PYROLYSIS OF MUNICIPAL PLASTIC WASTE

Nur Syafiqah Mohd Saidi and Rusmi Alias

Faculty of Chemical Engineering, Universiti Teknologi Mara, 40450 Shah Alam, Selangor.

***Abstract* - Since the over-used of plastic is becoming a major issue in the world nowadays, efforts of recycling the plastics into useful materials are being developed. One of the most common methods used in converting the plastic into valuable product is pyrolysis. This study aims to produce oil from the PET plastic bottles. The PET type of plastics is chosen as the raw material of the research since the plastic can be easily collected and recycled. The plastic slowly went through pyrolysis at four different temperatures of 300, 400, 500 and 600°C to produce the oil. At the first part of the study, the thermal degradation study was carried out with Thermogravimetric Analyser (TGA) from room temperature to 1000°C with heating rate of 10°C/min. The result from the TGA also is used to determine the content of moisture, volatile matter, fixed carbon and ash through proximate analysis and the appropriate range of temperature was determined. The pyrolysis process of the PET plastic in fixed bed reactor was done at the same condition in order to produce the solid, liquid and gas products. The highest yield of oil was produced at temperature of 400°C. The pyrolysis product was characterized by using FT-IR and GC-MS characterization techniques. Experimental results showed that pyrolysis could be an important method for the determination of the operating conditions and also an environmentally-friendly way for the transformation of the plastic wastes into valuable chemicals which later can be used as alternative fuel.**

Keywords— Fast Pyrolysis, Fixed Bed Reactor, Municipal Plastic Waste, PET Plastics, Waste-to-Energy,

I. INTRODUCTION

Plastic is widely used in many sectors including construction, automotive, packaging, electronic and healthcare. The demand for plastics keeps on increasing from day to day due to the growth in world population. Besides, the continuous demand of the plastics led to the increasing amount of municipal plastic wastes (MPW) in landfill and the uses of petroleum as the raw material for plastic production had caused the depletion of the fossil fuel. In the plastics production, different types of plastic such as, low density polyethylene (LDPE), polypropylene (PP), polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene-phthalate (PET), are developed in order to meet the needs of different industries. Usually, the highest amounts of available plastic types among MPW are PE and PS [1].

With the amount of plastics used and left to degrade in landfill, many efforts are being looked out to reuse the plastics waste. One of the plastic wastes that are currently being on research is Polyethylene-Phthalate (PET) plastic. PET plastic is widely used in plastic packaging of the food industry such as mineral water bottles, soft drink bottles and fruit juice container. Plastics can take up to billion years to degrade and the breakage of the bonds of many substances in the plastics occurs gradually. In order to reduce this massive breakout of plastic disposal, methods of reducing the production of waste are introduced. Methods such as recycling and reusing the plastic are not significant enough to be chosen as the best alternative. The rate of recycling for certain countries is still at the lowest. Recycling is proven to be difficult when the pre-treatment process needs a specific separation process. Only transparent plastics are usually desired by the manufacturers since they can be dyed easily to be transformed into new product [2].

Plastics are known to take up to billions of years to degrade naturally; thus the amount keeps on increasing year by year. The continuous disposal of plastics in landfill will then cause other environmental issues. Recycling always becomes an alternative when handling the plastic disposal but the world is in need for more reliable and sustainable method to overcome the problem. Some of the new resources had been discovered lately and it included the development of solar energy, wind power, geothermal and waste-to-energy (WTE) energy. The process of using waste to produce energy is one of the intelligent ways to meet the increased energy demand. An alternative should be used or invented in order to reduce the amount of plastic waste and to preserve the fossil fuel production. The conversion of the plastics to energy is possible since plastics are derived from petrochemical and pyrolysis can be one of the routes that helped the conversion. Therefore, this study aims to study the pyrolysis of Municipal Plastic Waste (MPW) by using Fixed Bed Reactor to produce liquid fuel product and characterization of the produced liquid fuel from the PET plastic bottles.

II. METHODOLOGY

A. Materials

1) Feedstock Preparation

The raw material which is PET plastic bottle is collected and cleaned using tap water before being further processed. Then, the water is completely wiped using a clean cloth. The bottles cut into small size for at least approximately 8 mm by using scissors. The pieces of PET plastics were divided into two parts, which are for raw material analysis and for pyrolysis process. For the analysis, a small amount of plastics are used to produce flaked PET plastic. About 200 grams of plastics were grinded in the polymer grinder to produce the flaked plastics, which later was sent for Thermal Gravimetric Analysis (TGA). Another 200 grams of plastic are fed to the reactor for every temperature tested. The plastics were ensured to be small and suitable for the process. The small pieces should be cut into equal size as they have to keep the size as constant variable.

2) Raw Material Analysis

Ultimate Analysis is conducted to determine the elemental composition of the raw material. The test is done by using CHNS-O analyzer (Model: Thermo Finnigan/ Flashea 1112). Each of the elements is tested with different condition. Those of C, N, and H were determined first, and the mass fraction of O was calculated by subtracting the ash contents of C, N, and H from the total mass of the sample. Proximate analysis of the raw material is tested by using Mettler Toledo, SDTA 851E, Thermogravimetric Analyser (TGA) where the moisture and ash content of the plastic are determined based on the standards; D3173-85 and D3174-82 ASTM standards, respectively [3]. 20mg of sample are used in determining the content of moisture, volatile matter, fixed carbon and ash. TGA is also used to study the thermal degradation of the PET plastics sample and any types of plastic. The analysis was carried out by using 10 micron grams of grinded PET plastic powder. Nitrogen gas was passed through at a rate of 50 ml/min for the room temperature to 1100^{o}C at the rate of 10^{o}C/min. The thermal degradation of the PET plastic bottles were then analysed by the graph provided from the analyser.

B. Pyrolysis Process

Pyrolysis of the PET plastic bottles was carried out in a pilot scale of packed bed reactor. It consists of pyrolysis reactor, thermocouple, nitrogen gas supply, condenser unit and a liquid product collection unit. The flaked plastics were fed into reactor and purging was done using nitrogen to create a reductive atmosphere for pyrolysis. The reactor was heated up to desired temperature with a fixed heating rate and this temperature was maintained till the process ended in 60 minutes. The volatiles formed passed through condenser where oil condensed and collected in a flask. The process flow of the pyrolysis process is shown in Figure 1 below.

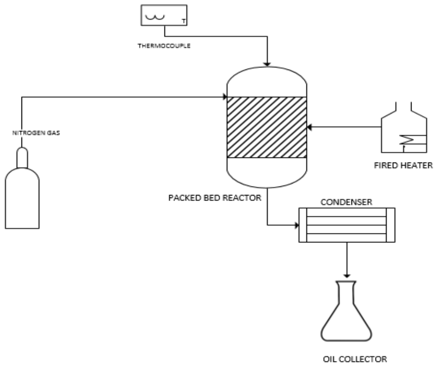


Figure 1 Process Flow Diagram of the Pyrolysis

The gas produced in the reactor is released at various intervals to avoid over-pressurized of the reactor. The char is also formed throughout the process, which settled down at the base of the reactor. The char was removed and weighed after the experiment ended to determine the percentage of product yield during the pyrolysis.

C. Product Analysis

For this research, the desired product was the liquid product of bio-diesel. The char are collected together with the oil but the gas will be released to the surrounding without being tested. FTIR is a technique used to obtain the chemical functional groups of the liquid bio-diesel product. The model used in the experiment is Perkin Elmer, Spectrum One. FTIR spectrum was collected in the range of 4000–440 cm^{-1} at a resolution of 4 cm^{-1}. Each peak from the FTIR result is studied thoroughly to determine the compounds existing in the oil produced. The liquid product, bio-diesel is further analysed by Gas Chromatography Coupled with Mass Spectroscopy (GCMS). The carrier gas is Helium gas and the initial temperature was set at 80°C for 5 minutes followed by a heating rate of 8°C/min to 305°C. Then, the temperature was held for 50 minutes.

III. RESULTS AND DISCUSSION

A. The Content of PET Plastics

The physical and chemical content of PET plastic bottle is tested in order to indicate and to determine the probability of yield from the pyrolysis process.

1) Proximate and Ultimate Analysis

The purpose of proximate analysis is to determine moisture, volatile, fixed carbon and ash content of materials. It is widely used in solid fuel characterization to show the ratio of combustible and incombustible component, and also to predict the combustion properties of solid fuel for instance its heating value. The TGA plot in Figure 1 shows the divided stages of the degradation. The proximate analysis is done by using the plot and is tabulated in Table 1.

Table 1
Proximate and Ultimate Analysis of PET

	Composition (wt%)
Proximate Analysis	
Moisture	0.15
Volatile Matter	81.06
Fixed Carbon	6.65
Ash	12.28
Ultimate Analysis	
C	75.21
H	3.90
N	4.89
O	16.01
Calorific Value(MJ/kg)	28.2

As shown in Figure 1, by following the ASTM, the moisture content is determined at the first stage of the plot. Drying takes place at temp 32.87°C to 180.84°C. The second stage is the volatilization of solid in nitrogen atmosphere from 157.51 to 937.47 °C. All of volatile matters were degraded in this stage. The third region is the combustion in oxygen environment at 940.27°C to oxidize all fixed carbon content leaving the ash at the end of the process. The fixed carbon content is determined by subtracting 100% content to the summation of percentage of moisture content, volatile matter and ash. Based on Table 1, the volatile matter of the PET plastic is relatively low compared to other studies on several other types of plastic. The lower amount of volatile matter leads to low liquid yield of pyrolysis process [4].

The ultimate analysis of the raw materials was obtained from Dayana and Shahruddin [5] and the results were also given in Table 1. The maximum C content was determined for the PET with the percentage of 75.21 %. After the elemental compositions were obtained calorific values for both plastic materials were calculated from the Dulong* equation as given.

$$HCV = 4.18 \times (78.4 \times C + 241.3 \times H + 22.1 \times S) \qquad (1)$$

The calorific value of PET was determined to be at 28.2 MJ/kg. Based on [6], the calorific value of the gasoline and diesel are at 42.5 MJ/kJ and 43.0 MJ/kg, respectively. To indicate a good commercial fuel grade, the calorific value of the PET plastic fuel should be close to the value of those commercial products. According to Anuar *et al* [7], the presence of benzoic acid, which contains aromatic ring, explained the low calorific value of PET.

2) *Thermal Behavior of PET Plastic*

Thermo gravimetric analysis (TGA) is one of the methods to determine the thermal decomposition or degradation of the raw materials. Figure 1 shows mass loss (TG) and derivative mass loss (DTG) curves with temperatures of the studied PET samples for the pyrolysis process. The thermo grams of the PET sample showed that overall degradation undergoes the first mass loss at the temperature between 32.87°C and 150.64°C.

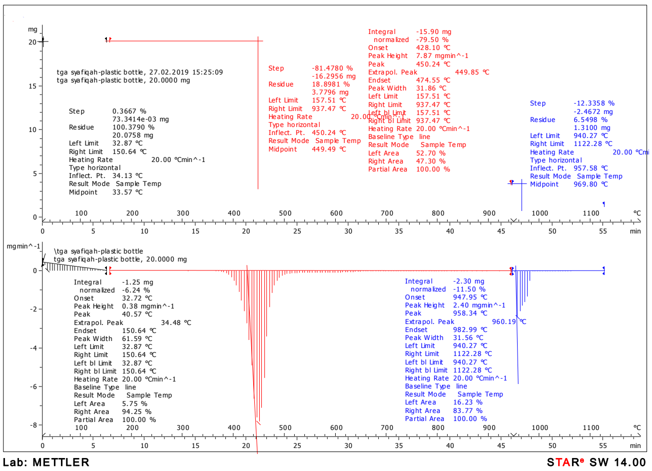


Figure 2 TG and DTG Plot of PET Sample

The most important degradation occurred at temperature 450.24°C and it can be clearly seen from the DTG curves of PET that it lost almost 79.50% of its initial weight. As a general, the plastic waste showed stable characteristics against increasing temperatures at the beginning of the process. However, with the increasing temperatures, the structural breakdown started and maximum weight losses occurred for both plastics. The decomposition temperature ranges were determined between 450-520 °C for PET.

After observing the TGA result for PET plastic, 450°C determined as a final high yield temperature for the fixed-bed pyrolysis with the help of the thermal behaviors of the plastics itself. As been mentioned previously, structural breakdown of the plastics were originated in the temperature range of 450-520 °C for PET and it lost most of their initial weight until the final temperature of 500 °C.

To compare the result with previous research, according to Putun and Cepeliogullar [4], they observed the main PET degradation started at 400°C with a very small weight change occurred when the temperature was in the range of 200–400°C. The maximum weight loss of the substance happened at temperature of 427.7°C. It was suggested that the thermal degradation of the plastic happened at temperature range of 350–520°C.

B. *Product Yield*

Pyrolysis produced three types of main products which are gas, liquid oil and char [3], [8]. The PET raw plastic used in the pyrolysis is approximately 200g for each temperature. The amount of product produced is weighed accordingly after the experiment was conducted. The composition for each product is tabulated in Table 2.

Table 2
The Composition of Pyrolysis Product

Temperature, °C	Product Composition (%)		
	Char	Oil	Gas
300	58.49	0.00	41.51
400	26.19	46.44	27.36
500	17.90	32.86	49.24
600	16.78	21.16	62.06

From Table 2, it is shown that the amount of product yield from each temperature is difference. This is because the process of pyrolysis is dependent on the temperature [9], [10]. It is observed that at the temperature of 300°C, the product only consisted of char and gas products. There is no oil produced at that temperature. This is maybe due to the compatibility of the temperature to break the bonds of the PET plastics. At temperature 300°C, the temperature is too low to start the pyrolysis of the plastic. The range of the pyrolysis of the plastic usually at the temperature of 400 to 700°C [11]–[13].

C. Analysis of the Oil Produced from Pyrolysis

1) FTIR Analysis

The oil produced from the pyrolysis process is a viscous liquid with a very dark brownish color. The smell of the oil is quite obnoxious at which, the use of mask is recommended. FTIR spectrum tested was done to the oil in order to determine the characteristics of the oil. The test was done to all the oil produced at different temperature of 400, 500 and 600°C.

Based on IR Spectrum Result in Figure 3, the characteristics and the wavelengths of the functional groups are shown through the stretching in the graphs. At temperature of 400°C, the intensity of the C-H wagging, C-H bending, C=C stretching, C-H stretching, and asymmetrical C-H bonds are the most extensive since the nature of the PET itself is from the hydrocarbon family. The =C-H alkene bonds appears at the range of 878.27cm^{-1} to 610.32 cm^{-1} which indicates the polymerization process of the PET. The polymerization of the raw material of PET, polyethylene, used ethylene as monomer for the production [14]; thus, the trace of alkene is detected in the pyrolysis oil of PET plastic bottles. Besides, the second high intensity of the result came from the peaks at 1581.35 cm^{-1} to 1420.54 cm^{-1}. The range indicated the presence of C=C bond stretching of aromatic compound. The aromatic compound at the range is the benzene ring compound that can be found widely in any PET products [15], [16]. This presence of the ring coupled with short aliphatic chain makes the polymer a stiff molecule as compared to other aliphatic polymers. At peak of 1026.21 cm^{-1}, the presence of amine with medium-weak intensity indicated the degradation of the polymer itself [17]. The presence of ether bond is also determined from the FTIR analysis at the intensity of 1127.4 cm^{-1}. The ether bond is related to the petroleum-based raw material of plastic substance which contained the aliphatic chain [17]. The oil also contains the O-H bond which indicated the presence of acidic component. Based on study by Cepeliogullar and Putun [4], it indicated that from their GCMS result, almost half of the PET oil composition contained benzoic acid which caused the acidic characteristic in the pyrolysis oil. The production of the oil continued for temperature 500°C and 600°C. The patent for the IR Spectra for both temperatures is almost the same with the same important

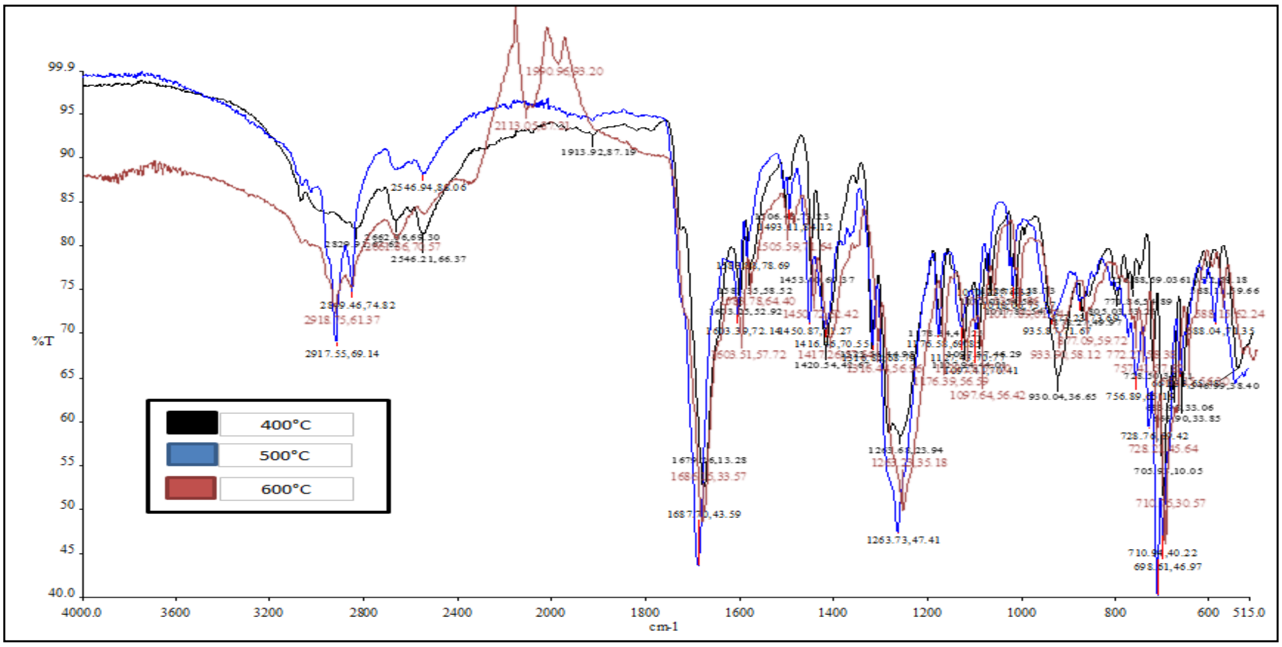


Figure 3: IR Spectrum of Oil at Different Temperature

peaks are observed and the common peaks for all the FTIR analyses are tabulated in Table 3. The absorption bands has been attributed to O-H bond stretching, C-H bond stretching (methylene groups), C=H bond stretching (carbonyl group), C=C bond stretching (Benzene) and C-O bond stretching (ether group formation). The similar stretching in the result shows the similar content and characteristics of the oil. The oil produced is of the same characteristic but the temperature used affected the yield of the oil.

Table 3
Lists of Bond in IR Spectrum at different Temperature

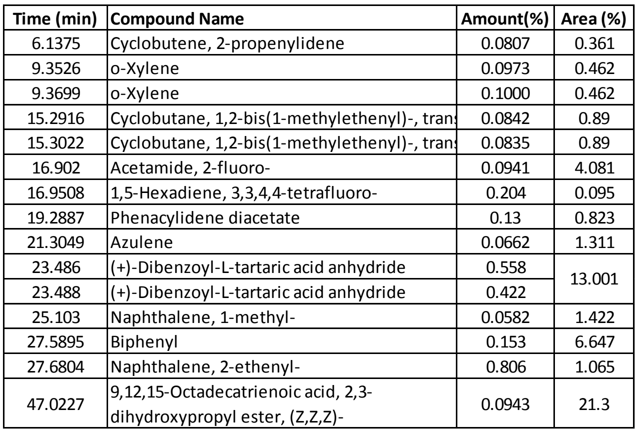
Bonding	***Intensity***
C-H (Alkane)	Strong
O-H (Acid)	Strong, Very Broad
C=C (Alkene)	Weak
C=C (Aromatic)	Weak
C-N (Amine)	Strong
C-O (Ether)	Strong
=C-H(Alkene)	Strong
C-Br (Alkyl Halide)	Strong

The result of the FTIR analysis from this study is supported with the result from the previous study by Cinelli et al [18]. The raw PET used in the previous research indicated the identical peaks as the product produced from the research. The C=O stretching and N–H bending, combined with C–N stretching are presented in the spectrum. The spectrum of PET also shows the typical C=O stretching and the C–O and C-O-C stretching bands.

2) *GCMS Analysis*

The gas chromatogram analysis was done by diluting the pyrolysis oil into benzene as solvent. The pyrolysis oil is viscous due to presence of wax or paraffin; thus, the dilution of the product is crucial in order to determine the composition of the oil. The result from the gas chromatogram is shown in Figure 4. The first peak in the analysis was observed after 6 minutes, which indicates the presence of cyclobutene, 2-propenylidene with the small amount of 0.0807 %. The high peak at around 17 minutes indicated the peak for Acetamide, 2-fluoro-. The presence of the material proved that the amine structure in the pyrolysis oil produced [19]. The second higher peak came after 21 minutes with the presence of azulene. Azulene is produced from the naphthalene isomer that contains a complex combination of hydrocarbons consists primarily of aromatic and phenolic compounds [20].

Table 4
List of Compounds in GCMS



Time (min)	Compound Name	Amount(%)	Area (%)
6.1375	Cyclobutene, 2-propenylidene	0.0807	0.361
9.3526	o-Xylene	0.0973	0.462
9.3699	o-Xylene	0.1000	0.462
15.2916	Cyclobutane, 1,2-bis(1-methylethenyl)-, tran	0.0842	0.89
15.3022	Cyclobutane, 1,2-bis(1-methylethenyl)-, tran	0.0835	0.89
16.902	Acetamide, 2-fluoro-	0.0941	4.081
16.9508	1,5-Hexadiene, 3,3,4,4-tetrafluoro-	0.204	0.095
19.2887	Phenacylidene diacetate	0.13	0.823
21.3049	Azulene	0.0662	1.311
23.486	(+)-Dibenzoyl-L-tartaric acid anhydride	0.558	13.001
23.488	(+)-Dibenzoyl-L-tartaric acid anhydride	0.422	
25.103	Naphthalene, 1-methyl-	0.0582	1.422
27.5895	Biphenyl	0.153	6.647
27.6804	Naphthalene, 2-ethenyl-	0.806	1.065
47.0227	9,12,15-Octadecatrienoic acid, 2,3-dihydroxypropyl ester, (Z,Z,Z)-	0.0943	21.3

After 23 minutes, the presence of anhydride component was detected as tabulated in Table 4. It may be from the amount of unwanted traces of catalyst from the previous experiment since the anhydride is known as a form of yellow solid particles. Besides, at retention time of 28 minutes, biphenyl compound is detected among the peaks which also determined in the previous study from Cepeliogullar and Putun [4]. From the gas chromatogram, the composition of the oil can be observed but it must be acknowledged that the values that are given do not represent the real composition of the compounds. They presented the differentiation of the composition of the oils [4]. Plastic materials were generally decomposed as different types of chemicals.

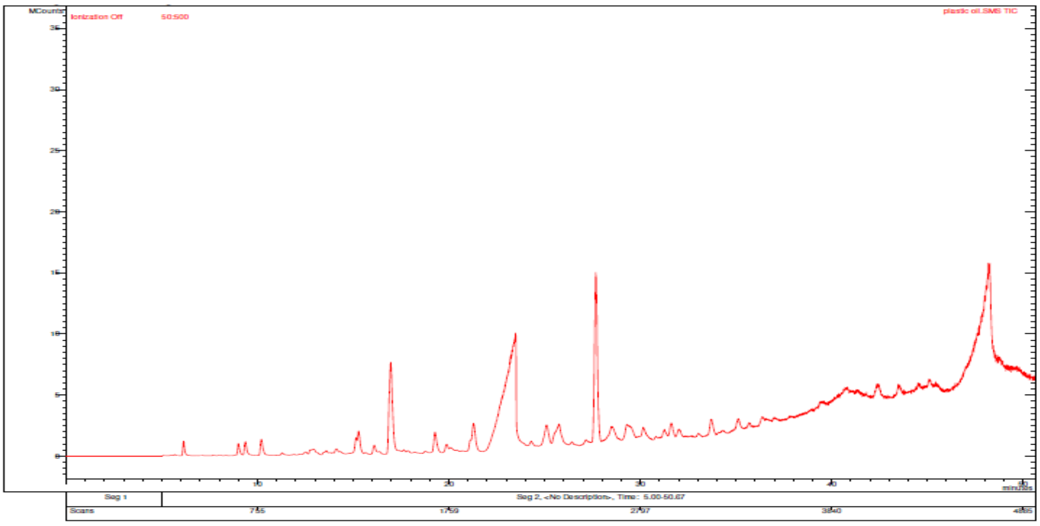


Figure 4: GCMS Result for Oil

IV. CONCLUSION

In this study, the wastes plastic material was selected as raw material in order to evaluate them in environmentally-friendly ways. Thermal behaviors and the proximate analysis of the plastic materials were determined by using TGA. Significant temperatures for the experiment were determined along with the amount of proximate quantitative materials. The raw materials were pyrolysed in order to obtain the oil product. The highest yield of the oil was determined at 400°C. At the final step of the study, pyrolysis products were characterized. Experimental results showed that pyrolysis is an important process for the understanding of the knowledge about all thermal activities of the PET plastic at high temperature regions. From the characterization of the oil produced from the plastic, the ability of the oil to be used as alternative oil can be observed and determined. Also, it can be an alternative technique for the recycling of plastic wastes in the suitable operating conditions.

ACKNOWLEDGMENT

Thank you to my supervisor, Dr Rusmi Alias for his guidance and to Universiti Teknologi Mara for the facilities provided. Besides, thank you to all those who actively involved in helping my team and I in finishing our research study.

REFERENCES

[1] J. A. Onwudili, N. Insura, and P. T. Williams, “Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time,” *J. Anal. Appl. Pyrolysis*, vol. 86, no. 2, pp. 293–303, 2009.

[2] E. Masanet, R. Auer, and D. Tsuda, “An Assessment and Prioritization of " Design for Recycling " Guidelines for Plastic Components.”

[3] A. López, I. de Marco, B. M. Caballero, M. F. Laresgoiti, and A. Adrados, “Pyrolysis of municipal plastic wastes: Influence of raw material composition,” *Waste Manag.*, vol. 30, no. 4, pp. 620–627, 2010.

[4] O. Cepeliogullar and A. E. Putun, *Utilization of two different types of plastic wastes from daily and industrial life*. 2013.

[5] S. Dayana, A. Sharuddin, F. Abnisa, W. Mohd, and A. Wan, “Energy recovery from pyrolysis of plastic waste : Study on non-recycled plastics (NRP) data as the real measure of plastic waste,” vol. 148, pp. 925–934, 2017.

[6] I. Ahmad *et al.*, “Pyrolysis Study of Polypropylene and Polyethylene Into Premium Oil Products,” *Int. J. Green Energy*, vol. 12, no. 7, pp. 663–671, Jul. 2015.

[7] S. Dayana, A. Sharuddin, F. Abnisa, W. Mohd, and A. Wan, “A review on pyrolysis of plastic wastes,” *Energy Convers. Manag.*, vol. 115, pp. 308–326, 2016.

[8] N. Dimitrov, L. Krato, and A. Pti, “Analysis of recycled PET bottles products by pyrolysis-gas chromatography,” vol. 98, pp. 972–979, 2013.

[9] P. T. Williams, S. Besler, and D. T. Taylor, “The pyrolysis of scrap automotive tyres: The influence of temperature and heating rate on product composition,” *Fuel*, vol. 69, no. 12, pp. 1474–1482, 1990.

[10] J. Růžičková *et al.*, “The influence of pyrolysis temperature on the chemical composition and the energy properties of char from tetrapak,” in *2017 IEEE International Conference on Environment and Electrical Engineering and 2017 IEEE Industrial and Commercial Power Systems Europe (EEEIC / I&CPS Europe)*, 2017, pp. 1–4.

[11] L. Diaz, A. McMahon, and A. Phan, *Benzoic acid recovery via waste poly(ethylene terephthalate) (PET) catalytic pyrolysis using sulphated zirconia catalyst*. 2018.

[12] T. Yoshioka, G. Grause, C. Eger, W. Kaminsky, and A. Okuwaki, *Pyrolysis of poly(ethylene terephthalate) in a fluidised bed plant*, vol. 86. 2004.

[13] S. M. Fakhrhoseini and M. Dastanian, “Predicting Pyrolysis Products of PE , PP , and PET Using NRTL Activity Coefficient Model,” vol. 2013, pp. 7–9, 2013.

[14] Y. Kissin and A. Goldman, *Chemistry and Mechanism of Alkene Polymerization Reactions with Metallocene Catalysts*, vol. 210. 2009.

[15] S. Vijayakumar and P. R. Rajakumar, “Infrared spectral analysis of waste pet samples,” vol. 4, pp. 58–65, 2012.

[16] S. Umamaheswari and M. Murali, “FTIR spectroscopic study of fungal degradation of poly (ethylene terephthalate) and polystyrene foam,” no. March 2014, 2013.

[17] S. Venkatachalam, S. G. Nayak, J. V Labde, P. R. Gharal, K. Rao, and A. K. Kelkar, “Degradation and Recyclability of Poly (Ethylene Terephthalate),” 2012.

[18] P. Cinelli, M. Schmid, E. Bugnicourt, M. B. Coltelli, and A. Lazzeri, “Recyclability of PET / WPI / PE Multilayer Films by Removal of Whey Protein Isolate-Based Coatings with Enzymatic Detergents.”

[19] Y. Ma, F. Feng, and B. Chen, “[Simultaneous determination of fluoroacetamide and tetramethylendisulfotetramin with gas chromatography-mass spectrography].,” *Wei Sheng Yan Jiu*, vol. 29, no. 6, p. 369,378, Nov. 2000.

[20] H. Xin and X. Gao, “Application of Azulene in Constructing Organic Optoelectronic Materials : New Tricks for an Old Dog,” pp. 945–956, 2017.