Identification of Kerosene Compounds from Used Lubricating Oil Pyrolysis Using GC-MS

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Abstract:- Due to the decreasing reserves of fossil fuels, efforts to produce fuels using various methods have been developed continuously. In this study, kerosene was produced through a microwave-assisted pyrolysis process from used lubricating oil. The compounds and compositions contained in kerosene were analyzed by GC-MS to ensure the presence of compounds with carbon chain lengths in the range of C_{10}-C_{16} as the main fraction that must be contained in kerosene. The identification results showed that the kerosene produced contained 89.98% C_{10}-C_{16}, while the fraction with the carbon chain length of less than C_{10} reached 10.05%. The types of compounds were dominated by 32.47% isoparaffin, 31.48% paraffin, 23.78% olefin, 10.03% cyclo-paraffin, and 2.18% aromatic.

Keywords:- Kerosene; Lignite; GC-MS; Microwave; Pyrolysis; used Lubricanting Oil.

I. INTRODUCTION

Fuel consumption increases continuously, but on the other hand, fossil-based fuel reserves continue to decrease because they cannot be renewed. One type of fuel that has experienced an increase in consumption is kerosene and jet fuel. S&P Global Commodity Insight reported that global jet fuel and kerosene demand was estimated to reach 8 million barrels per day with a demand growth rate of around 550,000 barrels per day until the end of 2024[1].

Efforts have to be pursued to overcome this circumstance, including producing kerosene using various methods. Kerosene has some benefits including as fuel in the commercial and military aviation industries and as a solvent in chemical industries [2].

Some investigators have shown the success of kerosene generation. Ekpenkhio converted jatropha curcas seeds into bio-kerosene via transesterification and pre-esterification operations [3]. Meanwhile, e-kerosene production through Fischer Tropsch and methanol pathways was compared and proposed the efficient process [4]. In 2020, Dujjanutat and Kaewkannetra developed catalytic hydrocracking of refined bleached deodorised palm to generate bio-hydrogenated kerosene [5] .

In this study, used lubricant oil (ULO) was treated to produce kerosene using the microwave-assisted pyrolysis

and exploited activated carbon that was generated from lignite, as microwave absorbent.

The composition of used lubricant oil (ULO) is 90% lube base oil and 10% additives. Heavy oil with long-chain hydrocarbons (C_{31} to C_{40}) is the fundamental component of lubricating oil that could be cracked into liquid fuel containing fuel fractions such as kerosene with a hydrocarbon chain between C_{10} - C_{16}.

This study aims to confirm the presence of kerosene compounds contained in the pyrolysis products. Identification was carried out using gas chromatography–mass spectrometry (GC-MS) instrument considering that the resulting product contained a mixture of complex compounds. GC-MS analysis has several advantages, including accurately detecting specific molecules by effectively separating and analyzing complicated combinations of substances. It also offers both quantitative and qualitative data, allowing for a thorough examination of the sample's constituent parts [6].

II. METHOD

➤ *Microwave Assisted Pyrolysis Process*

140 g lignite-activated carbon and 200 mL motorcycle's ULO was mixed in the pyrolysis reactor flask. After that, the reactor flask was linked to a series of condensers, and all materials were put in an 800 W microwave oven. A temperature controller was used to keep the temperature at 400 °C during the three-hour pyrolysis process. After pyrolysis, the vapor product was sent through a number of condensers to produce liquid fuel. The passage of vapor to the condenser was supported by a 200 mL/min nitrogen supply.

➤ *GC-MS Analysis*

A gas chromatography mass spectrometry (GS-MS), with the type of QP2010S Shimadzu, was carried out to analyze the kerosene result fraction. Instrument was operated with the following conditions: Helium (99.999%) was used as carrier gas at a constant flow of 27.3 cm/sec and an injection volume of 0.57 mL/min was employed (split ratio of 133.1) injector temperature 310°C; ion-source temperature 250°C. The oven temperature was set to start at 40°C (isothermal for 5 min), with an increase of 5°C/min, ending with a 15 min isothermal at 300°C. Mass spectra

were taken at 70 eV; a scan interval of 0.5 s and fragments from 28 to 600 Da.

> *Identification of Compounds*

The National Institute of Standards and Technology (NIST) and Willey Lab database were used to interpret the GC-MS mass spectrum. The unknown component's mass spectrum was contrasted with the known components' spectrums that were kept in the Willey and NIST libraries. The components of the test materials were identified by name, molecular weight, and structure.

III. RESULTS AND DISCUSSION

Figure 1 displays the chromatogram, which reveals a notable peak for pyrolysis product at a retention duration of 3–40 minutes. This illustrates the product has light hydrocarbons with a short carbon chain, generally $C_8 - C_{20}$ [7][8]. This demonstrates that ULO, which has a long carbon chain, has cracked into molecules with shorter carbon chains.
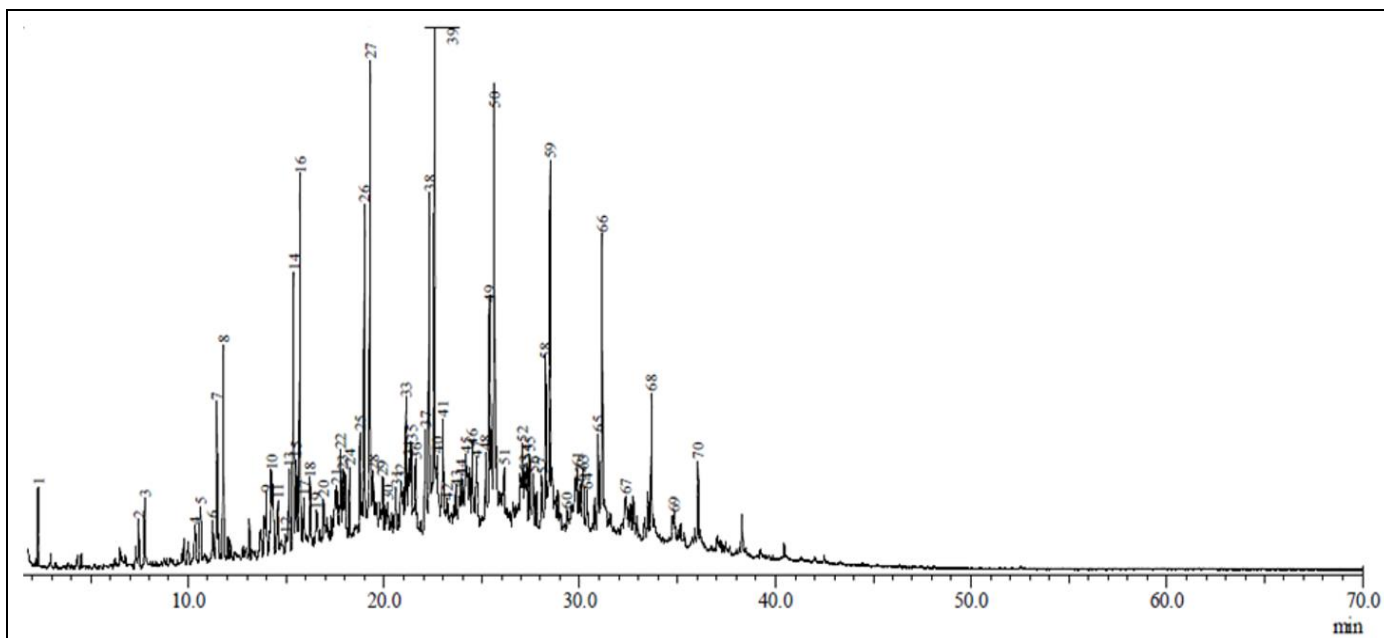

Fig. 1. GC Chromatogram of MAP Product using ULO Raw Material

Pyrolysis with microwave assistance was the method employed, in order to speed up and improve the efficiency of the heating process. In contrast to conventional heating, which spreads from the heat source to the material's surface, microwave heating originates inside the material and spreads uniformly throughout it as a result of molecular vibrations [9].

GC-MS analysis was utilized to identify the type of compounds and determine the kerosene fraction as presented in Table 1.

Table 1 Type of Compounds

No	RT	% Area	Formula	Name of Compound
1	2.326	0.63	C_6H_{12}	Cyclohexane
2	7.459	0.48	C_8H_{16}	1-Octene
3	7.783	0.71	C_8H_{18}	n-Octane
4	10.338	0.68	C_8H_{18}	n-Octane
5	10.628	0.84	C_9H_{20}	2,5-Dimethylheptane
6	11.237	0.5	C_9H_{18}	1-Octene, 2-Methyl
7	11.453	1.57	C_9H_{18}	1-Nonene
8	11.794	1.86	C_9H_{20}	n-Nonane
9	13.989	1.12	$C_{10}H_{20}$	1-Decene
10	14.241	1.77	$C_{10}H_{22}$	3,5-Dimethyloctane
11	14.579	0.77	$C_{10}H_{22}$	3-Methylnonane
12	14.975	0.48	C_9H_{12}	Benzene, 1,2,3-Trimethyl
13	15.162	0.79	$C_{10}H_{20}$	1-Nonene, 2-Methyl
14	15.387	2.38	$C_{10}H_{20}$	1-Decene
15	15.508	1.13	C_9H_{12}	Benzene, 1,2,4-Trimethyl
16	15.706	3.57	$C_{11}H_{24}$	n-Undecane
17	15.907	0.61	$C_{12}H_{24}$	4-Dodecene

18	16.225	0.83	$C_{12}H_{24}$	1-Decene, 2,4-Dimethyl
19	16.520	0.64	$C_{11}H_{24}$	Ddecane , 4-Methyl
20	16.904	0.63	$C_{12}H_{24}$	Cyclohexane, 1-Methyl-2-Pentyl,
21	17.581	0.77	$C_{12}H_{24}$	1-Nonene, 4,6,8-Trimethyl-
22	17.781	0.94	$C_{10}H_{22}$	Heptane, 3-Ethyl-2-Methyl
23	17.890	1.28	$C_{11}H_{24}$	Decane, 4-Methyl
24	18.243	0.61	$C_{12}H_{26}$	n-Dodecane
25	18.776	1.17	C_9H_{18}	1-Octene, 2-Methyl
26	19.001	3.31	$C_{12}H_{24}$	1-Dodecene
27	19.294	4.72	$C_{11}H_{24}$	n-Undecane
28	19.454	0.93	$C_{11}H_{22}$	2-Undecene
29	19.930	0.96	$C_{11}H_{17}$	Cyclohexadienylium, (1,1-dimethylethyl)methyl-
30	20.192	0.62	$C_{11}H_{24}$	n-Undecane
31	20.611	0.57	$C_{10}H_{14}$	Benzene, 1-methyl-4-(1-methylethyl)
32	20.852	0.67	$C_{12}H_{26}$	Decane, 2,9-Dimethyl
33	21.130	2.51	$C_{11}H_{22}$	Cis-3-Undecene
34	21.262	0.77	$C_{11}H_{22}$	1-Undecene
35	21.392	1.1	$C_{11}H_{24}$	n-Undecane
36	21.614	1.13	$C_{12}H_{26}$	Undecane, 4-methyl
37	22.108	1.06	$C_{10}H_{22}$	Nonane, 2-methyl
38	22.317	4.05	$C_{10}H_{22}$	Octane, 2,6-dimethyl
39	22.588	5.53	$C_{14}H_{28}$	1-Tridecene, 2-Methyl
40	22.725	1.32	$C_{12}H_{24}$	1-Dodecene
41	23.001	1.62	$C_{11}H_{24}$	Undecane
42	23.242	0.73	$C_{12}H_{24}$	4-Dodecene
43	23.689	1.08	$C_{10}H_{22}$	Octane, 3,5-dimethyl
44	23.933	1.57	$C_{13}H_{28}$	Undecane, 2,6-dimethyl
45	24.177	2.3	$C_{14}H_{30}$	Tetradecane
46	24.521	1.14	$C_{12}H_{26}$	Undecane, 2-methyl
47	24.732	1.03	$C_{12}H_{26}$	n-Dodecane
48	25.194	0.84	$C_{14}H_{28}$	1-Tridecene, 2-Methyl-
49	25.389	3.39	$C_{12}H_{24}$	1-Dodecene
50	25.638	5.38	$C_{11}H_{22}$	1-Heptyl-2-Methyl, Cyclopropane
51	26.136	0.98	$C_{12}H_{26}$	n-Dodecane
52	27.074	2.02	$C_{10}H_{20}$	Cis-3-Decene
53	27.158	0.64	$C_{13}H_{28}$	Undecane, 2,6-Dimethyl
54	27.292	0.73	$C_{14}H_{30}$	Tetradecane
55	27.435	0.87	$C_{14}H_{30}$	Tridecane, 2-Methyl-
56	27.637	0.6	$C_{10}H_{22}$	Nonane, 3-Methyl-
57	28.072	0.61	$C_{14}H_{28}$	1-tridecene, 2-Methyl-
58	28.257	1.68	$C_{12}H_{24}$	1-Dodecene
59	28.485	4.58	$C_{12}H_{26}$	Dodecane
60	29.342	0.98	$C_{10}H_{20}$	Cyclopropane, 1-Methyl-2-(3-Methylpentyl)-
61	29.877	1.45	$C_{11}H_{22}$	Cycloundecane
62	30.025	0.69	$C_{13}H_{28}$	Undecane, 4,8-Dimethyl-
63	30.163	0.72	$C_{12}H_{26}$	n-Dodecane
64	30.365	0.47	$C_{10}H_{22}$	Nonane, 3-Methyl-
65	30.945	0.96	$C_{12}H_{24}$	1-Dodecene
66	31.155	3.75	$C_{13}H_{28}$	Tridecane
67	32.351	0.52	$C_{16}H_{34}$	Tetradecane, 6,9-dimethyl-
68	33.666	1.23	$C_{13}H_{28}$	Tridecane
69	34.822	0.7	$C_{13}H_{28}$	Undecane, 2,6-Dimethyl-
70	36.045	0.67	$C_{12}H_{26}$	n-Dodecane

The list of compounds shown in table 1 detects that the types of compounds formed are paraffin, iso-paraffin, cyclo-paraffin and aromatic groups. However, it is still dominated by the iso-paraffin and paraffin groups as cumulatively in Table 2.

Table 2 Percentage of Compound Group

Compound Groups (%)				
Paraffin	Iso-paraffin	Olefin	Cyclo-paraffin	Aromatic
31.480	32.470	23.780	10.030	2.180

The result in Table 2 demonstrated that the reaction mechanism that occurred was primary cracking, which involved the breaking of carbon-carbon (C-C) bonds through a free radical mechanism followed by isomerization as secondary cracking. The presence of cyclo-paraffin and aromatic compounds indicates that a cyclization reaction also occurs as a secondary cracking [10].

In the end, the compounds were clustered based on the carbon chain length to confirm the presence of kerosene fraction. The kerosene fraction was determined as a compound with a carbon chain length of C_{10}-C_{16} [11], with the number of percentage in Table 3.

Table 3 Percentage of Kerose Fraction

Carbon Chain Length Percentage (%)		
< C_{10}	C_{10}-C_{16}	> C_{20}
10.05	89.89	0

The kerosene fraction produced can reach 89.89% and this value complies with fuel characteristic. There are no compounds with a carbon chain length of more than C_{20} were detected, indicating that the cracking process was effective.

The use of the MAP method with the addition of lignite-activated carbon as a microwave absorber can provide sufficient heat to direct cracks in the carbon chain length of the kerosene fraction without producing excessive light fractions.

IV. CONCLUTIONS

This study has established some key information related to the identification of MAP product compounds using ULO as the raw material namely:

- The microwave-assisted pyrolysis using lignite-activated carbon as microwave absorbent could be utilized as a method to convert ULO into kerosene fuel.
- The resulting type of compound consists of 32.47% iso-paraffin, 31.48% paraffin, 23.78% olefin, 10.03% cyclo-paraffin, and 2.18% aromatic.
- The kerosene fraction reaches 89.89% and the remaining 10.05% is a compound with a carbon chain length of less than C_{10}.

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