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Pyrolysis of Lubricant Waste into Liquid Fuel using Zeolite Catalyst

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Abstract— The number of means of transportation in Indonesia continues to increase from year to year. Along with this, the amount of used oil waste oil becomes something more useful by considering the high hydrocarbon content, namely the pyrolysis method with a raw material ratio of 1:1 to be converted into liquid fuel which is ready to be commercialized by catalytic cracking process using a zeolite catalyst of a certain amount. 25% by weight of the raw material which is useful for accelerating the reaction so as to save energy use and improve the quality of the resulting product. Observations were made by looking at the effect of temperature variations ranging from 250°C, 300°C, to the results of the pyrolysis process which aims to obtain the optimal process temperature

Keywords: catalyst, electric current, fuel, lubricant, pyrolysis, waste, zeolite

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1 INTRODUCTION

Motorized vehicles are now a primary need for society. Motor vehicle users in Indonesia are increasing every year. The increasing demand for motorized vehicles is followed by an increase in the need for oil as a vehicle lubricant. Oil can only be used for a certain period of time or based on the distance traveled by the vehicle. After that the oil must be replaced with a new one, so that the engine function is maintained in good condition.

Used motor vehicle oil that is not used must be discarded. So far, the used oil is simply thrown into the environment without being treated properly. Motor vehicle oil waste is included in the waste containing hazardous and toxic materials so that special handling is required. If motor vehicle oil waste is not treated properly and correctly, this will cause environmental pollution, especially on the quality of underground water. Underground water is a source of water for humans, so over time the effects of environmental pollution by used oil waste will have an impact on human health. This is a problem that needs to be addressed immediately so as not to have a systemic impact on environmental damage and human health. In tests of used lubricants studied, stated that the combustion process requires 4 important factors, namely, (a) available combustible fuel, (b) sufficient heat to raise the temperature of the fuel to the point of ignition, (c)) there is sufficient air to supply the oxygen needed to keep the combustion process running and maintain a sufficient heat supply so as to allow the ignition of the fuel and (d) the occurrence of a chemical chain reaction so that the combustion reaction can be sustainable [1].

Pyrolysis method is one method that can be used to reprocess used lubricating oil into fuel. In producing valuable liquid fuel products, pyrolysis can be carried out with or without the help of a catalyst. In this study, the pyrolysis process was carried out by heating lubricating oil and adding zeolite catalyst to a temperature of 350°C and heated for one (1) hour [2].

1.1 Lubricating Oil

Currently, energy sources still come from fossils, especially crude oil, natural gas or coal. Such sources of fossil fuels are expected to run out in the near future. According to some studies, it is estimated that crude oil will last only about another 80 years, gas fuels for 150 years, and coal for 230 years. Based on the above data coupled with the high cost of producing petroleum-based fuels, environmental hazards as a result of burning fossil fuels and the increasing demand for fuel, has prompted researchers to investigate the possibility of using alternative fuels instead of fossil fuels [3]-[6]. Alternative fuels must be technically feasible, economically competitive, environmentally friendly and have unlimited sources of availability [7].

Currently scientists and researchers around the world are working hard trying to develop new technologies that allow recycling or reusing waste as an energy source [8]. Waste treatment has become one of the most important problems in modern society to protect the environment [9]. In recent years, millions of tons of used oil have been dumped into the ground or water [10]. Used oil waste consists of used motor vehicle engine oil, used industrial engine oil, and used engine gear lubricants [11]. The production of waste motor vehicle oil is estimated at 24 million tons annually worldwide [12]. Meanwhile around 40 million metric tons per year of lubricating oil (grease) are produced worldwide. About 60%

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of the total production becomes waste [13]. In Turkey, it is estimated that more than 230,000 tons/year of waste industrial engine oil is illegally dumped in backyards or landfills by the public [14]. Illegal disposal of waste oil is an important and significant problem for modern society [15]. This should be a serious concern by the international community.

1.2 Pyrolysis

Converting used oil into fuel that resembles diesel or gasoline that can be used in engines without any side effects is very important [16]. Using waste oil as engine fuel is a way to increase efficiency from the point of view of energy use [17].Waste used oil can be reconstructed chemically by heating in an oxygen-free environment. This process is called pyrolysis [18]. Research on pyrolysis assisted by solid catalysts has been carried out by many previous researchers. From this research, it is known that the selectivity of this product is strongly influenced by the presence of a catalyst, the character of the catalyst, the presence of water vapor and gas in the used oil [19]. The presence of a catalyst or metal catalyst can affect the process temperature, yield and product composition [20]. Research on the processing of used oil waste into fuel by pyrolysis is very interesting and needs to be studied further [21].

Cracking is the process of breaking down or breaking large hydrocarbon molecules into small hydrocarbon molecules. The purpose of cracking is to improve the quality of the fraction. The process of converting plastic waste into oil can be done by the cracking process. The results of this plastic cracking process can be used as chemicals or fuel oil. There are three kinds of cracking processes, namely hydro cracking, thermal cracking and catalytic cracking:

1. Hydro Cracking

Hydrocracking is a cracking process by reacting plastic with hydrogen in a closed container equipped with a stirrer at a temperature between 423-673°K and a hydrogen pressure of 3-10 MPa. The hydrocracking process is assisted by a catalyst. To assist the mixing and reaction, 1-methyl naphthalene, tetraline and decaline are usually used as solvents.

2. Thermal Cracking

Thermal cracking is included in the pyrolysis process, namely by heating the polymer material without oxygen. This process is usually carried out at temperatures between 350°C and 900°C. This process produces charcoal, oil from condensation gases such as paraffin, isoparaffin, olefin, naphthene and aromatics, as well as gases that cannot be condensed.

3. Catalytic Cracking

This cracking method uses a catalyst to carry out the cracking reaction. With the presence of a catalyst, it can reduce the temperature and reaction time. The catalytic process can speed up the reaction, the process of breaking down large molecules into small molecules is carried out at high temperatures. The types of catalysts that are often used are silica, aluminum, and zeolite [22].

1.3 Catalyst

A catalyst is a substance added to a reaction system to speed up a reaction. Catalysts can provide active sites that function to bring reactants together and donate energy in the form of heat so that reactant molecules can pass the activation energy more easily. Because of its very important function, the use of catalysts is a very important requirement in various industries. The ability of a catalyst to accelerate the reaction rate is influenced by various factors. Factors that affect the performance of the catalyst; operating conditions such as temperature, pressure, flow rate, contact time; the type of bait used; the type of solid support used. Catalysts prepared in different ways will produce different activities and selectivity [23].

1.4 Zeolite

Zeolite as a catalyst only affects the reaction rate without affecting the reaction equilibrium because it can increase the difference in the molecular path of the reaction. Porous catalysts with very small pores will contain small molecules but prevent large molecules from entering. This molecular selectivity is called the molecular sieve which is found in natural zeolite substances [24].

Natural zeolites are formed due to complex chemical and physical processes from rocks that undergo various kinds of changes in nature. Geochemists and mineralogists estimate that zeolites are volcanic products that freeze into volcanic rocks, sedimentary rocks and metamorphic rocks which then undergo a weathering process due to the influence of heat and cold so that eventually zeolite minerals are formed [25].

Natural zeolite is a zeolite that is mined directly from nature. Thus the price is much cheaper than synthetic zeolite. Natural zeolites are minerals that are abundant in number but have an uneven distribution, such as clinoptilolite, mordenite, phillipsite, chabazite and laumontite. However, natural zeolite has several weaknesses, including many impurities such as Na, K, Ca, Mg and Fe and poor crystallinity. The presence of these impurities can reduce the activity of the zeolite. To improve the character of natural zeolite so that it can be used as a catalyst, absorbent, or other applications, activation and modification are usually carried out first. In addition to removing impurities found in natural zeolite, the zeolite activation process is also aimed at modifying the properties of the zeolite, such as surface area and acidity. The increased surface area and acidity will cause the catalytic activity of the zeolite to increase. One of the advantages of zeolite is that it has a surface area and acidity that is easily modified [25].

2 RESEARCH METHOD

2.1 Preparation of Catalyst

Zeolite was immersed in ion-free water while stirring with a magnetic stirrer for a day and a night (24 hours) at room temperature (25°C). The mixture was then filtered and the precipitate obtained was dried in an oven at 120°C for 12 hours.

Zeolite was then immersed in a 6M HCl solution for 30 minutes at a temperature of 50°C while stirring with a magnetic stirrer, then filtered and washed repeatedly, then dried at a temperature of 130°C for 3 hours in an oven, and immersed in a 1N NH4Cl solution at a temperature of 90°C for 3 hours per day within 1 week while stirring, then filtered, washed, dried and mashed.

2.2 Pyrolysis Process

Put 4 liters of used lubricant into Reactor I and 15.26 grams of zeolite catalyst into Reactor II. Putting used lubricant into reactor I which already contains glass wool then heated slowly with a temperature difference between reactor I and reactor II of 50°C. Then, increase the hydrogen gas pressure by 1 bar for every increase in temperature, with variations of 300°C, 350°C, 400°C, and 450°C. Then the used lubricant will mix with hydrogen gas with the aim that the hydrogen gas will break down the molecules in the used lubricant, and some of the steam used lubricant mixed with hydrogen gas will be flowed into reactor II which contains a catalyst and flowed to the condenser to produce liquid fuel products, finally opening the liquid fuel product valve.

2.3 Product Analysis

The physical properties analyzed were density, kinematic viscosity (cSt), flash point (°C), and calorific value (cal/gr).

3 RESULT AND DISCUSSION

From the research that has been done, the results of observations with variations in temperature in the process of Hydrocracking Pyrolysis of Lubricant Waste are obtained.

2.3 The Relationship between the Effect of Temperature on product Yield

The effect of temperature on product yield is carried out at a temperature of 300-450°C with a Zeolite catalyst added 5% from used lubricant raw materials as shown in Figure 1. From Figure 1, it can be seen that temperature has a fairly important influence on the Hydrocracking pyrolysis process, at a low temperature of 300°C the yield of 8.4% of the product is produced and the resulting yield also increases with the increase in temperature, namely at a temperature of 400°C of 12.06 %.

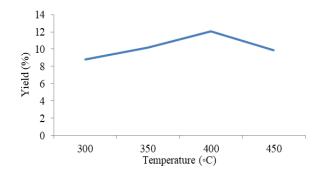


Fig. 1. The relationship between temperature and product yield

The increase in yield can be interpreted as an increase in the cracking reaction that occurs. A cracking reaction is an endothermic reaction where this reaction involves the process of breaking the carbon chain, where to be able to break a bond requires a large amount of heat energy. This is also the case in the research where the yield of the liquid product obtained increases with increasing temperature, but at a temperature of 450°C the yield value of the resulting product decreases by 33.37% this is because at a temperature of 450℃ with a lower temperature. Higher levels of coke will make more coke formed in reactor 2 due to the decarboxylation reaction, which converts carboxylic acids from monoglycerides, diglycerides, and free fatty acids. become straight chain alkanes, then release CO2 and decarbonylation reactions, namely producing alkanes through the reaction of carboxylic acids on monoglycerides, diglycerides, and free fatty acids. with hydrogen, then form CO and H2O as by-products. At high temperatures will increase the rate of molecular kinetics so that the diffusion of reactants into the catalyst will also be better. If the diffusion is better, more reactants can enter the pores of the catalyst so that more compounds contained in the feed are cracked.

3.2 The Relationship between the Effect of Temperature on Density

The density of the product increases with the addition of temperature, at a temperature of 300°C the density of the product is 0.7789 gr/ml while at a temperature of 450°C the density of the product is 0.7834 gr/ml. This is due to the formation of coke residue in the reaction cracking so that the molecular weight of the compound analyzed increases. This Coke residue can be seen clearly in the dark brown-black cracking reaction product and carbon deposits in reactor 2. This precipitate was not found in the cracking reaction at lower temperatures. This Coke residue was included in the density test of the cracking reaction product so that the density obtained was produced is larger. It can be seen in Figure 2.

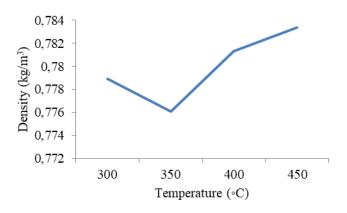


Fig. 2. The relationship between temperature and density product

3.3 The Relationship between the Effect of Temperature on Viscosity

Viscosity is the viscosity of a fluid. Viscosity is related to the friction between layers of fluid when one layer moves to another layer. In this study, the viscosity of Hydrocracking Pyrolysis was measured based on the time taken by the nickel iron alloy ball across the hoppler viscometer with a distance of 10 cm. Measurement of a viscosity aims to determine the viscosity of the oil at a certain temperature so that the oil can flow at that temperature. The lighter the petroleum fraction, the smaller the viscosity. On the other hand, the heavier the oil fraction, the greater the viscosity.

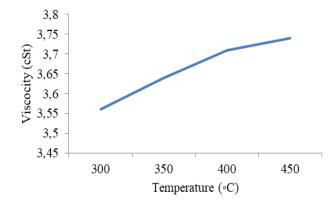


Fig. 3. The Relationship between the Effect of Temperature and Viscosity Product

The observed viscosity is the kinematic viscosity, which is the ratio between the dynamic viscosity and the density of a product. Similar to the results of the density test of the cracking reaction product, the cracking reaction product which gives the smallest viscosity value at a temperature of 300°C. Occurs between the reactant molecules and the catalyst surface resulting in lighter cracking products. However, the product of the cracking reaction which took place at a temperature of 450°C showed an increase in viscosity due to the formation of carbon deposits so that by naked eye the cracking reaction product looked thicker.

3.4 Effect of Hydrotreating Temperature on Flash Point

The flash point is the lowest temperature at which the oil will ignite when exposed to a spark. The flash point measurement is done using a flash point tester. The higher the flash point, the easier the fuel storage process. °API or API Gravity is a measure of how heavy or light a petroleum liquid is compared to water. In Figure 4 you can see °API. The highest was obtained at 60.05 at a temperature of 450°C and the smallest at 45.525 at the actual temperature of the reactor at 300°C. The °API value obtained in this study based on ASTM D1298 belongs to lights oil or light oil. Light oil is a liquid petroleum that has a low density. It has a viscosity, which is low and has a high API gravity. Evidently, in this study, the pyrolysis product has a low viscosity, the value of which can be seen in Figure 4. This is due to the high proportion of light hydrocarbon fractions and generally very low paraffin content.

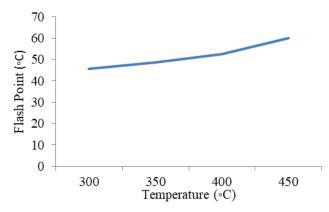


Fig. 4. The Relationship between Temperature and Flash Point Product

3.5 Caloric Value Analysis of Green Diesel

The calorific value is the amount of heat energy released per unit mass. In this study, measurement of calorific value was carried out on 4 samples with 5% natural zeolite catalyst and 1 sample without treatment. The calorific value obtained from untreated used lubricant is 5513.0125 cal/gram, then at a temperature of 300°C the calorific value is 6388,8610, at 350°C the heating value is 6740.4665, at 400°C the calorific value is 7213.8833 and the temperature is 450°. C obtained calorific value of 8041.3191. The higher the calorific value of a fuel, the more efficient the energy produced, because it produces more heat with less mass.

3.6 Analysis of the Cetane Number of Green Diesel

Hydrocracking Pyrolysis products were then tested for cetane numbers using the Octane and Fuel Analyzer Zeltex. The Satanic number indicates the ability of the fuel to selfignite (auto ignition). With a temperature of 350°C it has a cetane number of 62.2 CN and at a temperature of 450°C it has a cetane number of 76.2. The scale for the cetane number usually uses a reference in the form of a mixture of normal cetane ($C_{16}H_{34}$) with alpha methyl naphthalene ($C_{10}H_7CH_3$). Normal cetane has a cetane number of 100, alpha methyl naphthalene has a cetane number of 0. This shows that hydrocarbon fuels with a straight chain atomic structure have a higher cetane number than fuels with a complex atomic structure.

4 CONCLUSION

Hydrocracking Tank Reactor with hydrogen gas as a pressure increase while helping the cracking process in SAE 5W-30 Lubricants which can break down the molecules contained in used lubricants. Temperature affects the resulting product. The higher the temperature, the more results are formed, which is due to the more volatile, the higher the production speed.

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