolved in water during heating, then evaporated with water.

Table 1. GC-MS results of WCO and hydrolysis products

Substances	WCO		Substances	HDR	
	RT	Content (%)		RT	Content (%)
Palmitic Acid	11.77	27.89	Lauric Acid	8.88	33.72
Oleic Acid	12.93	58.83	Myristic Acid	10.41	56.81
Palmitic Acid Chloride	13.82	2.57	Palmitic Acid	11.99	0.12
Oleylaldehyde	14.83	3.81	Oleic Acid	13.17	0.19
16-Dehydropregnonolone	14.91	2.46	Petroselenic Acid	13.62	1.57
1-Monopalmitin	15.02	1.89	1-Mono-Olein	14.62	0.18
2,3-Dihydroxypropyl elaidate	16.22	1.37	1-Methyl-4-Phosphorinanone	14.88	0.48
Squalene	17.34	1.18	2-Ethylbutyric Acid, eicosyl ester	14.99	0.75
			1-Monopalmitin	15.12	4.99
			3-butyl-thiophene-1,1-dioxide	16.01	0.38
			1-Mono-Stearin	16.49	0.44
			(acetoxymethyl)methyl [(trimethylsilyl)methyl]silane	16.13	0.36

3.2. Green Diesel Synthesis Through Hydrodeoxygenation

Hydrodeoxygenation was carried out under two different operating conditions, at 375°C with 12 bar pressure (HDO12) and 400°C with 15 bar pressure (HDO15). Table 2 shows that green diesel has met all the specifications of diesel fuel based on Indonesia National Standard (SNI) of biodiesel and diesel fuel, except the acid number. It means that there are still many free fatty acids that have not been converted into alkanes, so the reactions have not run optimally. A decrease in the iod number indicates that the double bond on green diesel has been reduced compared to waste cooking oil feedstock.

The decrease in the density value due to long carbon chain bonds in the waste cooking oil has been broken into short carbon chains so that the molecular weight of green diesel products will decrease. While the decrease of viscosity caused by the breaking of carboxylic bond from the waste cooking oil containing carbonyl (CO) and hydroxyl (-OH). The increase of cetane index on green diesel shows better combustion quality compared to SNI of biodiesel and diesel.

Table 2. Properties comparison of Green Diesel and Other Product

Sample	Iod Number	Acid Number	Density	Viscosity	Cetane Index
HDO12	80.37	3.14	0.87	4.80	51.23
HDO15	66.83	1.35	0.83	4.50	55.68
HDR (hydrolysis product)	-	146.31	0.92	40.26	-
WCO (feedstock)	106.60	4.94	0.93	40.80	-
SNI of Biodiesel	115.00	0.80	0.85-0.89	2.30-6.00	51.00
SNI of Diesel	170.00	0.60	0.82-0.87	2.00-5.00	40.00

Functional groups of the product investigated by FTIR. Figure 2 shows that on the spectra of waste cooking oil (WCO) and hydrolysis product (HDR), there are still a C=O and C-O groups which are carboxylic acid. Whereas in the spectra of HDO12 and HDO15, the C=O group has been decreased and C-O group has disappeared. It means that the carboxylic acid has been well disentangled. There is also a decrease in the =CH₂ group of the waste cooking oil, the hydrolysis reaction, to the hydrodeoxygenation reaction, in which the group is identified as an alkene. It can be concluded that the alkene has been able to broke properly through hydrodeoxygenation into alkane. From properties of green diesel and FTIR result, the optimum condition of green diesel production is at 400°C and 15 bar.

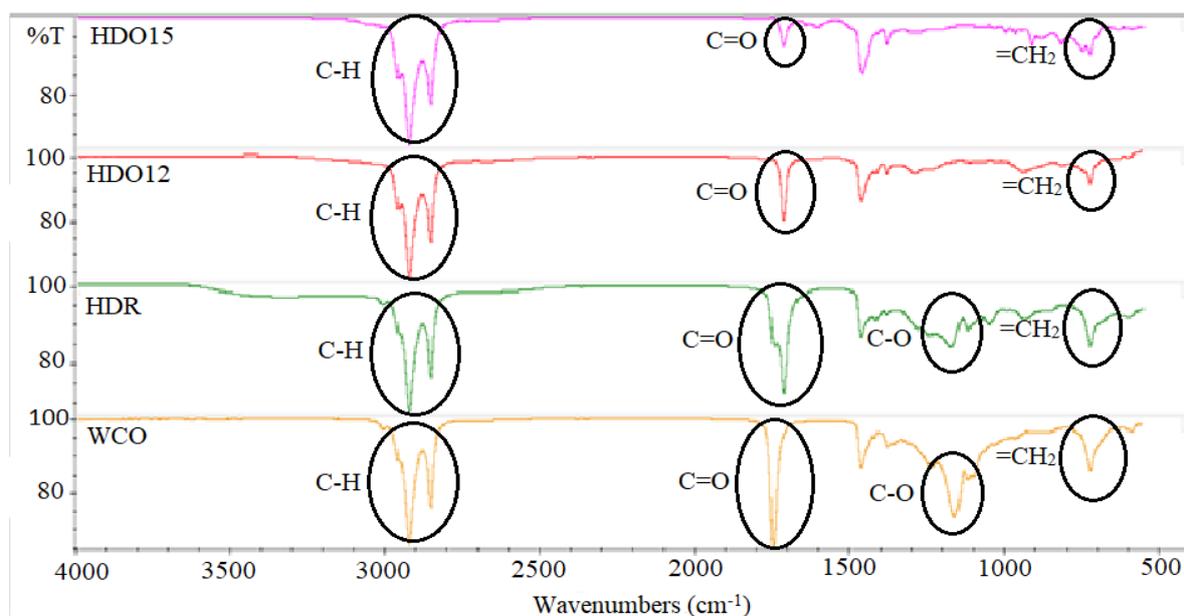


Figure 2. FTIR result of green diesel

Figure 3 and 4 shows that CO gas formation is larger than CO₂ and CH₄ which means NiMo/Al₂O₃ catalyst leads to the catalytic decarbonylation reaction compared to decarboxylation and methanation, where the reaction requires hydrogen to produce heptadecane, CO gas, and water. The presence of gas and water generated from the main reaction encourages the formation of water-gas shift side reactions, where the CO gas and water produced from the decarbonylation reaction reach equilibrium conditions and produce CO₂ and H₂ gases. The use of a particular catalyst may cause the reaction to be reversible, so that the CO gas will increase. From the GC-TCD test results, it can be concluded that the use of NiMo/Al₂O₃ catalysts has been able to direct to the main reaction, although it still requires a lot of H₂ gas for the decarbonylation reaction compared with decarboxylation.

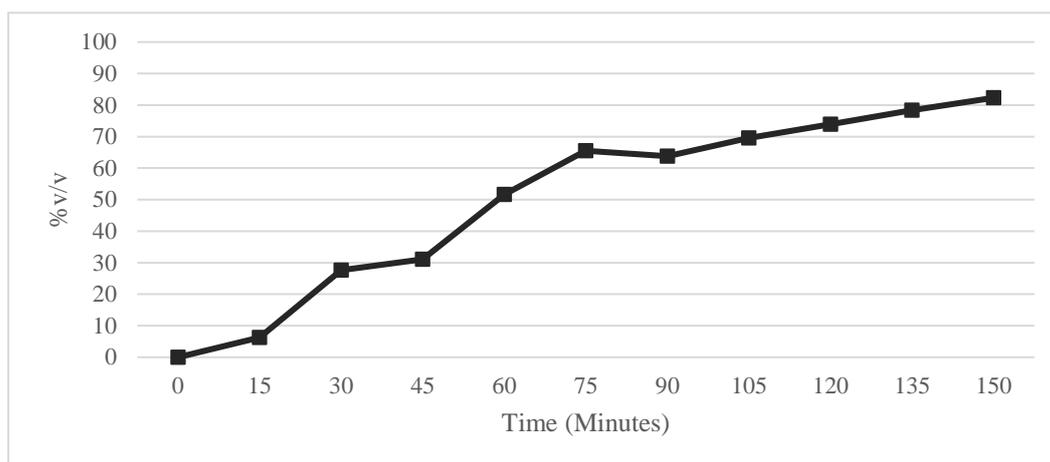


Figure 3. Graph of gas consumption rate

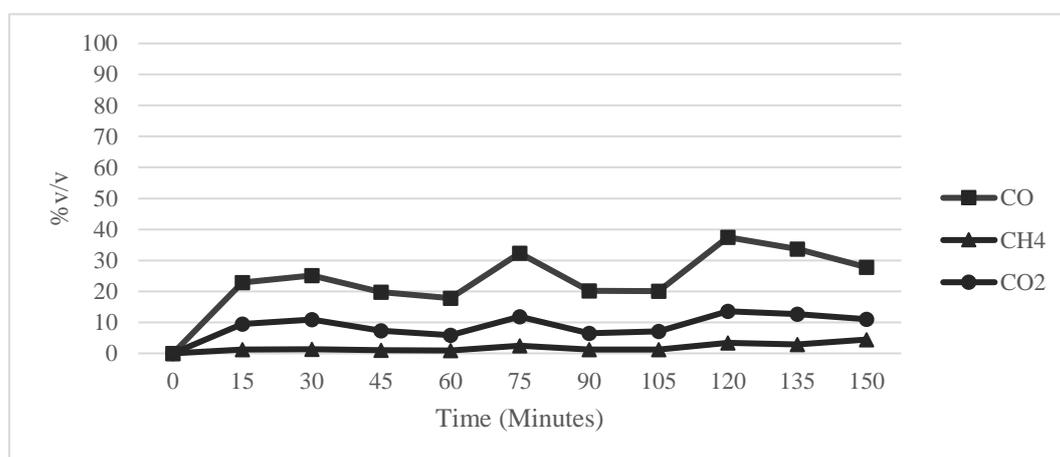


Figure 4. Formation of hydrogenated gas

Conversion, selectivity, and yield are the success parameters of hydrodeoxygenation process in producing green diesel product. The greater the value of the three parameters, the better hydrodeoxygenation process. Table 3 shows that the largest percentage of selectivity, yield, and conversion of green diesel occurred at HDO15. It means that the optimum operating condition of hydrodeoxygenation achieved at 400°C and pressure of 15 bar.

Table 3. Selectivity, yield, and conversion of distillation product

Product	% Selectivity	%Yield	%Conversion
Biogasoline	8.44	8.36	
Biokerosene	7.17	7.10	82.15
Green diesel	69.58	68.87	
Lubricant	11.93	11.81	

4. Conclusion

In this study, green diesel is produced through hydrolysis and hydrodeoxygenation reaction using NiMo/Al₂O₃ catalyst. Characterizations of green diesel have shown that both of hydrodeoxygenation products have met the specifications of diesel, except the acid number with optimum operating condition at 400°C and pressure of 15 bar. These conditions with NiMo/Al₂O₃ activated led to dominant yield of 68.87% of diesel fraction, selectivity of 69.58%, and conversion of 82.15%.

5. Acknowledgement

Director of Research and Community Service through International Indexed Publication Grant for Student Thesis (PITTA) Universitas Indonesia 2017 is acknowledged for the financial support to carry out the present study.

6. References

- [1] Rogelio S B, Fernando T Z, and Felipe D J H L 2012 *Hydroconversion of Triglycerides into Green Liquid Fuels*. *InTech* 338
- [2] Rogelio S B, Yanyong L and Tomoaki M 2010 *Production of Green Diesel by Hydrocracking of Canola Oil on Ni-Mo/Al₂O₃ and Pt/zeolitic based catalysts 2-7*
- [3] Bambang H S, Muhammad B P, and Muhammad H S 2016 *Synthesis of renewable diesel through hydrodeoxygenation reaction from nyamplung oil (Calophyllum Inophyllum oil) using NiMo/Z and NiMo/C catalysts with rapid heating and cooling method*. *IOP Conf. Ser. Mater. Sci. Eng.* **162** 12009
- [4] Luciana P T, Carine T A, Ednildo A T, Heloysa M C A, Fernando L P P and Silvio A B V D M 2015 *Hydrolysis of waste frying oils in subcritical water for biodiesel production by esterification using a heterogeneous catalyst*. *Chem. Eng. Trans.* **43** 565–570
- [5] Bambang H S, Mohammad N and Andri W 2014 *Synthesis of Renewable Diesel through Hydrodeoxygenation Using Pd/zeolite Catalysts*. *Procedia Chem.* **9** 139–150