Energy Balance of non-catalytic Pyrolysis of Plastic Wastes to produce Liquid Fuel

Harwin Saptoadi[1*], Anjar Kresna Putra[1,] Wega Trisunaryanti[2], Zainal Alimuddin[3],
Mochamad Syamsiro[4], Kunio Yoshikawa[4]

[1] Dept. of Mechanical and Industrial Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia
[*] Email : harwins@ugm.ac.id
[2] Dept. of Chemistry, Universitas Gadjah Mada, Yogyakarta, Indonesia
[3] Dept. of Mechanical Engineering, Universiti Sains Malaysia, Penang, Malaysia
[4] Dept. of Environmental Science and Technology, Tokyo Inst. of Technology, Tokyo, Japan

Abstract: A simple pyrolysis of HDPE plastic wastes has been carried out in order to obtain alter-native liquid fuel. About 900 g of plastic was pyrolyzed at constant temperatures varied from 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, The gases were condensed in two consecutive liquid containers separated by a water-cooled condenser. The liquid yield rates were observed and concluded that higher temperature delivered higher rate, between 1.1 ml/min and 5.05 ml/min. Higher temperature produced more liquid in the first container but less in the second container. Several physical characteristics of the liquid were investigated, such as specific gravity. Distillation and GC-MS tests have been conducted to those oils. All products in the second container contained light fractions of hydrocarbons (between C5 and C15), thus almost similar to gasoline. Meanwhile those in the first container contained heavier fractions (between C15 and C24), except pyrolysis at 450 °C, therefore they were closer to diesel fuel. A simple calculation of energy balance was done, where the pyrolysis at 550 °C seemed to be the best, because the generated thermal energy from pyrolytic oil was already higher than the required electric energy for pyrolysis. However several improvements must always be made in order to save more energy and to bring the results into commercialization.

Keywords: Energy balance, Liquid fuels, Plastic wastes, Pyrolysis, Temperature variation

1. Introduction

Plastics made from HDPE (high-density-polyethylene) and LDPE (low-density-polyethylene) are very popular due to its low cost, good processability, high impact resistance, excellent chemical resistance and electrical insulating properties. Their most common use is as films for general packaging, mainly bags and food wrappings, and also as bottles for foodstuffs and household chemicals. PE represents the largest constituent of plastics waste and one of the most commonly recycled polymers [1]. Currently waste plastics disposal in landfill areas is not popular anymore. They must be reutilized as materials or fuels. For this purpose, pyrolysis appears to be very favorable because its products can be used for raw materials in chemical industries or for fuels. It is predictable because plastics are actually petroleum derived materials [2]. Pyrolysis is a thermal decomposition process by heating in inert atmosphere to yield hydrocarbons in solid, liquid and gaseous phase. It can be conducted at various temperature levels, reaction times, pressures, and in the presence or absence of catalysts. The apparent advantage is that it allows the treatment of mixed, contaminated, or hard to recycle plastic wastes [3]. The most significant process variable is temperature, because it influences both the polymer conversion and the product distribution, i.e. oils, gases, waxes, and solid residue. As temperature rises, the gas fraction will increase and conversely the liquid fraction will decrease [4 and 5]. The production of gasoline, kerosene and diesel oil from waste plastics' pyrolysis is an emerging technological solution to the huge amount of plastics which can not be recovered economically. Pyrolytic recycling of plastic wastes has already been achieved successfully on commercial scale in several plants [6].

A previous research has been conducted in a simple way, without any catalytic reforming, in order to find out the influence of pyrolysis temperature during attempts to convert HDPE wastes into liquid fuels which are expected to be appropriate to gasoline or diesel engines applications [7 and 8]. Liquid fuels have been obtained successfully, however energy balance calculations must be carried out to make sure that the required energy for pyrolysis is still lower than the energy contained in the produced liquid fuel, otherwise such a process could never be broadly commercialized.

2. Research Methodology

The research is carried out using the experimental unit shown in Fig. 1. Around 900 g of HDPE as raw materials are placed in a tightly sealed cylindrical feedstock container (D 8 cm, H 48 cm) and pyrolyzed in a cylindrical reactor (stainless steel, D 30 cm, H 50 cm) with temperature variations of 450 ^{o}C, 500 ^{o}C, 550 ^{o}C, 600 ^{o}C and 650 ^{o}C [7 and 8]. The high temperature is brought about by a 1200 W heater, which consists of electric resistance wires and controlled with the help of thermocouples. A stainless tube will direct the pyrolytic gases into the Container I where some parts condense naturally. The rest which are still in gaseous phase will flow further through a Condenser (D 2.5 cm, L 48 cm) supplied by cooling water in ambient temperature, where some parts of the gas condense in the Erlenmeyer flask (Container II). The remaining gas is then flared to avoid emission of combustibles into the atmosphere.

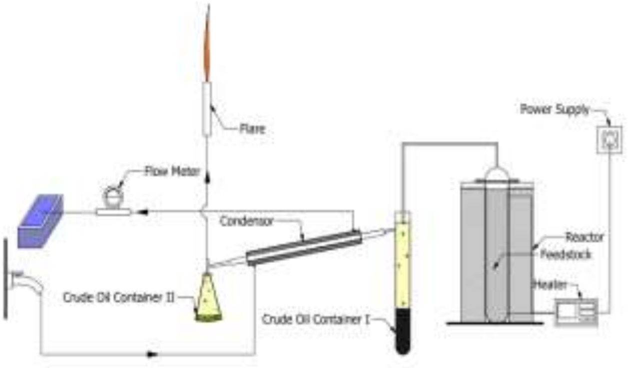


Figure 1. Schematic diagram of the experimental unit

Initially the cylindrical reactor is heated until the desired temperature is reached, then the feedstock tube is placed inside. The experiment is terminated if there is no further oil condensation in both containers. The pyrolysis products are solids (left inside the feedstock tank), liquid (in the container I and II) and flared gas. However, the research focuses only on oil (and wax) products due to their considerable potential as fuels. Unexpectedly, at pyrolysis temperatures of higher than 550 ^{o}C, the liquid in both containers become wax after several minutes. The oils and waxes are then sent to laboratories for analysis in terms of physical parameters, especially Specific Gravity, in order to estimate their Heating Values.

3. Results and Discussions

3.1. *Liquid Production*

Liquid productions, both from Oil container I (before condensor) and Oil container II (after condensor), as a function of time and process temperature are shown in Figure 2.

Low temperature pyrolysis (at 450 ^{o}C and 500 ^{o}C) yields no oil in the container II but the highest amount of oil is obtained in the container I, i.e. 924 ml and 889 ml by the end of pyrolysis at 450 ^{o}C and 500 ^{o}C, respectively. The condensor does not help to obtain more oil. However at higher temperatures, oil begin to yield in the container II, i.e. 60 ml, 336 ml and 349 ml by the end of pyrolysis at 550 ^{o}C, 600 ^{o}C and 650 ^{o}C, correspondingly. On the contrary, those collected in the container I become lesser with higher temperature, i.e. 786 ml, 427 ml and 359 ml. It means that the condensor begins to play its role. More gases, which are not condensable in ambient temperature, can then be liquefied by the condensor at lower temperatures.

The total liquid productions (from both containers) are obviously decreasing with higher pyrolysis temperatures, i.e. 924 ml, 889 ml, 846 ml, 763 ml and 708 ml, at 450 ^{o}C, 500 ^{o}C, 550 ^{o}C, 600 ^{o}C and 650 ^{o}C, respectively. However the higher oil yields at lower temperatures are associated with longer process durations. It takes around 840 minutes for the pyrolysis at 450 ^{o}C, 630 minutes at 500 ^{o}C, 360 minutes at 550 ^{o}C, 230 minutes at 600 ^{o}C and only 140 minutes at 650 ^{o}C. Therefore, in terms of oil production rates, higher temperatures are kinetically preferable, because they amount to 1.1 ml/min, 1.41 ml/min, 2.35 ml/min, 3.31 ml/min and 5.05 ml/min, at 450 ^{o}C, 500 ^{o}C, 550 ^{o}C, 600 ^{o}C and 650 ^{o}C, correspondingly. The steeper curves at higher temperatures, as displayed in Figure 2, validate the phenomena.

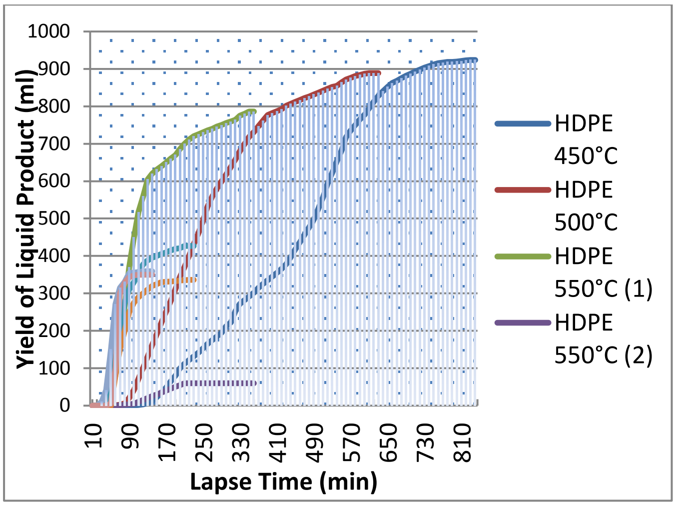
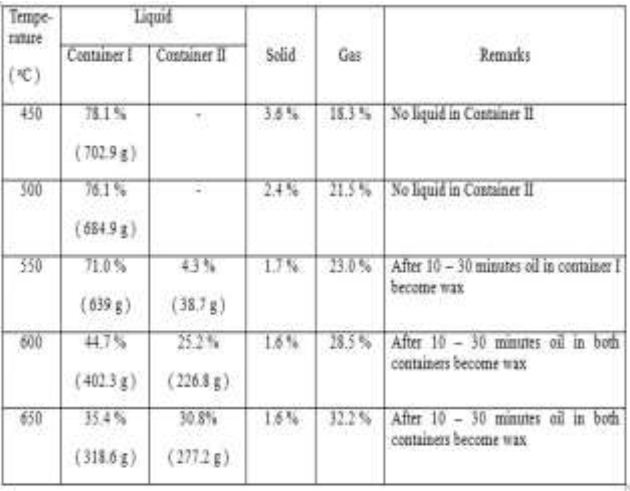


Figure 2. Oil yield as a function of time

3.2. *Composition of Pyrolysis Products*

Pyrolysis products exist in liquid, solid and gaseous phase. The oil and char products are weighed in order to identify their mass percentages, while the percentage of the uncondensed, flared gas is simply the rest. Char is the solid residue left at the bottom of the cylindrical feedstock container at the end of the process. The following Table 1 reveals product compositions as a function of pyrolysis temperature.

Table 1. Product fractions at various process temperatures



Tempe-rature (°C)	Liquid		Solid	Gas	Remarks
	Container I	Container II			
450	78.1 % (702.9 g)	-	3.6 %	18.3 %	No liquid in Container II
500	76.1 % (684.9 g)	-	2.4 %	21.5 %	No liquid in Container II
550	71.0 % (639 g)	4.3 % (38.7 g)	1.7 %	23.0 %	After 10 – 30 minutes oil in container I become wax
600	44.7 % (402.3 g)	25.2 % (226.8 g)	1.6 %	28.5 %	After 10 – 30 minutes oil in both containers become wax
650	35.4 % (318.6 g)	30.8% (277.2 g)	1.6 %	32.2 %	After 10 – 30 minutes oil in both containers become wax

Certain liquids solidify and become wax after several minutes because of natural cooling. This is a typical phenomenon for HDPE wastes which is a difficult material in the pyrolysis process by treatment at high temperature, because of its high degradation temperature and high viscosity products, such as low quality wax [3]. However, the wax can be liquefied again with appropriate heating prior to its utilization. While liquid and solid products tend to decrease with higher pyrolysis temperatures, non condensable gases increase. Higher temperatures are obviously more capable to decompose plastic wastes into light hydrocarbon fractions which are more difficult to condense. If cooling water for the condenser is available at lower temperature, apparently more oil could be obtained and less gas could be flared.

3.3. Specific Gravity of Oil and Waxes

Oil and wax characteristics are those which are important for commercial fuels, since the pyrolytic oils are intended for use in internal combustion engines. They include Specific Gravity, Kinematic Viscosity, Reid Vapour Pressure, Flash Point and Distillation. However, only Specific Gravity gets the special attention in this investigation. For comparison purposes, properties of conventional fuels, such as gasoline, kerosene and diesel fuel, are intentionally attached in the reports. Figure 3 displays some of the mentioned properties.

In general, waxes have higher specific gravity, i.e. more than 0.828, which is reasonable because they are solid. On the contrary, oils have specific gravities of between 0.745 and 0.77. Waxes are more similar to diesel fuel and kerosene, while oils, especially that in the container II of 550 ^{o}C pyrolysis, closely resemble gasoline.

Actually, accurate information about Heating Values of these oils is inevitably required in order to calculate the energy balance. However no measurement with bomb calorimeter has been carried out. Instead, a common approach can be conducted by considering that there is a proven relationship between Specific Gravity and Higher Heating Value of any fuel [9], as seen in the following formulas.

$$Specific\ Gravity = \frac{141.5}{131.5 + {}^{\circ}API} \qquad (1)$$

$$Higher\ Heating\ Value = 17{,}660 + (\ 69\ x\ {}^{\circ}API\ ) \qquad (2)$$

Equation (1) converts Specific Gravity into ^{o}API. Equation (2) is applicable for uncracked distillate or residues yielded from this pyrolysis, because no catalyst is used. Heating values obtained from equation (2) is in Btu/lb unit.

Figure 3. Specific gravities of oils and waxes

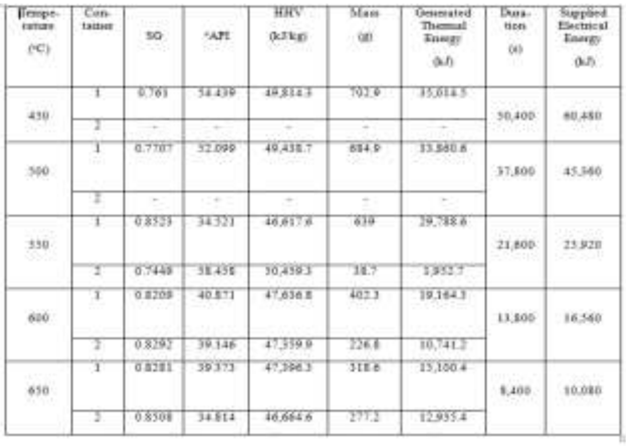
3.4. Simple Energy Balance

Pyrolysis provides evidence that it can successfully convert HDPE wastes into useful liquid fuel. Even the noncondensable gas can be flared, which shows clearly that combustible hydrocarbons are yielded in all phases from this thermal decomposition process. The produced liquid fuel contains energy which can be released later from combustion process, as can be seen from its Heating Value. The char and gas contain energy as well, however it is not included in the energy balance.

In order to generate heat for pyrolysis process a 1,200 Watt electric resistance heater is installed in the feedstock container wall. Due to its thermostatic control, where the heater will be automatically switched off when the desired temperature is achieved and on again when the temperature is lower than the expected, the electricity is fortunately not supplied continuously, but interruptedly. Pyrolysis at 450 °C, for example, was in the reality not supplied by electricity for 840 minutes long, but much lesser. Again, in this simple energy balance it is not considered either.

The following Table 2 shows the calculation results.

Table 2. Energy Balance at various pyrolysis temperatures



Temperature (°C)	Container	SG	°API	HHV (kJ/kg)	Mass (g)	Generated Thermal Energy (kJ)	Duration (s)	Supplied Electrical Energy (kJ)
450	1	0.761	54.439	49,814.5	702.9	35,014.5	50,400	60,480
	2	-	-	-	-	-		
500	1	0.7707	52.099	49,438.7	684.9	33,860.8	37,800	45,360
	2	-	-	-	-	-		
550	1	0.8523	34.521	46,617.6	639	29,788.6	21,600	25,920
	2	0.7449	58.456	50,459.3	38.7	1,952.7		
600	1	0.8209	40.871	47,636.8	402.3	19,164.3	13,800	16,560
	2	0.8292	39.146	47,359.9	226.8	10,741.2		
650	1	0.8281	39.373	47,386.3	318.6	15,100.4	8,400	10,080
	2	0.8508	34.814	46,664.6	277.2	12,935.4		

It is obvious that at lower temperatures the energy balance is awfully negative. At 450 °C there is a deficit of 25,465 kJ, while at 500 °C the shortage is 11,499 kJ. Fortunately at higher temperatures those figures are promising because it becomes more and more positive. At 550 °C there is a surplus of 5,821.4 kJ, while at 600 °C the excess is 13,345.5 kJ, and at 650 °C it is even increased to 17,955.9 kJ.

Actually, thermal energy is not comparable to electrical energy although quantitatively they have the same amount. Thermal energy is low quality energy, while electrical is high quality. Roughly thermal energy must be multiplied by 0.4 prior to balancing with electrical energy, considering an average efficiency of 40% in modern steam power plants. In this case, only pyrolysis at 650 ^{o}C fulfills the requirement because the supplied electricity of 10,080 kJ is compensated by the generated electricity of 11,214 kJ, therefore a surplus of 1,134 kJ still remains.

If electrical energy is considered expensive, other types of energy sources, such as LPG, kerosene, charcoal, biomass wastes, etc., can be used. It seems that successful commercialization of the system can be immediately realized.

4. Conclusions

1. Simple pyrolysis without catalysts can be used to obtain liquid fuels from HDPE wastes.

2. At low pyrolysis temperatures the energy balance is not favorable, where deficits occur. However at higher temperature the deficit diminishes.

3. At the pyrolysis temperature of 650 ^{o}C the energy balance is positive.

4. The energy balance could be made more accurate by considering several factors which were neglected, such as Energy contents of char and gas, Using Lower Heating Values instead of Higher Heating Values, The real operation time of electric heater, etc.

5. Other types of cheaper energy sources, such as LPG, kerosene, charcoal, biomass wastes, etc., can be used so that successful commercialization of the system can be immediately realized.

5. References

[1] La Mantia, F. (2002) *Handbook of Plastics Recycling*, Rapra Technology Ltd., Shropshire, UK.

[2] Aguado, J. and Serrano, D. (1999) *Feedstock Recycling of Plastic Wastes*, RSC Clean Technology Monograph, Cambridge, UK.

[3] Scheirs, J. and Kaminsky, W. (2006) *Feedstock Recycling and Pyrolysis of Waste Plastics, Converting Waste Plastics into Diesel and Other Fuels*, John Wiley & Sons Ltd., West Sussex, UK.

[4] Paradela, F., Pinto, F., Gulyurtlu, I., Cabrita, I. and Lapa, N. (2009) Study of the Co-pyrolysis of Biomass and Plastic Wastes, *Clean Techn. Environ. Policy*, 11, pp 115-122.

[5] Syamsiro, M., Prawisudha, P., Hu, W. and Yoshikawa, K. (2011) Co-production of Liquid and Gas Fuels from Waste Plastics, *Proceedings of the 4th AUN/SEED-Net Regional Conf. on New and Renewable Energy*, pp 104-107.

[6] Fukushima, M., Shioya, M., Wakai, K. and Ibe, H. (2009) Toward Maximizing the Recycling Rate in a Sapporo Waste Plastics Liquefaction Plant, *J. Mater Cycles Waste Manag.*, 11, pp. 11-18.

[7] Putra, A.K. (2012) *Characteristics Analysis of Oil and Wax from Pyrolysis of HDPE Wastes at Various Temperatures*, Undergraduate thesis, Department of Mechanical and

Industrial Engineering, Gadjah Mada University, Yogyakarta.

[8] Saptoadi, H., Putra, A.K., Trisunaryanti, W., Alimuddin, Z., Syamsiro, M., Yoshikawa, K. (2013) Potentiality of oil and wax products from pyrolysis of High-Density-Polyethylene wastes as automotive fuels, *Proceedings of the 6th AUN/SEED-Net Regional Conference on Energy Engineering*, Bandung.

[9] Singer, J.G (1991) *Combustion : Fossil Power*, 4th edition, Combustion Engineering Inc., Connecticut, USA.

Acknowledgement

The paper describes preliminary results of a research funded by JICA/AUN/SEED-Net in a CRI program for fiscal year 2011 and 2012. Another considerable contribution is also obtained from the Dompet Dhuafa Foundation. Their supports are herewith gratefully acknowledged. Special thank goes to Nosal Nugroho Pratama, master student of the first author, for his excellent performance as a research assistant.