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Synthesis of Bio-Jet Fuel from Coconut (*Cocos nucifera*) Oil Through Hydrodeoxygenation Using NiMoP/Al₂O₃ Catalyst

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Abstract. The increasing of scarce of petroleum availability, unstable prices, and potential environmental damage due to the use of fossil fuel encourage the development of alternative fuels that can replace fossil fuels, including jet fuel. Bio-jet fuel is a renewable fuel that has similar characteristics to jet fuel. The potential raw material for bio-jet fuel production in Indonesia is coconut oil. The composition of fatty acids in coconut oil corresponds to the range of carbon atomic chain of jet fuel. Indonesia is also the country with the second-largest share of coconut oil exports in the world which shows that the use of coconut oil in Indonesia is very less. In this study, bio-jet fuel was synthesized from coconut oil through hydrodeoxygenation reaction to convert fatty acids to hydrocarbons by removing oxygen. The catalyst used in this reaction was NiMoP/Al₂O₃ catalyst. The hydrodeoxygenation reactions were carried out with variations of pressure and temperature, at pressures of 10, 15, and 20 bar, and temperatures of 375, 385, and 400°C. The reactions were stopped if they had reached equilibrium based on GC-TCD analysis of the gas product. The hydrodeoxygenation reaction at 400°C and 20 bar was able to produce high conversion (92.56%), much hydrocarbon content (91.91%), high selectivity and also yield of bio-jet fuel (82.93% and 54.34%). Liquid products were distilled to obtain jet fuel fraction products. From the results of the density, viscosity, acid number, heating value, and freezing point analysis of the bio-jet fuel distillate, good values were obtained.

INTRODUCTION

Since 2005, Indonesia's aviation fuel consumption has been greater than national production so that a portion of jet fuel needs must be fulfilled through imports. Indonesia's aviation fuel consumption continues to increase with an average increase of 4.62% per year from 2012 to 2016. In 2016, Indonesia's aviation fuel consumption reached 4.67 million kiloliters, while national production was only 3.62 million kiloliters so that the balance jet fuel commodities recorded a deficit of 1.05 million kiloliters or 22.48% [1].

Bio-jet fuel is an aircraft fuel with the main composition is hydrocarbons which have 9 to 15 carbon atoms, which can be produced from vegetable oils [2]. One of the potential raw materials for bio-jet fuel production in Indonesia is coconut oil. Most fatty acids in coconut oil have carbon chains that are within the range of bio-jet fuel carbon chains (C9 to C15) so that high selectivity and yield of bio-jet fuel are expected to be obtained. In terms of availability, Indonesia is the second-largest coconut oil producer in the world and also the country with the second-largest share of coconut oil exports in the world (31.68% in 2016) [3].

The conversion of coconut oil into bio-jet fuel can be done through a hydrodeoxygenation reaction which aims to remove oxygen from a reactant using hydrogen [4]. NiMo/Al₂O₃ catalyst is one of the main catalysts in the hydrodeoxygenation process. Addition of phosphorus (P) as a secondary promoter was able to improve the activity and selectivity of the catalyst [5], as well as being one of the innovations of this study because no bio-jet fuel synthesis studies were found using NiMoP/Al₂O₃ catalysts.

Eller et al. [6] performed hydrodeoxygenation reactions on coconut oil using NiMo/Al₂O₃ catalyst in a continuous reactor with LHSV between 1.0 and 3.0 h⁻¹, temperature between 260 and 380°C, while the pressure was 30 bar and the H₂/feedstock volume ratio was 600Nm³/m³. The highest bio-jet fuel fraction selectivity was 58% which was obtained by reaction at 360°C and LHSV 1.0 h⁻¹.

In this study, bio-jet fuel from coconut oil was synthesized through the hydrodeoxygenation reaction using NiMoP/Al₂O₃ catalyst. This research is expected to be an alternative solution in the development of Indonesian aviation fuel.

MATERIALS AND METHODS

Materials

Refined, bleached, and deodorized coconut oil was purchased from Okusi Biotech (Indonesia). Materials used to prepare the catalyst, such as Ni(NO₃)₂·6H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, Al₂O₃, and H₃PO₄ were purchased from Merck.

Hydrodeoxygenation Reaction

All reactions were processed in a 330 ml batch stirred reactor integrated with a condenser and furnace. 100 g of coconut oil and 5 g of NiMoP/Al₂O₃ catalyst which had been prepared by impregnation method were added to the reactor for each reaction. The mixture was heated to 375°C under 10 bar of H₂ pressure. Stirrer speed was kept constant at 800 rpm. The hydrodeoxygenation reactions were carried out with variations of pressure and temperature, at pressures of 10, 15, and 20 bar, and temperatures of 375, 385, and 400°C. The reactions were stopped if they had reached equilibrium based on GC-TCD analysis of the gas product. The hydrodeoxygenation reactions were coded according to Table 1.

Characterization of the Raw Material and Products

Coconut oil (as the raw material), gas product, and liquid product of the hydrodeoxygenation reaction were characterized by GC-MS Claurus 680/SQ8T to identify the component fraction, FTIR ThermoFisher Scientific Nicolet iS5 to identify the functional groups, and GC-TCD to identify the gas product composition and gas consumption during the reaction. The properties of distilled jet fuel from hydrodeoxygenation reaction were investigated through acid number, density, kinematic viscosity, heating value, and freezing point analysis.

RESULTS AND DISCUSSION

Characterization of the Raw Material

Table 2 shows the fatty acid (FA) composition of the coconut oil used in this study. The fatty acid composition in coconut oil was mostly within the range of the bio-jet fuel carbon chain (C9 to C15). Therefore, the cracking process was not needed as an advanced stage of the hydrodeoxygenation process, so the technology used was simpler and can reduce production costs. Also, 83.09% of fatty acids in coconut oil were saturated fatty acids so that less hydrogen was consumed to convert double bonds in coconut oil into saturated chains.

Characterization of the Hydrodeoxygenation Products

The product obtained from the coconut oil hydrodeoxygenation reactions consisted of gas products and liquid products. The gas product formed can show the dominant reaction pathway and can show that the reaction has reached equilibrium. Whereas liquid products consisted of bottom products and condensate, and there was a little residual reactant (residue).

Gas Chromatography-Thermal Conductivity Detector

The analysis of gas products using GC-TCD aimed to prove that hydrodeoxygenation reactions work well, to determine when the reaction has reached equilibrium, and to determine the composition of the gas product so that the dominant hydrodeoxygenation reaction pathway can be known. From the overall hydrodeoxygenation reaction, the dominant gas product was CO. This indicates that the operating conditions and catalysts of NiMoP/Al₂O₃ directed the reaction towards decarbonylation which produces hydrocarbons with one carbon less than the fatty acid carbon atoms.

with the by-products are CO and H₂O. Thus, most hydrocarbons in hydrodeoxygenation liquid products had the odd number of carbons because the raw material of coconut oil was entirely even number of carbons.

TABLE 1. Coding of Hydrodeoxygenation Reactions

Code	T (°C)	P (bar)	Time (minutes)
HDO1	375	10	75
HDO2	375	15	135
HDO3	375	20	180
HDO4	385	10	60
HDO5	385	15	105
HDO6	385	20	150
HDO7	400	10	30
HDO8	400	15	45
HDO9	400	20	60

TABLE 2. Fatty Acid Composition of the Raw Material

Fatty Acid	% m/m
C6:0	0.38
C8:0	5.60
C10:0	6.34
C12:0	29.46
C14:0	18.92
C16:0	15.94
C18:0	6.32
C18:1	13.48
C18:2	3.22
C18:3	0.16
C20:0	0.13
C20:1	0.05

In Table 1, the reaction time of each hydrodeoxygenation reaction has been listed. Differences in operating conditions greatly affected the reaction time to achieve equilibrium. At the same operating pressure, increasing operating temperature resulted in decreasing of reaction time. This happened because the reactions were endothermic, so the reaction rate increased with increasing reaction temperature. Whereas, at the same operating temperature, increasing operating pressure resulted in increasing of reaction time. Increased pressure caused higher availability of H₂ in the reactor. The higher availability of H₂ gas slowed down the reaction to equilibrium, especially the reaction between gas products where the increase in pressure and the number of moles of the reactant side shifted the equilibrium towards the product which has a smaller number of moles of gas, they were CH₄ (methanation) and CO₂ (water-gas shift).

Fourier-Transform Infrared Spectroscopy

FTIR test result on coconut oil sample (Fig. 1) shows a high absorbance of 1742 cm⁻¹ which is characteristic of the C=O function group in the form of esters, such as triglycerides which are dominant in coconut oil. From the FTIR results of the hydrodeoxygenation products, peaks at 1742 cm⁻¹ were not found which indicates that the breakdown of the carbon-oxygen bond from the reactant had been successful.

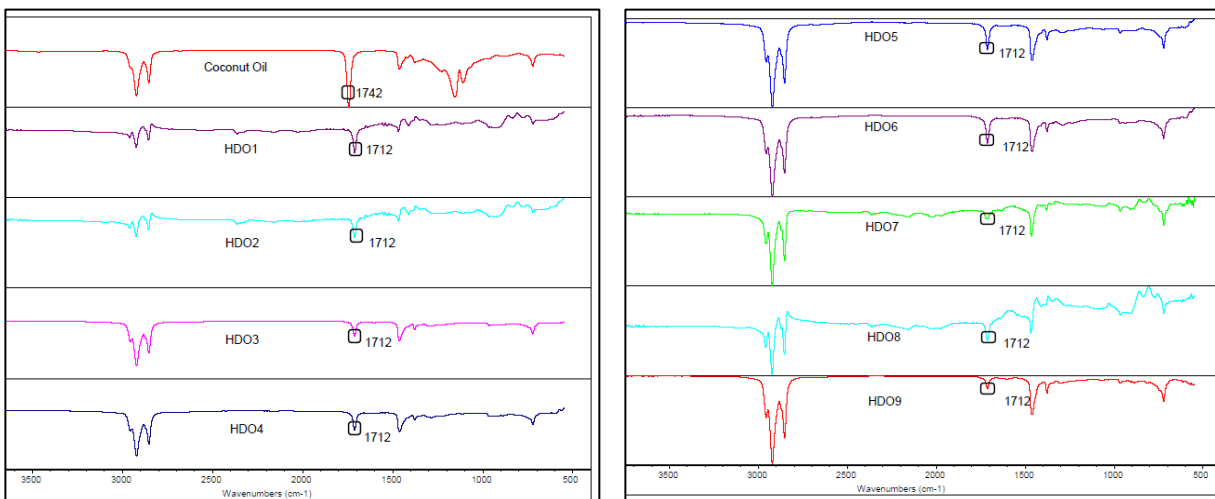


FIGURE 1. IR Spectra of the Reactant and HDO Products

Although the C=O group in the form of esters had been lost, there was still a functional group C=O in the form of carboxylic acid which is characterized by the presence of absorbance of 1712 cm^{-1} . Carboxylic acid or free fatty acids were the products of triglycerides cracking reaction before finally free fatty acids were converted to hydrocarbons through the hydrodeoxygenation reaction. The presence of C=O carboxylic acid in the hydrodeoxygenation product indicates that the conversion of free fatty acids was not completely done. Some of the free fatty acids were remaining and unconverted.

Gas Chromatography-Mass Spectroscopy

The liquid products from each hydrodeoxygenation reaction were analyzed by GC-MS to identify the components contained in the sample semi-quantitatively. Figure 2 to Figure 5 respectively show the conversion of reactants, hydrocarbon content, the selectivity of bio-jet fuel, and yield of bio-jet fuel from each hydrodeoxygenation reaction based on GC-MS results that will be obtained by distillation of hydrodeoxygenation liquid product.

The high conversion value (Fig. 2) proves that all hydrodeoxygenation reactions had been able to convert coconut oil into liquid products with alkane, alkene, aromatic and oxygenate components, and gas products in the form of CO, CO₂, H₂O, and CH₄. The percentage of hydrocarbon content in liquid products for all the hydrodeoxygenation reaction (Fig. 3) was also high so that it can be concluded that all the hydrodeoxygenation reactions carried out in this study had successfully converted coconut oil into hydrocarbons.

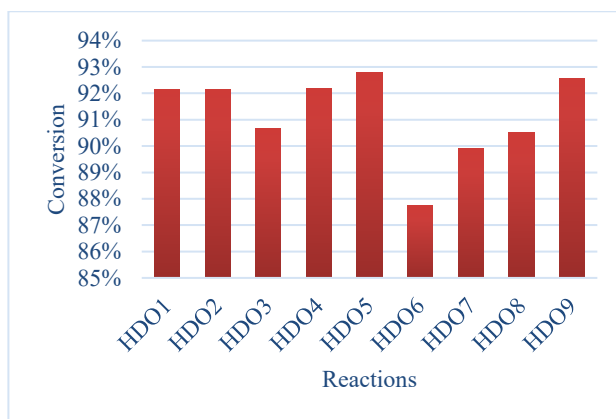


FIGURE 2. Conversion of Raw Material for Each Hydrodeoxygenation Reaction

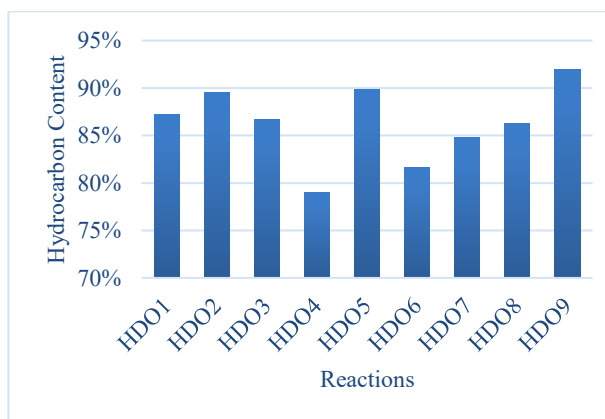


FIGURE 3. Hydrocarbon Content of All Hydrodeoxygenation Liquid Product

Figure 4 shows the selectivity of bio-jet fuel for each hydrodeoxygenation reaction. The selectivity of bio-jet fuel is the percentage of hydrocarbons in jet fuel fraction contained in the hydrodeoxygenation liquid product. The selectivity of bio-jet fuel for each reaction was relatively high. This indicates that all the hydrodeoxygenation reactions in this study did not cause any carbon chain cracking in the bio-jet fuel carbon number.

The entire hydrodeoxygenation reaction was also capable of producing a fairly good yield value, as shown in Fig. 5. The yield of bio-jet fuel is the ratio between the bio-jet fuel mass based on bio-jet fuel selectivity value and the mass of the converted reactants. The mass of the liquid product obtained from each hydrodeoxygenation reaction has a large enough difference with the mass of the reactants. This proves that there was loss of mass during the reaction as gas products. This was logic because the oxygen compounds in the reactants almost completely disappear in the liquid product. This loss of mass caused the yield of bio-jet fuel value to be considerably smaller than its selectivity.

Some of these parameters indicate that HDO9 (400°C; 20 bar) was the best operating condition for running the hydrodeoxygenation reaction of coconut oil into bio-jet fuel. HDO9 has the highest value of hydrocarbon content, the yield of bio-jet fuel (which is only defeated by HDO1), with relatively fast reaction time (60 minutes). HDO1 (375°C; 10 bar) can also be a good alternative for hydrodeoxygenation reactions, with the lowest operating temperature and operating pressure still having high hydrocarbon content and yield of bio-jet fuel, and fast operating time (75 minutes). Figure 6 shows the composition of hydrocarbons grouped into several biofuels based on their carbon chain length, such as gasoline (5 to 10 carbon atoms), jet fuel (9 to 15 carbon atoms), diesel oil (10 to 25 carbon atoms) [2]. Meanwhile, Figure 7 shows the comparison of HDO9 hydrocarbon components and conventional jet fuel.

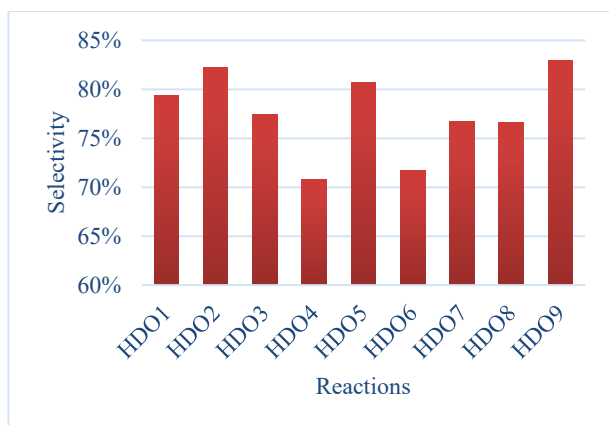


FIGURE 4. The Selectivity of Bio-Jet Fuel in Liquid Products

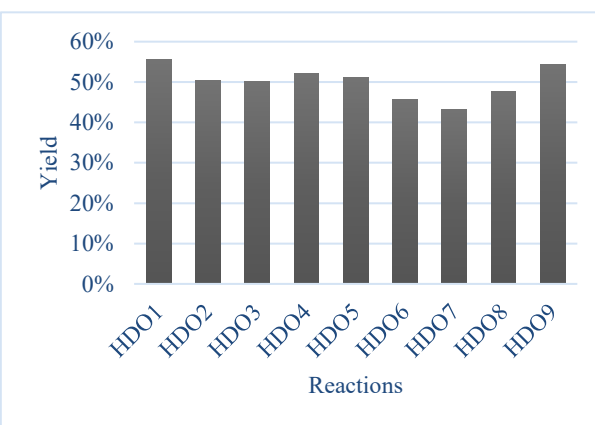


FIGURE 5. The Yield of Bio-Jet Fuel for Each Hydrodeoxygenation Reactions

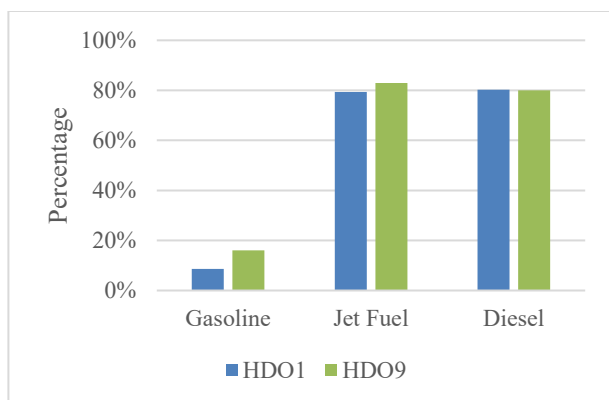


FIGURE 6. Comparison of Biofuel Fractions in Liquid Product of HDO1 and HDO9

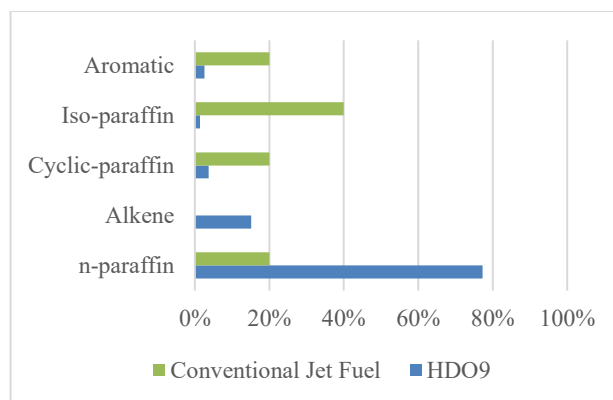


FIGURE 7. Comparison of Hydrocarbon Groups Content in HDO9 and Conventional Jet Fuel

Density

The density of distilled bio-jet fuel from HDO9 (BJ9) was much lower than the raw material. The loss of most oxygen atoms in coconut oil and cracking in long carbon chains gave a significant difference in density value of BJ9. However, the density of BJ9 (0.762 g / ml) still did not meet the ASTM standard for jet fuel (0.775-0.840 g / ml). This was caused by the composition of hydrocarbons which were mostly n-paraffin (Fig. 7). n-paraffin has the smallest density compared to other hydrocarbon groups.

Kinematic Viscosity

From the results of kinematic viscosity analysis, BJ9 (1.58 mm²/s) has met the ASTM D1655 standard (max. 8 mm²/s). Termination of the C=O bond by the hydrodeoxygenation reaction caused a significant decrease in kinematic viscosity on the BJ9 of the raw material.

Acid Number

BJ9 acid number (28.97 mg KOH/g) was far above the maximum standard according to ASTM D1655 (0.1 mg KOH/mg). This proves the results of FTIR and GC-MS analysis which also identified the presence of an amount of free fatty acids in the BJ9 sample. The high BJ9 acid number indicates that some of the oxygenates and free fatty acids

have boiling points that were in the temperature range of bio-jet fuel distillation so that the concentration of free fatty acids in BJ9 distillate was higher than the concentration in the hydrodeoxygenation liquid product.

Heating Value

BJ9 heating values (45.19 MJ/Kg) exceeded the minimum standard of commercial jet fuel (42.8 MJ/Kg). It has been shown in Fig. 8 that the hydrocarbon content in BJ9 was mostly n-paraffin and contained only a few aromatic compounds. This hydrocarbon composition gave BJ9 a high heating value because n-paraffin has a high heating value.

Freezing Point

The freezing point of the BJ9 sample was -33°C, still not meeting the ASTM D1655 standard which sets a maximum freezing value of -47°C. As previously stated, the largest hydrocarbon content in BJ9 was n-paraffin. n-paraffin is a group of hydrocarbons with the highest freezing point so that the freezing point of BJ9 was not low enough to meet ASTM standards. To obtain iso-paraffin, cyclo-paraffin, or aromatics with higher concentrations, a catalyst which can direct the results of the reaction towards the hydrocarbon group is needed.

CONCLUSION

The hydrodeoxygenation reaction at 375, 385 and 400°C and pressures of 10, 15, and 20 bar using NiMoP / Al₂O₃ catalyst had been able to convert coconut oil into hydrocarbons in bio-jet fuel fractions with the dominant reaction pathway was decarbonylation. The hydrodeoxygenation reaction that was able to provide the highest conversion, hydrocarbon content, selectivity, and optimum yield of bio-jet fuel was the reaction at 400°C and 20 bar for 60 minutes. The conversion value, hydrocarbon content, selectivity, and yield of bio-jet fuel respectively were 92.56%, 91.94%, 82.93%, and 54.34%. The value of viscosity and heating value of the distillate of the bio-jet fuel fraction met the ASTM D1655 standard. While the value of acid numbers still far exceeded the standard due to the content of free fatty acids in distillates. In addition, the density and freezing point of the bio-jet fuel distillate did not meet the standard because the n-paraffin content was too dominant compared to other hydrocarbon groups.

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