

# Synthesis of bioavture through hydrodeoxygenation and catalytic cracking from oleic acid using NiMo/Zeolit catalyst

Michelle Flavin Carli<sup>1</sup>, Bambang Heru Susanto<sup>1,\*</sup>, and Thareq Kemal Habibie<sup>1</sup>

<sup>1</sup>Chemical Engineering Department, University of Indonesia, Kampus Baru Universitas Indonesia, Depok 16424;

**Abstract.** Currently, fossil fuels are still the primary source of fuel. As has been known, fossil fuel especially aviation fuel is limited resources and can increase greenhouse gas emissions. This condition encourages replacement efforts of avture into bioavture fuel. In this research, bioavture is synthesized through hydrodeoxygenation and catalytic cracking from oleic acid as a model compound using NiMo/Zeolite catalyst. Hydrodeoxygenation carried out under operating conditions: at temperature of 375°C, under 15 bar pressure and for 2.5 hours. The chain of hydrocarbons from the result of hydrodeoxygenation has been cracked by catalytic cracking reaction for 1.5 hours. Variation operating condition used are 360, 375, and 390°C. The liquid product is tested its chemical characteristic, ie acid number, FTIR and GC-MS and its physical characteristics, ie density test and viscosity. Bioavtur that synthesized by catalytic cracking have met the specifications of bioavtur, except the acid number with optimum temperature at 375°C. These conditions with NiMo/Zeolite activated led to dominant yield of 36.32%, selectivity of 38.05%, and conversion of 84.30%. Percentage of yield and selectivity of bioavtur are still low caused by performance of catalyst that is still can not optimum. While, high percentage of conversion caused by high temperature used for catalytic cracking.

## 1 Introduction

Every year, the national energy sector always faces challenges in the utilization of fossil fuels especially fuel oil, which shows the increase of consumption continually. One of fuel oil is the aviation fuel, commonly called avture or jet fuel. From 2005 to 2011, the consumption of aviation fuel in Indonesia is almost always greater than the production that must be fulfilled through imports. Indonesia's aviation fuel consumption in 2014 reached 4.2 million kiloliters (KL) while production from domestic refineries reached only 3.3 million KL, so the balance of aviation commodities recorded a deficit of 0.9 million KL [1]. This condition encourages the search effort of alternative aviation fuels as a substitute for petroleum-based energy supply.

As has been known, bioavture is a fuel aircraft similar avture (aviation turbine) which generally use vegetable oil as raw materials. One of the most abundant vegetable oils in Indonesia and widely used as feedstock for biofuel production is palm oil.

Source of raw materials used for bioavture production in this study is a compound model one of the unsaturated fatty acids contained in vegetable oil, namely oleic acid (C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>). The use of oleic acid as a raw material aims to represent one of the double bonds of fatty acids contained in vegetable oils, thereby the characterization of bioavture production process, optimum operating conditions, and pathways of reaction can be obtained easier and these parameters can be used as reference for conversion vegetable oils to bioavtures.

Oleic acid can be converted by some methods, such as thermal cracking, catalytic cracking, hydrocracking, hydrodeoxygenation, etc.

In this research, oleic acid converted by hydrodeoxygenation and catalytic cracking. Hydrodeoxygenation method is a hydrogenolysis process that aims to remove oxygen from a material buy cutting off the carbon-oxygen bonds using hydrogen pressure. During the hydrodeoxygenation (HDO) process, oils and fats essentially consisting of triglycerides, which are molecules with higher levels of oxygen, are subjected to high H<sub>2</sub> pressures and high temperatures in the presence of metal catalysts. At the end of the process, n-paraffins are produced as the constituents of gasoline, jet fuel, and diesel. The principal chemical reactions that occur during the HDO process are: decarboxylation, decarbonylation, and hydrogenation [2].

Decarboxylation reaction is the expected reaction during the hydrodeoxygenation process. Decarboxylation is the reaction of the breaking of the carboxylic bond in the vegetable oil. The success of the decarboxylation is the parameter of success in generating bioavtures. Cabon dioxides gas produced during the production process is the number of carboxylate groups that have been disconnected from the reactants.

Meanwhile, catalytic cracking is reaction breakdown of hydrocarbon compounds that have large molecules into smaller molecules at high temperatures with the aid of a catalyst. The process of catalytic cracking is a simple method and effective for the manufacture of biofuel [3]. In the catalytic process of the compound

\* Corresponding author: [bambanghs@che.ui.ac.id](mailto:bambanghs@che.ui.ac.id)

with high molecular weight in raw material will be broken down into compounds with a small molecular weight such as gasoline, kerosene, and diesel with use catalyst [4] [5].

Commonly used catalysts are nickel metal catalyst (Ni) and molybdenum (Mo). The core of catalyst needs to be distributed on a surface of support catalyst, one of which is zeolite. The use of zeolite as a support catalyst is due to three-dimensional structure of a highly porous zeolite and has a fairly wide pore space which is indicated by the large volume and pore diameter of the zeolite [6]. The type of zeolite used in this study is natural zeolite, because of its abundant availability in nature and has an affordable price.

## 2 Methodology

### 2.1 Materials

The materials used in this experiment are: Oleic Acid Technical Grade was purchased from TnT Chemical (Bandung, Indonesia), NiMo/Zeolite, ethanol (Merck), barium hydroxide (Merck), phenolphthalein (Merck), kalium phthalat (Merck), and aquadest (Merck).

### 2.2 Hydrodeoxygenation

Hydrodeoxygenation 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. Nitrogen gas purged for 30 minutes. To ensure the activity of catalyst, 1.5 g NiMo/Zeolite which has been prepared by impregnation method was maintained in the reactor at 300 °C under 10 bar of H<sub>2</sub> pressure for 1 h. After that, 150 ml oleic acid was added. The mixture was heated to 375 °C under 15 bar of H<sub>2</sub> pressure for 2.5 h. Stirrer speed during the reaction was kept constant at 800 rpm. To check the reaction has occurred or not, the gas product was taken every 15 minutes and tested with GC-TCD. In this step, the double bonds and the oxygen that were present in the triglycerides were saturated with hydrogen gas. The gas products were condensed and collected as condensate.

### 2.3 Catalytic Cracking

Catalytic cracking was performed in the same reactor with same equipment as hydrodeoxygenation. Hydrodeoxygenation product and NiMo/Zeolite 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 three different operating conditions i.e. 360°C, 375°C and 390°C. The temperature of the reactor reached was adjusted to desired value. The reaction was occurred for 1.5 h. In this step, the chain of hydrocarbons of hydrodeoxygenation product were cracked into shorter chains. 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 [7].

## 2.4 Characterization of HDO and CC Product

Hydrodeoxygenation and catalytic cracking 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 bioavtur were investigated through acid number to know the amount of free fatty acids in the products. Acid numbers were determined by titration with KOH. The samples were assayed in triplicate and the analysis was conducted in accordance with ASTM D3242. Physical properties of bioavtur were investigated through density, and viscosity to know the quality of the products.

## 3 Result and Discussion

### 3.1 Synthesis of Bioavtur

Products produced from synthesis through hydrodeoxygenation and catalytic cracking reaction is divided into two, top product formed in the gas form and bottom product in the liquid form. Then, bottom product that have been distilled is characterized to determine the optimum operating condition.

#### 3.1.1 Density of Bioavtur

Physical properties that become one of the parameters in the quality of fuel is the density, which is the unit of fuel weight per unit volume.

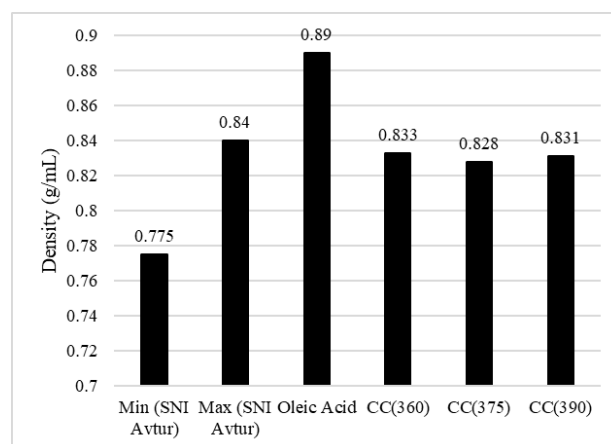


Fig. 1. Comparison of Density

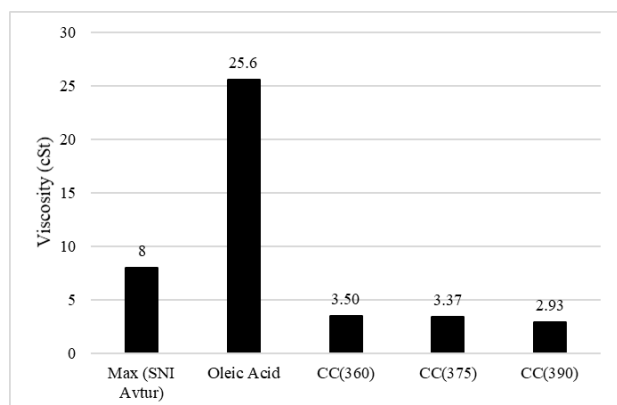
Figure 1 shows the decrease in density from raw material in the form of oleic acid to bioavtur. This change indicates that hydrodeoxygenation and catalytic cracking reactions have occurred over the NiMo/Zeolite catalyst. The decrease in the density value due to long carbon chain bonds in the oleic acid has been broken into short carbon chains so that the molecular weight of bioavtur products will decrease. From Figure 1, we can

also see that catalytic at 375°C has better density than catalytic cracking at 360°C and 390°C and meets the specifications of commercial avtur..

### 3.1.2 Viscosity of Bioavtur

Viscosity is a resistivity parameter possessed by a fluid discharged in a capillary tube, expressed in units of time required to travel a certain distance.

Figure 2 shows that the product's viscosity of catalytic cracking at 360, 375 and 390°C are respectively 3.50, 3.37 and 2.93 which are still in the range of commercial avtur viscosity referring to ASTM D1655. The graphs also shows the decrease in viscosity from raw material in the form of oleic acid to bioavtur. The decrease of viscosity caused by the breaking of carboxylic bond from the waste cooking oil containing carbonyl (CO) and hydroxyl (-OH). The presence of a hydroxyl group on a carboxylic bond may form a hydrogen bond with a carbonyl group that causes the bonding between molecules become stronger and higher viscosity value [8].

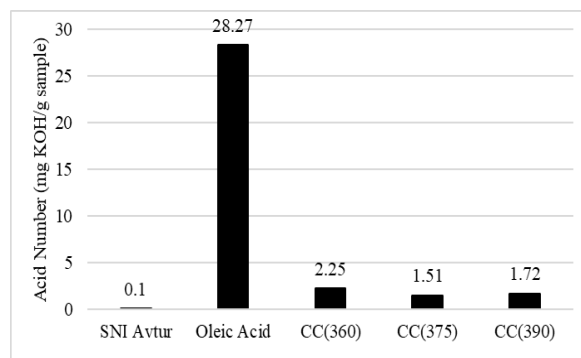


**Fig. 2.** Comparison of Viscosity

### 3.1.3. Acid Number of Bioavtur

The higher the acid number indicates that there are still many free fatty acids in a sample.

Figure 3 shows that all products of bioavtur have not met the specifications of avture based on Indonesia National Standard (SNI) for the acid number parameter. It means that there are still many free fatty acids that have not been converted into alkanes, so the reactions have not run optimally. Figure 3 also shows a decrease in the value of the acid number in the products, indicates the catalytic cracking occurred well and cracked the carboxylic acid group contained in the raw material into alkane hydrocarbons.



**Fig. 3.** Comparison of Acid Number

### 3.1.4. Fouried-Transform Infrared Spectroscopy

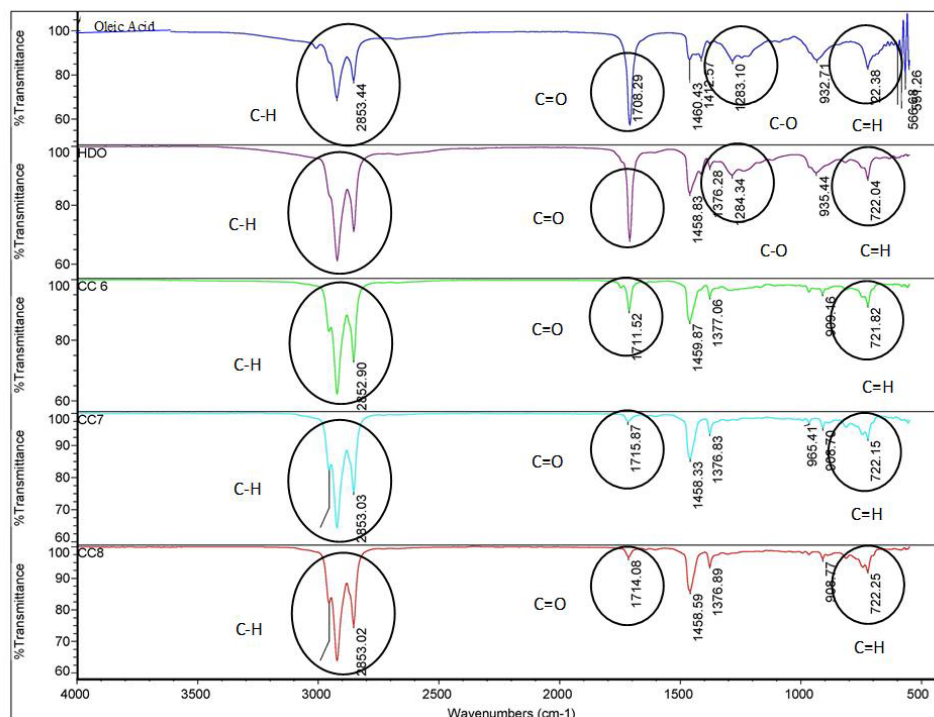
The functional groups of hydrodeoxygenation and catalytic cracking products are detected by FTIR. In Fig. 4, it can be seen that oleic acid, hydrodeoxygenation product, and catalytic cracking products which is bioavtur, have absorption at the wavelength range of 2921  $\text{cm}^{-1}$ , indicates the presence of alkane group (C-H). From Table 1, it can be seen that the decrease of the transmittance value of the alkane group is followed by the increase of the transmittance value of the alkene group. This change indicates that the alkenes have been cracked become alkane groups.

Table 1 also shows on the raw material and bioavtur product, there are carbonyl group (C = O) which read at the wavelength of 1700-1750  $\text{cm}^{-1}$ , where there is a significant increase of transmittance value from raw material in the form of oleic acid to the final product of bioavtur. This indicates that the carboxylate group has been cracked in the raw material. However, once those peaks did not disappear completely, it means that there was no full conversion when using the tested experimental conditions.

### 3.1.5 Gas Chromatography-Mass Spectroscopy

To evaluate the compounds synthesized in the HDO and CC reactions, the gas chromatography technique coupled with mass spectrometry was used.

The CC reaction products can be used to formulate biogasoline (5 to 8 carbon atoms), jet fuel (9 to 15 carbon atoms), green diesel (16 to 20 carbon atoms) and lubricant (21 to 25 carbon atoms) [9]. The semi-quantitative proportions of these biofuels were calculated using GCMS data and hydrocarbon chain sizes. The result are shown in Table 2.



**Fig. 4.** FTIR Result

The percentage of green diesel composition still dominates, especially in product of CC(390). This result indicates that oleic acid have been converted into alkanes but the chain is still quite long. As for the percentage of biogasoline composition is still quite high, especially in product of CC(375). This phenomena can be caused by a more reactive thermal cracking reaction than catalytic cracking at high temperatures.

**Table 1.** FTIR Transmittance Comparison of Bioavture and Other Product

Sample	Transmittance (%)			
	C-H	C=O	C-O	C=H
	2830-3000 cm <sup>-1</sup>	1700-1750 cm <sup>-1</sup>	1100-1300 cm <sup>-1</sup>	675-1000 cm <sup>-1</sup>
CC6 (360°C)	62.306	89.916	-	91.475
CC7 (375°C)	64.286	97.346	-	92.014
CC8 (390°C)	63.810	96.686	-	92.100
HDO	61.528	68.529	90.182	88.998
Oleic Acid	69.465	57.505	86.329	83.236

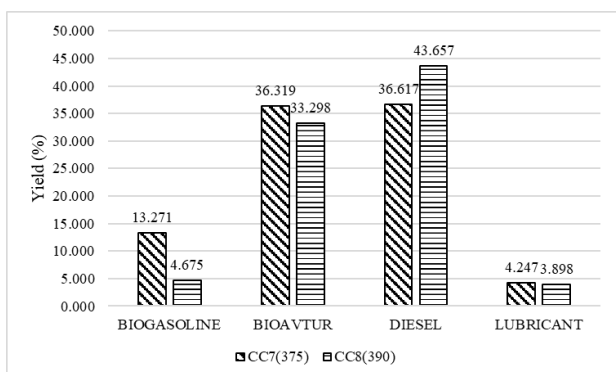
**Table 2.** GC-MS Results

Sample	CC(375)	CC(390)
Biogasoline	13.90	4.95
Bioavture	38.05	35.29
Green Diesel	38.37	46.27
Lubricant	4.45	4.13

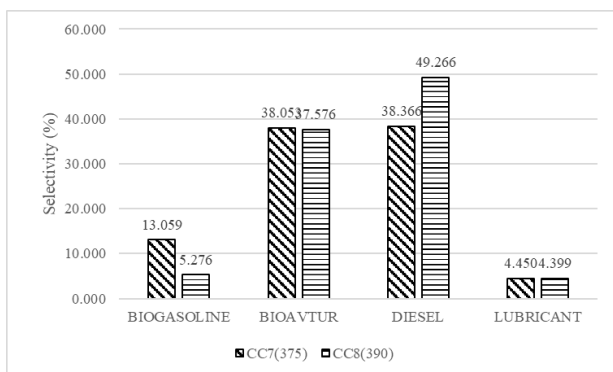
The results presented in Figure 5 shows that the oleic acid have good enough potential for the production of bioavture with range of yield is about 30%. This result indicates that the NiMo/Zeolite catalyst used is less selective for producing bioavtures, both in catalytic cracking reactions and in hydrodeoxygenation reactions. In addition, less optimal yield and selectivity of bioavture in this study could also be due to the low ratio of catalysts used in the catalytic cracking reaction, ie 1%.

Conversion, selectivity, and yield were also calculated using GCMS data. These are the success parameters of hydrodeoxygenation and catalytic cracking process in producing bioavtures. Fig.5 and Fig.6 show that the largest percentage of yield and selectivity of bioavtur occurred at CC(375). It means that the optimum temperature of catalytic cracking in this study achieved at 375°C. While, from Figure 7 it can be seen that the CC(390) conversion value is higher than CC(375), because the higher temperature will induce the hydrodeoxygenation reaction and the catalytic cracking

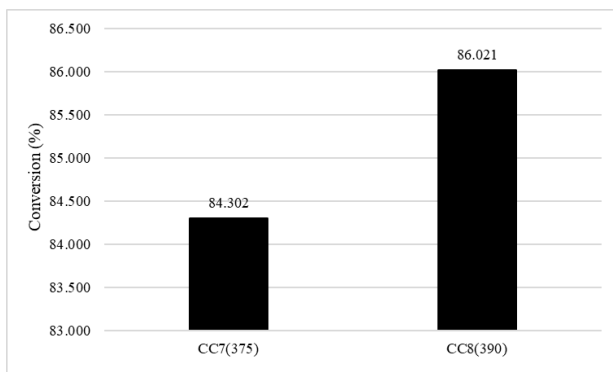
toward the product, especially the endothermic reaction. In addition, high temperatures will also cause a thermal cracking reaction that can increase the number of products.



**Fig. 5.** Yield Comparison of Catalytic Cracking Product



**Fig. 6.** Selevtivity Comparison of Catalytic Product



**Fig. 7.** Conversion Comparison of Catalytic Product

## 4 Conclusion

Characterizations of bioavture have shown that hydrodeoxygenation and catalytic cracking products have met the specifications of bioavtur, except the acid number with optimum temperature at 375°C. These conditions with NiMo/Zeorlit activated led to dominant yield of 36.319% of bioavture fraction, selectivity of 38.053%, and conversion of 84.302%. This study has shown the optimum temperature of catalytic cracking for bioavture synthesis, but the catalysts used are less selective, both in hydrodeoxygenation and catalytic

cracking reactions. So it is necessary to re-research to find a more selective catalyst for bioavture synthesis.

Director of Research and Community Service through International Indexed Publication Grant for Student Thesis (PITTA) Universitas Indonesia 2018 with contract No. 2388/UN2.R3.1/HKP.05.00/2018 is acknowledged for the financial support to carry out the present study.

## References

1. D. E. Nasional, "Outlook Energi Indonesia 2016," Sekretariat Jenderal Dewan Energi Nasional, 2016.
2. S. M Krar, L. Kovacs, L. Boda, A. Leveles, Thernesz, J. Wahlne and Hancsok, "Fuel Purpose Hydrotreating of Vegetable Oil on NiMo/Al<sub>2</sub>O<sub>3</sub> Catalyst," pp. 107-111, 2009.
3. S. Hassan, Y. Sani, A. A. R. Abdul, N. Sulaiman and W. M. A. W. Daud, "Biogasoline: an out of the box solution to the food for fuel and land use competitions," *Energy Conversion and Management*, vol. 89, pp. 349-367, 2015.
4. Y. K. Ong and S. Bhatia, "The current status and perspectives of biofuel production via catalytic cracking of edible and non edible oils," *Energy*, vol. 35, pp. 111-110, 2010.
5. Nurjannah, A. Roesyadi and D. H. Prajitno, "Biofuel Production from Catalytic Cracking of Palm Oil," *Jurnal Reaktor*, vol. 13, pp. 37-43, 2010.
6. B. Bognadov, D. Georgiev, I. Markovska and Y. Hristov, "Synthetic Zeolites: Structure, Clasification, Current Trends in Zeolite Synthesis Review," *International Science Conference*, 2009.
7. B. H. Susanto, M. Nasikin and A. Wiyo, "Synthesis of Renewable Diesel through Hydrodeoxygenation Using Pd/Zeorlite Catalysts," *Procedia Chemical*, vol. 9, p. 1390150, 2014.
8. B. H. Susanto, M. B. Prakasa and M. Nasikin, "Synthesis of Renewable Diesel from Palm Oil and Jatropha Curcas Oil Through Hydrodeoxygenation Using NiMo/ZAL," *International Journal of Technology*, Depok, 2016.
9. F. De Sousa, C. Cardoso and V. Pasa, "Producing Hydrocarbons for Green Diesel and Jet Fuel Formulation from Palm Kernel Fat Over Pd/C," *Fuel Processing Technology*, p. 143, 2016.