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Organic chemistry field received articles from the entire spectrum of synthetic organic, bioorganic, physical-organic chemistry, and natural products.

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Biofuel from Pyrolysis Waste Lube Oil of Refinery Unit III using Fly Ash of Coal Combustion as a Catalyst

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Abstract

Lube oil waste obtained from Utilities Unit, Crude Distillation Unit, and Crude Distillation & Light End Unit at Refinery Unit III Plaju Palembang South Sumatra. The process of pyrolysis of lube oil waste using fly ash catalyst is expected to produce fuel oil. Lube oil waste pyrolysis uses Fly Ash catalysts with a total catalyst of 500 g with a temperature range variation of 0-85, 85-16, 165-250, 250-300, and 300-350 °C, while pyrolysis of waste lube oil without catalysts with a variation in the temperature range of 0-85, 85-165, 165-250, 250-300, and 300-350 °C. Temperature range variations are referenced based on boiling route solvent fraction (0-85 °C), premium fraction (85-165 °C), kerosene fraction (165-250 °C) and diesel (250-350 °C). Solvent fraction cannot be analyzed because there is no product result whether it is pyrolysis process using catalyst or without catalyst, Premium Fraction is only produced using catalyst, analysis result Octane Number 76.6. Sulfur content, Density and flash point analysis of pyrolysis products using catalysts and without catalysts in accordance with kerosene products in the market. Solar fraction of pyrolysis process using catalyst and without catalyst, Analysis results cetane numbers 43.2 and 45.6 have not met the specifications of solar products.

Keywords: pyrolysis, Lube oil waste, Fly Ash catalysts.

Abstrak (Indonesian)

Limbah *lube oil* diperoleh dari Unit Utilitis, Unit *Crude Destilasi*, Unit *Crude Destilasi & Light End* di *Refinery Unit III* Plaju Palembang Sumatera Selatan. Proses pirolisis limbah *lube oil* menggunakan katalis *fly ash* diharapkan menghasilkan bahan bakar minyak. Pirolisis limbah *lube oil* menggunakan katalis *Fly Ash* dengan jumlah katalis 500 gr dengan variasi range temperatur 0-85, 85-16, 165-250, 250-300, dan 300-350 °C, sedangkan pirolisis limbah *lube oil* tanpa katalis dengan variasi range temperatur 0-85, 85-165, 165-250, 250-300, dan 300-350 °C. Variasi range temperatur dijadikan acuan berdasarkan trayek didih fraksi *solvent* (0-85 °C), fraksi premium (85-165 °C), kerosine (165-250 °C) dan solar (250-350 °C). Fraksi solvent tidak bisa dianalisis karena tidak ada hasil produk baik itu proses pirolisis menggunakan katalis maupun tanpa katalis, Fraksi Premium hanya dihasilkan menggunakan katalis, Hasil analisis Bilangan Oktan 76,6 vs (88,0) belum memenuhi spesifikasi bahan bakar Premium. Hasil analisis Sulfur content, Density dan flash point dari produk pirolisis menggunakan katalis dan tanpa katalis sesuai dengan produk kerosine di pasaran. Fraksi solar dari proses pirolisis menggunakan katalis dan tanpa katalis, Hasil analisis spesifikasi produk solar bilangan setana 43,2 dan 45,6 belum memenuhi spesifikasi produk solar.

Kata Kunci: Pirolisis, Limbah Lube Oil, Katalis Fly Ash.

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INTRODUCTION

Lube Oil is a petroleum product that includes heavy distillate fractions and has a boiling point route of 300 °C. Lubricating oil is one of the petroleum products. Lubricating oil functions include: reduce friction and wear, cool components [1]. Lube oil waste at PT Pertamina Refinery Unit III has been managed by a designated waste management company to manage it, which every month requires additional costs.

Lube oil waste can be processed by various methods, one alternative method of handling lube oil waste is by converting lube oil waste into liquid fuel. It is expected that using this method can provide solutions to the above problems and can provide more benefits in the form of liquid fuel that can be used as fuel. Technology to convert lube oil waste into liquid fuel is by cracking process or also called pyrolysis [2].

This pyrolysis process uses raw materials in the form of lube oil waste and catalysts from coal fly ash. Flying ash can be used as a catalyst to speed up the process because it is composed of several porous oxides such as, SiO_2, Al_2O_3, Fe_2O_3, MgO, and CaO. On the other hand, the utilization of coal flying ash is still very lacking in the steam power plant industry (PLTU) whereas coal flying ash has a high enough market value if used to be a catalyst in the pyrolysis process. Another method of processing lube oil waste is chemical purification of lube oil waste using sulfuric acid media (H_2SO_4)and sodium hydroxide (NaOH) to produce fuel[3].

The increasingly rapid industrial activity today, various types of heavy metal waste produced can be a serious problem for health and the environment [4]. The limitation of fossil energy requires diversification of energy resources in order to guarantee the availability of energy. Then the use of new and renewable energy must be intensified [5]. In this study converted lube oil waste with pyrolysis process using fly ash catalyst into liquid fuel [6]. By using fly ash catalysts, it will be reviewed against the yield of each fraction of hydrocarbons produced by the influence of reaction temperature on the process of pyrolysis of lube oil waste.

The expected hydrocarbon fraction of the compound is the fraction of gasoline, kerosene and diesel (gasoil). Furthermore, the right number of catalysts and temperature ranges for optimum operating conditions will result in the yield and quality of hydrocarbon fractions in accordance with the specifications of the director general of oil and gas. As well as research conducted to trigger the spirit of students and the community to develop biomass technology that is expected to support government programs to overcome energy problems and realize the development of energy diversification.

Based on waste criteria issued by the Ministry of Environment, lube oil waste belongs to the category of Toxic and Hazardous Materials waste (B3). Lube oil waste is produced from lube oil used by refinery unit III, for petroleum processing. Basically lube oil waste is composed of long chain hydrocarbon organic components that are very possible to produce valuable liquid products. Lube oil waste is one of the sources of pollutants that can contaminate groundwater, and will damage the soil water content, can even kill microorganisms in the soil and lube oil waste can inhibit the biological oxidation process of the environmental system. Although lube oil waste can still be used, if not managed properly, it can harm the environment [7].

Catalyst is a substance that accelerates the rate of chemical reactions at a certain temperature, without being altered or used by the reaction itself. A catalyst plays a role in the reaction not as a reaction or a product. Catalysts allow reactions to take place faster or allows a reaction at a lower temperature due to changes it triggers to the reaction. Catalyst provides a preferred path with lower activation energy. Catalysts reduce the energy needed for a reaction to take place. Fly ash is one of the materials that can be used as catalysts [8].

Fly ash is a solid waste resulting from the use of coal as an energy resource. The potential for fly ash presence in Indonesia is considerable with increased coal consumption where the potential availability of coal ash is 10% of total coal consumption, with 80% details being fly ash [9].

According to SNI 03-6414-2002 the definition of fly ash coal is waste from burning coal in steam power plants furnaces that are smooth, round and pozolanic. Fly ash is a material that has a fine grain size, grayish color and obtained from the combustion of coal.

Pyrolysis is heat energy that encourages oxidation so that complex carbon molecules decompose, mostly into carbon. Another term of pyrolysis is destructive distillation or dry distillation. Pyrolysis is an irregular decomposition process of organic matter caused by heating without being associated with outside air [10].

Pyrolysis is also known as thermolysis, thermal fracturing, dry distillation, destructive distillation, etc.; however, there are differences in those terms. During this pyrolysis process, it produces 3 main products that can be classified as follows: [11,12]

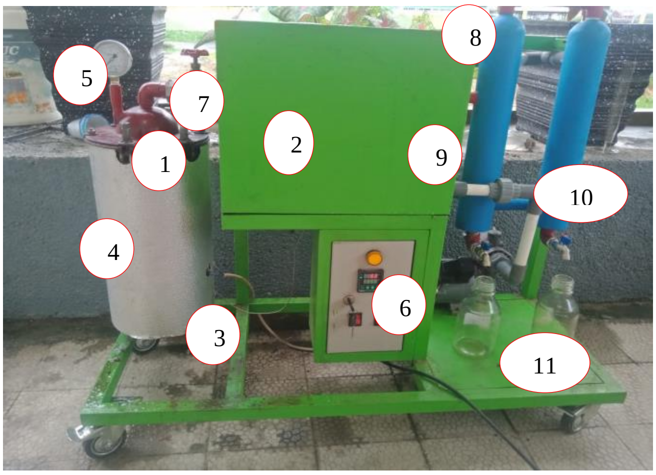
1. Solid residues (which consist mainly of carbon and ash) known as char
2. Gas (mainly CO,CO_2,CH_4,H_2 and other mild hydrocarbons)

3. Steam/liquids known as bio-oils or bio-crudes (especially oxygenate, aromatic, water, low polymerization level products, tar, etc.)

MATERIALS AND METHODS

Materials

Lube oil waste obtained from Utilities Unit, Crude Distillation Unit, Crude Distillation & Light End Unit at Refinery Unit III Plaju Palembang South Sumatra. Fly Ash from Bratachem, (Palembang, Indonesia). All other chemicals used were obtained from Refinery Unit III Plaju Palembang South Sumatra.



Caption:
1. Reactor,
2. Condenser,
3. Preheater,
4. Stainless steel shell,
5. Pressure control,
6. Thermal Control,
7. Control Valve,
8. Water cooler (inlet),
9. Water cooler (outlet),
10. Output Product,
11. Liquid fuel product tank

Methods

Waste-lube-oil is done the process of marriage using pyrolysis process and fly ash catalyst which is one of the process of greed using high temperatures without air or limited air. In this study the pyrolysis process uses a temperature range (0-85, 85-165, 165-250, 250-300, 300-350 ^oC) with raw materials of 5 litres and catalysts of 0, 250, 500, 750, 1000 g. The temperature range set on the heater uses 5 variations of the set point range temperature (0-85, 85-165, 165-250, 250-300, 300-350 ^oC) which aims to obtain hydrocarbon fractions that correspond to the specified temperature range. The result of this pyrolysis process will be accommodated in the container and will be analysed the content of sulphur, Density, sulphur Mercaptan, Octane Number, Cetane Number, End Point and Flash Point.

Density is one of the critical parameters in determining the quality of biodiesel products produced. It has the function of knowing how combustion reactions occur in diesel engine combustion chambers [13,14].

In some countries during winter, the water content in diesel may form crystals that can block the fuel flow into the engine injector. Furthermore, water can cause corrosion and growth of micro-organisms which can also block fuel flow into the combustion chamber. In addition, sediments can cause blockage and damage to the engine [15,16].

Flash point is the temperature at which the sample is burned, and the fire is marked by the appearance of sparks. The fire point is the temperature at which the sample is burned as the fire occurs. Flash and fire point experiments were carried out to find out the flashpoint temperature and the hotspot temperature of the sample [17].

RESULTS AND DISCUSSION

Characteristic of Fly Ash as Catalyst

Characteristic test was conducted against fly ash catalyst which is coal fly ash from combustion in boiler combustion chamber. Characteristic test is conducted to find out the elements contained in the fly ash catalyst using ICP instrument (*Inductivity Coupled Plasma*).

ICP OES is a tool for the analysis of metal elements in a material. The material to be analyzed must be a homogeneous solution. There are about 80 elements that can be analyzed using this tool. The advantage of this tool is that it is very selective and can be used to measure several elements at once in each measurement. In Table 1, it can be seen that the results of fly ash analysis without activation of Al Content 7.52% and Si 24.44%.

Based on Table 1, the content of Fe and Si elements is greater percentage than other elements. And can be concluded based on the composition fly ash entry class f (SiO_2 + Al_2O_3 + Fe_2O) > 70% derived from bituminous coal.

Characteristic of Waste-Lube-Oil

A characteristic test of lube oil waste was conducted to determine the water and sulfur content to be compared with pyrolysis results obtained from this study, can be seen in Table 2.

Table 1. The results of the analysis of the characteristics of the Fly Ash catalyst using ICP (*Inductivity Coupled Plasma*)

Sample	Analysis Parameters	Method	Unit	Results
Fly Ash	Al	IP 501/ASTM D 5184	%	7.52
	Si		%	24.44
	Fe		%	46.18
	Ca		%	16.36
	K		%	0.32
	Mn		%	0.44
	Ni		%	0.88
	Cu		%	0.08
	Zn		%	0.01
	V		%	0.01

Table 2. Characteristics of Lube Oil Waste

Sample	Analysis Parameters	Method	Unit	Results
Waste Lube Oil	SG 60/60 °F	ASTM D-4052	-	0.842
	Sulfur Content	ASTM D-2622	ppm	254
	Water Content	ASTM D-6304	ppm	377

Effect of catalyst and temperature on oil volume from pyrolysis

The volume of products resulting from pyrolysis is directly affected by the activeness of the catalyst used. The more catalysts used, the more active sites are available for reaction. However, the increase in the volume of product results will decrease even if there is no increase at all at the time of the addition of catalysts. The same goes for the effect of temperature on the volume of products produced. In accordance with the Arrhenius equation, the higher the temperature, the greater the value of the thermal decomposition constant as a result of which the rate of pyrolysis increases and conversion will increase as seen in figure 1.

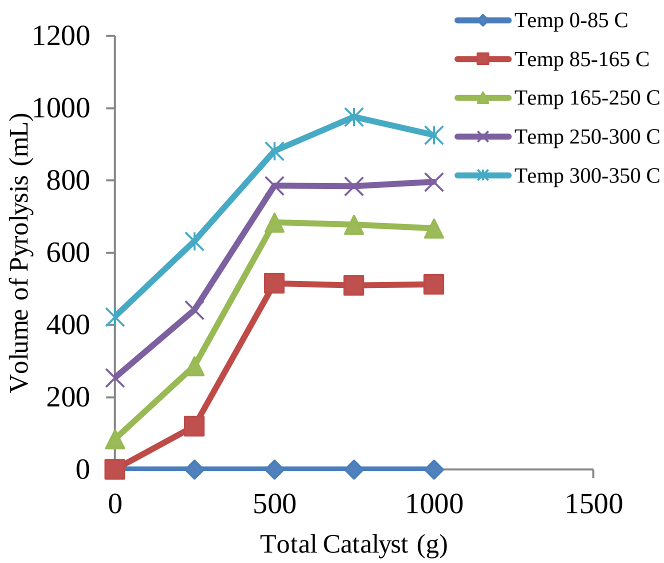


Figure 1. The volume of oil produced from the pyrolysis process against the number of catalysts added to each variation in the temperature range.

Oil produced from a variety of temperature ranges of 0-85 °C amounted to 0 mL, 85-165 °C totalled 1657 mL, 165-250 °C totalled 2400 mL, 250-300 °C totalled 3062 mL, and 300-350 °C totalled 3839 mL. So it can be concluded that the higher the temperature produces oil with a greater volume as well[18]

This is because, at higher temperatures, waste-lube-oil will react faster and evaporate resulting in more yields after condensation. On the other hand, the different temperatures used in this study produced different hydrocarbon fractions because hydrocarbon bonds that are weaker than higher temperatures will result in more hydrocarbon bonds than lower temperatures resulting in fewer hydrocarbon bonds. From the picture can also be seen that the variation of the temperature range that has the most optimal volume is at 300 -350 °C [16] to produce more yield and the resulting product in the form of bio-diesel. Following explanation below:

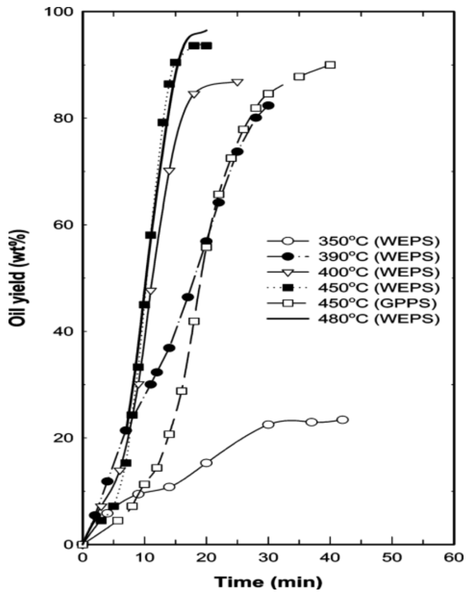


Figure 2. Effects of reaction temperature on the oil yield of non-catalytic pyrolysis [19].

Effect of Catalysts on% Yield of Pyrolysis Products

Yield is the comparison between the mass of the resulting product to the mass of the initial raw material used in a process. Yield is used to determine the overall performance of a process. Percent yield of a process can be affected by several process variables such as temperature, time, reaction, catalyst and so on. In this study the percent value of the yield will be based on each number of catalysts from the pyrolysis process. The effect of catalysts on the number of %yields of pyrolysis products can be seen in Figure 4.

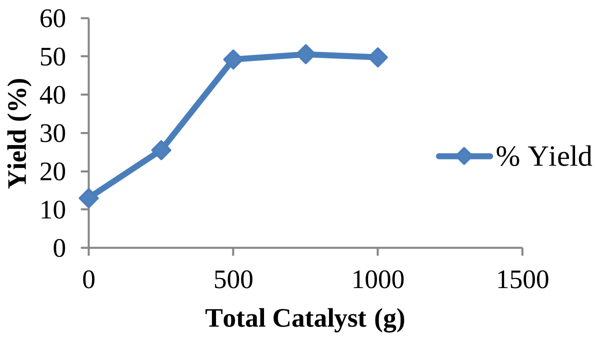


Figure 3. Effect of Total Catalyst on %Yield of Pyrolysis Products

From the picture above it can be known that % yield is strongly influenced by the number of catalysts the process catalyst. The increase in %yield is directly proportional to the addition of the number of pyrolysis catalysts, but when it reaches the maximum limit of the amount of 500-800 g of catalyst %yield will be constant or tend to decrease. This is due to the constant feed of lube oil waste so that when catalysts are added more oil or products are produced tend to be less.

Effect of Catalyst on the Amount of Residue from Pyrolysis

One of the most important points of the pyrolysis process is not only how much oil can be obtained but also how much waste lube oil can be decomposed. This can be observed by knowing how much residue or residue is in the reactor at the end of the pyrolysis process. The effect of catalysts on the amount of residue produced by pyrolysis can be seen in the picture below:

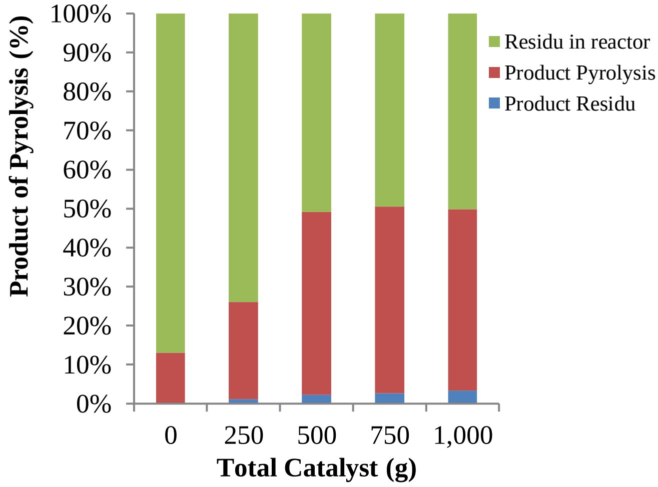


Figure 4. Pyrolysis products using a catalyst

The amount of residue produced based on the graph above has a significant difference depending on the number of catalysts in each variation of the temperature range. When viewed in terms of the economic pyrolysis tool in decomposing *waste lube oil* then the optimal point is at 500 g catalyst because the energy used is smaller than the energy in the number of other catalysts. Residual contributors from pyrolysis are the catalysts included in the product.

CONCLUSION

Based on the research that has been done, it can be concluded that the fuel oil produced from the pyrolysis of waste lube oil Refinery Unit III is a premium, kerosine and solar fraction with the use of catalysts of 500 g of fly ash. The quality of kerosene fraction is the same as the market, the premium fraction has not met the specifications but the solar fraction meets the market standards.

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