Green diesel production from Crude Palm Oil (CPO) using catalytic hydrogenation method

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Abstract. Green diesel is an alternative solution for solving problems using biomass energy as a fuel source. The advantages of this second-generation green diesel or biodiesel (Gen-2nd) are capable of reaching cetane numbers 70-90, far higher than the Gen-1st biodiesel performance of cetane numbers 50-65, respectively. The production process is through hydrogenation reactions with hydrogen injection of 4-9 MPa, the use of heterogeneous NiMo/Al2O3 catalysts, and takes place in temperatures of 280 - 380°C. The need to design this catalytic hydrogenation reactor to convert crude palm oil (CPO) into green diesel fuel is good and safe when operating at high pressures and temperatures. The optimum operation was obtained by varying the amount of CPO oil raw material and NiMo/Al2O3 catalyst used in producing the best percent yield and green diesel characterization. At a temperature of 315°C, the highest yield was 68.2%, where the number of products began to decline above these temperature conditions. The green diesel specifications obtained have met diesel oil standards (Directorate General of Oil and Gas, 2016) by testing density, kinematic viscosity, water content, flash point, calorific value, and cetane numbers.

1. Introduction

Technological products are needed in a continuous search for improved sources of energy, and green diesel is an alternative solution for solving problems using biomass energy as a fuel source. This renewable green diesel fuel has efficiently, the same energy densities as petroleum, derived fuels due to the removal of oxygen contents and equal carbon-carbon percentage [1]. The advantages of this second-generation biodiesel or green diesel (Gen-2nd) are capable of reaching cetane numbers 70-90, far higher than the Gen-1st biodiesel performance of cetane numbers 50-65, respectively.

Green diesel is produced with hydrodeoxygenation vegetable oil (triglycerides) or animal fats through catalytic processing with hydrogen, produced a mixture of straight-chain and branched saturated hydrocarbons which typically contain 15 to 18 carbon atoms per molecule (C15 to C18) [2]. Hydrodeoxygenation can be a very expensive process due to hydrogen injection of 4-9 MPa, the use of heterogeneous NiMo/Al2O3 catalysts, and takes place in temperatures of 280–380°C. In hydrogenation process, the C-O bond will be cut using H2 gas, the carboxylic functional group is disconnected into the form of CO2 compound by decarboxylation process, and CO and H2O compounds were released through decarbonylation process [3].

Compared to the transesterification of triglyceride reactions to the Gen-1st biodiesel, methyl or ethyl esters compounds, catalytic cracking and hydrogenation have several advantages such as low
processing costs, and energy consumption for the process separation. In addition to producing diesel fuel types, this reaction (fig.1) also produces light hydrocarbon such as propane, gasoline, and kerosene. However, this cracking process usually requires high operating conditions (temperature and pressure), and it becomes a major consideration on its process safety [4].

![Diagram of triglycerides into green diesel synthesis]

**Figure 1.** The synthesis of triglycerides into green diesel [5]
Future biorefineries are expected to be projected to enhance sustainable and integrated bioenergy products. Therefore, research continues to be conducted, and catalysts play an important role in increasing the conversion of vegetable oil in producing the desired product. The selection of the catalysts for the hydrodeoxygenation process depend upon the activity, stability, and importantly the selectivity of metal and support catalyst as well as its high surface area and extensive range of high porosity. The new catalysts to process vegetable oils may be synthesized taking into account the following considerations: a) high activity toward deoxygenation, b) minimization of coke formation, c) water resistance, d) capability to regenerate in single processes, e) high tolerance to chemical poisons, f) scalability in any commercial process [6].

The activity of monometallic Ni/Al2O3, Mo/Al2O3, and NiMo/Al2O3 sulphided catalysts were studied for comparative hydroprocessing activity of sunflower oil. Harnos et al. [7] compared the activity of sulphided catalysts with the non-sulphided catalysts. They tested both sulphided and non-sulphided Pd/activated C, Pd/Al2O3, Ni/Al2O3, and bimetallic solid acid catalysts NiMo/Al2O3. The reaction conditions were set at 613.15 K under the pressure of 21 bars of H2 gas. The major products distribution were found to be C17, C18 and small alkanes with different catalyst.

The content of NiMo/γ-Al2O3 in each catalyst was about waste cooking oil 5 wt%. A maximum of 77.97% green diesel yield was achieved at nearly complete conversion of WCO using NiMo/γ-Al2O3 at a temperature of 400°C, a pressure 60 bar, and 4 hours of reaction time. The oxygen content was decreased from 14.25 wt% to 13.35 wt%, at a temperature of 400°C, a pressure of 30 bar and 1 hour of reaction time [8].

2. Methodology

2.1. Material

The materials used in this research are Crude Palm Oil (CPO), hydrogen gas, Ammonium Heptamolibdate Tetrahydrate, Nickel (II) Nitrate Heksahidrat, Aluminium Oxide. CPO produced from PT Perkebunan Mitra Ogan which is circulating in the area of Palembang, South Sumatera.

2.2. Experimental procedure

This study began with the process of making catalysts, nickel molybdenum with support of alumina (NiMo/Al2O3). The raw materials used are Nickel (II) Nitrate Hexahydrate (Ni(NO3)2.6 H2O) as for Ni, Ammonium Heptamolybdate Tetrahydrate ((NH4)2(24 MoO24.4 H2O) as for Mo, and alumina commercial Al2O3. The process of making this catalyst consists of impregnation, drying, and calcining.

The Aluminium Oxide (Al2O3) commercial is heated at 120°C for 2 hours and then cooled in the desiccator. Ammonium heptamolybdate tetrahydrate (NH4)2(24 MoO24.4 H2O) 0.87 M as much as 10 ml and Nickel (II) Nitrate Hexahydrate (Ni(NO3)2.6 H2O) 2M as much as 10 ml is impregnation with 12 gr of Al2O3 which has been activated. The mixture is stirring and heated at a temperature of 80°C to dry, then more drained in the oven with a temperature of 120°C for ± 4 hours. The mixture is calcined in a furnace with a temperature of 600°C for 5 hours. After that, the mixture can be used in hydrodeoxygenation reaction as a NiMo/Al2O3 catalyst.

Hydrodeoxygenation reaction of 300 ml CPO uses 0.15 gr NiMo/Al2O3, and 25 psia hydrogen, the process is performed during 1 hour of operation in the temperature in the range 270 – 330°C. Analysis condensate of green diesel products through the analysis of physical (qualitative and quantitative) and chemical properties.

3. Results and Discussion

The cracking product consists of organic liquid products, water, gas, and coke. The organic liquid product contains a large number of components of liquid hydrocarbons [9]. This hydrodeoxygenation reaction occurs at constant pressure in 55 bars, Figure 2 shows the percent yields of green diesel products that continue to rise with the higher operating temperature, the temperature of 315 °C is the
optimum condition of the result at 68.2%. Yield is the ratio of the weight of condensate products obtained by the amount of crude palm oil used as raw material.

![Figure 2. Effect of reaction temperature on the percent yield of green diesel](image)

Under optimum temperature, CPO has not been fully converted into green diesel products, so that while the condensation product is excreted many of the vapor is detached. However, at a temperature of 330 °C there is a decrease in the quantity of products produced, this is because the temperature is too high resulting in the occurrence of hydrocarbons that have formed carbon deposits (coke) and aromatic compounds, this is shown from the more blackish colors and odors of products. Coke formation was observed for all catalytic cracking of used palm oil [10] and will affect the density (Fig.3-a) and viscosity (Fig.3-b) of the product.

![Figure 3. Effect of reaction temperature on the product density (a) and viscosity (b) of green diesel](image)
Table 1. Green diesel product specifications

| Characteristics           | Unit   | Standard* | Research | Test Method |
|---------------------------|--------|-----------|----------|-------------|
| Density @ 15 °C           | gr/ml  | 0.8150 – 0.8600 | 0.8101   | ASTM D 1298 |
| Kinematic Viscosity @ 40 °C | cSt    | 2.0 – 4.5 | 4.27     | ASTM D 445  |
| Flash Point               | °C     | 52        | 58       | ASTM D 93   |
| Cetane Number             |        | 48        | 75       | ASTM D 613  |

* The standard and quality of diesel fuel from the Directorate General of Oil and Gas RI 2016 [11]

The density and viscosity of the product are strongly influenced by the number of paraffin hydrocarbons that are formed, the shorter the chain then the more the value. Figures 3 are shown, at the optimum temperature of the density is 0.8101 gr/ml and the viscosity is 4.27 cSt, and this is still in the specification of the diesel fuel (Table 1). The amount of value is increased with the high operating temperature, coke has started to form. Increased density of thermal cracking product fluid followed by increased viscosity of the fluid. The test of the flashpoint product (ASTM D-93) is still above standard, which is 58°C, but still in the limit of 52–96°C from diesel fuel. The ignition delay is caused by still not pure diesel product that is analyzed and the content of oxygen. The presence of oxygen, in water molecules and acid, reduces the stability and quality of the fuel. Deoxygenation process does not last perfectly, can be caused by the amount of hydrogen injected is still limited. At the test of the heating value, obtained the value of 10693 cal/gr. The heating value product is close to the standard of green diesel fuel, 44 MJ/kg [8] or equivalent to 10516 cal/gr, the resulting fuel products has approached its standard value.

In chemical composition testing with GC-MS analysis (Fig.4), it was obtained that the resulting product was dominated by the paraffin chain C15-C18 39.63%, range of diesel fuel. While other compositions are gasoline, kerosene, and naphtha (17.55%), lubricating oils (6.28%), paraffin (3.82%), and other compounds (33.44%).

![Figure 4. GC-MS analysis of green diesel product](image-url)
Compounds from the C5-C14 chain contained in the product due to the continuous thermal cracking reaction to convert the compound into a lighter fraction, and also formed a myristic acid which has a chemical formula \(C_{14}H_{28}O_2\). Meanwhile, the hydrocarbon > C18 is due to the large molecular fatty acids in the feed such as oleic acid (fig.1) not yet fully crack by the process. Da Mota, et al. (2014) in their research on the scale pilot plant produces green diesel by using CPO, through GC-MC analysis product obtained including 91.38% (w/w) of hydrocarbons such as normal paraffin, naphthenic, Olefin and 8.62% (w/w) oxygenation compounds [12].

4. Conclusion
The optimum temperature of the hydrogenation of crude palm oil using NiMo/Al2O3 catalyst to produce the green diesel fuel is 315 °C, with a product yield of 68.2%. The physical and chemical properties have fulfilled the specification of diesel fuel, which is density 0.8101 gr/ml, kinematic viscosity 4.27 cSt, flash point 58 °C, cetane number 75, and calorific value is10693 cal/gr.

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