Preparation of Kerosene from Lubricating Oil Waste using Microwave-assisted and Activated Carbon Pyrolysis from Lignite

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Abstract: This study discusses one method that offers a simultaneous solution to reduce lubricating oil waste while providing fuel. Both the treatment of lubricating oil waste and supply of fuel are classic problems in developing countries such as Indonesia, but require serious handling because they will become crucial problems in the future. Lubricating oil waste is classified as hazardous and toxic material, and particularly the amount of motorcycle lubricating oil waste reaches 1.2 GL. which will continue to increase from year to year. The goal of this study is to convert lubricating oil waste, specifically from motorcycles, into kerosene through microwave-assisted pyrolysis and using activated carbon from lignite sized 12 mesh as microwave absorbent. The experiment was conducted in various absorbent mass i.e. 80, 90, 100, 120, and 140 g, then each was added in 200 mL of lubricating oil waste. The mixture then took place in glass reactor and was heated in 800 W powered of microwave at constant temperature of 400 ºC for 3 hours. The vapour product of pyrolysis was cooled in a series of condenser to obtain fuel. Fraction similarity of kerosene was analysed with GC-FID, meanwhile its classification of the carbon chain length compound was identified by GC-MS. Properties were measured for its density (15 ºC) using ASTM D-1298 method and specific energy using bomb calorimeter. 140 g mass of absorbent produced the most similar chromatogram to kerosene standard and was able to obtain the composition of C_9-C_{15} fraction in amount of 90.61%. This product has density of 817.363 kg/m^3 and specific energy of 45.49 MJ/kg. It is important to develop this research to increase the kerosene fraction by examining the effect of temperature to control the endothermic thermal cracking reaction.

1 INTRODUCTION

Because people still rely heavily on private transportation, Indonesia becomes a country with relatively high motorcycle users reaching 112,771,136 units in 2019 (Badan Pusat Statistik Indonesia, 2020) and will grow to about 6% per year. This circumstance effects on the increasing amount of both of lubricating oil waste and also fuel needs. The data above then could be used to predict Indonesia's potential of lubricating oil waste in that year i.e. 1.2 GL

Lubricating oil waste is categorized into hazardous and toxic material so that it requires the proper handling method. One of the methods that can be developed is to process lubricating oil waste into fuel as well as kerosene through cracking technique. This method is capable of cutting long hydrocarbon chain (C_{31}- C_{40}), which is the main compound of lubricating oil waste, to be hydrocarbon compound of kerosene which has shorter hydrocarbon chain (C_9-C_{15}). Kerosene that is processed in this way can be an alternative source of fuel supply that complements the source of fossil fuel which is non-renewable energy. Kerosene has a variety of utility such as being a precursor for aviation turbine gasoline, for illumination, as well as for tractor vaporizing oil (Jones & Pujado, 2008).

Cracking techniques as previously described have been investigated through the catalytic cracking process using sulfated zirconia catalyst and can produce kerosene fraction as much as 9,04% (Permsubscul, Vitidsant, & Damronglerd, 2007). Moreover, other researchers has been using Fe/SiO_2-Al_2O_3 for catalytic cracking process and able to produce kerosene fraction of 15.71%

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(Makvisai, Promdee, Tanatavikorn, & Vitidsan, 2016). Even though these experiments do not produce kerosene in particular, but both have succeeded to show the potential of cracking lubricating oil waste into fuel including kerosene.

Cracking process of lubricating oil waste into kerosene can be done through microwave-assisted pyrolysis method. This technique is one of the most promising methods of enhancing and accelerating chemical reactions (Motasemi & Afzal, 2013). Microwaves can heat materials at specific targets because heat is generated from within the material itself through the mechanism of polar molecular agitation under the effect of an oscillating electricity or magnetic field, so that heating can take place effectively (Taylor, Singh, & Minhas, 2005). Therefore the using microwave heating required less energy (del Mundo, Cavarlez, Pe, & Roces, 2018). However, this method can be potently carried out using microwave absorbent to overcome the low dielectric property of lubricating oil waste. Microwave absorbents can be made from a variety of raw materials that are cheap and easy to obtain, like coconut shells, coal, or banana peels, if treated further into activated carbon. The capability of activated carbon as a microwave absorbent is very reliable because it is supported by relatively high dielectric characteristics (Menéndez et al., 2010).

The success of the microwave-assisted pyrolysis process using activated carbon absorbents has been proven by the following researchers. Bu et al., (2013) has developed the microwave pyrolysis process of Douglas fir sawdust pellets using activated carbon from lignite coal. Meanwhile Lam, Russell, Lee, & Chase, (2012) has developed pyrolysis process to crack high density polyethylene into liquid product that is matching with petrol and diesel using microwave-assisted process and commercial activated carbon (Aquacarb 207EA, Chemviron). In addition, Rahim, (2017) has also developed microwave-assisted pyrolysis to convert waste from lubricating oil from motorcycles to gasoline using activated carbon absorbent from lignite. On the other hand, activated carbon from coconut husk was used and succeed to transform waste shipping oil into a diesel-like fuel via microwave-assisted pyrolysis (Mahari et al., 2017). The term pyrolysis refers to the process by which material decomposes thermally in the absence of oxygen (Rabiu, Auta, & Kovo, 2018).

In particular, this study aims to treat lubricating oil waste into product that has a rich kerosene fraction through microwave-assisted pyrolysis techniques by observing the effect of the microwave absorbent mass made from lignite. Cracking process of heavy fraction

hydrocarbon is the complex reaction and since the specific target of the hydrocarbon structure to be generated is substances type with the C_9-C_{15} chain length, this research becomes important to carry out. The amount of absorbent utilized can influence the amount of microwaves absorbed and then released as heat that can lead to the desired reaction.

In this research lignite was chosen as activated carbon raw material for absorbing microwave due to lignite is one of the feedstock with potential amount in Indonesia but less beneficial if use as fuel with combustion directly. British Petroleum, (2020) has released the data that Indonesia's total proved reserves of low rank coal, including lignite, reach 29.4% at end 2019. Indonesian lignite, especially at East Kalimantan Province, has relatively high enough fixed carbon that is 31.55% (Patmawati, Alwathan, & Ramadani, 2020).

2 MATERIALS AND METHODS

The main materials, namely lubricating oil waste and lignite, were obtained from motorcycle garage and coal mining areas located in Samarinda City, East Kalimantan Province. The study began by first preparing activated carbon from lignite, as a microwave absorbent, using the method in detail described by Rahim and Fitriyana, (2018).

Furthermore 200 mL of lubricating oil waste from motorcycle was mixed with various absorbent mass of activated carbon sizing 12 mesh in the reactor flask. Mass variations used were 80, 90, 100, 120 and 140 g. The material mixture was then placed in 800 W microwave and then the reactor flask was connected to a series of condensers. The pyrolysis process was carried out for three hours and the temperature was maintained at 400°C with a temperature controller. Vapour product from pyrolysis was then passed through a series of condensers to get liquid fuel. Nitrogen flow of 200 mL/min was used to support flowing process of vapour to the condenser. The kerosene result fraction of each variation was analysed using a gas chromatography flame ionization detector (GC-FID) and gas chromatography mass spectrometry (GC-MS), while the characteristics of the resulting kerosene product were measured through the density (15°C) also calorific value respectively using the ASTM D-1298 and bomb calorimeter methods.

3 RESULT AND DISCUSSION

The results of GC FID chromatogram from the fuel products obtained were compared to similarity with the standard chromatogram of lubricating oil waste and kerosene. Chromatograms data were processed using Origin 7 software. The illustration of the chromatogram peaks is shown in figure 1.

When viewed from the characteristics of the retention time and the peak formed, it is seen the difference on the chromatogram of the product with the lubricating oil waste chromatogram. The output of the gas chromatography analysis in figure 1 (a) shows a significant peak for lubricating oil waste occurring at a retention time of 40 - 60 minutes. This shows lubricating oil waste containing heavy fractions with long carbon chain hydrocarbons.

While the chromatogram for the product resulting from the process of pyrolysis of lubricating oil waste, shows those significant peaks in figure 1 (b) to 1 (f) occur at shorter retention times, which are on average of 3 - 50 minutes. This indicates that there has been cracking process of long chain hydrocarbons to hydrocarbons with shorter chains.
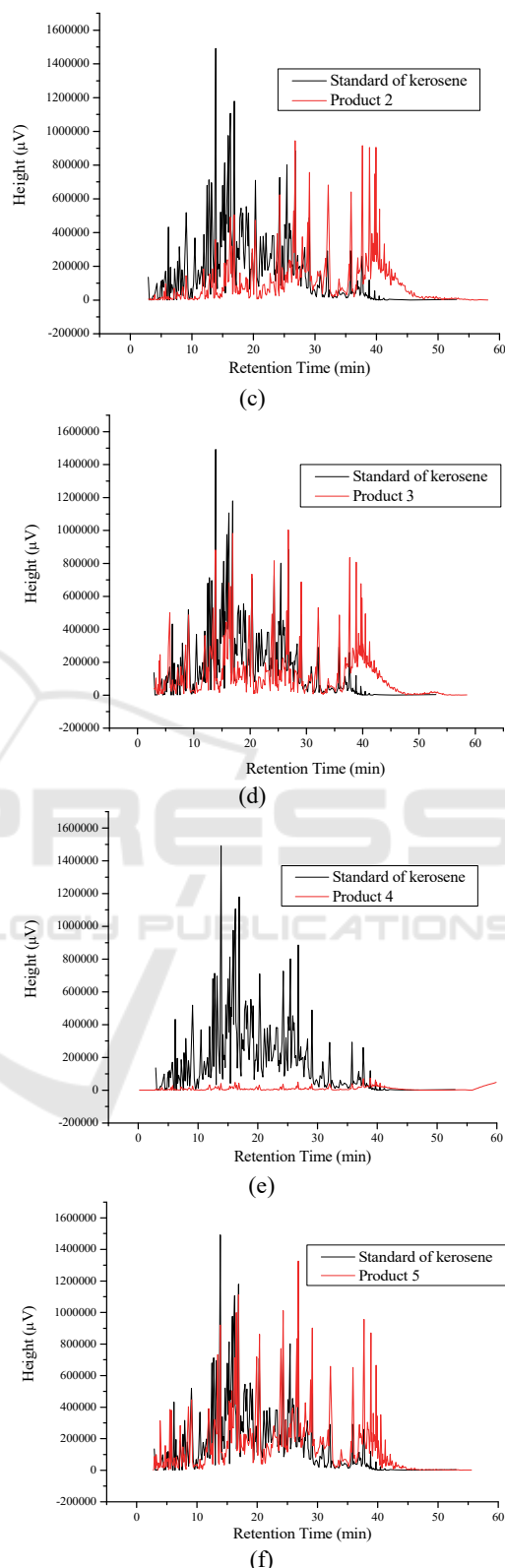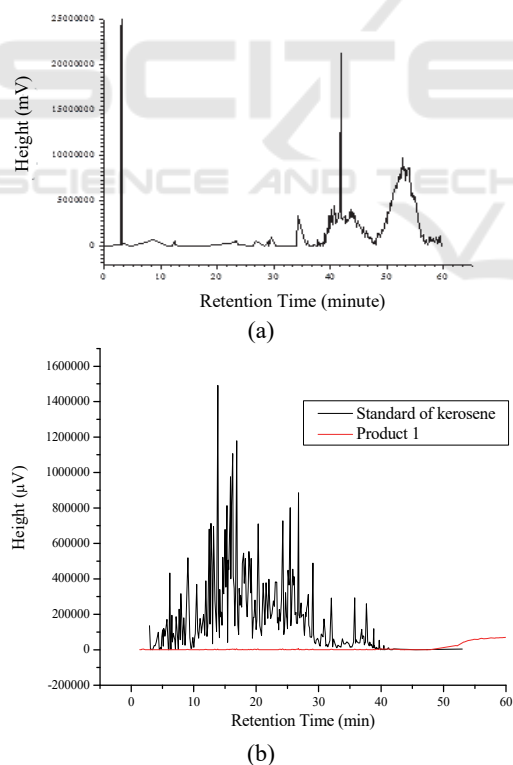

Figure 1: Chromatograms of (a) Lubricating oil waste; product compared with standard kerosene for absorbent mass (b) 80 g; (c) 90 g; (d); 100 g; (e) 120 g; (f) 140 g.

The results of the product chromatogram which are considered to represent the kerosene fraction are those that show significant peaks at the retention time of 3 - 40 minutes as shown by the standard kerosene chromatogram. While chromatograms that appear at retention times lower than 3 minutes are expressed as lighter fractions of kerosene and vice versa that appear at retention times higher than 40 minutes are considered to be heavier fractions of kerosene.

In the use of a relatively low absorbent mass that is 80 g, the expected pyrolysis has not been occurred yet completely which is evident from none emergence of significant peaks of the product chromatogram at 3-40 minutes retention time as showed in figure 1 (b). This exhibits that the absorbent mass utilized is not sufficient to produce heat that can crack the long hydrocarbon chain.

Table 1: Composition of hydrocarbon compound.

Hydrocarbon compound (%)	Mass of absorbent (g)				
	80	90	100	120	140
Paraffin	60.54	55.48	44.53	44.81	38.70
Isoparaffin	17.37	17.01	16.79	19.56	23.11
Olefin	19.56	23.19	32.12	28.97	32.51
Cycloparaffin	0.00	1.64	0.86	0.93	3.38
Aromatic	1.98	1.96	4.97	5.03	1.61

Table 2: Composition of carbon chain length.

Carbon chain length (%)	Mass of absorbent (g)				
	80	90	100	120	140
$C_5 - C_8$	3.54	3.17	9.79	8.20	7.25
$C_9 - C_{12}$	73.59	74.53	84.60	84.30	88.32
$C_{13}-C_{15}$	17.13	16.14	2.58	4.29	2.29
$C_{16}-C_{20}$	4.19	5.44	2.30	2.51	1.45
C_{26}	1.00	-	-	-	-

Although the cumulative composition of C_9-C_{15} could reach 90.72% but product still contain heavy fraction (C_{13}-C_{15}), in range kerosene fraction, quite much namely 17.13%, and lighter fraction (C_9-C_{12}) only reach 73.59%. Meantime the heaviest fraction (C_{16}-C_{26}) reach 5.19%. Although the C_{16}-C_{26} fraction appeared at retention time of 3-40 minutes, the carbon chain length produced was not a kerosene fraction, as can be looked in the distribution of composition of carbon chain length in table 2. Based on data in table 1, the hydrocarbon compound is still dominated by paraffin species as much as 60.54%.

On the use of more absorbent mass i.e. 90 to 140 g, significant chromatogram peaks appear at 3-40 minutes retention times and it has indicated the formation of compounds with hydrocarbon chain of kerosene fraction. This also further tends increasing the composition of the C_9-C_{12} fraction up to 88.32% on the utilization of 140 g mass of absorbent as well as the amount of C_{13}-C_{15} and C_{16}-C_{20} could be reduced till 2.294% and 1.45% respectively. The escalation in absorbent mass, that listed in table 1, also causes trend of raising the composition of hydrocarbon in olefin and isoparaffin species which exhibits that the stages of primary cracking reaction lead to olefin formation an also drive isomerization as secondary reaction. As it is known the secondary reactions, such as reforming, isomerization, alkylation, and polymerization, occur in thermal cracking (Speight, 2015). This phenomenon is a nature of endothermic thermal cracking reactions. Where the utilization of greater absorbent mass will further increase the absorption of microwaves and then released as greater heat into lubricating oil waste. As a consequence, primary and secondary reactions can take place more quickly.

An interesting result is shown in the utilization of 120 g absorbent mass. Previously, it was expected that the chromatogram resulted would be closer to the standard kerosene chromatogram along with the increasing mass of the absorbent used. Although the cumulative result of products in the kerosene fraction range is quite high at 88.59%, the elevation of the product chromatogram peaks tends to be very low compared to the standard kerosene peaks so as to form a flat chromatogram as shown in figure 1 (e). The product obtained shows the tendency of the formation of compounds in the range of kerosene fractions with more diverse types of compounds, as consequence there are no compounds with high composition. The results of GC MS analysis have identified 98 types of compounds that appear in this product.

The product chromatogram that is most similar to the kerosene standard chromatogram is the product chromatogram that used the most absorbent mass of 140 g as shown in figure 1 (f). In the use of this absorbent mass can be absorbed microwaves which then produce sufficient heat to break the chain of hydrocarbons so as to result a product that mostly has a carbon chain length in the range of hydrocarbon chains for kerosene.
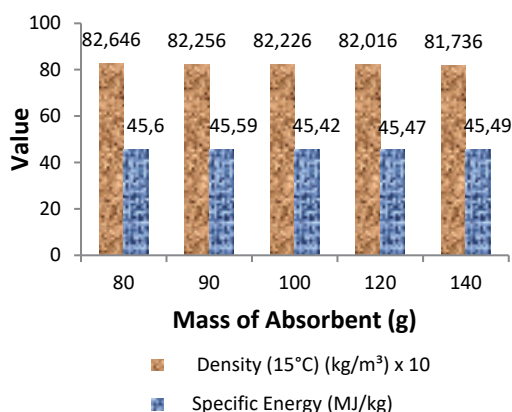
Figure 2: Properties value of product.

Refer to the data that showed in figure 2, it is seen that the mass of activated carbon as a microwave absorbent influences the density value of pyrolysis products. The higher mass of activated carbon causes the pyrolysis product density inclines to decrease which indicates that the pyrolysis product formed has the smaller molecular weight. All of products density has value lower than raw material which has a density of 871.114 kg/m^3.

Specific energy is one of important characteristic of kerosene as fuel. The specific energy of products was not influenced significantly by the elevation of mass absorbent and those values are in the range 45.42 – 45.60 MJ/kg. However, it seems that this property is influenced by the quantity of paraffin and isoparafin compounds formed. Overall the specific energy of the products are convenient of kerosene value based on Defence Standard 91-091 which requires a minimum value of 42.80 MJ/kg (Ministry of Defence, 2019).

This research can be developed to further improve the kerosene fraction (C_9-C_{15}), and reduce the lightest fraction (C_5-C_8) and the heaviest fraction (C_{16}-C_{26}). This can be conducted by examining the effect of temperature, because the thermal cracking reaction is endothermic.

4 CONCLUSIONS

This research has provided some key information related to pyrolysis of lubricating oil waste into kerosene with assisted microwaves, namely:
1. Active carbon from lignite is potential as a microwave absorber to generate heat to crack long chain hydrocarbon of lubricating oil waste.
2. The mass of activated carbon as much as 140 g can generate adequate heat to result a stable

product in the kerosene fraction hydrocarbon range (C_9-C_{15}) as much as 90.61%.
3. This product has properties of density and specific energy values are 817.363 kg/m^3 and 45.49 MJ/kg consecutively.
4. In general, the experimental results obtained in this research indicate the potential for conversion of lubricating oil waste into kerosene.

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