STUDY ON GC-MS PROFILE OF FUELS PRODUCED FROM PLASTIC WASTE CONVERSION VIA THREE-CONDENSER PYROLYSIS REACTOR

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ABSTRACT

The problem of plastic waste is very flourished in the current era of modern life. In this study, a three-condenser pyrolysis reactor was applied to obtain fuels in the form of oil#1, oil#2, and oil#3 from plastic waste. Gas Chromatography-Mass Spectroscopy (GC-MS) technique was carried out to analyze the fuel for profiling study. Characterization using GC-MS indicated the domination of hydrocarbon compounds was found oil#1. The existence of hydrocarbon compounds from oil#2 and oil#3 was displayed by chromatogram and MS database from Library Wiley 7.LIB. Meanwhile, alcohol, ether, and fatty acid were detected from oil#1 based on the chromatogram and MS database. Therefore, the samples were categorized as fuel. The result of this study corresponded to the concept of pyrolysis and be able to be implemented as an alternative energy source.

Keywords: fuel, GC-MS profile, plastic waste, three-condenser pyrolysis reactor

I.INTRODUCTION

The utilization of plastics is significantly flourished in the current era of modern life. However, both the function and pollution from plastics are like two sides of a coin, which become a challenge in recent decades. In general, plastic waste generation rates are affected by economic development, the degree of industrialization, public habits, and others (Hoornweg and Bhada-Tata, 2012). Global plastic waste generation by sector reported around 343 million metric tonnes in 2018 (Geyer, 2020). Of the Basel Convention data reported after 2015, Indonesia produced plastic waste approximately 9.6 million metric tonnes, after China about 61 million metric tonnes and the United States around 34.5 million metric tonnes per year in 2018 (Tsakona and Rucevska, 2020). Plastic waste originated from packaging plastic is estimated 275 million tonnes. More than 10% is dominated by a large amount of landfilled waste (Cassou, 2018). Based on other data, plastic waste around the world approximately 12% was incinerated, 9% was recycled, and more than 60% was discharged in landfills or the environment, including on the ocean (Jambeck et al., 2015; Geyer et al., 2017).

The term "plastic" derived from the Greek word "plastikos" meaning fit for molding. (Tulashie et al., 2019). According to the American Chemistry Council, plastic is a type of synthetic or polymer, similar to natural resins found in trees and other plants (American Chemistry Council, 2015). Nowadays, there are more than 30 types of primary plastic combined with several different additives, so that thousands types of plastics give diverse plastic materials. Around 97-99% of these plastics derives from fossil fuel feedstock (Center for International Environmental Law, 2017), while remaining 1-3 % comes from bio-based plastics (European Bioplastics, 2016). Commonly, one of the plastics that have frequently been found is Polyethylene (PE) : low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and the other plastic is Polypropylene (PP); Polyvinylchloride (PVC); Polystyrene (PS); Polyethylene terephthalate (PET); Polylactic acid (PLA), Polycaprolactone (PCL), Bio polymerspolybutylene succinate (PBS), Polyvinyl alcohol (PVA), Polytrimethylene terephthalate (PTT), and others (Anuar Sharuddin et al, 2016; Tsakona and Rucevska, 2020).

Today, thermochemical recycling of plastics, thermal cracking or pyrolysis, has been conducted across countries and regions (Panda et al, 2010; Tsakona and Rucevska, 2020). However, Indonesia's energy recycling based on plastic, meaning conversion of plastic into fuel, is not available yet, and recycled plastic material is only 11% of a total plastic waste (Quina et al, 2019). Commonly, most of the plastics can be recycled into liquid fuel, although the effect of plastic waste types of pyrolysis process is very significant on the yield and quality of produced oil (Almeida and Marque, 2015; Miandad et al, 2017).

Recycling plastic faces many challenges. Both costeffectiveness and efficient recycling of mixed plastic are some of the problems. Key parameters that have to notice for the quality assessment of recycled plastic are the degree of mixing (polymers cross-contamination), the degree of degradation, and the contamination levels (Vilaplana et al, 2007). In addition, there are some aspects to recycle plastic waste into fuel depend on technical/ method, economic, environmental, political, and others (Lazarevic et al, 2010).

To recycle plastic waste, there are some of the methods, which are mechanical recycling, chemical recycling : hydrogenation, gasification, pyrolysis, chemical depolymerization, etc and energy recovery. Each recycling methods have advantages and disadvantages depend on kinds of used plastic polymers (Panda et al, 2010; Kumar et al, 2011; Grigore, 2017; Antelava et al, 2019).

Pyrolysis is deûned as irreversible thermochemical process of anaerobic decomposition on the material at elevated temperature (300+ °C) (Singh and Ruj, 2016; Faussone, 2018; Sharuddin et al., 2018; Tulashie et al., 2019). The pyrolysis technique is considerable be applied to obtain liquid oil and char solid fractions (López et al., 2011; Sharma et al., 2014) as well as gas (Erkiaga et al, 2013; Wilk and Hofbauer, 2013). Many types of the pyrolysis reactors have been used to produce liquid fuel and its derivate products. The parameters such as mixing plastic and catalyst (Syamsiro et al, 2014), co-reactant or co-pyrolysis, temperature (Wu and Williams, 2010; Dewangan et al., 2016), operation time, heat transfer (Singh and Ruj, 2016), and efûciency of the reaction towards achieving the ûnal desired product have been studied (Hazrat et al, 2014). Most of the plastic pyrolysis in the labscales have performed in batch, semi-batch, or continuous-ûow reactors such as ûuidized bed, ûxed-bed reactor, and conical spouted bed reactor (CSBR) (Wong et al, 2015; Anuar Sharuddin et al, 2016; Kunwar et al, 2016; Othman et al, 2017; Sharuddin et al, 2018).

Kinds of compounds in the fuel from plastic waste have been reported that mainly categorized like hydrocarbon and followed by minor compounds such as hydrocarbon cyclic, alcohols, esters, oxirane, acids, ketones, nitrogen-containing compounds and chloro-containing compounds (Dewangan et al, 2016; Tulashie et al, 2019).

As the comparison of fuel oil applicated, especially according to various fuels and carbon ranges, there is the characterization of some petroleum product. Gasoline or petrol is a flammable petroleum liquid consists mostly of hydrocarbons with a range of C₄ - C₁₂ per molecule. Classification of gasoline is automobile gasoline, aviation gasoline, and technical (solvent) depending on use. Kerosene or paraffin oil is a highly flammable colorless liquid with a strong odor, distilled from petroleum which is a mixture of about ten different types of fairly simple chain hydrocarbons with a range $\rm C_6$ - $\rm C_{16}$ per molecule. It is less volatile than gasoline that is applied as burned in lamps, heaters, and furnaces, as well as jet fuel. Kerosene-type jet fuel (including Jet A and Jet A-1) has a carbon number distribution $\rm C_8$ - $\rm C_{16'}$ and wide-cut or naphtha-type jet fuel (including Jet B) has a range $C_5 - C_{15}$. Jet fuel is a type of aviation fuel designed for use in aircraft powered by gas-turbine engines. The most commonly used fuels for commercial aviation are Jet A and Jet A-1 which are produced to a standardized international specification. Fuel oil is a fraction obtained from petroleum distillation, either as a distillate or a residue that is made of long hydrocarbon chains, particularly alkanes, cycloalkanes, and aromatics. Fuel oil is classified into six classes, numbered 1 through 6, according to its boiling point, composition, and purpose. Containing C_{0} - C_{70} , the fuel oil has a long carbon chain and a boiling point ranging from 175 - 600 °C. Diesel oil is a type of fuel oil. It is produced from the fractional distillation of crude oil, resulting in a mixture of carbon chains, typically contain $C_8 - C_{21}$ per molecule (Tulashie et al, 2019; ALS (Australian Laboratory Services) Global, 2020).

Analysis method, a gas chromatography-mass spectroscopy (GC-MS) technique, has been widely applied for the samples measurement in several fuel products. GC-MS gives advantages in realistic measurement, and is a valid technique for the analysis of fuel even that can be used in complex mixtures of samples to identify the release of volatile compounds (Sharma et al, 2014).

To provide innovative solutions in tackling the problem of plastic waste, a three-condenser pyrolysis reactor, which means the pyrolysis reactor with three condensers, has been developed to be functionated for converting plastic waste into three types of fuel oils. As far as our literature survey could ascertain, no study was found about the three-condenser pyrolysis reactor that used to convert plastic waste into fuel In this study, a threecondenser pyrolysis reactor has been applied to obtain fuel oils from plastic waste via the pyrolysis method. The fuel oils were characterized by the GC-MS technique to study profile component.

II. MATERIALS AND METHODS

Types of plastics used for the pyrolysis process was collected from plastic packaging, mainly beverages such as mineral water, soft drink bottle, and fruit juice containers, which were from Polyethylene terephthalate (PET) waste. The plastic waste was washed with detergent and water to clean dirt and oil. The treatment was conducted so that not affect the chemical properties of oil. The plastic waste was dried, and then cut into pieces to the size of about 0.5–2.0 cm using scissor (Tulashie et al, 2019).

2.1. Pyrolysis of Plactic Waste using Threecondenser Pyrolysis Reactor

Pyrolysis apparatus to convert plastic waste into fuel oil was carried out using a lab scale threecondenser pyrolysis reactor. The part of it was described in Figure 1.

Before the pyrolysis process was conducted, the heating source, using a gas stove, was assembled to a reactor/boiler (1). To monitor heat, a thermostat was paired in the reactor lid (2). The aerator, filled with cold water, was connected to three condensers (3, 4, 5). Each liquid oil/fuel exit place pipeline (6, 7, 8) was positioned receptace under the storage tank for oil#1, oil#2, and oil#3, respectively.

As many as 2 kg of plastic waste samples were filled in the pyrolysis reactor (tank). Started from around 30 °C, the pyrolysis reactor was heated up to 350 °C during the whole process. After the reactor temperature had reached the set limit, the process started and lasted for 2 hours. Vapor from the tank flowed in the pipeline toward condensers one, two, and three was condensed using cold water and was obtained three different oils. The pyrolysis products, three types of oil, were measured in mL using a measuring cylinder. And then, the reactor lid opened when the temperature of the reactor had reached under 40 °C to remove the residual solid material (Tulashie et al, 2019).



- Annotation : d = Internal diameter
- h = Total hight
- 1 = Total length
- 1. Reactor/Boiler (d = 58 cm; h = 60 cm)
- 2. Reactor Lid
- 3. Condenser 1 (d = 30 cm; h = 40 cm)
- 4. Condenser 2 (d = 15 cm; h = 25 cm) Condenser 3 (d = 15 cm; h = 25 cm)
- Condenser 3 (d = 15 cm; h = 25 cm)
 8 Storage Tank (d = 10 cm; h = 17 cm)
- 6 8.Storage Tank (d = 10 cm; h = 17 cm)
 9. Heating Source (Gas Stove)
- 10. Cantilever
- 11. Pipeline (Reactor to Condenser) (d = 8 cm; 1 = 25 cm)
- 12. Pipeline (Condenser to Condenser) (d = 5 cm; 1 = 20 cm)
- 13. Pipeline (Condenser to Storage Tank) (d = 3 cm; h = 15 cm)

Figure 1. A Three-condenser Pyrolysis Reactor

2.2. Characterization of Fuel Using GC-MS Analysis

The samples of oil from the pyrolysis process of plastic waste were analyzed using GC-MS, respectively. With the specification of the GCMS-QP 2010 Ultra variant equipped with capillary column HP-PONA ($50 \text{ mLx} 0.25 \text{ mm I.D.}, 0.50 \mu \text{m}$), chromatographic condition was raised with a gradient temperature of 2 °C/min until the limit set temperature (Shimadzu, 2011).

III. RESULTS AND DISCUSSION

By the process of pyrolysis conducted for 2 hours at 350 °C using a three-condenser pyrolysis reactor, three different oils, which categorized as oil#1, oil#2, and oil#3, acquired from three disparate condensers. As many as 2 kg of plastic waste samples obtained 2 L of a total oil based on 1200 mL of oil#1 from condenser one, 300 mL of oil#2 from condenser two, and 500 mL of oil#3 from condenser three, respectively. The three samples of oil were investigated using the GC-MS technique to discover the characterization of it. Either identification or quantification on the chromatogram profile of three types of oil was interpreted based on MS data from the Wiley 7.LIB Library. Through observation of chromatogram and MS data interpretation, the profiles of each oil were compared with fuel oil (ALS Global, 2020) both by chemical compound names and by range carbon (Tulashie et al., 2019). In Figure 2, the chromatogram profile of oil#1 revealed three peaks that explained three chemical compounds in the oil sample. The three chemical compounds were $C_{14}H_{20}O$ of 1-Tetradecanol (41.42%), $C_{18}H_{26}O_{2}$ of Stearic acid (39.28 %), and $C_9H_{16}O_2$ of 2-Butoxy-3,4-dihydropyran (19.30 %) (see Table 1). Comparing with carbon range, it can be concluded that oil#1 of plastic waste pyrolysis was like the diesel oil range ($C_8 - C_{21}$) according to (ALS Global, 2020). But, in component, oil#1 contained alcohol, fatty acid, and ether as reported by (Tulashie et al., 2019).

In Figure 3, as many as seven peaks appeared on the chromatogram profile of the oil#2 sample. The hydrocarbon compounds represented by six peaks (total of 52.2 %), and only one peak of the ketone compound (47.80 %). Six kinds of hydrocarbon compounds have a carbon range (C_6 and C_{12}) of alkanes hydrocarbon meanwhile only C_6 of the alkenes hydrocarbon. The ketone compound contained in the sample was C_3H_6O . In detail, the chemical compounds of oil#2 were summarized



Figure 2. GC-MS Chromatogram Profile of Oil#1 from Pyrolysis of Plastic Waste. Peaks: (1) 1-Tetradecanol; (2) 2-Butoxy-3,4-Dihydropyran; (3) Stearic Acid



Figure 3. GC-MS Chromatogram Profile Of Oil#2 From Pyrolysis Of Plastic Waste. Peaks: (1) 2-Propanone; (2) 2,3-Dimethylbutane; (3) N-Hexane; (4) 2-Methyl-1-Pentene; (5) 1-Hexene; (6) 4,6,8-Trimethyl-1-Nonene; (7) 7-Methyl-1-Undecene



Figure 4. GC-MS Chromatogram Profile of Oil#3 from Pyrolysis of Plastic Waste. Peaks: (1) n-Pentadecane; (2) Cis-1,3-Dimethoxycyclopentane; (3) n-Eicosane; (4) n-Heptadecane; (5) Dioctylphthalate; (6) n-Tricosane; (7) n-Pentacosane; (8) n-Hexadecane; (9) n-Hexatriacontane; (10) n-Octacosane

Tabel 1. Composition of Oil#1 from Pyrolysis of Plastic Waste

Name of Compound	Peaks	*RT (min)	%Area	Molecular Formula
Fatty Acid				
Stearic acid	3	24.610	39.28	$C_{18}H_{36}O_2$
Alcohol				
1-Tetradecanol	1	19.787	41.42	$C_{14}H_{30}O$
Ether				
2-Butoxy-3,4-dihydropyran	2	22.218	19.30	C9H16O2

*RT, Retention Times of Gas Chromatography in minutes

Tabel 2. Composition of Oil#2 from Pyrolysis of Plastic Waste

Name of Compound	Peaks	*RT (min)	%Area	Molecular Formula
Alkanes Hydrocarbon		·		
2,3-Dimethylbutane	2	2.300	7.80	C_6H_{14}
n-Hexane	3	2.345	6.07	C_6H_{14}
4,6,8-Trimethyl-1-nonene	6	8.387	10.50	$C_{12}H_{24}$
7-Methyl-1-Undecene	7	8.620	13.43	$C_{12}H_{24}$
Alkenes Hydrocarbon				
2-Methyl-1-pentene	4	2.413	6.06	C_6H_{12}
1-Hexene	5	2.483	8.34	C_6H_{12}
Ketones				
2-Propanone	1	2.230	47.80	C_3H_6O

*RT, Retention Times of Gas Chromatography in minutes

in Table 2. To investigate oil#2, compared according to (ALS Global, 2020) that oil#2 has a carbon range $C_6 - C_{12}$ indicated like kerosene-type jet fuel ($C_5 - C_{15}$).

As shown in Figure 4, the chromatogram profile of oil#3 displayed ten types of peaks that represented ten chemical compounds. Alkanes hydrocarbon $(C_{15} - C_{36})$ represented by eight peaks have dominated in quantities (95.65%) and followed by

other minor components such as $C_{24}H_{38}O_4$ of Dioctylphthalate (4.32%), and $C_7H_{14}O_2$ of Cis-1,3-Dimethoxycyclopentane (0.03%). If the chemical compounds contained in oil#3 (see Table 3) were compared as claimed by (Tulashie et al, 2019; ALS Global, 2020), the highest composition of chemical compounds, alkanes hydrocarbon, would not exhibit like gasoline with a range of $C_4 - C_{12}$ per molecule, but fuel oil ($C_9 - C_{70}$) or hydraulic oil for phthalate substance.

Name of Compound	Peaks	*RT (min)	%Area	Molecular Formula
Alkanes Hydrocarbon				·
n-Pentadecane	1	19.564	1.48	$C_{15}H_{32}$
n-Hexadecane	8	23.786	15.63	$C_{16}H_{34}$
n-Heptadecane	4	21.272	13.62	$C_{17}H_{36}$
n-Eicosane	3	20.437	6.98	$C_{20}H_{42}$
n-Tricosane	6	22.078	14.60	$C_{23}H_{48}$
n-Pentacosane	7	22.901	16.72	$C_{25}H_{52}$
n-Octacosane	10	25.853	11.86	$C_{28}H_{58}$
n-Hexatriacontane	9	24.752	14.77	C ₃₆ H ₇₄
Ester				
Dioctylphthalate	5	21.823	4.32	$C_{24}H_{38}O_4$
Ether				
Cis-1,3-Dimethoxycyclopentane	2	20.375	0.03	C7H14O2

Tabel 3. Composition of Oil#3 from Pyrolysis of Plastic Waste

*RT, Retention Times of Gas Chromatography in minutes

Overall, each sample, which is oil#1, oil#2, and oil#3, indicates the pyrolysis oil from plastic waste containing chemical compounds such as hydrocarbon compounds, fatty acids, alcohols, ketones, esters, and ether. Although the characteristic of pyrolysis oil was not investigated more yet like other parameters, viscosity, boiling point and specific gravity, that can be used to claim as fuel specifically, the oil of plastic waste pyrolysis has the potential to be used as a combustible fuel source as reported by (Sharma et al., 2014; Dewangan et al., 2016; Tulashie et al., 2019).

IV. CONCLUSIONS

In this study, converting plastic waste into fuel using three-condenser pyrolysis reactor technology is very prospect to be implemented for reducing plastic waste which is obtained about 2 L of total oil from 2 kg of plastic waste. Overall, the chemical compounds, which are indicated as fuel like hydrocarbon compounds, fatty acids, akohols, ketones, esters, and ethers, are discovered from oil#1, oil#2, and oil#3 samples. Therefore, the oil of pyrolysis product, especially fuel from plastic waste, has the potential to be used as an alternative energy source.

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