CHARACTERISTICS OF PYROLYSIS OIL BATCH POLYETHYLENE AND POLYSTHYRENE PLASTIC WASTE AT VARIOUS TEMPERATURES

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Abstract

Efforts are being carried out in order to utilize polyethylene (PE) and polystyrene (PS) plastic waste by converting them into fuel or oil. One technology that can be used is pyrolysis. This study aims to (1) determine the quantity and the characteristics of oil from the results of pyrolysis polyethylene (PE) and polystyrene (PS) plastic waste at various temperatures which include characteristics of physics (specific gravity, heating value, flash point, pour point, and kinematic viscosity) and chemical characteristics (composition compounds in oil), (2) determine the optimal conditions of process pyrolysis related to the quality and quantity of oil by pyrolysis, and (3) determine the potential treatment of PE and PS plastic waste by pyrolysis method.

The materials used in this study were the type of polyethylene (plastic bags) and polystyrene/styrofoam (for fruits or vegetables) plastic waste. The selected temperature variations are T = 400°C, 450°C, and 500°C. Pyrolysis oil was weighed and measured its volume to obtain v/w_o and yield.

The results showed that the quantity of pyrolysis oil from polyethylene (PE) plastic waste at temperatures of 400, 450, and 500°C based on v/w_o (ml/g) respectively were 0.3429 ml/g; 0.5129 ml/g; and 0.199 ml/g while the results of polystyrene (PS) plastic waste at temperatures of 400, 450, and 500°C respectively were 0.89 ml/g; 0.905 ml/g; and 0.915 ml/g. The results of pyrolysis oil based on yield of polyethylene (PE) plastic waste at temperatures of 400, 450, and 500°C respectively were 33.33 wt%; 38.61 wt%; and 15.55 wt% while polystyrene (PS) plastic waste at temperatures of 400, 450, and 500°C respectively were 80.94 wt%; 79.79 wt%; and 80.14 wt%. While the characteristics shown by the results of pyrolysis oil from PE plastic with a temperature of 400°C were closer to kerosene while at temperatures of 450 and 500°C were closer to the characteristics of diesel fuel. As for pyrolysis oil results of PS plastic with temperatures of 400, 450, and 500°C were closer to the characteristics of gasoline. Optimal conditions of pyrolysis oil related to the quantity of pyrolysis of PE plastic at a temperature of 450°C was obtained when the highest of v/w_o and yield respectively were 0.5129 ml/g and 38.16 wt%, while for the pyrolysis of PS did not have any optimal conditions. For, oil produced was relatively constant despite the increasing temperatures. Based on technical analysis, handling PE and PS plastic waste using pyrolysis methods provides benefits to society making it feasible to do.

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1. Introduction

Waste is the result of human activity that cannot be used any longer. However, that view has changed over the development of this era. Nowadays, waste is seen as an untapped resource. It is called a resource because it has a potential to be utilized. Most common waste of which is plastic waste, be it polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and so on. Plastic waste is an environmental pollutant that is difficult to decompose and it takes a very long time to biodegrade, so it has the potential to pollute the environment.

An effort that can be carried out in order to take advantage of plastic waste is to convert plastic waste into fuel or oil. One of the technologies that can be used and meet the zero waste concept is pyrolysis, where the products of pyrolysis itself generally consists of solid, liquid and gas, all of which can be used according to the raw materials used, can be either natural materials of plant material (biomass) or form of the polymer. The raw material is one of the process variables that affects the final product of pyrolysis. In addition to raw materials, final products of pyrolysis are also influenced by process variables such as temperature, heating rate, moisture content, particle size, residence time, catalyst, and so forth.

In this study, the selected process variable is the temperature of the PE and PS waste plastic. This selection is based on the purpose of this study which is to obtain oil products derived from waste plastics as much as possible. To obtain these products, selected raw materials chosen are plastic bags and styrofoam. Those are plastic waste that cannot be broken down or decomposed in a very long time, no market demand, and are also materials from petroleum. Therefore, when they are heated at a certain temperature, they can produce petroleum products. They can be acquired the most at certain temperatures at the temperature range of 400°C to 500°C.

2. Methodology

2.1 Scheme of Research Tools

Scheme of research tool is shown in Figure 1 as follows:

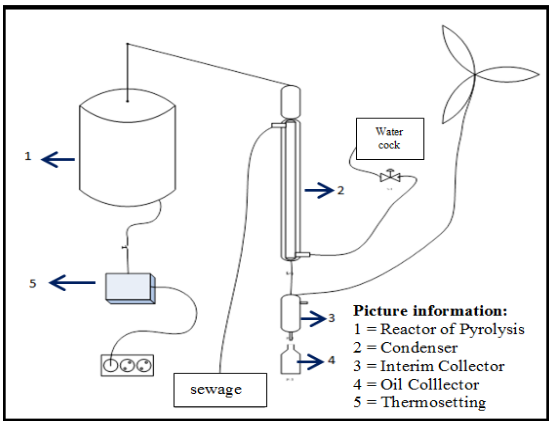

Figure 1. Scheme of Research Tools

2.2 Material of Research

The materials used in this study is polyethylene plastic waste (plastic bags) and polystyrene / styrofoam (boxes of fruit/vegetables).

2.3 Procedures of Research

Procedures of Pyrolysis Process

The raw materials of polyethylene plastic waste were shredded and weighed about 350 grams. The enumeration can be resized to fit into the reactor. Materials were put into the reactor and the reactor lid was locked tightly so that there was not any direct contact with the air. The condenser was filled with water, after that the electricity was turned on, and the temperature was set at T = 400ºC, 450ºC and 500ºC. The steps were repeated for raw materials as much as 50 grams of polystyrene waste. Then, the pyrolysis oil was taken after cooling until it reached room temperature.

Procedure Analysis of Pyrolysis Process Results

Pyrolysis oil volume and weight were measured. The results of pyrolysis oil volume (v) compared with the initial weight of material (w_0) are as the equation (1) below:

$$\frac{volume}{initial\ weight} = \frac{v}{w_0}\ (\frac{ml}{g}) \qquad (1)$$

Futhermore, the result of weight of pyrolysis oil (w_t) compared to the initial weight of the materials (w_0) to obtain the yield are as thw equation (2) below:

$$yield = \frac{w_t}{w_0} \times 100\% \qquad (2)$$

Pyrolysis oil was analyzed in physics including the specific gravity, heating value, flash point, pour point, and kinematic viscosity. Moreover, chemical identification was also carried out to determine the composition of compounds on the oil by GC-MS.

3. Results and Discussion

In this study, the pyrolysis reactor used was still in laboratory scale with 36 cm height, the 9.5 cm of base diameter, height and diameter of heater respectively was 40 cm and 30 cm. At these dimensions, charging 350 grams raw materials of PE plastic was carried out to obtain the average density of PE plastic inside the reactor tube of 0.19 g/cm^3 (0.19 g/ml), while for PS plastic, it was given mass of 50 grams so the average density in the tube reactor was 0.02 g/cm 3 (0.02 g/ml).

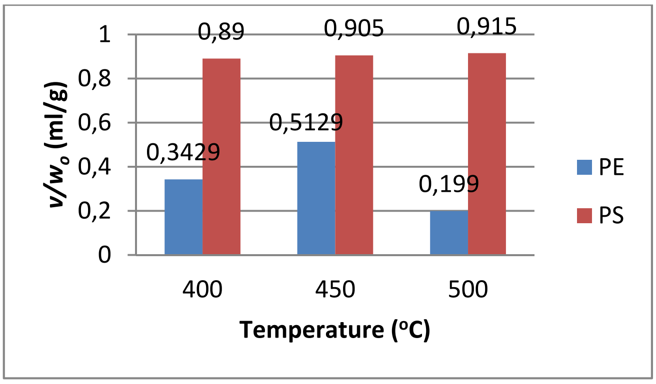

Figure 2. Comparison of average v/w_0 generated on pyrolysis of PE and PS plastic

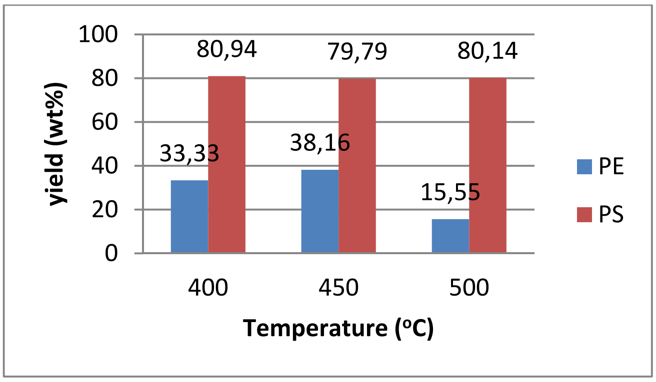

Figure 3. Comparison of average yield on pyrolysis of PE and PS plastic

Figure 2 shows the increase in temperature which resulted in the increase in the number of v/w_o (ml/g) up to a certain limit and then it decreased so that there was maximum conditions for v/w_o (ml/g) PE plastic, whereas PS plastic tended to be at a constant state. The v/wo (ml/g) of PS plastic pyrolysis oil was far more than the v/wo (ml/g) in PE because PS plastic is the result of the polymerization of styrene monomers that has a liquid phase while PE plastic is produced from ethylene monomers that has a gaseous phase. Therefore, when polystyrene is polymerized, it will produce more liquid product.

Figure 3 shows the yield on pyrolysis of PE and PS plastic, which for PE plastic increased and then decreased with increasing temperatures indicating that the resulting PE plastic yield is a function of temperature f(T) while the PS plastic, the resulting yield was relatively constant although the temperature was increased (by an additional yield, but the amount is very small/not significant and can be considered constant). At PS plastic, v/wo (ml/g) of oil produced and the yield were relatively constant but there were differences in behavior. The difference in the behavior showed a decrease in the mass of oil produced, in which the temperature of 500ºC, oil mass became lighter when it had more volume. Similarly, the oil mass from pyrolysis results of PS plastic at the temperature of 500ºC where the volume was greater than the temperature of 400ºC was smaller than the pyrolysis oil of PS plastic at the temperature of 400ºC. This happened with regard to the density of the plastic oil from pyrolysis results of PS plastic which was at the temperature of 450°C and 500°C. The density value is smaller than the density of the plastic oil from pyrolysis results of PS plastic at the temperature of 400°C.

The amount of energy required and the energy produced in the pyrolysis of 350 gram PE plastic with at the temperature of 450°C and pyrolysis of 50 gram PS plastic at the temperature of 500°C are consecutively shown in Figure 4 and Figure 5.

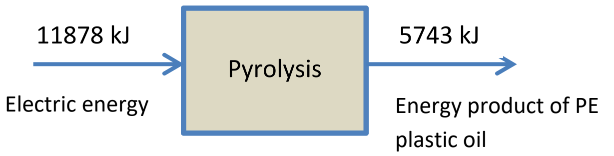

Figure 4. Energy balance of PE plastic pyrolysis at temperature of 450°C

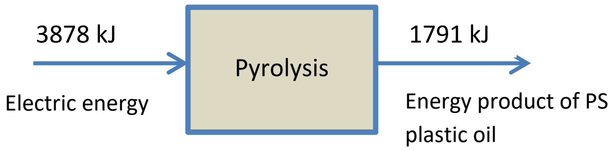

Figure 5. Energy balance of PS plastic pyrolysis at a temperature of 500°C

Based on the amount of energy required and produced, it is seen that the energy produced from pyrolysis of PE plastic was 0.48 times less than the energy required, while the energy produced from pyrolysis of PE plastic was 0.46 times less than the energy required.

The comparison of the results of pyrolysis PE and PS plastic oil in this study with the other researchers is shown in Table 1.

Table 1. Comparison of the results of pyrolysis PE and PS plastic oil with the other studies

	Parameter							
	Density (15°C)	SG at 60/60 °F	API Gravity at 60 °F	Kinematic viscosity	Gross Heating Value	Flash Point	Pour Point	Water Cont.
Unit	gram/ml	-	-	mm²/s	BTU/lb	°C	°C	% vol
Black plastic oil with catalyst zeolite(a,b)	0,767	0,7578	52,8	1,376 (30°C)	20091	10°C	Unverified	Nil
Black plastic oil with catalyst bentonit(b)	0,8394	0,8402	36,8	45,79 (30°C)	19651	30,5° C	Unverified	Nil
Black plastic oil without catalyst(a,b)	0,7789	0,7797	50	1,703 (30°C)	20022	10°C	Unverified	Nil
PS oil(c)	0,931	0,9315	20,4	1,005 (40°C)	19025	20,5	< -24	Unmeasuring
PS+PE oil(c)	0,89 until 0,92	0,8911 until 0,9211	27,3 until 22,1	0,981 until 1,008 (40°C)	19098 until 19300	< 10	< -24	Unmeasuring
PS+PP oil(d)	0,88 until 0,92	0,8812 until 0,9174	29,1 until 22,7	0,912 until 0,995 (40°C)	19124 until 19369	< 10	< -24	Unmeasuring
PE oil 400°C	0,767	0,7687	52,6	4,706 (50°C)	20086	46,5	36	Unmeasuring
PE oil 450°C	0,788	0,7879	48,1	1,994 (40°C)	18540	30,5	27	Unmeasuring
PE oil 500°C	0,809	0,8087	43,5	1,261 (40°C)	18540	24,5	15	Unmeasuring
PS oil 400°C	0,925	0,9257	21,3	1,027 (40°C)	19079	34,5	< -33	Unmeasuring
PS oil 450°C	0,921	0,9217	22	0,942 (40°C)	19108	32,5	< -33	Unmeasuring
PS oil 500°C	0,905	0,9052	24,8	0,991 (40°C)	19222	28,5	-6	Unmeasuring

All the results of the study by Ramadhan, 2014, Laksono, 2014, Reynaldy, 2012 and Efendi, 2012, compared to this study indicate that the specific gravity value is in accordance with the theory, which is the specific gravity of oil is generally lower than the specific gravity of water, between 0.74 to 0.96 and the API Gravity value of pyrolysis oil was greater than the API Gravity of water which is 10, wherein the API Gravity of oil materials is also greater than 10. Heating value of this research and a study by Ramadan, 2014 and Laksono, 2014 show the results of pyrolysis oil plastic bag (PE) without catalyst have a similar heating value which is about 20,000 BTU/lb, but the heating value at 450 and 500°C is slightly different and still within the range of heating value of oil, which is usually ranging from 18,300 to 19,800 BTU/lb. The addition of catalysts gives different effects. The addition of zeolite catalyst increases the heating value of the oil, while the addition of bentonite catalyst lowers the heating value of oil. Researches by Reynaldy, 2012, and Efendi, 2012, compared to this study, both of which showed the heating value of PS oil about 19,000 BTU/lb. Furthermore, the value of the flash point in this study compared to other studies, where the results show different values, the results of pyrolysis oil produced has a higher flash point in this study, while in the other studies show lower flash point which means that oil which was investigated by Ramadhan, 2014, Laksono, 2014, Reynaldy, 2012 and Efendi, 2012, was highly flammable. The difference in the value of the flash point may probably occur because of differences in the type and composition of the raw materials used. The pour point values in this study and the other studies indicate that PS oil pour point values are very low, which means that the oil is still in form of liquid at the very low temperatures, so it can still be used even if it is stored at low temperatures because the oil does not freeze.

The analysis results of the oil from pyrolysis of PE and PS plastic in this study were then compared with some kerosene, diesel, gasoline, HFO and LFO as in Table 2.

Table 2. Comparison of the results of pyrolysis PE and PS plastic oil with kerosene, diesel, gasoline, HFO and LFO

	Parameter					
	SG at 60/60 °F	Kinematic viscocity (40°C)	Kinematic viscosity (50°C)	Gross Heating Value	Flash Point	Pour Point
Unit	-	mm²/s	mm²/s	BTU/lb	°C	°C
Kerosene[1,2,3,4,9,10]	Max. 0,835	1,2 (30°C) 2,71 (20°C)	--	18642,61	Min 38	-47 *)
Diesel [5,8,9]	0,82 until 0,87	1,3 until 4,1	--	18470,79	60 until 80	-35 until 15
Gasoline [2,6,7,9]	0,724	0,88	--	18900,34	-43	-3
HFO [4,7,9]	0,9782	--	177	17654,64	74	-10
LFO[3,9]	0,89	30 (30°C)	--	17998,28	79	
PE Oil 400°C	0,7687	--	4,706	20086	46,5	36
PE Oil 450°C	0,7879	1,994	--	18540	30,5	27
PE Oil 500°C	0,8087	1,261	--	18540	24,5	15
PS Oil 400°C	0,9257	1,027	--	19079	34,5	< -33
PS Oil 450°C	0,9217	0,942	--	19108	32,5	< -33
PS Oil 500°C	0,9052	0,991	--	19222	28,5	-6

The characteristics shown by the results of pyrolysis oil from PE plastic with a temperature of 400°C were closer to kerosene from the specific gravity and flashpoint value, whereas at the temperatures of 450 and 500°C, it was closer to the characteristics of diesel fuel from the kinematic viscosity and gross heating value. It was also similar for PE plastic pyrolysis oil. It was also seen approaching the characteristics of solar at the temperature of 500°C which was viewed from kinematic viscosity, gross heating value and pour point, while the results of PS plastic pyrolysis oil with temperatures of 400, 450 and 500°C was seen closer to the characteristics of the gasoline in terms of its kinematic viscosity, gross heating value, flash point and pour point.

In this study, the result of PE plastic pyrolysis oil tends to approach the characteristics of diesel which has long carbon atoms (C12 to C18) where the number of carbon atoms PE itself is C2, while the result of PS plastic pyrolysis oil tends to be close to the characteristics of gasoline that has shorter carbon atoms (C4 to C12) where the number of PS carbon atom itself is a C8. This happens because of the possible of PE pyrolysis process, cracking happening does not convert polyethylene into ethylene monomers but it remains polyethylene (it is possible because the temperature is not high enough), whereas for PS pyrolysis, cracking that occurs can already convert polystyrene into styrene monomers which have shorter carbon chains.

The results of research conducted by Ramadhan, 2014 and Laksono, 2014, in doing pyrolysis of black plastic bag at a temperature of 350°C produces oil which has similar characteristic to kerosene than diesel. Based on a research carried out by Pratama, 2013, in doing pyrolysis of plastic waste for alternative fuels, it was concluded that the compositions of plastic waste strongly influence the formation tendency of the distribution of the number of carbon atoms in hydrocarbon of pyrolysis oil. PE plastic type can direct the formation of the atomic fraction from medium (C12-C20) to long (> C20), the diesel fraction can be formed more than plastic pyrolysis oil derived from a single type of PE plastic as raw materials. The use of a mixture of waste plastics such as PP, PS, PET and others can reduce the tendency of the formation of compounds of long carbon atoms. On the other hand, it increases the tendency of formation compounds of short carbon atoms with carbon atoms that have lower number.

In the analysis of the chemical characteristics using GC-MS, it is shown that not all PE and PS plastic pyrolysis oil was tested, but only selected plastic pyrolysis oil with temperature of 500°C with the assumption that at that temperature, PE and PS plastic have been decomposed in a maximum point. Chromatogram of the results of PE and PS plastic oil sample pyrolysis is shown in Figure 6.

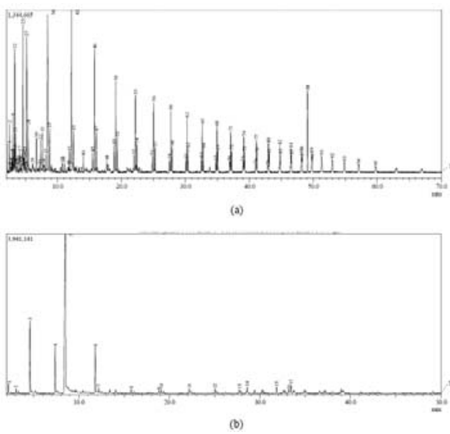

Figure 6. Chromatogram of the results of oil sample pyrolysis (a) PE, (b) PS

The test results using GC-MS showed that PE plastic pyrolysis oil with the most 1-Nonene compounds (7.34%) and 1-Decene (5.44%), whereas the PS plastic pyrolysis oil had the most compounds which were stirene (60.84 %), toluene (11.21%), alpha-methylstyrene (8.75%), ethylbenzene (8.41%) and others (10.79%) as in Table 3.

Table 3: GC-MS of results of PS plastic pyrolysis oil at a temperature of 500°C

No.	Name	% weight
1.	Stirene	60,84
2.	Toluena	11,21
3.	Alpha-metilstirena	8,75
4.	Etilbenzena	8,41
5.	Benzene, 3-butenil- (CAS) 3-Butenilbenzene	1,69
6.	Bibenzil	1,34
7.	1,3-Diphenilpropane	1,24
8.	Others	6,52

A research conducted by Reynaldy, 2012, for the pyrolysis of waste polystyrene, it obtained the same GC-MS analysis with this research which resulted in the highest compounds of styrene (56.9%) followed by toluene (12.09%). The number of stirene compounds in the pyrolysis oil results of this PS plastic caused distinctive aroma in the oil, given that styrene is an aromatic compound.

Based on the results of GC-MS analysis towards the PS plastic pyrolysis oil results, it contained styrene by 61%. Dominant content of styrene can be used as raw material for the chemical industry and the manufacture of plastic materials and synthetic rubber. In the chemical industry, raw material for styrene is a material such as polystyrene, ABS, styrene-butadine rubber (SBR), styrene-butadiene latex, styrene-isopropene-styrene (SIS), styrene-ethylene/ butyene-styrene, and so forth. These materials are used in industries including rubber, plastic, insulation, fiberglass, pipes, automotive parts and food containers. Styrene has the molecular formula of C_8H_8 or C_6H_5-C_2H_3. It needs an advanced process to separate styrene from other compounds in order to obtain pure styrene in the form of oily clear liquid (Reynaldy, 2012).

Besides containing styrene, PS plastic pyrolysis oil also contains toluene at 11.21%, in which toluene (C_7H_8) is colorless clear liquid that is not soluble in water with a smell like paint thinner and has like-benzene aroma. Solvent is liquid, solid, or gas that dissolves other solution, either in the form of solids, liquids and gases and produces a solution. Toluene can be used for the manufacture of benzoic acid, the material of making trinitro toluene (TNT) and as a solvent carbon compounds (Reynaldy, 2012).

The results of GC-MS analysis for PE plastic pyrolysis oil was composed of 95 peaks that showed 95 compounds contained in the oil products in which the amount (weight %) of each compound has a low profile and provides a product that does not spread like the PS plastic pyrolysis oil. In this study, it was limited to the final product oil, so that the composition of gas product was not investigated.

4. Conclusion

1. The quantity of pyrolysis oil from polyethylene (PE) plastic waste at the temperatures of 400, 450, and 500°C based on v/w_o (ml/g) respectively were 0,3429 ml/g; 0,5129 and 0,199 ml/g, while the results of polystyrene (PS) plastic waste at temperatures of 400, 450, and 500°C respectively were 0,89 ml/g; 0,905 ml/g and 0,915 ml/g. The result *yield* (wt%) of pyrolysis oil of polyethylene (PE) plastic waste at the temperatures of 400, 450, and 500°C respectively were 33,33 wt%; 38,61 wt% and 15,55 wt%, while polystyrene (PS) plastic waste at the temperatures of 400, 450, and 500°C respectively were 80,94 wt%; 79,79 wt% and 80,14 wt%.
2. The characteristics shown by the results of pyrolysis oil from PE plastic with a temperature of 400°C were closer to kerosene from the specific gravity and flashpoint value, whereas at the temperatures of 450 and 500°C, it was closer to the characteristics of diesel fuel from the kinematic viscosity and gross heating value. It was also similar for PE plastic pyrolysis oil. It was also seen approaching the characteristics of solar at the temperature of 500°C which was viewed from kinematic viscosity, gross heating value and pour point, while the results of PS plastic pyrolysis oil with temperatures of 400, 450 and 500°C was seen closer to the characteristics of the gasoline in terms of its kinematic viscosity, gross heating value, flash point and pour point.
3. Optimal conditions of pyrolysis process associated with quantity of oil of PE plastic pyrolysis at the temperature of 450°C was obtained when v/w_o and the highest yield were at 0.5129 ml/g and 38.16 wt%.
4. Based on technical analysis, handling PE and PS plastic waste using pyrolysis methods provides benefits to society making it feasible to do.

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