

Optimization of Plastic Pyrolysis for Liquid Fuel

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Abstract

Pyrolysis of post-consumer plastics, comprising of high density polyethylene, low density polyethylene, polystyrene and polypropylene, is investigated for temperatures up to 1000°C. The mixture is representative of the major polymeric materials found in municipal plastic waste stream. This research focused on the influence of reaction conditions on the pyrolysis process, and the products of liquid and gaseous fuels for each individual plastic material. Ultimately the pyrolysis reaction and product from pyrolyzing of mixed plastics were investigated. The first stage of the project involved a comparison of waste plastics and virgin plastic. The space temperature in the pyrolyzer and the product were measured simultaneously. The results indicated that pyrolysis occurred mainly at about 400°C (wall temperature of the reaction channel). The pyrolysis products can be decomposed into low molecular weight products by increasing the reaction temperature and extending the retention time.

1. INTRODUCTION

Plastics are widely used and provide a fundamental contribution to all main daily activities: agriculture, automobile industry, electricity and electronics, building materials and packaging. Since only a small amount of waste plastic is recycled and most plastics are not biodegradable, all these activities have led to the generation of an increased amount of plastic waste, particularly in more industrialised countries. Plastics make up 7-15% of New Zealand's waste stream by weight but up to 20% of landfill space because plastics are lighter than many other materials. This results in approximately 190,000 tonnes of plastic waste disposed to New Zealand landfills each year. Measures have to be implemented to reduce their negative impact on the environment. If this situation is not dealt with in an effective way, the

enormous accumulation of quantities of plastic could cause serious ecological problems.

Raw plastics are derived from by-products of the petrochemical industry and are essentially a non-renewable fissile based resource. There are six main plastics occurring in New Zealand's municipal solid waste, high density polyethylene (HDPE); low density polyethylene (LDPE); Polypropylene (PP); polyvinyl chloride (PVC); polystyrene (PS) and polyethylene terephthalate (PET).

On the other hand, the fossil fuel has been a major concern over the world due to its declining resources. Recycling plastic waste by way of chemical reaction process such as pyrolysis has made it possible to be one of the new energy resources. There are many methods used to treat plastic waste, such as land filling, incineration, materials recycling and pyrolysis. Pyrolysis is one of the best methods for treating plastic waste in addition to preserving petroleum resources.

The objective of this project is to convert plastic waste into diesel fuel for transport through pyrolysis without catalyst. Chloride in PVC is undesirable in both liquid and gaseous fuel products thus being excluded in this project. Polyethylene, polystyrene and polypropylene was then selected as the main component of the feedstock for pyrolysis in this project. The sample is post-consumer plastic waste with a mixture of 50% PE, 25% PS and 25% PP. The collected waste plastics were washed and chipped to sizes of 5 to 10 mm for the experiments.

The objectives of the project were to investigate the pyrolysis kinetics, to analyse the product compositions and to identify the effects of the operational conditions. The kinetic study of pyrolysis reaction is essential to understand the degradation mechanism, to quantify the rate of reaction, to determine the affecting parameters and to predict the composition of the products. The preliminary experiments were done at lab scale apparatus.

2. EXPERIMENTS AND PROCEDURES

2.1. Experiment Apparatus

The equipment used in this project is illustrated in **Figure 1** and the actual equipment set up is shown in **Figure 2**.

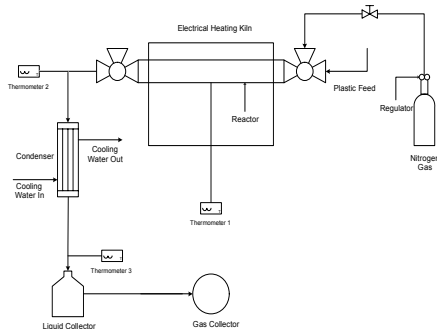


Figure 1 Line diagram of the apparatus



Figure 2 Actual equipment set-up

The pyrolysis reactor consists of a stainless steel tube with a dimension of 2.5 cm in diameter and 34 cm long, a furnace heated by built-in electrical elements, a stainless steel carrier and temperature detectors as shown in **Figures 1** and **2**. The plastic carrier which is introduced inside of the reactor has

three separated zones with a gap on one end to insert the temperature detector. Due to the most efficient heating area in central region of the reactor, the plastic is placed in the middle zone of the carrier. Because of the removable characteristic, there are some advantages to use the carrier: it is easy to feed the plastic to the tube and fix the plastic position inside the tube; it is also easy to clean up the residue after the reaction instead of washing the whole tube. The temperature detector has a long stainless steel hose to support the inside thermocouple which is to measure the temperature of the pyrolysis atmosphere.

2.2. Materials and Procedures

The waste plastic mixture used in this experiment was supplied by *Green Fuels Technologies Ltd*, with a composition of 50 wt% PE, 25 wt% PP and 25 wt% PS. Although the waste plastic has been pre-treated such as washing and drying, there are some residual like the label paper or viscous liquid. Those may have some effect on the product yield or the composition.

A series of runs of the mixture pyrolysis with maximum amount of 10grams were carried out at final temperature of 300°C and 500°C with different heating rate.

After these tests, further experiments were performed using virgin plastics of each type of the future plastics and the mixture.

The volatility of liquid product was analysed by heating in a vacuum oven with different temperatures of 50°C, 80°C, 110°C, and 140°C. The composition of liquid product was analysed using a gas chromatograph (GC-R1A). The gases were analysed by Micro gas chromatograph (Micro-GC).

3. RESULTS AND DISCUSSION

The preliminary experiment results showed that some plastic chain broke down when the space temperature reached about 100°C space temperature (**Error! Reference source not found.**). The wall temperature corresponding to the space temperature at 100°C is at about 400°C. The temperature at which plastic starts pyrolyzing is similar to that previously reported by Bockhorn et al. (1998); Kiran et al. (2000) and Miranda et al. (2001). An interesting finding from this work is

that the peak value of space temperature after about 20 minutes from the start of heating. It is believed that this is due to the evaporation of pyrolysis product during the fast plastic decomposition. Energy is needed in the breaking-down of the molecular chains of the solid plastics. The activation energy on the polymer breaking-down decreases with decrease in molecular weight of the polymer (Miranda et al. 2001).

A separate test to heat pure nitrogen in the apparatus was performed to compare the space temperatures and it was found the peak temperature at about 20 minutes was absent without plastics. This confirms the plastic causes the temperature peak during the plastic decomposition. The accelerating of the space temperature increase towards the peak value is an indication for the actual pyrolysis occurrence. The drop of the space temperature after the peak value may indicate that the majority of the pyrolysis has completed. The peak space temperature corresponds to a wall temperature of about 500°C.

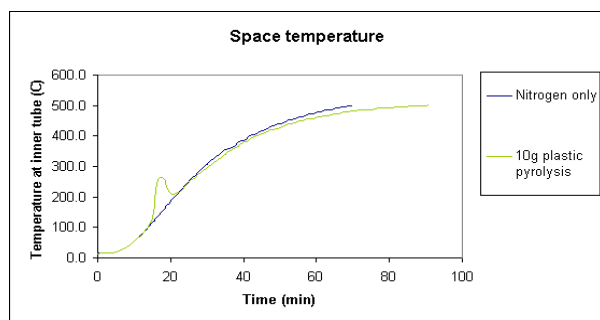


Figure 3 The influence of plastic on inner space temperature

Similar experiments were done with different virgin plastic. The pyrolysis starting temperature of PE, PS and PP are all at about 100°C (**Error! Reference source not found.**). The heat released from PS, which has pyrolyzed first, will influence other types of plastic. Therefore, pyrolysis of all plastic will start at about the same time and form only one peak in the space temperature curve (Figure 1, Figure 5). Demirbas found the same result through a similar pyrolysis experiment (Demirbas 2004).

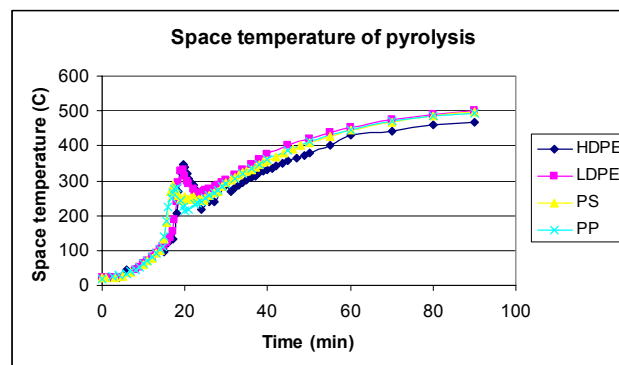


Figure 4 Space temperature in the pyrolyzer of plastic pyrolysis

During the period of pyrolysis (from the start to the end of the peak), all plastics convert into oil product and small amount of gas product (Figure 5). The oil products was generated and evaporated immediately at 500 °C wall temperature. The oil vapour increased the inner space temperature quickly and formed the peak on the curve (**Error! Reference source not found.**). At the wall higher temperature from 500 to 1000°C, the heavy oil product can be degraded to light oil and gas products. This has been found in many other studies (Demirbas 2004; Demirbas 2005; Saha and Ghoshal 2005).

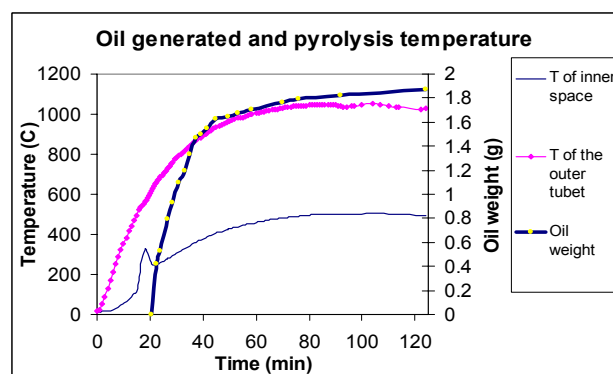


Figure 5 The amount of oil generated and temperature profile throughout pyrolysis (T_1 , wall temperature; T_2 , inner space temperature)

Ash, char, wax, oil, non-condensable gases, was produced from plastic pyrolysis. It was found the proportion of ash in plastic waste was higher than virgin plastic. The percentage of char in both waste and virgin plastic was less than three percent. The composition and the proportion of wax, oil and non-condensable gases are controlled by three factors: reaction temperature, pyrolysis retention time, and condenser performance.

Product	Final pyrolysis temperature	
	500°C	300°C
Weight Percentage [%]		
Oil	22.4	26.5
Gas	52.7	45.5
Wax	10.7	14.1
Ash	14.2	13.9
Total	100	100

Table 1 Product yields under different pyrolysis temperature

Note that: the weight of gas is a secondary value that is calculated by the difference of mass.

- Wax is the product condensed at relatively high temperature and relatively low retention time.
- The composition and the proportion of oil product are determined by oil steam retention time, pyrolysis temperature, and condensation temperature. Longer retention time or higher reaction temperature tempts to break the polymer into smaller fragments. The components in the oil can be separated by using fractional condenser.
- There was small amount of non-condensable gases generated with oil products. The oil and wax can be further pyrolyzed into non-condensable gases under high temperature.

The proportion and the composition of the liquid products were analysed with gas chromatography (GC-R1A; Table 2).

Liquid product (500°C)	
Time [min]	Conc. [mass %]
5.18	3.9
8.24	13.1
13.96	18.3
23.1	8.7
27.63	45.7

Table 2 liquid products distribution analysis

The main components in the liquid products were identified to be styrene (45.7 wt%), toluene (18.3 wt%), heptane (13.1 wt%), nonane (8.7 wt%), and hexane (3.9%). At 500 °C, most products pyrolyzed from PP, HDPE and LDPE have been further decomposed to non-condensable gases and light oil

(Table 2). Styrene is one of the pyrolysis products from PS, which need higher temperature than 500 °C to be further decomposed, so there is a relatively large proportion of styrene in the liquid products.

The volatility of liquid product was analysed by using a vacuum oven with different temperatures.

Temperature [°C]	Accumulated evaporation [wt%]
15	-
50	66.87
80	72.88
110	78.87
140	84.78

Table 3 Volatility of liquid products

The effects of the three factors on the composition and the proportion of the pyrolysis products are going to be quantified in the next stage. The experiment will be applied on semi-commercial scale apparatus.

4. CONCLUSION

Four types of plastics and a mixture of 25 % each type were pyrolyzed using a batch pyrolyzer with nitrogen gas. Based on the results, the following conclusions have been made:

- All of the four types of plastic start pyrolyzing at a similar temperature, about 400°C. The temperature when polystyrene starts pyrolyzing is slightly lower than the other three. All plastic was decomposed into lower molecular weight products at this stage.
- The products with relatively high molecular weight such as wax and heavy oil can be further pyrolyzed into low molecular weight products. It depends on the retention time and the reaction temperature.
- 22.4% oil, 52.7% gas, 10.7% wax and 14.2% ash was produced with the pyrolyzer at 500 °C final pyrolysis temperature. Less oil and wax was pyrolyzed at 300 °C than that at 500 °C (Table 1).

5. REFERENCES

Bockhorn, H., A. Hornung, et al. (1998). "Stepwise pyrolysis for raw material recovery from plastic

- waste." Journal of Analytical and Applied Pyrolysis **46**(1): 1-13.
- Demirbas, A. (2004). "Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons." Journal of Analytical and Applied Pyrolysis **72**(1): 97-102.
- Demirbas, A. (2005). "Recovery of chemicals and gasoline-range fuels from plastic wastes via pyrolysis." Energy Sources **27**(14): 1313-1319.
- Kiran, N., E. Ekinci, et al. (2000). "Recycling of plastic wastes via pyrolysis." Resources, Conservation and Recycling **29**(4): 273-283.
- Miranda, R., Y. Yang, et al. (2001). "Vacuum pyrolysis of commingled plastics containing PVC. I. Kinetic study." Polymer Degradation and Stability **72**(3): 469-491.
- Saha, B. and A. K. Ghoshal (2005). "Thermal degradation kinetics of poly(ethylene terephthalate) from waste soft drinks bottles." Chemical Engineering Journal **111**(1): 39-43.
- SPI, T. S. o. t. P. I. (1999). "The SPI resin identification code." Retrieved Nov/24, 2005, from <http://www.plasticsindustry.org/outreach/recycling/resincodes.htm>.
- Williams, E. A. and P. T. Williams (1997). "Analysis of products derived from the fast pyrolysis of plastic waste." Journal of Analytical and Applied Pyrolysis Proceedings of the 1996 12th International Symposium on Analytical and Applied Pyrolysis, Oct 14-18 1996 **40-41**: 347-363.