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Characterization of Green Diesel Product in the Hydrotreating Process of Crude Palm Oil using Ni/Bentonite Catalyst

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ABSTRACT
The main issues faced by many developed and developing countries in the world today are future energy availability and better utilization of natural resources. Production of green diesel using hydrotreating process at 4 bar pressure, 3000 ml CPO was injected with hydrogen gas using 3% catalyst to accelerate the reaction. The non-static variables used in this research are pressure and temperature. After obtaining optimum conditions for pressure variations of 18 bar and 20 bar with the best operating temperature variations of 300℃, 310℃, 330℃, 350℃, 380℃. The use of pressure 20 bar and at a temperature of 350℃ per 3000 ml is the optimum condition in this study and produces a percentage yield of 39.83%. The physical properties obtained are density at 20 bar pressure is 777 kg/m^3 - 795 kg/m^3, kinematic viscosity at 20 bar pressure 2.14 cSt - 2.21 cSt and flash point at 18 bar pressure 56-60℃ and at 20 bar pressure 55℃ - 66 ℃, Cetane number at 20 bar pressure is 75.1, at 20 bar pressure heating value is 42.91 MJ/kg which meets European standards ENI5940: 2016 / AL: 2018.

Keywords: *Crude Palm Oil, Hydrotreating, Green Diesel, Characteristics.*

1. INTRODUCTION

The government is currently working to increase the use of biofuels as an environmentally friendly energy source to reduce dependence on fossil fuels. The choice is based on the fact that renewable energy is a proven technology, undergoing rapid development, and has the potential to have a zero carbon footprint. Biodiesel is a future energy source that is renewable, environmentally friendly and its raw materials are widely available in Indonesia [1].

Palm oil is an oil that has environmentally friendly characteristics at a low price that can be used as an alternative fuel source. One of the potential resources that can be utilized as alternative energy is the utilization of vegetable oil obtained from the extraction of vegetable oil-producing plants. There have been many studies conducted to find potential vegetable oils to be used as alternative fuels, such as the utilization of palm oil (CPO), coconut oil, castor bean oil, etc. In terms of economics and availability, palm oil (CPO) is the most potential biodiesel feedstock, where Indonesia is the number one CPO producing country in the world (50% of world production) with a total CPO production in 2019 of around 34 million tons towards global CPO consumption needs [2].

Green diesel is a biologically derived product with less impact on atmospheric CO_2 accumulation and unlike petroleum diesel, it is free of aromatics or naphtha and produces cleaner combustion. Unlike biodiesel, green diesel does not contain oxygen so it is more stable, non-corrosive, and has a calorific value similar to petroleum diesel. Green diesel also has superior cold weather behavior compared to biodiesel, does not increase NOx emissions and has a higher cetane number (CN) which facilitates engine starting [3].

Method in making green diesel by hydrotreating process, which is a hydrodeoxygenation reaction involving hydrogen gas [4]. There is a side reaction from the hydrotreating process, namely coke forming, which can deactivate the catalyst [5]. Catalysts work by changing the path of the reaction mechanism, generally the catalyst used for the hydrotreating process is a type of heterogeneous catalyst, which is a catalyst with a different phase from the reactants. Catalyst has three components: the active component, the carrier, and the promoter. In the hydrodeoxygenation reaction, the type of catalyst can affect the yield of the product produced [5].

The hydrotreating process is generally carried out in a reactor with high temperature (300-450°C) and high pressure and hydrogen is supplied to the reactor along with the feedstock [4]. Hydrotretaing processes typically involve the use of heterogeneous catalysts, such as Ni-Mo, Co-Mo, Pt, Pd and zeolites, with catalysts that have a high acid density being more desirable due to their ability to remove oxygen through C-O cleavage of fatty acids, helping to speed up the reaction and increase the acid density [4]. In this process there are five reaction pathways namely hydrogenation, hydrogenolysis, hydrodeoxygenation, decarbosylation and decarbonylation. Green diesel using the triglyceride hydroprocess has propane as a by-product. This makes green diesel considered more economical and attracts the world's attention [6].

Research conducted by [7] discusses the production of green diesel at optomum temperatures, CPO has not been fully converted into environmentally friendly diesel products, so that when the condensation product is removed, a lot of steam is released, but at 330 °C there is a decrease in the amount of product produced, this is due to high temperatures resulting in hydrocarbons that form carbon deposits (coke) and aromatic compounds, this is indicated by the increasingly blackish color and smell of the product. The optimum temperature of crude palm oil using $NiMo/Al_2O_3$ to produce environmentally friendly diesel fuel is 315°C, with a product yield of 68.2%. The physical and chemical properties met the diesel fuel specifications of density 0.8101 gr/ml, kinematic viscosity 4.25 cSt, cetane number 75, and calorific value 10693 cal/gr.

Research conducted by [8] Ni-BZS 0.5 catalyst has the highest activity and selectivity in the conversion of coconut oil to biogasoline. The conversion value of the liquid product obtained was 52.82% (w/b), and the selectivity to the gasoline fraction was 30.52% Carbon deposition was reduced on the Ni-BZS 0.5 catalyst due to the presence of Ni metal. This metal breaks down hydrogen or allows hydrogen spillover, although it is not as good as precious metals such as platinum and palladium.

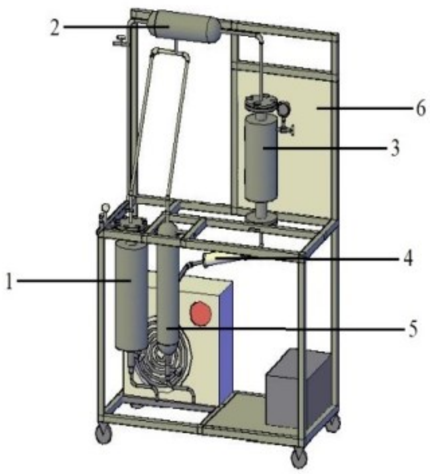
The presence of Ni provides resistance to carbon deposition carbon or the formation of carbon residues. In addition, the Lewis acid sites of Ni can increase the adsorption of feed on the catalyst resulting in an optimized cracking process. This shows that increasing the acidity value can indeed increase catalyst activity, but acidity is not the only determinant of conversion yield.

Based on the description above, the title of this research is "Characterization of Green Diesel Product in The Hydrotreating Process of Crude Palm Oil Using Ni/Bentonite Catalysts". The purpose of this research is to produce green diesel from crude palm oil through hydrotreating process using Ni/Bentonite catalyst. In addition, this research also aims to analyze the characteristics of the best green diesel product by reviewing the parameter of % yield of products obtained from crude palm oil raw materials. This research will also include quality parameters such as density, kinematic viscosity, flash point, cetane number, calorific value, and conduct analysis using GC-MS to provide a more comprehensive picture of the quality of green diesel produced.

2. MATERIAL AND METHODS

2.1 Materials

The materials used in this study were used crude palm oil (CPO), hidrogen (H_2), nickel (Ni), bentonite clay, H_2SO_4, NaOH and aquadest.The tool used in the research on the conversion of crude palm oil into green diesel fuel is a hydroprocessing tool. This tool has several main components, namely:



Description:

1. Feed Tank	4. Condenser
2. Accumulator Tank	5. Separator Tank
3. Reactor 1	6. Control Panel

Figure 1. Unit Hydrotreating

2.2 Method

The research was conducted at the Chemical Engineering Laboratory and Energy Engineering Laboratory at Politeknik Negeri Sriwijaya Palembang. This research was carried out for 5 months, starting from March to July 2024.

This research on making green diesel using Crude palm oil with the hydrotreating method consists of several stages of the process, namely the preparation of raw materials, the manufacture of catalysts, the research process and the analysis stage of the products produced will be carried out in the chemical engineering laboratory and the energy engineering laboratory of Politeknik Negeri Sriwijaya.

For the preparation of Nickel Catalyst and NaOH in a ratio of 1: 1. then filtered while doused with NaOH solution then dried at room temperature for 24 hours after that calcined at 300ºC with 3 hours in the furnace.Then bentonite catalyst preparation prepare bentonite clay with a size of 170 mesh. then mix bentonite clay with H_2SO_4 solution in a ratio of 1: 10. After that let the bentonite solution stand at room temperature for 24 hours. then filter the bentonite clay. then activation of bentonite clay in a furnace with a temperature of 300ºC within 3 hours.

Wet impregnation of Ni/bentonite catalyst is nickel mixed with 50 ml NaOH solution, then put bentonite clay into the nickel salt solution, stir until smooth, then filtered, then form a small round, then dry at 100ºC for 24 hours. after that activate the catalyst at 450ºC within 2 hours in the furnace.

In the process of making green diesel using Crude palm oil by hydrotreating method, there are various variations of pressure 18 bar and 20 bar with the best operating temperature variations of 300°C, 310°C, 330°C, 350°C, 380°C. The product obtained will then be analyzed based on the parameters of green diesel, which consists of Density by Method ASTM D1298, Kinematic Viscosity (mm^2 /S) by Method ISO 12058, Flash Point (ºC) by Methode ASTM D93, Cetane Number by Method ASTM D5865-11a, Calorific Value by ASTM D5865-11a, and GC-MS TSP.

3. RESULTS AND DISCUSSIONS

The results from the analysis were that they are key factors that hugely influence to the results of the green diesel produced. Physical properties and yields can be seen in the following table:

Table 1. Physical Properties of Green Diesel Product Research Results

Sampel	Test Parameters: Density (kg/m^3)	Kinematic Viscosity (cSt)	Flash Point (ºC)
Standard EN15940:2016/A1:2018	765 – 800	2 – 4,5	Min 55
S.1	794, 9	2,08	56
S.2	794,6	2,12	58
S.3	789,1	2,14	59
S.4	783,6	2,20	60
S.5	778, 9	2,07	59
S.6	795	2,16	55
S.7	793	2,15	57
S.8	788,06	2,18	59
S.9	782	2,21	66
S.10	777	2,14	60

Table 2. Yield of Green Diesel Product

Sample	Pressure (Bar)	Temperature (ºC)	Product Volume (ml)	Yield (%)
S.1		300	850	28,3
S.2		310	930	31,0
S.3	18	330	1050	35,0
S.4		350	1140	38,0
S.5		380	1100	36,67
S.6		300	975	32,5
S.7		310	1020	34,0
S.8	20	330	1145	38,17
S.9		350	1195	39,83
S.10		380	1155	38,50

3.1 The Effect of Temperature on Green Diesel Yield

The reaction occurred at constant pressures of 18 bar and 20 bar. Fig 2 shows the percentage of green diesel product yield that continues to increase with higher operating temperatures. Temperature 350°C is the optimal condition with a yield of 39.83% at a pressure of 20 bar and at a pressure of 18 bar the optimal temperature at 350°C the yield obtained is 38%. Percent yield in the manufacture of green diesel from crude palm oil indicates the percentage of green diesel product mass produced compared to the amount of CPO used. Where in this study in making green diesel using raw materials in the form of crude palm oil 3 liters.

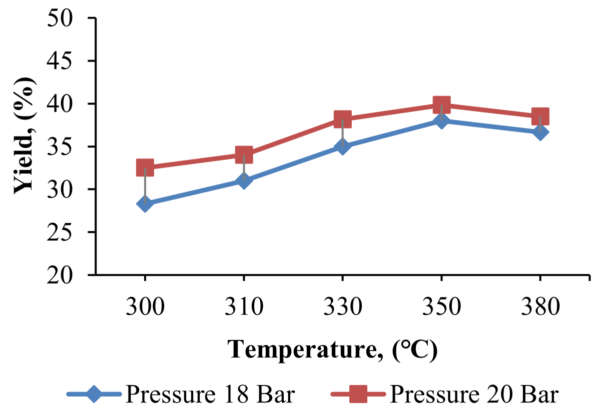


Figure 2. The Effect of Temperature on Green Diesel Yield

At the optimum temperature of 350°C, CPO has not been fully converted into green diesel products, so when the condensation product is removed, a lot of steam is released. However, at 380°C there is a decrease in the amount of product produced, this is because the temperature is too high resulting in the formation of carbon deposits (coke), this is indicated by the blackish product and has a pungent odor.

3.2 Analysis of Green Diesel Product Characteristics

Density

Density is the measurement of mass per unit volume of an object, as each substance has a different density [9], Density is one of the physical properties that can be used as an indication in knowing the type of product or compound. Based on Green Diesel European Standars, Green Diesel has a density range between 765-800 kg/m^3. The higher the density of an object, the greater the mass per volume [10].

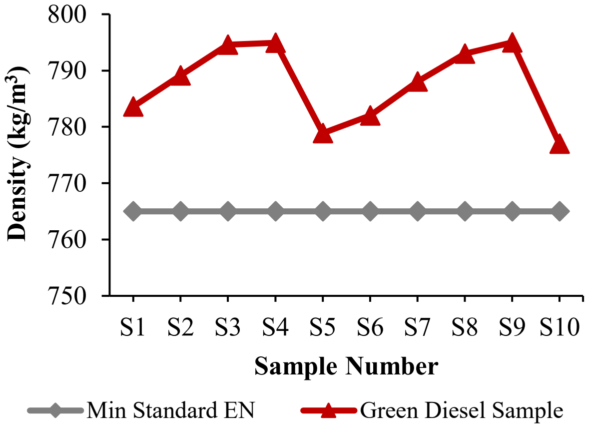


Figure 3. Density Chart of Green Diesel Product

From table 1, it can be seen that the density value obtained from the research falls into the range of European Standard EN15940: 2016/A1: 2018. Density at 20 bar pressure conditions the highest density is 795 Kg/m^3 and at 18 bar pressure the highest product density is 794,9 Kg/m^3. Density is affected by process temperature and pressure. Where the higher the temperature will increase the pressure so that it can cause coke formation in the catalytic process and can affect the density value of a product [5]. Density values that are too high can cause incomplete combustion reactions that can increase emissions and engine wear [11].

Viscocity

Viscosity is the viscosity of a fluid. The greater the viscosity of the fluid, the more difficult it is for an object to move in the fluid. Viscosity in liquid that plays a role is the cohesion force between liquid particles [12].Viscosity is also a measurement of the resistance of a fluid that is altered by either pressure or stress. Kinematic viscosity is measured using the DIN 53015/ISO 12058 method. The kinematic viscosity measurement results compared to the European Standard can be seen in the following table and grafic.

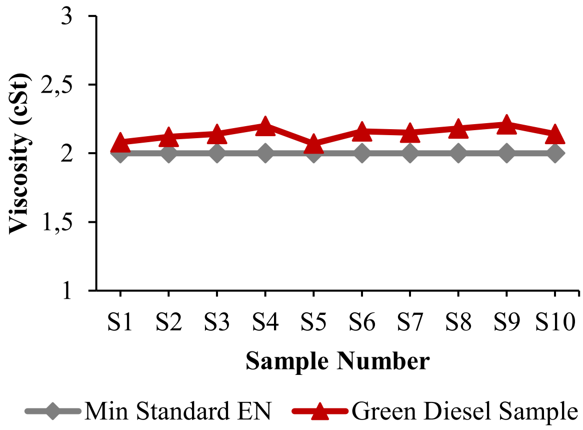


Figure 4. Viscosity Chart of Green Diesel Product

From the Fig. 4 and Table 1, it can be seen that the viscosity value obtained from the research falls into the european standard range with a range of 2-4.5 viscosity under pressure conditions 20 bar the highest density is 2.21 cSt and at a pressure of 18 bar the highest product density is 2.20 cSt.

Flash Point

Flash point is the lowest temperature at which oil will ignite when exposed to sparks, Incomplete combustion and even explosions occur because the flash point is too low to cause fuel injector failure [13]. Flash point is tested using the ASTM D93 method. The flash point value is related to the safety and storage of a fuel, the greater the flash point value, the easier the fuel storage.

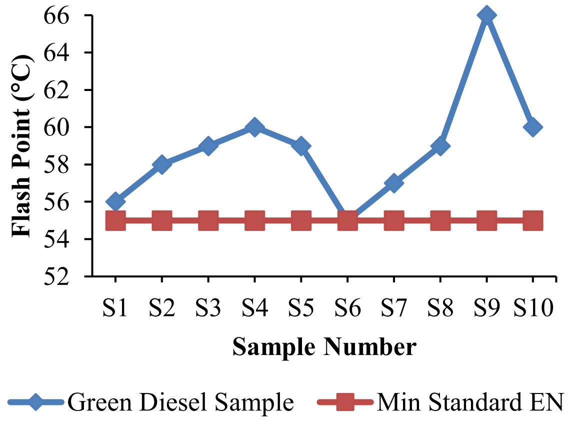


Figure 5. Flash Point Chart of Green Diesel Product

From the Fig. 5 and Table 1, flash point measurement is carried out using a flash point tester. Flash point determination is related to the safety of fuel storage. The flash point test results were obtained between 55°C- 66°C which meets the requirements of the Green Diesel European Standard. Flash point is related to the volatility of the fuel as a result, this will affect the amount of light fraction present in the fuel sample [14].

Cetane Number

Cetane Number is a number that indicates the burning quality of diesel fuel, According to Liu, et al 2011 The higher the yield sometimes, the higher the quality of the diesel fuel. Conversely, low levels of diesel fuel can cause the engine to run slower. Cetane number indicates the ability of the fuel to self-ignite (auto ignition). Based on table 4.6, the cetane number in sample 1 is with a pressure of 18 bar, which is 72.3. And sample 2 at a pressure of 20 bar has a cetane number of 75.1 CN, this is in accordance with Green Diesel European Standars EN15940: 2016/A1: 201 with a minimum cetane number of 70 CN.

Table 3 Cetane Number of Green Diesel Product

Testing Type	Standard EN15940:2016/A1:2018	Test Results	
		S.4	S. 9
Cetane Number	Min 70	72,3	75,1

Calorific Value

Calorific value is the amount of heat energy released per unit mass. HHV heating value, is the heating value obtained experimentally using a calorimeter bomb where the combustion of fuel is cooled to room temperature so that most of the water vapor formed from burning hydrogen condenses and releases its latent heat. LHV calorific value, is the calorific value of fuel without latent heat from condensation of water vapor [15]. In this study, calorific value measurements were made on samples with 18 bar pressure with a calorific value of 41.04 MJ/kg and 20 bar pressure having a calorific value of 42.91 MJ/kg or 9804.4041cal/gram. This calorific value is close to the calorific value of Green Diesel European Standars EN15940:2016/A1:201 of 43.70-44.5 MJ/kg. The higher the calorific value of a fuel, the more efficient the energy produced, because it produces more heat with less mass [16].

Table 4. Calorific Value of Green Diesel Product

Testing Type	Standard EN15940:2016/A1:2018	Test Results	
		S.4	S. 9
Calorific Value	Min 43,70 - 44,5	41,04	42, 91

Gas Chromatography-Mass Spectrometry

Gas Chromatography (GC) serves to separate mixtures of compounds based on their physical and chemical properties. In this study, green diesel product samples were analyzed using GC-MS to identify the chemical compounds and composition of the yield from the crude palm oil hydrotreating catalytic process with 3% activated Ni/Bentonite catalyst. The samples represent the whole sample with various hydrogen pressures used in the process.

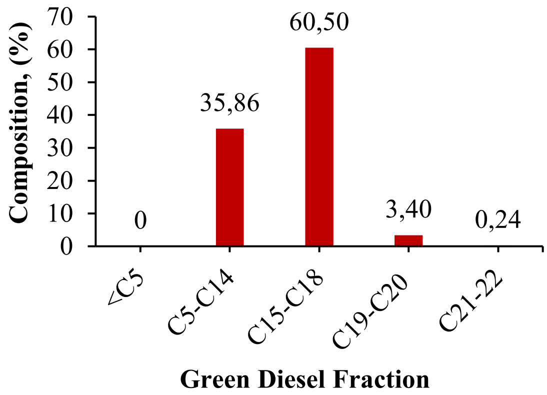


Figure 6. Green Diesel Product Fraction and Composition Chart

Green Diesel product from Catalytic Hydrotreating crude palm oil process using 3% activated Ni/Bentonite catalyst, 4 bar H_2 gas injection, 350°C reactor temperature through GC-MS TSP analysis is dominated by C15-C18 chain 60.50% which is the fraction of diesel fuel. This is not much different from the research conducted by [5] by using crude palm oil, zeolite catalyst, and 12 bar H_2 at 375°C through GC-MS analysis the product obtained is dominated by C15-C18 chains 55.93%.

From Fig. 6, it is known that the green diesel product produced does not contain fractions <C5 because hydrocarbons below C5 cannot be condensed and evaporate into the air. The 35.86% C5-C14 fraction is a fraction of naphtha, gasoline, and kerosene. The C5-C14 chain compounds contained in the product are due to continuous cracking reactions and converting the compounds into lighter fractions. It also forms myristic acid which has the chemical [5]. In addition, there is also a C19-C20 fraction of 3.40% which is lubricating oil and the C21-C22 fraction of 0.24% is paraffin/wax which is formed due to the cracking process on crude palm oil not yet fully into diesel products.

4. CONCLUSIONS

Based on the results of research on the characteristics of Green Diesel products from the Crude palm oil hydrotreating process using Ni/Bentonite catalysts, it can be concluded. From the optimum conditions for making green diesel through the hydrotreating process, the highest percent yield at a pressure of 18 bar is at an optimal temperature of 350°C, which is 38.0% yield. And at a pressure of 20 bar and an optimal temperature of 350°C the yield is 39.83%, 777 kg/m^3-795 kg/m^3, at a pressure of 18 bar density from 778.9-794.9, viscosity at a pressure of 18 bar 2.07 cSt - 2.20 cSt, viscosity at a pressure of 20 bar 2.14 cSt - 2.21 cSt and flash point at a pressure of 18 bar 56 - 60 and at a pressure of 20 bar 55°C - 66°C, Cetane number at 18 bar pressure is 72.3, Cetane number at 20 bar pressure is 75.1 and heating value at 18 bar pressure is 41.04 MJ/kg and at 20 bar pressure heating value is 42.91 MJ/kg which meets European standard ENI5940: 2016/Al:2018.

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