 https://doi.org/10.1051/e3sconf/202560503050

Physical characterization of used lubricating oil as fuel production feedstock

Zami Furqon[1*], *Didi* D. Anggoro[2], and *Heri* Sutanto[3]

[1]Doctoral Program of Environmental Science, School of Postgraduate Studies, Diponegoro University, Semarang 50241, Central Java, Indonesia
[2]Chemical Engineering Department, Faculty of Engineering, Diponegoro University, Semarang 50241, Central Java, Indonesia
[3]Physical Science Department, Faculty of Basic Science, Diponegoro University, Semarang 50241, Central Java, Indonesia

Abstract.. These articles aim to identify the physical characteristics of the hydrocarbons in used lubricating oil, which is required as feedstock for process designs, and to address certain issues with the equipment used in the catalytic cracking process in the future. The data can be used to determine specific parameters to refine used lubricating oil into fuel. Used lubricating oil falls into the medium-heavy oil category based on the results of the characteristic tests. The physical test findings determined the sample's fluidity and volatility qualities such as the ASTM D 92 flash point, ASTM D 97 pour point, ASTM D 4052 specific gravity test, ASTM D 1160 distillation, and ASTM D 445 viscosity. Based on test results, the following values were found: initial boiling point: 160°C, flash point: 198°C, specific gravity (60°F): 0.864, viscosity (100°C): 34.9 Centi Stoke, and pour point: > -30oC. Based on the collected data, the KUOP value is more than 12.5 where the value shows paraffinic hydrocarbon type and the API gravity value is 32.3.

1 Introduction

Lube base oil is a term used to describe lubricants made from the gas oil fraction, a byproduct of petroleum processing, which boils between 200 and 350 degrees Celsius. Two types of base oil sources are used in lubricant products: synthetic base oils and mineral oil based on fossils with paraffinic, naphthenic, and aromatic characteristics spanning from carbon atoms C_{20} to C_{40}. Every compound is unique and can be employed in a way that best suits the requirements of the intended climate system. While five different types of chemicals dominate the synthetic oil base market, they include olefin oligomers, particularly polyalphaolefins (PAOs); esters (polyols); alkylated aromatics; Specialty lubricants are

*Corresponding author: zamifurqon@students.undip.ac.id

hydrocarbons that have been substituted with fluorine, chlorine, or polyether [1]. Depending on the product composition, lubricant is made up of 90–100% oil and 0–30% additives. Antioxidants, anti-wear, antistatic, detergents, dispersants, foaming agents, friction modifiers, anticorrosion, inhibitors, and other roles are all possible for additives. Lubricants are currently widely used in a variety of industries, including heavy machinery, automotive, oil and gas, mining, ports, power plants (both hydropower and conventional), and others. In industrial equipment and machinery, lubricants are employed as hot fluid in thermal oxidizers, as heating media or coolants in pumps and compressors, as lubricants in automobile engines, and for other purposes [2].

A variety of additives are used in the lubricant manufacturing process to enhance the physical and chemical characteristics of the finished product. An oil lubricant's additive content can reach 20%, with detergents and dispersants accounting for the majority at 15% of the oil weight. Certain substances found in oil additives are known to be dangerous environmental pollutants. Molybdenum disulfide, zinc di aryl or diallyl di thiophosphates, heavy metal soaps, and other organometallic compounds containing heavy metals are examples of substances that contain heavy metals. Because of this, current motor oils have a relatively high zinc content—they contain about 1500 mg of zinc per kilogram and 87 mg of cadmium per kilogram. The heavy metal concentration is one of the more significant distinctions between fresh and old motor oil. Since several of these metals have the potential to be extremely damaging to organisms, it is crucial to know how much metal is present in old motor oil. Motor wear and gasoline are the sources of these metals. Pb, Zn, Ca, Ba, and Mg are found in high concentrations in used motor oil, while Fe, Na, Cu, A1, Cr, Mn, K, Ni, Sn, Si, B, and Mo are found in lower concentrations. Polyaromatic hydrocarbons (PAHs), another class of substance found in used motor oil, are extremely dangerous to human health because some of them are carcinogenic and mutagenic [3].

Hazardous toxic waste refers to substances or other items that pose a direct threat to the ecosystem and can jeopardize the health and sustainability of living beings and the environment. The heavy metal chromium from car engines can be found in used lubricating oil, along with other harmful and dangerous substances like sulfur, nitrogen, chlorine, bromine, and oxidized compounds. If this substance gets inside the body, it can cause cancer, damage to the kidneys, and nerve damage [4].

Taking this into consideration and applying it to waste oil, the following actions make up the environmental protection solution:

1.1. Preventing the production of waste lubricating oil;
1.2. Organizing the collection of waste lubricant; and
1.3. Reusing used lubricants through a variety of recovery techniques. Additionally, inappropriate or illegal waste oil disposal might pose a threat to the environment. This is because mineral-based oils, which make up the majority of waste oil, have a low biodegradability [5].

It is feasible to approximate the approximate ratio of different types of hydrocarbons in the same oil after use by using information on the structure of hydrocarbons in new oil. Used lubricating oil experiences numerous chemical and physical transformations throughout normal engine operation. For instance, the same analytical method is used to re-analyze a machine that uses a certain brand of new lubricating oil. The chemical composition of the oil samples was assessed by elemental analysis (CHNS/O analysis), nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and gas chromatography-mass spectrometry (GC-MS). An intermediate correlation was observed between the chemical parameters of the collected fresh and used oils when the findings were compared. Both oil FTIR spectra showed bands associated with the presence of carbonyl groups and amine-containing compounds. Contrary to the fresh oil, phenols were not found in the used oil. According to the NMR spectra obtained, the paraffinic hydrocarbons of the fresh oil were more linear and had longer chains than those in the used oil [6].

Following the Minister of Environment Regulation No. 6 of 2021, due to its hazardous nature, used oil requires special handling to avoid adverse impacts caused by this waste. In Indonesia, used lubricating oil is categorized as hazardous waste which is regulated by Law No.32 of 2009, which regulates environmental protection and management. And Government Regulation No.22 of 2021 contains environmental approval, protection and management of water quality, protection and management of air quality, protection and management of marine quality, environmental damage control, hazardous waste management, and non-hazardous waste management. The processing is also regulated by the Minister of Environment and Forestry Regulation No.18 of 2020 regarding the utilization of hazardous waste because lubricating oil is dangerous toxic waste.

Reusing spent lubricating oil can be done in a few different methods, such as recycling it to make base oil once more or processing it to make fuel energy products [7]. For example, when lubricating oil is converted into another type of hydrocarbon product produced is similar in quality to diesel and gasoline products, pyrolysis and catalysis technology can be employed to obtain fuel. Many articles discuss only the process technology without including the characteristics of the feedstock to be refined. Recognizing the physical characteristics of feedstock can be directed to what type of hydrocarbon products will be produced. Obtaining data on the physical characteristics of feedstock will help us to solve some cases in the operation next.

In the new era, pyrolysis and catalysis process technology are overlapping. Without catalyst, the pyrolysis products of old lubricating oil are gas, liquid fuel, and coke with yields of 5.4 wt.%, 90.6 wt.%, and 4 wt.%, respectively; however, when 2% by weight of aluminum oxide catalyst is employed, the yields of gas, liquid fuel, and coke from the same product are 4 wt.%, 90.7 wt.%, and 3.2 wt.% [8]. Hydrocarbon ($C_{12}H_{26}$) - ($C_{32}H_{66}$) was catalytically cracked at 500°C for 5 seconds using B-Zeolite and Y-Zeolite catalysts, feed 0.2 mg, and catalyst 1.5 mg at 0.45 MPa He in the Curie Point Analyzer (CPA). The percentage of gasoline yield increased greatly, and the number of branched-chain hydrocarbons, such as isomeric hydrocarbon types iC_5H_{12}, iC_6H_{14}, iC_7H_{16}, and iC_8H_{18}, increased significantly as a result of the Y Zeolite catalyst [9]. In a stirred reactor, pyrolysis was performed both catalytically and non-catalytically at 300 RPM and temperatures of 430, 460, 480, and 520 degrees Celsius. SiO_2 (64.86%), Al_2O_3 (22.6%), Fe_2O_3 (0.14%), MgO (0.45%), and Sulfate (0.70%) were the catalysts that were employed, along with kaolin type. Consequently, the yield of the solid product is 3.9%, the liquid product is 90%, and the product gas is 6.9%. Diesel fraction, with a flash point of 38 °C, is the end product [10]. The yield of pyrolysis by thermal cracking ranges from 85% to 91%, while the yield percentage is not significantly affected by pyrolysis utilizing catalysts [11].

2 Characteristics of used lubricating oil

From the qualitative aspect of other characteristics, used lubricating oil has a different color compared to new lubricating oil. Color degradation occurs from light color to dark color due to the influence of heat and time. Changes in lubricant color can be seen in Figure 1 below. The inclusion of additives alters the fluidity and volatility properties of lubricant products, influencing their physical and chemical properties. When additives are added to base oil, the lubricant product will function well in the mechanical system of the machinery and be resistant to various working circumstances. Lubricating oil must be characterized and its physical and chemical qualities must be evaluated for various purposes following processing in combustion engine equipment. Characterization in this context involves merely examining physical properties; chemical properties are addressed. The inclusion of potentially soluble metals including Pb, Zn, Ca, Ba, and Mg, Fe, Na, Cu, Al, Cr, Mn, K, Ni, Sn, Si, B, and Mo causes used lubricating oil to become more viscous, which lowers its fluidity properties [12].

Used lubricating oil is a toxic waste that contains dissolved heavy metals and several aromatic compounds that can harm soil and water environmental ecosystems and hurt human health. Processing is therefore necessary to extract compounds with economic value and separate undesirable chemicals or substances. Used lubricating oil is a hydrocarbon with a typical boiling point of 150 to 570 degrees Celsius that can be used as feed in process equipment as liquid hazardous waste. Its characteristics are based on both physical and chemical characteristics, where physical characteristics include fluidity and volatility, while chemical characteristics include K UOP or K Watson or K factor to determine what type of hydrocarbon (PNA), carbon, oxygen, sulfur, and metal concentration, among others [13].

Fig.1. Used lubricating oil

Physical tests are conducted to determine how spent lubricating oil can be used to generate fuel energy. These tests include numerous operating characteristics that are necessary for operating system design. With an initial boiling point (IBP) of 160 degrees Celsius, vacuum distillation circumstances yield the distillation value of used lubricating oil; however, the reading device's FBP value is no longer measurable. Used lubricating oil with a flash point of 198°C, a fire temperature of 242°C, and a viscosity in the heavy range is categorized as non-flammable. It is inefficient and needs a very high operating temperature to convert into high-yield fuel. Catalytic cracking is the method used in the heavy oil business to process hydrocarbons. The hydrocarbon feedstock to be treated is described, and a small-scale feasibility study of the production process is carried out. The design of the processing process's operating parameters, the kind of catalyst that will be employed, and the end products that will be generated will all be determined by physical testing of spent lubricating oil [14].

The physical test results of various parameters, including density, viscosity, distillation, flash point, API gravity, and K UOP value, can be used to determine the characteristics of used lubricating oil, just like other heavy oil hydrocarbons. From these results, one can determine which type of hydrocarbon compound belongs to which category. When designing the specifications of the raw materials to be used, the type of process to be chosen, the desired operating conditions, and the products to be produced, the characteristics derived from the physical test results can be used as justification for the processing process. They can also be used to estimate the problems that will arise in the processing and products.

3 Used lubricating oil testing

It is necessary to conduct tests on several test factors, including the fluidity and volatility characteristics of used lubricating oil, to determine the viability of this material as a substitute source of feedstock for the production of fuel. By the standard procedure, the ASTM D 4052 density test, ASTM D 445 viscosity, ASTM D 1160 distillation, ASTM D 97 pour point, and ASTM D 92 flash point are conducted using the American Society for Testing Material, or ASTM method [13]. Another standard can be used if we have limitations on finances by using manual ASTM standards for density and viscosity such as ASTM D 1298 and ASTM D 88 for saybolt viscosity as well as other test standards. Industrial testing needs precision and accurate results based on demand from consumers.

Fluidity properties

Density and viscosity

Fluidity is the state in which a liquid or gas has the physical characteristics that permit it to flow. The mass of a material divided by its volume yields the density of that material. where the following is the general equation

$$Density(\rho) = \frac{Massa\ (m)}{Volume\ (v)} \quad (1)$$

Density can be defined as the ratio of the used lubricating oil's density to that of an equivalent volume of water. Since density varies with temperature, it is necessary to know the temperature at which the density is measured. The chemical makeup of the oil has an impact on density. Specific gravity rises when the number of aromatic compounds in the oil increases while specific gravity falls when the number of saturated compounds increases. When the number of particles in used engine oil grows, so does the specific gravity of the used engine oil.

Density, pressure, and temperature all affect viscosity. Viscosity and temperature have an inverse relationship: viscosity will rise when engine oil temperature drops and vice versa. Testing for viscosity can reveal whether old engine oil is contaminated. Engine oil viscosity can be increased by dissolved and suspended oxidized and polymerized products, whereas a decrease in viscosity suggests fuel contamination.

Fig.2. Density Meter ASTM D 4052 and Viscosity ASTM D 445

To provide quick and precise test results, density testing is done using an automatic density meter, ASTM D4052. In contrast, the ASTM D 1298 manual density test requires accuracy from the person and takes a lengthy time. It is advised that an automatic testing apparatus be used when the test sample is sufficiently large. The ASTM D445 viscosity test with manual test apparatus works in a similar manner.

Pour Point

The lowest temperature at which used lubricating oil or fuel oil can still flow by itself under test conditions. it is a very important property that can determine how the oil will flow at a certain temperature. Determination of the pour point serves to determine whether or not the type of pump is suitable for moving fractions from one place to another at a certain temperature. By knowing the pour point of the fraction, it can be known at what temperature the fraction can be flowed with a pump during the transportation process.

Fig. 3. Pour Point ASTM D 97

Volatility Properties

Distillation and Flash Point

Volatility is a substance's propensity to evaporate or its rate of evaporation. At a given temperature, a substance having a greater vapor pressure will evaporate more readily than one with a lower vapor pressure. A substance's vapor pressure indicates its volatility. Vapor pressure, flash point, and distillation all serve to illustrate the different ways that hydrocarbons can be volatile. Only distillation and flash point were evaluated for used lubricating oil. The process of distillation is used to separate different hydrocarbon compounds according to how easily the compounds in hydrocarbons may be evaporated or how differently their boiling points range. A combination of chemicals is heated to a boil, causing it to evaporate; the vapor is then cooled to return to liquid form in the distillation process. Heavy oil is the raw material used in vacuum distillation ASTM D 1160 so that the used lubricating oil will evaporate more quickly when vacuum pressure requirements are met. Using atmospheric distillation, which has a high boiling point based on the properties of the used lubricating oil, is different. Engine oil's flash point is the lowest temperature that, under certain circumstances, must be heated to release enough vapor to combine with air to form a mixture that a certain flame can spontaneously ignite. Flashpoint and firepoint are not the same things, even though they are tested using the same ASTM D 92 procedure. The length of ignition is the primary distinction.

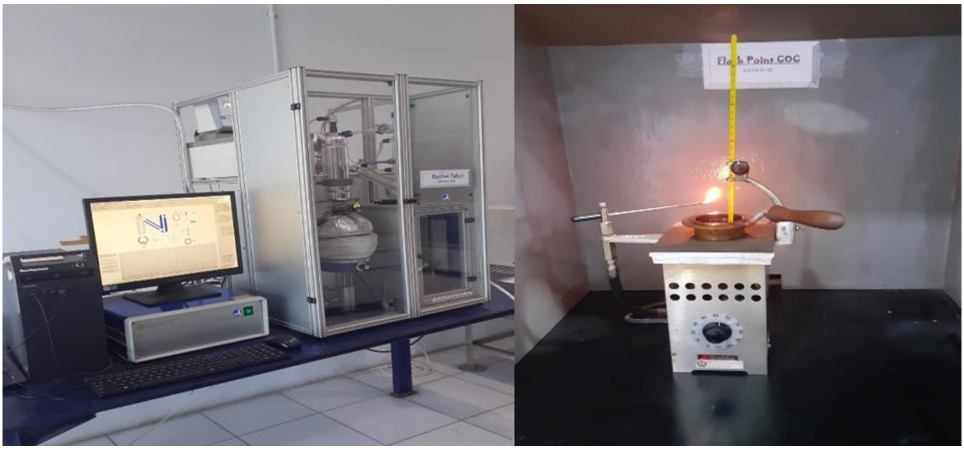

Fig. 4. Distillation ASTM D 1160 and Flash Point Cleveland Open Cup ASTM D 92

4 Results

When comparing the densities of petroleum liquids, API gravity is used to determine how heavy or light a petroleum liquid is to water. It is also known as the inverse measure of a petroleum liquid's density to water; that is, the greater the API gravity of a petroleum liquid, the less dense the other is. Most petroleum liquids have an API gravity of between 10^{o} and 70^{o}. The ASTM D 4052 specific gravity test results are used to determine the API gravity value of used lubricating oil. This number is then entered into the formulation for calculation, as indicated by the equation below. The temperature indication used during testing provides the value for additional test parameters, such as distillation ASTM D 1160, pour point ASTM D 97, flash point ASTM D 92, and fire point ASTM D 92. Variations in the findings obtained from ASTM D 445 viscosity tests, often known as kinematic viscosity tests, which measure the fluid's flow velocity at 210°F or 100°C. The most widely used viscosity units are m^2/second, stoke (St), and Centi stoke.

$$\boldsymbol{API\ Gravity} = \frac{141.5}{SG\ (60oF)} - 131.5 \quad (2)$$

$$\boldsymbol{API\ Gravity} = \frac{141.5}{0.864} - 131.5 = 32.3 \quad (3)$$

Table 1. Parameter test results of used lubricating oil

NO	PROPERTY	OBSERVATIONS	METHODE
1	Specific Gravity, 60^{o}F	0.864	ASTM D 4052
2	API Gravity	32.3	Calculated
3	Pour Point, ^{o} Celsius	>-30	ASTM D 97
4	Flash Point COC, ^{o} Celsius	198	ASTM D 92
5	Fire Point COC, ^{o} Celsius	242	ASTM D 92
6	Viscosity 100^{o}C	34.9 Centi stoke	ASTM D445
7	Distillation, IBP ^{o} Celsius	160	ASTM D1160
8	K UOP	>12.5	UOP 375

K Factor or K UOP Value

a systematic way of classifying crude oil according to its paraffinic, naphthenic, intermediate, or aromatic nature. 12.5 or higher indicates a crude oil of predominantly paraffinic constituents, while 10 or lower indicates a crude of a more aromatic nature. As seen in Figure 5, the association between viscosity at 100ºC or 210ºF and API Gravity yields the UOP Characterization Factor, K. The specific gravity value from the density measurement device (Figure 2) density meter must be determined before calculating the API gravity value. Next, determine the viscosity at 210°F, or 100°C. See the viscosity on the vertical scale on the left of the graph and the gravity on the horizontal scale at the bottom of the graph for API. At 210ºF (100ºC), connect the API gravity and kinematic viscosity values, and locate the place where the graph's vertical and horizontal lines join. The curve number nearest to this point should be read. The characterization factor, also known as the K factor or K UOP, is the value that has been interpolated and corrected for the point's distance from this curve. K factor value can be used to know what type of hydrocarbon is paraffinic, naphthenic, and aromatic. Fuel product has different characteristics than feedstock especially used lubricating oil. To obtain the final product as the fuel needed K UOP value so that can be estimated what type of product will be produced and what type of process technology will be used depending on fixed process design. From the result K UOP value > 12.5 it shows hydrocarbon type is paraffinic. Paraffinic is the favorite hydrocarbon as a potential feedstock to be refined because can produce different types of products so that the refinery unit can operate more flexibly and more efficiently.

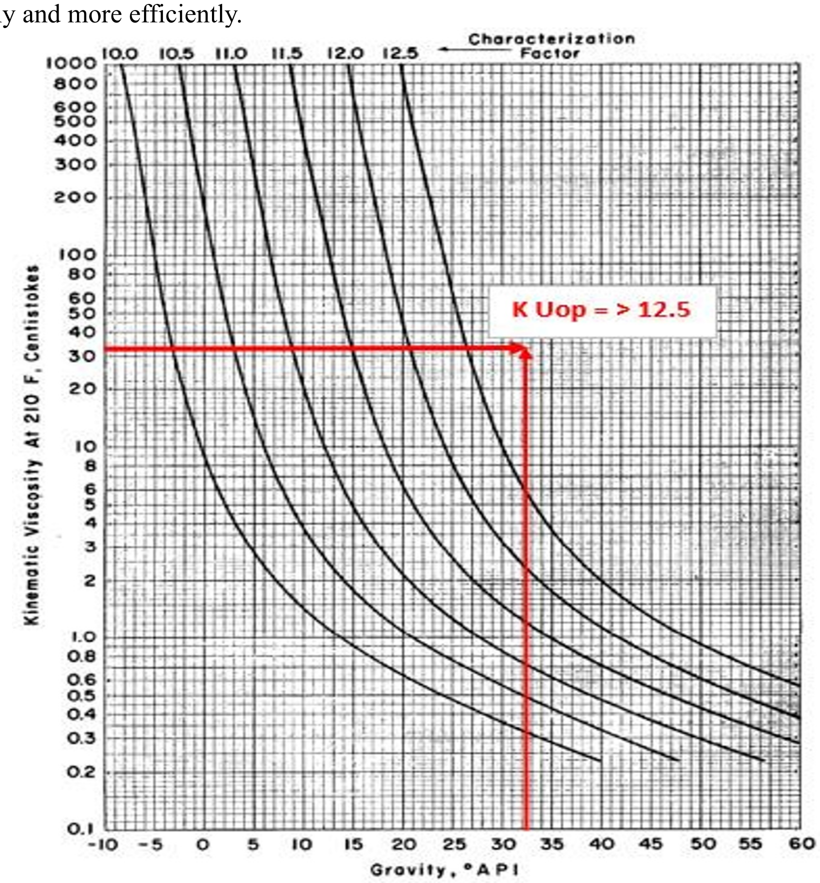

Fig. 5. Correlation Graph of API Gravity and Kinematic Viscosity Values at 210ºF or 100ºC

 https://doi.org/10.1051/e3sconf/202560503050

5 Discussion

Catalytic cracking feedstock properties depend on physical properties and chemical properties that are closely related. Hydrocarbons in crude oil feedstocks are classified as light, medium, or heavy hydrocarbon types according to the measured API gravity. Light crude oil has an API gravity higher than 31.1° with a density value that is, less than 870 kg/m3, medium oil has an API gravity between 22.3 and 31.1°. Heavy crude oil has an API gravity below 22.3°, or 920 to 1000 kg/m3, where the density value is 870 to 920 kg/m3. Extra heavy oil has an API gravity below 10.0°, or more than 1000 kg/m3. The average boiling point of the distillate and the API gravity value can be correlated to find the K UOP value for crude oil feedstocks with accessible distillation data.

$$K\ Uop = \sqrt[3]{1.8Tb/SG} \quad (4)$$

where: Tb = volume, or average normal boiling point in R (Rankine degrees), and SG = specific gravity at 15.6°C (60°F). The volume average boiling point (VABP) is used to calculate K UOP or Watson. Depending on the value of the Watson characterization factor, crude oils are classified as paraffinic (Kw = 11-12.9), naphthenic (Kw =10-11), or aromatic (Kw <10). To find the K UOP value of used lubricating oil feedstock in this activity, a different approach was taken. The approach was carried out using the UOP Company characterization method which requires the results of physical properties test data specific gravity 60ºF: 0.864 and viscosity 210ºF or 100ºC: 34.9 Centi stoke. Where the API Gravity value can be determined and the K UOP value can also be obtained if you have viscosity value data [14]. As a comparison of used lubricating oil characteristics are the characteristics of heavy oil for refinery catalytic cracker (RFCC) feedstock which has paraffinic hydrocarbon properties as shown in Table 2.

Table. 2. Comparison of used lubricating oil and heavy oil feedstock characteristics test results

NO	SPESIFIKASI	FEEDSTOCK		METODE
		Heavy Oil	Used Engine Oil	
1	Specific Gravity (60ºF)	0.888	0.864	ASTM D 4052
2	API Gravity	27.8	32.3	Calculated
3	Viscosity 100ºC, Centi stoke	-	34.9	ASTM D 445
4	Distillation			ASTM D 1160
	IBP, º Celsius	248	160	
	10% vol, º Celsius	378	412	
	30% vol, º Celsius	418	>440	
	50% vol, º Celsius	440	-	
	70% vol, º Celsius	465	-	
	90% vol, º Celsius	-	-	
	FBP, º Celsius	-	-	
5	K UOP	>12,5	>12,5	UOP 375

The recovery of used lubricating oil is tested on some parameters like crude oil as a feedstock in the refinery to determine the value of density, viscosity, flash point, and distillation before going to process so that can be compared characteristics between them. Based on the results of the used lubricating oil characteristic test, the K factor or K UOP value of used lubricating oil is categorized as paraffinic hydrocarbons. When compared with the specifications of the test of characteristics of heavy oil raw materials or heavy oil at the existing refinery in the catalytic cracker unit, it is possible for used lubricating oil to be processed into fuel. It means the result of the specification can be used as justification to select used lubricating oil as an alternative feedstock to substitute heavy oil in the industry.

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