PYROLYSIS OF POST-CONSUMED WASTE PLASTICS FOR THE RECOVERY OF BTX-AROMATICS USING A FLUIDIZED BED REACTOR

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Abstract: Waste plastics have been usually disposed on landfill sites or been utilized energetically, for instance, incineration. Modern Society, however, requires reasonable alternatives to cope effectively with needs for energy- and environmental conservation. Researchers consider the pyrolysis of plastic wastes to be an alternative, and intensive researches have been carried out [1]. Via pyrolysis, plastic wastes can be converted into chemical feedstock which can be used to produce new valuable products such as oils and gases of high caloric value. In this study, fractions of waste polypropylene and polyethylene and mixed waste plastics, were pyrolyzed in a laboratory scale pyrolysis plant equipped with a fluidized bed reactor and a char removal system, under different conditions. In experiments, the influence of the reaction temperature, the feed rate, and the kind of fluidizing medium on the product spectrum was investigated to optimize reaction conditions for the maximum recovery for BTX-aromatics. Pyrolysis of the PP fraction produced oils up to 43 wt% of the product. With respect to the PE fraction, the maximum oil yield was above 60 wt% of the product. The target compound was BTX aromatics, whose amount in the oils reached 53 wt% for the PP fraction and 32 wt% for the PE fraction. The oils that were obtained in the experiments almost had no metal and chlorine contents.

1. Introduction

Waste plastics cause considerable problems in the world due to their large volume and the difficulty of treating them. Incineration and landfill, which are traditional treatment methods for waste plastics, cannot solve the problem regarding the treatment of plastic wastes because suitable depots are expensive and because incineration stimulates the emission of harmful gases [1]. Furthermore, waste plastics can only be partly recycled into new products due to their contamination [2].

A promising treatment process for waste plastics is pyrolysis. The thermal and catalytic pyrolysis of waste plastics into fuel-like hydrocarbons or monomer under different conditions has been well investigated by some researchers [3-5]. The pyrolysis of the polyolefin plastics

LDPE, HDPE, and PP yields an oil product consisting mainly of alkenes, alkanes, and alkadienes; a gas product consisting of hydrogen, alkanes, and alkenes; and negligible char [6,7]. Many researches on the pyrolysis of waste plastics have been carried out in a fluidized bed reactor. Pyrolysis in a fluidized bed reactor, which offers high heat and mass transfer and consequently almost a constant temperature, provides a more uniform spectrum of products due to the shorter residence times in the reactor. As a result of the uniformity of the product spectrum, the possibility of applying the process at a relatively small scale gives rise to a wider range of investment alternatives [8].

The annual generation of waste plastics in Korea currently amounts to 4.6 million ton/year, and is continually increasing. Polypropylene and polyethylene are the main components of such plastic wastes. In this study, three waste fractions of polypropylene, polyethylene, and mixed plastics, were pyrolyzed in a pyrolysis plant equipped with a fluidized bed reactor and a char removal system. The aim of this study was to find out the optimal temperature for a high yield of BTX aromatics and to reduce the chlorine content in the pyrolysis oils by applying additives, such as CaO, $Ca(OH)_2$, rice straw and oyster shell.

2. Experiments

2.1 Feed material

Three pellet-type fractions of waste plastics, polypropylene, polyethylene and mixed, were used in the experiments. To capture HCl liberated during pyrolysis, CaO, $Ca(OH)_2$, rice straw and oyster shell were premixed with waste plastics. The main properties of the feed materials including chlorine contents are shown in Tab. 1.

Tab. 1 Specifications of feed material

Proximate analysis (wt.%)	PP	PE	Mixed	Ultimate analysis (wt.%)	PP	PE	Mixed
Moisture	0.15	0.1	1.37	C	80.3	81.8	79.85
Volatile matter	95.08	98.87	92.9	H	13.2	13.6	12.26
Fixed carbon	1.22	0.04	1.14	O	1.7	1.9	5.08
Ash[a]	3.55	0.99	4.59	Cl	0.06	0.01	1.13

[a] by difference

2.2 Pyrolysis plant and Procedure

The pyrolysis plant consisted mainly of a feeding system, a fluidized bed reactor, a char removal system, a quench system, and a gas-circulating system. The feeding system was equipped with two screw feeders with variable feed rates, so they would input uniformly. The reactor, which was indirectly heated by electricity, was made of a sus-316 steel tube with a height of 300 mm and an inner diameter of 80 mm. The reaction temperature was determined based on the average value taken from the three thermocouples in the reactor. The gas distributor was made of steel, with 49 bending tubes designed to prevent the fluidizing quartz sand (0.4 mm) from falling through the plate. The char removal system was made up of a cyclone and a hot filter designed to capture particles bigger than 10 and 2 μm, respectively. The quench system, which was cooled to -30 °C using ethanol, consisted of four glass condensers for the precipitation of oil and of an electrostatic precipitator by which the aerosols were captured. The non-condensable gas was recycled using a compressor, and was used as the fluidizing gas. During the pyrolysis, the non-condensable gas was sampled, using teflon gas bags (2L) at 10 min intervals, to analyze their composition. The excess gas was burned in a flare stack to regulate the pressure. A schematic diagram of the pyrolysis plant is shown in Fig. 1.

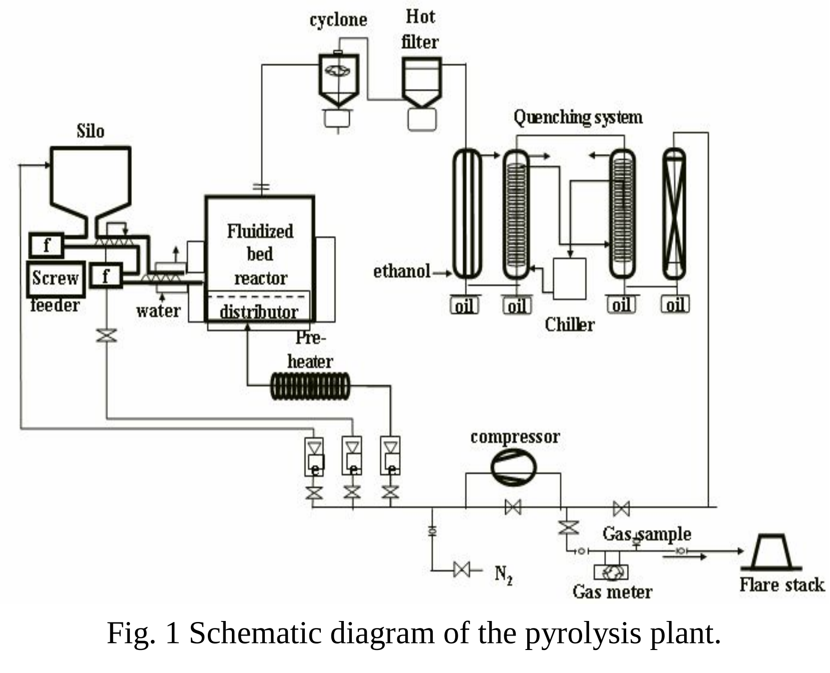

Fig. 1 Schematic diagram of the pyrolysis plant.

2.3 Reaction Conditions

In each experiment, the input of the feed material was 0.5 kg, and 1.5 kg quartz sand was used as the fluidized bed material. The experiments from Run1 to Run4 for all the fractions were performed to determine the influence of the reaction temperature on the aromatics yield. To achieve a high yield of BTX aromatics, reaction temperatures ranging from 660 °C to 780 °C were selected. The reaction conditions of the experiments are shown in Tab.2.

Tab. 2 Reaction conditions

Parameters	Polypropylene				Polyethylene				Mixed			
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4
Reaction temperature (°C)	668	703	727	746	660	680	704	728	677	710	735	773
Feed rate (g/min)	4.5	4.5	4.5	4.5	5.2	5.2	5.2	5.2	6.7	6.7	6.7	6.7
Flow rate (NL/min)	29	28	27	26	29	28	28	27	53	50	48	46

3. Results and Discussions

3.1 Organic Mass Balance

In establishing organic mass balance, the product oil and char yields were determined by weighing after the pyrolysis experiments. The amount of gas production was calculated, along with the gas density and the measured gas volume. Thereafter, distillation with the product oil was conducted to separate the light oil from the viscose residue. The light distilled oil and the viscose fraction were designated as oil and distillation residues, respectively. Finally, the char and distillation residues were burnt in a furnace to find out the amount of organic mass in them. The organic mass balance from Run1 to Run4 is shown in Tab. 3.

Tab. 3 Organic Mass Balance of the Pyrolysis Experiments

Product	Polypropylene				Polyethylene				Mixed			
	Run1	Run2	Run3	Run4	Run1	Run2	Run3	Run4	Run1	Run2	Run3	Run4
Oil	43.1	35.9	34.7	29.6	60.9	56.6	43.6	38.2	35.2	32	29.7	25.9
Gas	54.4	57	61.7	65.9	36.6	42.8	54.6	59.3	57.8	61.2	61.9	64.4
Char	2	6.9	3.1	4	0.7	0.3	0.3	2	5	4.5	6.3	7.2
Distillation residue	0.5	0.2	0.5	0.5	1.8	0.3	1.5	0.5	1.9	2.3	2.1	2.5

3.2 Chlorine Content in Pyrolysis Oil

Additives, such as CaO, $Ca(OH)_2$, oyster shell and rice straw, was pre-mixed with mixed waste plastics that contains relatively high amount of chlorine in them. Fig. 2 presents the effect of the various additives on the chlorine content. It can be seen that CaO, $Ca(OH)_2$ and oyster shell were significantly influence on the chlorine removal but rice straw was slightly decreased.

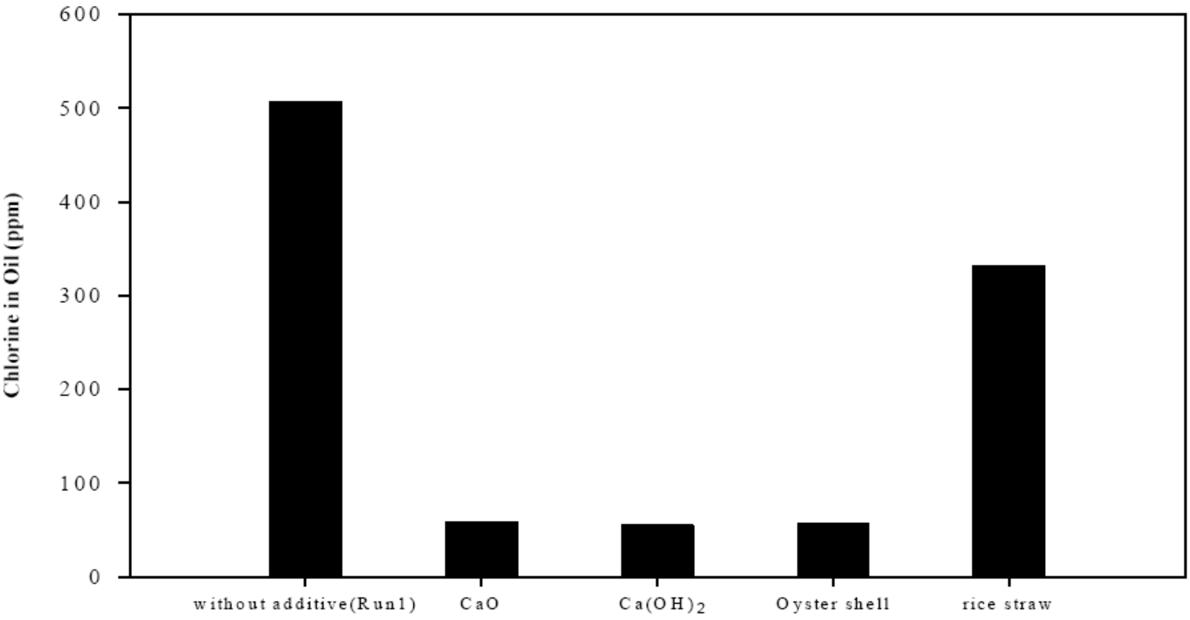

Fig. 2 Effect of additives on the chlorine content

4. Conclusions

Pyrolysis of waste plastics (PP, PE and mixed fractions) was carried out in a fluidized bed reactor equipped with a char removal system, under various reaction temperatures. The oil that was obtained in the experiments consisted of aliphatics and mono- and polyaromatic compounds. For the target compounds (BTX aromatics), up to 53 wt% was obtained for the PP fraction in the oil, and up to 32 wt% for the PE fraction, up to 51 wt% was obtained for the mixed fraction in the oil. For PP and PE fractions, it was found that the concentration of BTX aromatics in the oil increased along with the reaction temperature but the mixed fraction was slightly decreased at the reaction temperature 773°C. The main compounds of the pyrolysis gas were methane, ethene, ethane, propene, butadiene, and butane, and the maximum heating value of the gas obtained in both cases was about 50 MJ/kg. Therefore, the pyrolysis gas seems to be appropriate for use as a heating source in a pyrolysis plant. Ethene and propene, if separated from the other gas components, can be utilized as chemical feedstock for the production of polyolefin. The oils that were obtained in the experiments almost had no metal content. The metals were concentrated in the char and in the distillation residue. In addition, the amount of chlorine in the oil was below 10 ppm for both the PP and PE fractions. Due to the lower metal and chlorine contents of the oil, it seems that the environmental problems caused by the burning of the oil would not be serious. Chlorine content of mixed fraction was decreased about up to 50 ppm by addition of additives (CaO, $Ca(OH)_2$ and oyster shell). The char and distillation residue produced in the experiments consisted mainly of inorganics, whose utilization remains a challenge. Pyrolysis char, however, has potential for use in road surfacing and as a building material.

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