Manufacturing Liquid Fuel from Cooking Oil using Pyrolisis Process Review of Temperature and Reaction Time

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Abstract: Indonesia has abundant renewable energy sources, but they have not been utilized optimally compared to with the use of fossil fuels. For this reason, it is necessary to develop other energy sources as cheap and renewable alternatives to reduce dependence on fuel oil (BBM). One of the renewable energies that can be developed is liquid fuel produced from used cooking oil. This study aims to obtain the optimum reaction temperature and time that produces the highest %yield . Liquid fuel is made from 1000 ml of used cooking oil and 10% zeolite catalyst through a pyrolysis process at temperatures of 290oC, 310oC, and 330oC with reaction times of 70 minutes, 90 minutes, 110 minutes and 130 minutes atreactor catalytic cracking. To determine the quality of liquid fuel, density, viscosity, flash point, cetane number and GC-MS analysis were conducted. Based on % yield of 2,9776% at a temperature of 310oC and a time of 130 minutes, the resulting liquid fuel production has a density value of 837.08 kg/m3, a viscosity value of 2.84 mm2/s and a cetane number. of 71.6. The results of the GC-MS analysis show that in liquid fuel pyrolysis of used cooking oil there is a gasoline fraction (C5 – C12) of 26.3%, a kerosine fraction (C13 – C14) of 15.4%, and a diesel fraction (C15 – C19) of 46.2%.

Keywords: pyrolisis, cooking oil, liquid fuel, zeolite catalyst, biodiesel

1. Introduction

Fuel oil is a very important need in life. The fuel used so far comes from crude oil taken from the bowels of the earth, while petroleum is a non-renewable fuel, so it will experience difficulties in the future. For this reason, it is necessary to develop other energy sources as cheap and renewable alternatives in order to reduce dependence on fuel oil. production biofuel can reduce dependence on fossil fuels and its use is more environmentally friendly. Currently, biofuels can be found in solid, liquid and gaseous forms produced from organic materials either directly from plants or indirectly from industrial, commercial, domestic processes or agricultural residues.

Utilization of waste from the food industry process as a raw material for making alternative fuels is one of the best solutions that can be done. The food industry waste in question is used cooking oil. Used cooking oil has considerable potential to be developed into biodiesel fuel because it has the fatty acids of used cooking oil. Like animal fats, vegetable oils can also be made by cracking methods into shorter chain carbon compounds such as biogasoline.

The cracking process (pyrolysis) is a process in which unsaturated long chain compounds with large molecules will be broken down into shorter chain compounds such as gasoline, kerosene and diesel using a catalyst. Pyrolysis reactions in general can be described by the following formula:

$$C_nH_mO_p \ (biomassa) \xrightarrow{\text{heat}} \Sigma \ liquid \ C_xH_yO_z + \Sigma \ gas \ C_aH_bO_c + H_2O + C \ (\text{char})$$

The product in the form of a liquid is the main product of the pyrolysis process, commonly referred to as pyrolysis oil or bio-oil. Bio-oil can be used in the production process of liquid fuels or chemicals. The initial products formed from the pyrolysis process are condensed gas and solid fuel. The condensed gas may decompose further into noncondensable gases such as CO, CO_2, H_2 and CH_4, liquids and solid fuels.

Temperature determines the rate of material decomposition, residence time in the reactor and pyrolysis results. The rate of decomposition and damage to the structure of the constituent material increases with increasing temperature of the pyrolysis reaction. Reaction time is related to the length of time the material holds in the reactor. If the residence time is long enough, the pyrolysis process will be perfect for converting raw materials into gas and liquid.

2. Materials and Method

2.1. Materials

The manufacture of liquid fuel in this study uses cooking oil as much as 1000 ml each and 10% zeolite catalyst from the raw material is inserted into the catalytic cracking reactor.

2.2. Method

This research started with the preparation of used cooking oil and zeolite catalyst. The used cooking oil prepared as much as 1000 ml is carried out by a filtering process to remove the impurities contained in the used cooking oil, then the catalyst Zeolite in granular form is crushed into powder.

Then the zeolite was sieved using a 60 mesh sieve. The sifted zeolite was immersed in 1 N HCl solution for 80 minutes while stirring. Zeolite was washed with distilled water until the pH was neutral. Zeolite was calcined in an oven at 300oC for 2 hours. The pyrolysis process of 1000 ml of cooking oil uses a 10% zeolite catalyst with temperature variations of 290°C, 310°C, 330°C and reaction times of 70 minutes, 90 minutes and 110 minutes and 130 minutes. Liquid fuel product analysis includes %yield, density, viscosity, flash point, cetane number and GC-MS analysis.

3. Results and Discussion

3.1. Yield Percentage

Yield percentage is the ratio of the mass of the product produced to the mass of the raw material that is fed. The percentage yield resulting from the cracking process can be seen in Figure 4.1.
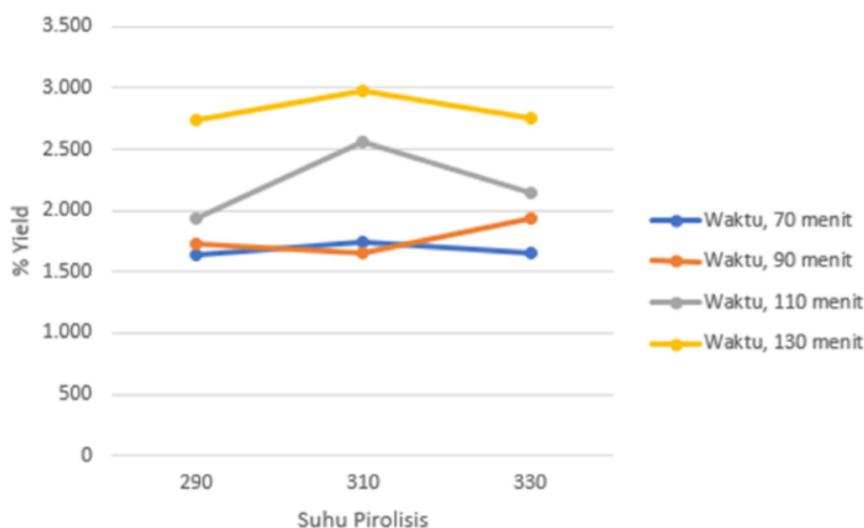
Fig. 1. Effect of Pyrolysis Temperature (^{o}C) on Yield Percentage at Various Pyrolysis Time

Figure 1 shows that the %yield of liquid fuel tends to increase as the pyrolysis temperature increases. This is because at high temperatures the decomposition of raw materials will be more perfect so as to produce a higher % yield of liquid fuel as well.

However, in this study there was also a decrease in yield as the temperature and time of pyrolysis increased, namely at a pyrolysis temperature of 330°C and a pyrolysis time of 130 minutes. The decrease in % yield was due to the high temperature and pyrolysis time of 130 minutes. This decrease in % yield occurs because at high temperatures and too long a time will result in greater loss of weight.

3.2. Density

Density or specific gravity is defined as the mass of a material per unit volume of the material. The purpose of determining this density is to determine the density value of the liquid fuel product resulting from the pyrolysis process.
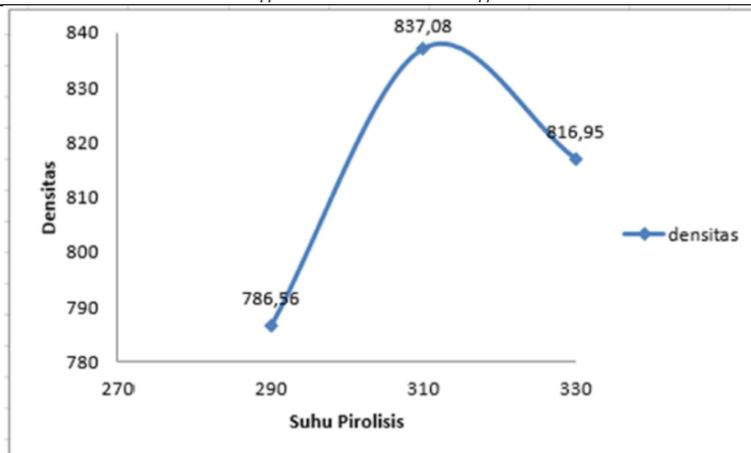
Fig. 2. Effect of Pyrolysis Temperature (^{o}C) on Density at Various Pyrolysis Times

The results of the pyrolysis process on the quality of density can be seen in Figure 2 which shows an increase in density at a temperature of 310oC and a decrease at a temperature of 330°C and 390°C. At a temperature of 310°C and a time of 130 minutes, the density value is 837, 08 kg/m3. The increase in density is due to pyrolysis at low temperatures there is a re-cracking of used cooking oil. As for the decrease in density at a temperature of 330°C because there are no more saturated fatty acid compounds that will decompose and also evaporation of substances that have been decomposed which causes the density value to decrease.

Based on the Indonesian National Standard (SNI) 8968: 2021, the minimum density of liquid fuel 765 kg/m3. Overall, the density value of the liquid fuel produced from the pyrolysis of beef fat has met the Indonesian National Standard (SNI) 8968: 2021.

3.3. Viscosity

Viscosity is the property of a liquid (fluid) due to friction between the molecules of the liquid with the force on the liquid. Viscosity aims to determine the value of the viscosity of a liquid, the greater the viscosity, the slower the flow.
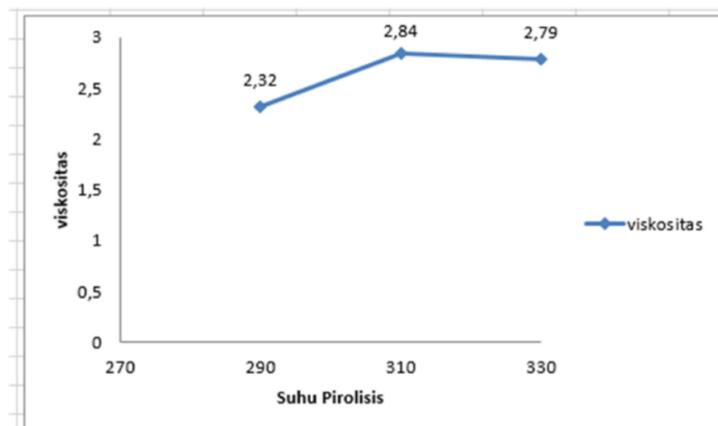
Fig. 3. Effect of Pyrolysis Temperature (^{o}C) on Viscosity at Various Pyrolysis Times

The results of the pyrolysis process on the quality of the viscosity can be seen in Figure 3 which shows an increase in temperature of 310°C and then decreases at a temperature of 330°C. The increase in the value of the viscosity of the liquid is influenced by increasing heating and burning time. Increasing the temperature in the pyrolysis process will produce oil that has a greater viscosity value. The largest viscosity in the sample at a temperature of 310°C with a time of 130 minutes is 2.84 mm2/s. The decrease in the viscosity value at a temperature of 330^C is due to the fact that there are no more saturated fatty acid compounds that will decompose and also evaporation from decomposed substances which causes the viscosity value to decrease.

Based on the Indonesian National Standard (SNI) 8968: 2021, the viscosity of liquid fuel ranges from 2,0 to 4,5 mm2/s. Overall, the viscosity value of liquid fuel produced from the pyrolysis of beef fat has met the Indonesian National Standard (SNI) 8968: 2021.

3.4. Flash Point

The flash point is closely related to the ease with which the fuel is ignited and the speed of the combustion process. Flash point is a phase with which a material will be able to extinguish a fire in the form of a vapor. The lower the flash point temperature, the easier it will be for the material to burn.
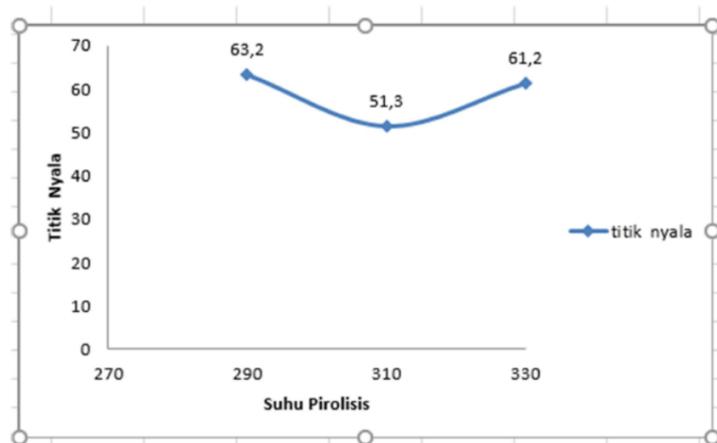
Fig. 4. Effect of Pyrolysis Temperature (^{o}C) on Flash Point at Various Pyrolysis Times

The results of the pyrolysis process on the quality of the flash point can be seen in Figure 4 above which shows the higher the temperature, the higher the flash point value. This is because the oil resulting from pyrolysis at low temperatures has a simpler carbon chain. The lowest flash point is obtained at a temperature of 310°C and a time of 130 minutes which is $51,3^{o}$C and the highest flash point is obtained at a temperature of 290°C and a time of 130 minutes which is $63,2^{o}$C.

Based on the Indonesian National Standard (SNI) 8968: 2021, the flash point of liquid fuel is at least 55°C. Overall, the flash point value of the liquid fuel produced from the pyrolysis of cooking oil does not meet the Indonesian National Standard (SNI) 8968: 2021.

This is because the flash point test uses an open bowl that allows contact with air to be one of the factors for flammable liquid fuel and has a low flash point. The presence of volatile matter in the product can also reduce the flash point of the product so that it cannot reach the SNI 8968: 2021 standard.

3.5. Cetane Number

Cetane Number or Cetane Number is a measure that indicates the quality of the fuel for diesel. In a diesel engine a higher cetane number fuel will have a shorter ignition period than a lower cetane fuel. The higher the cetane number the easier it is for the fuel to burn in compression. With combustible fuel it will reduce the knock from the diesel engine, so the engine will be smoother. Therefore, a fuel that has a higher cetane number will usually cause the engine to run smoother and quieter. This is different if the cetane number is lower then there will be a delay so that it adds knocks to the combustion process.

The results of the Cetane Number measurement on liquid fuel products are found to be 71,6, compared to the standard for hydrocarbon diesel oil as a result of the Decree of the Director General of New, Renewable Energy and Energy Conservation in 2021 which is worth 70 so that it can be concluded that liquid fuel products meet the Standards.

Indonesian National Standard (SNI) 8968 : 2021. The cetane number value is influenced by the fatty acid composition of the used cooking oil, the more unsaturated the oil, the lower the cetane number. Cooking Oil has saturated fatty acids as much as 89.75% in the form of caprylic acid, acorbic acid, acetyl salicylic acid, decanoic acid, stearic acid, oleic acid, margaric acid and aricidonic acid. High saturated fatty acids result in a highcetane number. The higher the cetane number , the better the combustion quality of the diesel engine (Naimah et al, 2017).

Results of GC-MS Analysis of Beef Fat Raw Material

Fig. 5. Cooking Oil Raw Material Chromatogram

In Figure 5 it can be seen that the results of GC-MS identify used cooking oil raw materials that have a retention time of 18 minutes. The retention time at each peak represents the compounds contained in the used cooking oil raw material. From the retention time of each peak, the % area is obtained which is the composition of saturated and unsaturated fatty acids in the raw material of used cooking oil.

GC-MS analysis results show that saturated fatty acids in cooking oil can be classified into 14 groups, namely caprylic acid by 3.47%, corbic acid by 32.6%, acetylsalicylic acid by 13.04%, decanoic acid by 6.52% , stearic acid by 4.34%, oleic acid by 2.17%, aricidonic acid by 2.17%, margaric acid by 38.59%.

This is in accordance with research in the integrated research and testing laboratory (2013) which states that the content of saturated fatty acids in new cooking oil and waste cooking oil each has an insignificant effect (P>0.05) on saturated fatty acid levels, and unsaturated fatty acids. Fresh oil contains 99.930% fat, 1.790% saturated, and 90.275% unsaturated. Fat content in waste cooking oil is 99.882%, saturated fatty acids 25.564%, and unsaturated fatty acids 72.113%. The highest saturated fatty acid content is M.Palmitate 25.69% while the unsaturated fatty acid Cis-9-octadecanoate is 48.06%.

3.6. Results of GC-MS Analysis of Liquid Fuel Products
The results of GC-MS analysis for liquid fuel products based on the highest % yield are at a temperature of 310oC, pyrolysis time of 130 minutes.

Fig. 5. Liquid Fuel Products Chromatogram

In Figure 5, it can be seen that the GC-MS results identify the pyrolysis oil that has a retention time of 18 minutes. The retention time at each peak represents the compounds present in the liquid fuel product. From the

retention time of each peak, the % area is obtained which is the composition of hydrocarbon compounds in liquid fuel products.

GC-MS analysis results show that the liquid fuel fraction produced is classified into 4 groups, namely the gasoline fraction ($C_5 - C_{12}$) of 26.3%, the kerosine fraction ($C_{13} - C_{14}$) of 15.4%, and the fraction diesel ($C_{15} - C_{19}$) by 46.4%. Most of the fatty acids in used cooking oil are cracked and turned into compounds of the alkane group, alkene and aromatic group compounds with the highest number of carbon chains, namely $C_{15} - C_{19}$, equivalent to diesel fuel.

4. Conclusion

The best operating conditions to produce liquid fuel with the highest % yield are at a temperature of $310^{\circ}C$ and a reaction time of 130 minutes. The resulting liquid fuel production has a density, viscosity and cetane number that has met the Indonesian National Standard (SNI) 8968: 2021, Based on the highest % yield, the results of the GC-MS analysis show that in the liquid fuel pyrolysis used cooking oil there is a gasoline fraction ($C_5 - C_{12}$) of 26.3%, a kerosine fraction ($C_{13} - C_{14}$) of 15.4% , and the diesel fraction ($C_{15} - C_{19}$) was 46.2%.

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