

Synthesis of Green Diesel From Waste Cooking Oil Through Hydrodeoxygenation Technology With NiMo/ γ -Al₂O₃ Catalysts

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Abstract. Hydrodeoxygenation (HDO) of waste cooking oil (WCO) and trapped grease over sulfide catalysts was examined to produce high quality transportation fuel from low-grade resources. The hydrodeoxygenation of waste cooking oils was carried out in a high pressure of 30 and 60 bar and high temperature of 300 – 400 °C in a batch reactor autoclave. NiMo/ γ -Al₂O₃ catalyst was prepared and for the first time tested in hydroprocessing of waste cooking oil. The content of NiMo/ γ -Al₂O₃ in each catalyst was about WCO 5 wt.%. A maximum of 77,97 % green diesel yield was achieved at nearly complete conversion of waste cooking oil using NiMo/ γ -Al₂O₃ at temperature of 400°C, pressure 60 bar and 4 hours of reaction time. The oxygen content was decreased from 14,25 wt.% to 13,35 wt.%, at temperature of 400°C, pressure of 30 bar and 1 hour of reaction time. The Hydrodeoxygenation process was much influenced by temperature, pressure, and time.

1 Introduction

Today energy needs continue to rise but inversely proportional to energy substitutes such as petroleum, natural gas that can not be optimized. The amount of available energy sources currently is sourced from fossil fuels accounted for 94% of the national energy mix mix, comprising 47% of petroleum, 26% coal and 21% natural gas [1]. With an economic growth of 6.3 to 6.8 per year, energy demand is projected to grow around 6% per year until 2014. Fuel oil will continue to be preferred in the final energy demand, because in addition to the fact that fuel-based technologies are more efficient, fuel prices can still continue to compete if compared to other fuels such as coal and natural gas. More over, fuel oil still dominates the use of final energy, especially in the transportation sector, because the use of fuel more practical and efficient and can not be replaced by other fuels.

Considering Indonesia is the largest palm oil producer in the world with oil palm production in 2014 reaching 33 million tons so that the potential of cooking oil produced is quite large [2]. In 2007 used cooking oil (MGB) from various sources as much as 3.9 tons has not been fully utilized. This gives a huge opportunity to make Indonesia as a country that has a strong energy resistance by processing it into greendiesel with hydrodeoxygenation method, in addition to producing high fuel quality compared to biodiesel and petrodiesel, also environmentally friendly [3].

2 Literature Review

2.1 Waste Cooking Oil

Waste cooking oil is waste oil that can be made from various types of cooking oil such as corn oil, vegetable oil, samin oil and so on which when viewed from the chemical composition of the compounds are carcinogenic. In addition to the environmentally destructive wastes the chemical content formed can be harmful to human health. The first sign of cooking oil damage is the formation of acrolein in cooking oil. This acrolein causes itching in the throat when eating fried foods using cooking oil repeatedly. Acrolein is formed from the hydration of glycerol that forms an unsaturated aldehyde.

2.2 Green Diesel

Green diesel is a straight-chain hydrocarbon fraction similar to that produced by the hydrogenation of triglycerides from vegetable oils [4]. The injection of hydrogen with the support of a bimetallic catalyst for the hydrotreating reaction of the triglyceride compound is capable of breaking the ester or carboxylic group bond of the glycerol group [5,6]. Then followed the breaking of carboxylic groups from the existing fatty acid bonds as well as the saturation reaction of the double chain carbon bonds into straight chain hydrocarbon compounds [7, 8, 9].

2.3 Hydrogenation and Hydrodeoxygenation

Hydrogenation technology or Hydrotreatment is a branch of hydroprocessing such as catalytic reactions using hydrogen to eliminate the atoms heterogeneous (heteroatoms) such as sulfur,

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nitrogen, and oxygen, each of which is contained in the compound hydrogen sulfide (H₂S), ammonia (NH₃) and water (H₂O) in a process feedstock [10, 11]. Hydrogenation process usually followed by hydrodeoxygenation reaction (HDO), decarboxylation (DCO), and decarbonylation (DCN) or combination of them [11].

Hydrodeoxygenation (HDO) is a process for eliminating oxygen hydrogenolysis of a material by cutting the carbon-oxygen bond using hydrogen gas [12, 13]. The content of oxygen in organic compounds has a very important role in estimating the characteristics of the fuel to be generated. Oxygen levels in vegetable oils that can reach more than 50% by weight, have an impact on the low calorific value, low thermal stability, corrosive, can not be mixed with fossil fuels and the increasing tendency towards polymerization reaction [14].

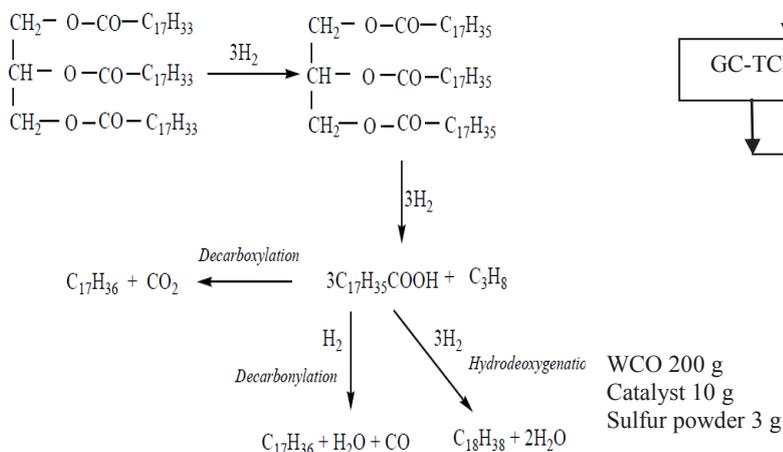
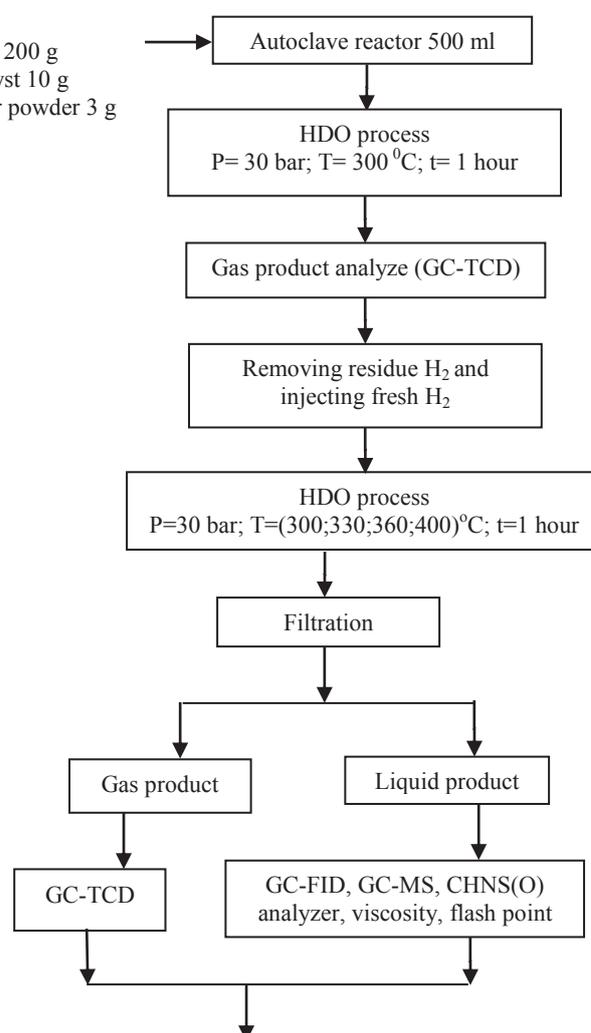
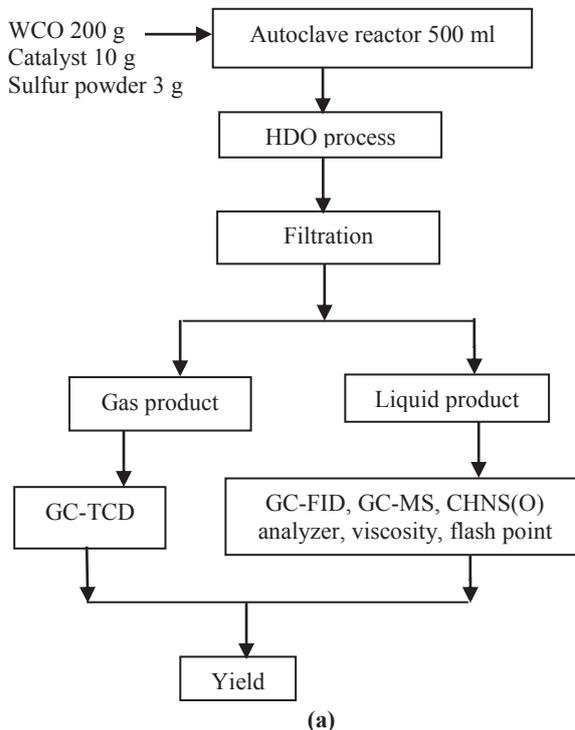


Fig. 1. Reaction pathway of hydrotreatment

3 Methodology

The procedure in this study was including 10 grams of NiMo/γ-Al₂O₃ catalyst passed 200 mesh, 3 grams of sulfur powder and 200 grams of waste cooking oil into the autoclave reactor. Then HDO processes were varied on time, temperature, pressure, and number of reaction stage with rotation speed of 800 rpm. After the HDO process was finished, the product was filtered off and separated between liquid and gas for analysis step. However, in the 2-stage, after the first stage was finished, gas in the reactor was replace by fresh hydrogen, then the reaction was continued in the second stage with the same pressure and time variations but with different temperatures. After the reaction process was completed, product gas was analyzed using GC-TCD Shimadzu GC-2014. The liquid product was separated from solid material by filtering. Liquid product was analyzed using GC-FID. More over the physical and chemical properties of liquid product was also to be

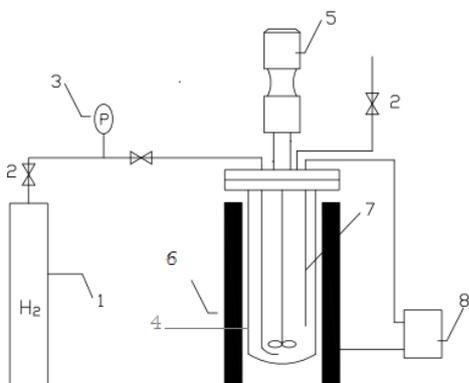
analyzed in accordance to ASTM Standard such as viscosity, flash point and elemental analysis. The operating conditions of each experiment were followed below:



Yield

(b)

Fig. 2. Green Diesel Synthesis Scheme (a) Single reaction (b) Two steps reaction



1-steel bottle; 2-valve; 3-pressure gauge; 4-reactor;5-electrical machine; 6-jacket; 7-thermocouple; 8-controller

Fig. 3. Schematic and Equipments of Experimental

Table 1. Operating Conditions

Run	Stage amount	Operating Condition					
		Temperature (°C)		Initial pressure		Time (hour)	
		T1	T2	P1	P2	t1	t2
1	1	300	-	30	-	1	-
2	1	330	-	30	-	1	-
3	1	360	-	30	-	1	-
4	1	400	-	30	-	1	-
5	1	300	-	60	-	1	-
6	1	330	-	60	-	1	-
7	1	360	-	60	-	1	-
8	1	400	-	60	-	1	-
9	2	300	300	30	30	1	1
10	2	300	330	30	30	1	1
11	2	300	360	30	30	1	1
12	2	300	400	30	30	1	1
13	1	300	-	60	-	4	-
14	1	400	-	60	-	4	-
15	1	300	-	30	-	4	-
16	1	400	-	30	-	4	-

4 Discussion

4.1 Pressure and Temperature Profile

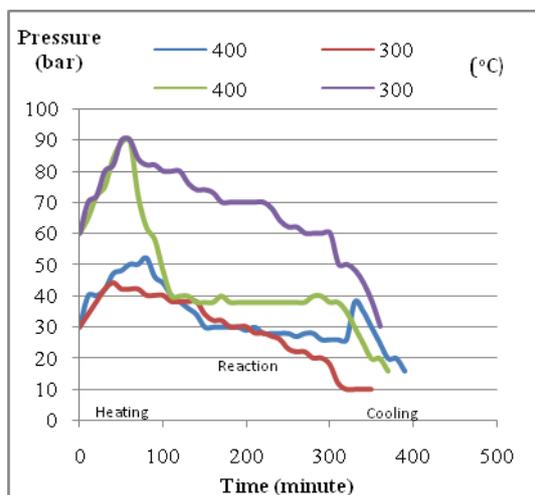


Fig. 4. Pressure profile on the time

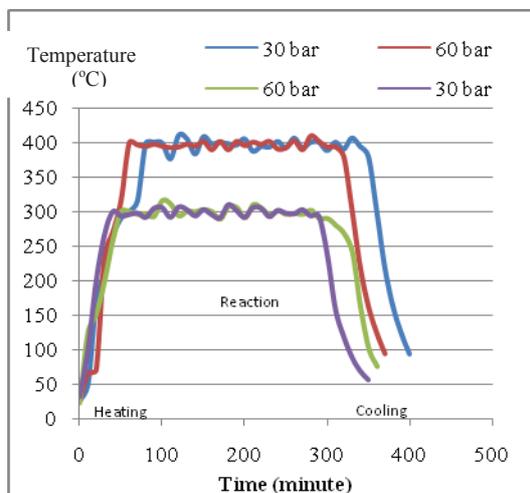


Fig. 5 Temperature Profile on The Time

The pressure and temperature profile of the above reaction was observed at 4 hours reaction time. By controlling the temperature of the coil heater in the reactor it was desirable that the reaction temperature was immediately achieved and kept constant during the reaction. The observation of the condition of the process pressure was seen fluctuating even pressure drop on the graph above. This pressure drop phenomenon follows the Joule Thompson Effect theory. The hydrogen gas stored in a guarded tube at a pressure of about 200-250 bar to remain in the gas phase was then injected into the reactor at a pressure of 30 or 60 bar. As a result of this pressure drop, the gas became inflate and the rapid

pressure drop was practically not allowing the occurrence of external heat propagation into the system and vice versa ($Q = 0$). As a result of this adiabatic development the gas underwent temperature changed both up and down (fluctuations).

4.2 Effect of Temperature on Green Diesel Yield

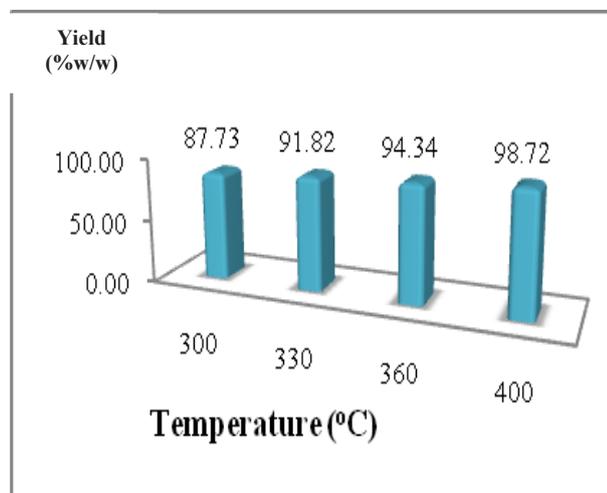


Fig. 6. Effect of Temperature on Green Diesel Yield

At the initial pressure condition of 30 bar and 1 hour reaction time, the highest result is obtained at 400°C operating temperature of 98.72% considering green diesel C₁₃-C₂₂. This is because when the temperature is increased then the cracking process will occur more easily and optimally. It is also caused by the addition of greater heat energy.

4.3 Effect of Initial Pressure Reaction to Green Diesel Yield

At 400 °C and a reaction time of 1 hour, the green diesel produced at a pressure of 60 bar is lower than the pressure of 30 bar. It is predicted that at higher pressures the incorporation of alkyl in short carbon chains results in long-chain hydrocarbons C₂₃⁺ which are not green diesel but it was a small part of the wax [15].

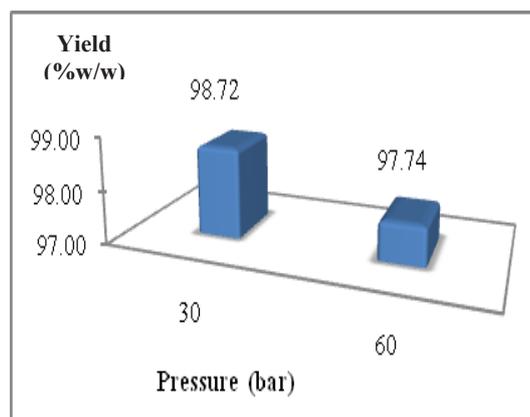


Fig. 7. Effect of Initial Pressure Reaction to Green Diesel Yield

4.4 Effect of Reaction Time to Green Diesel Yield

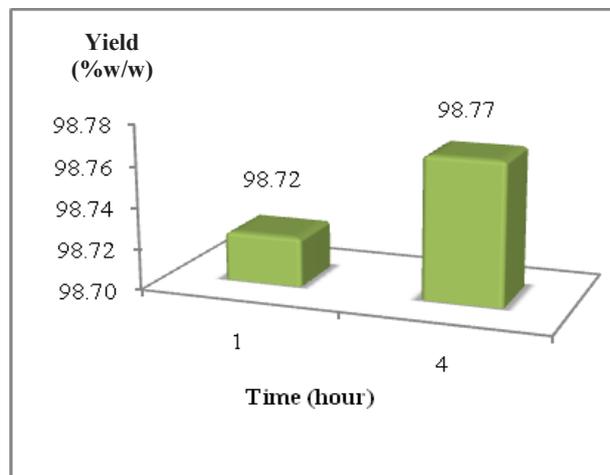


Fig. 8. Effect of Reaction Time on Green Diesel Yield

Results at 4 hours of operating time are higher than the operating time of 1 hour only. The longer the reaction time, the cracking process also occurs more optimally because the contact between reactants and catalysts longer to produce more products that also cause the green diesel increased.

4.5 Effect of Number of Stages of Reaction to Green Diesel Yield

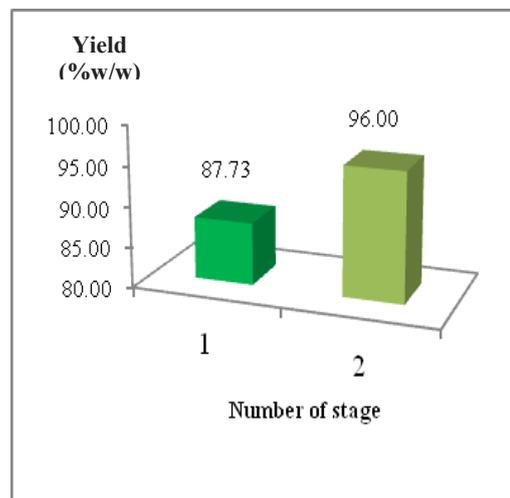


Fig. 9. Effect of Number of Stages of Reaction to Green Diesel Yield

Results at 2 stages are higher than the reaction result of only 1 stage. This is due to the cracking process at 2 stages occurs longer where every 1 stage is given 1 hour so that if 2 stage then happened 2 hour reaction of cracking. In addition, replacement with fresh hydrogen makes the cracking process more optimal.

4.6 Effect of Reaction Temperature on Decreasing Oxygen Content

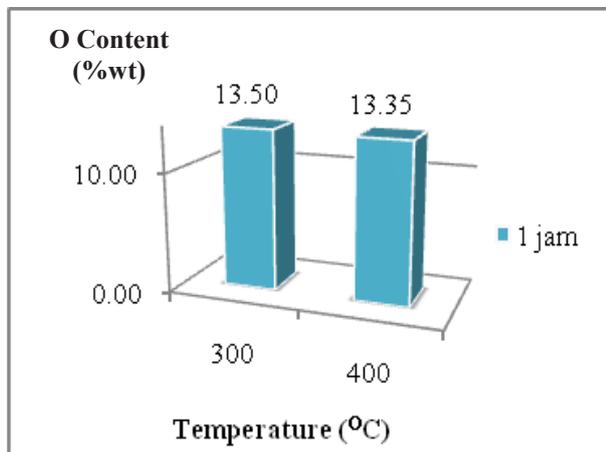


Fig. 10. Effect of Reaction Temperature on Decreasing Oxygen Content

In a reaction that lasted 1 hour, waste cooking oil which originally contained 14.25% oxygen can be reduced to 13.5 and 13.35% oxygen at reaction temperature of 300 and 400°C respectively. Although only less than 1% but with increasing reaction temperature, it is possible to remove oxygen contained in the fatty acid chain in waste cooking oil.

5 Conclusion and Suggestion

5.1 Conclusion

Based on the research that has been done, obtained some conclusions include:

1. The highest yield was obtained under operating conditions with 2 stage reaction, where $T_1 = 300\text{ }^\circ\text{C}$, $T_2 = 400\text{ }^\circ\text{C}$, $P_1 = P_2 = 30\text{ bar}$, $t_1 = t_2 = 1\text{ hour}$ that was equal to 98,93%
2. Factors affecting green diesel yields were pressure, temperature, number of stages and time.
3. Oxygen levels decreased from 14.25% to 13.35% at $T = 400^\circ\text{C}$, $P_1 = 30\text{ bar}$, $t = 1\text{ hour}$.

5.2 Suggestions

Suggestions that can be submitted for further research include:

1. In order to improve the quality of green diesel product produced, it is necessary to learn more about the hydrodeoxygenation operation condition made from used cooking oil, especially operating pressure and operating temperature need to be increased.

2. Should be further studied related to raw material pretreatment method, product separation, catalyst used and product treatment before analyzed in order to obtain more optimal result.
3. Need further study related to isomerization reaction to get more comprehensive green diesel result.
4. Required product quality analysis such as GCMS, calorific value and FTIR, cetane number measure the success of research that has been done.

Acknowledgments

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