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Pyrolysis of Mixed Plastic Wastes for the Recovery of Benzene, Toluene, and Xylene (BTX) Aromatics in a Fluidized Bed and Chlorine Removal by Applying Various Additives

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Mixed plastic wastes are very difficult to mechanically recycle into new products because of their non-homogeneity. Therefore, pyrolysis and gasification seem to be very effective in the extraction of energy from mixed plastic wastes in the form of oil and gas. In this study, a fraction of mixed plastic wastes was pyrolyzed in a bench-scale plant equipped with a fluidized-bed reactor and a char removal system. This study has two aims. The first is to find out the optimum reaction temperature for a high yield of benzene, toluene, and xylene (BTX) aromatics. The second is to find out the best additive for chlorine removal. To find out the optimum reaction temperature for the maximum BTX content, experiments at a temperature range of 660–780 °C were carried out. The pyrolysis oils that were obtained from the experiments were composed of aliphatics and mono- and polyaromatic compounds. The reaction temperature had a positive effect on the BTX aromatics yield. The maximum BTX aromatics yield was obtained at 719 °C, with a value of 18 wt % of the organic product. The pyrolysis oils had almost no metal content. The metals that were present in the feed material were concentrated in the solid product, the char. It seems that the char removal system, which was composed of a cyclone and a hot filter, almost perfectly removed the char particles. Besides the pyrolysis oil, a combustible gas was also obtained. The main components of the gas were CH_4, C_2H_4, C_3H_6, C_4H_6, and C_4H_{10}. The higher heating value of the product gas was about 50 MJ/kg. To absorb the hydrogen chloride that was formed from the degradation of the polyvinyl chloride (PVC) in the mixed plastic wastes, additives (calcium oxide, calcium hydroxide, crushed oyster shells, and rice straw) were added to a fraction of the mixed plastic wastes. In the experiments without any additive, the chlorine contents of the pyrolysis oils were 350–500 ppm. When the additives, especially calcium oxide, calcium hydroxide, and crushed oyster shells, were applied, the chlorine content of the pyrolysis oils significantly decreased to 50 ppm. The results of this study suggest that the use of oyster shells as a HCl absorbent can stimulate the recycling of waste oyster shells, which are abundant in Korea.

1. Introduction

Plastics are widely used in everyday life as well as in high-tech industries as an indispensable ingredient. The production of plastics has increased according to demand from society, and accordingly, the amount of waste plastics has also increased. Landfills and incineration are the most widely used among the existing methods of processing waste plastics. Direct disposal of waste plastics in landfills is now almost impossible in developed countries because of legislation pressures and high costs. Incineration stimulates the emission of harmful gases, such as dioxin, furans, and acid gases, and heavy metals that can cause damage to the environment and health.[1] Furthermore, incineration emits carbon dioxide, which causes global warming. Therefore, there is an increasing need to recycle waste plastics. Toward this end, various technologies have been developed that can recover energy from waste plastics and use such energy as petrochemical feedstock or fuel oil.[2] Pyrolysis is a promising process for treating waste plastics, because it produces liquid and gas products with higher heating values (HHVs), which can help solve the problem of high oil prices.[3] In recent years, other process variants in the pyrolysis of plastics have been investigated, such as (1) low-temperature cracking of plastics at 500–650 °C to produce waxes and oils that are potential feedstock in refineries, (2) pyrolysis of plastics in an inert-gas stream at a temperature range of 650–800 °C to obtain mostly light olefins, such as ethene, propene, and butadiene, from mixed plastics, (3) pyrolysis at 600–800 °C, using pyrolysis gases as fluidizing media, which yield heat-content gases and benzene, toluene, and xylene (BTX)-rich oils, and (4) monomer recovery from pure plastics, such as poly(methylmethacrylate) (PMMA), polystyrene (PS), polytetrafluoroethylene (PTFE), and poly(ethylene terephthalate) (PET), by heating the plastics at 450–550 °C.[4] In addition, there is also a great deal of research on the catalytic pyrolysis of plastics.[5–7]

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The pyrolysis of plastics has been carried out with various reactors, such as melting vessels, blast furnaces, autoclaves, tube reactors, rotary kilns, and fluidized-bed reactors. Fluidized-bed pyrolysis appears to be one of the most promising feedstock recycling technologies, for several reasons. Fluidized-bed pyrolysis is characterized by its excellent heat and mass transfer, as well as its maintenance of a constant temperature throughout the reactor.[8] Accordingly, it is marked by a uniform spectrum of higher quality products. In fluidized-bed pyrolysis, several factors influence the mass balance of the product, such as the temperature, feed rate, feed size, and kind of fluidizing medium. Among these factors, the most significant is the reaction temperature. Particularly, it is well-known that the formation of aromatics in the pyrolysis of polyolefin is stimulated above 600 °C.[9]

On the other hand, pyrolysis oil with less halogen elements has been one of main aims in the pyrolysis of waste plastics. In particular, HCl generated during pyrolysis can cause problems, such as corrosion and dioxin formation. A lot of research has been carried out to capture chlorine with basic additives.[10,11]

The amount of waste plastics that are currently generated in Korea is 4.6 million tons/year and is continually increasing. In this study, a fraction of mixed plastic wastes was pyrolyzed in a pyrolysis plant equipped with a fluidized-bed reactor and a char-removal system. Experiments were conducted to find out the optimum reaction temperature for a high yield of BTX aromatics and the best additive for chlorine removal. To find out the optimum reaction temperature for high-yielding BTX aromatics, experiments were carried out at a temperature of 650−800 °C. To absorb the hydrogen chloride that was generated during the degradation of polyvinyl chloride (PVC), additives (calcium oxide, calcium hydroxide, crushed oyster shells, and rice straw) were applied to the feed material.

2. Experimental Section

2.1. Feed Material. A recycling center in Korea provided the fraction of pellet-type mixed plastic wastes that was used in this study. According to the recycling center, the mixed plastic wastes were composed of polyethylene, polypropylene, PS, and other minor plastics, such as PMMA and PET. The mixed plastic wastes, at first, were sieved to reduce their particle size to 2−3.4 mm and fed in the experiments. To analyze the feed material, it was again cryogenically ground using liquid nitrogen and the final powder-type material was analyzed several times for accuracy. The additives that were used to remove the HCl from the mixed plastics were calcium oxide, calcium hydroxide, oyster shells, and rice straw. Calcium oxide and calcium hydroxide were powder-type. The oyster shells were crushed into fine particles for a better reaction. The rice straw was cut into a rectangular form with a diameter of up to 5 mm. The proximate analysis of the mixed plastic fraction showed that its volatile matter and ash content were about 93 and 4.6 wt %, respectively. It also had a high chlorine content of 1.13 wt %. Additionally, the HHV of the plastics, which was calculated by Dulong's formula, was about 44 MJ/kg. The characteristics of the mixed plastic wastes are listed in Table 1.

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Table 1. Main Properties of the Mixed Plastic Wastes

proximate analysis	wt %	elemental analysis	wt %
moisture	1.37	carbon	79.9
volatile matter	92.9	hydrogen	12.6
fixed carbon	1.14	oxygen	5.1
ash[a]	4.59	chlorine	1.13
		HHV(MJ/kg)	44.4

[a] By difference.
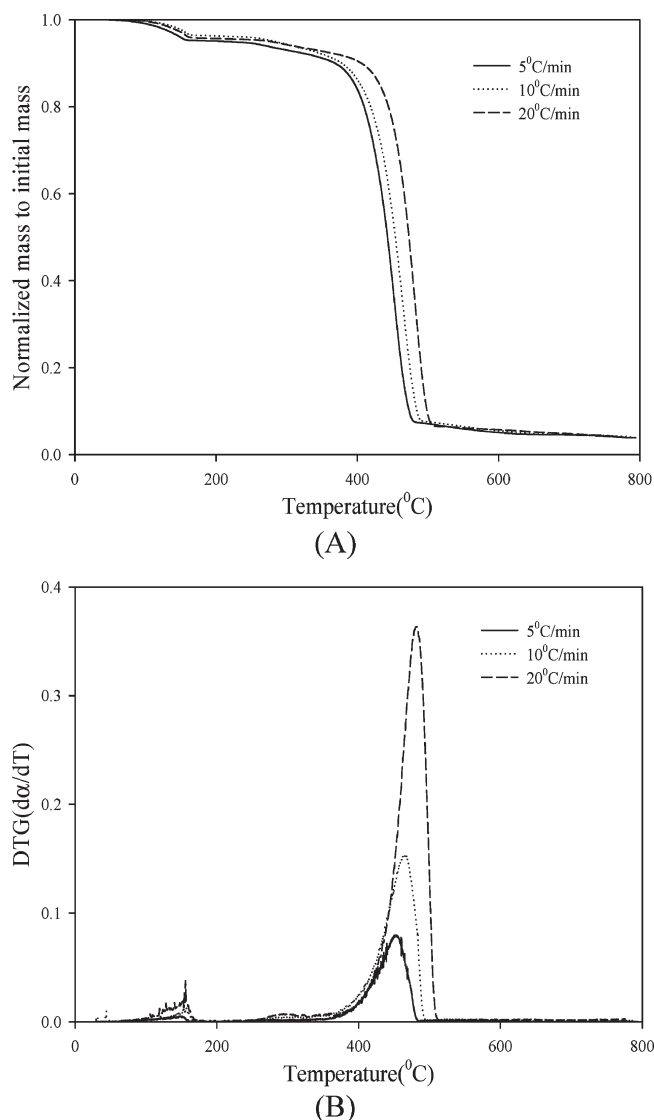
Figure 1. TGA of the feed material: (A) TGA and (B) DTG.

2.2. Thermogravimetric Analysis (TGA) and Differential Thermogravimetry (DTG) Experiments. To investigate the thermal degradation property of the feed material, a TGA was carried out with a thermogravimetric analyzer (TGA 2050, TA Instruments). The experiments were conducted initially at 30 °C and then up to 800 °C, at heating rates of 5, 10, and 20 °C/min. The sample amount was 10−20 mg, and nitrogen gas as a purge gas was made to flow at a rate of 100 mL/min. The TGA and DTG curves that were obtained are shown in Figure 1. As the heating rate increased, the temperature range at which weight loss took place also increased. The main thermal degradation took place at 400−500 °C, which is also clearly shown in the DTG curves. At 800 °C, the TGA curves reveal that the degradation residue amounted to approximately 5%, which coincides with the ash content in the proximate analysis.
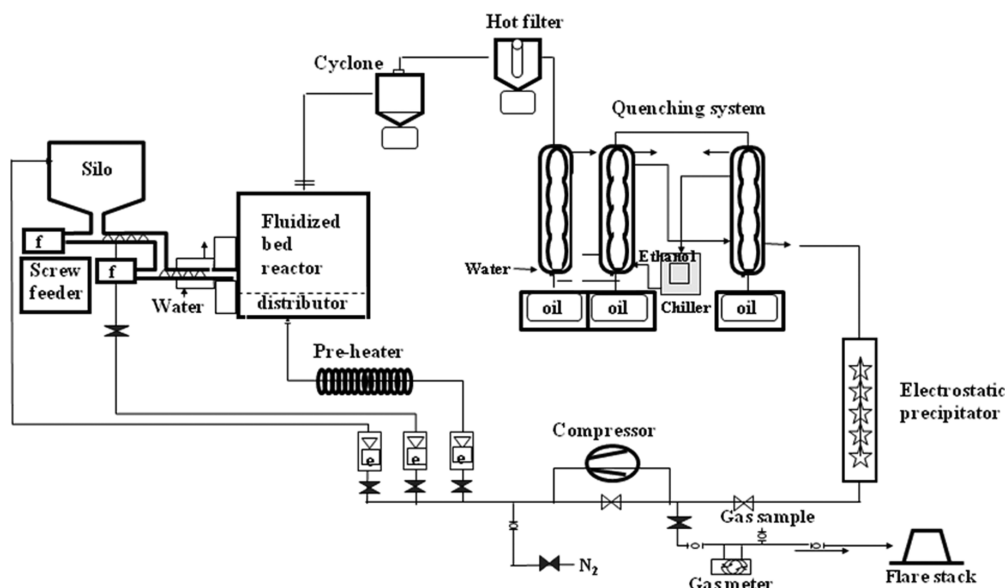
Figure 2. Schematic diagram of the pyrolysis plant.

Table 2. Reaction Conditions

parameter	run 1	run 2	run 3	run 4	run 5	run 6	run 7	run 8	run 9	run 10
reaction temperature (°C)	677	710	735	773	690	711	712	719	711	722
additive			none		CaO	CaO	Ca(OH)$_2$[a]	Ca(OH)$_2$[b]	oyster shell	rice straw
input additive(g)			none		42.75	42.75	28.23	28.23	76.35	24
feed rate (g/min)	6.7	6.7	6.7	6.7	8	7.7	7.2	5.7	7.1	6.1
flow rate (nL/min)	53	50	48	46	52	50	50	50	50	50

[a] The specific surface area of Ca(OH)$_2$ in run 7 is 38−40 m^2/g. [b] The specific surface area of Ca(OH)$_2$ in run 8 is 11−15 m^2/g.

2.3. Pyrolysis Plant. The bench-scale pyrolysis plant was designed to have a throughput of up to 1 kg/h. The plant consisted mainly of a feeding system, fluidized-bed reactor, char-removal system, quench system, and gas-circulating system. The feeding system was equipped with two screw feeders that helped uniformly feed the plastics. The core of the plant was the fluidized-bed reactor, which was indirectly heated with electricity and was made up of a sus-316 tube with an inner diameter of 110 mm and a height of 390 mm. To determine the reaction temperature, three thermocouples were installed in the reactor. The reaction temperature is defined as the average value that was taken from the thermocouples. Quartz sand (3.8 kg) with a diameter of about 0.4 mm was used as the fluidized-bed material. The gas distributor was made of steel, with bubble cap tuyeres that were designed to prevent defluidization from coke formation during pyrolysis. A cyclone and a hot filter constituted the char removal system, which could capture particles bigger than 10 and 2 μm, respectively. The quench system consisted of one steel condenser that was operated with cool water and two glass condensers that quenched gaseous products with ethanol and operated at −25 °C. Aerosols after the quenchers could be captured with an electrostatic precipitator. Noncondensable gas was circulated into the fluidized bed with a compressor. Some noncondensable gas was sampled using Teflon gas bags (2 L) at intervals of 15 min to analyze its composition. The remaining gas stream was burned in a flare stack after its gas volume, pressure, and temperature were measured. A schematic diagram of the pyrolysis plant is shown in Figure 2.

2.4. Reaction Conditions. Pyrolysis experiments (runs 1−4) were carried out to find the optimum reaction temperature for a high yield of BTX aromatics. The reaction temperature was selected from 660 to 780 °C, because the formation of aromatics from the pyrolysis of polyolefin is stimulated above 600 °C. Experiments (runs 5−10) were also conducted to find the best

additive for chlorine removal. For this, additives were applied to the feed material and then mixed well. Runs 5 and 6 were carried out to investigate the effect of calcium oxide at different reaction temperatures. Runs 7 and 8 were performed to investigate the effect of calcium hydroxide with different specific surface areas. Runs 9 and 10 were conducted to find out the influence of oyster shells and rice straw on chlorine removal. Except for run 5, the experiments (runs 6−10) were carried out at 711−722 °C. The amount of feed material in each experiment was 0.8 kg. The residence time of the pyrolytic gases in the reactor in all of the experiments, which was 0.5−1 s, was calculated according to ref 12. The flow rate of the fluidizing gas in all of the experiments maintained more than twice the minimum fluidizing velocity. The reaction conditions are summarized in Table 2.

2.5. Product Analysis. The product of the pyrolysis of the mixed plastic wastes was divided into gas, oil, and solid residue (char). A fraction of the oil product from each run was distilled in a distillation apparatus under reduced pressure (210 °C and 130 mbar) to separate a light fraction of the oil and the distillation residue. After the distillation, the distilled light oil that was designated in this study as a pyrolysis oil was quantitatively and qualitatively analyzed by comparing the peak that appeared under identical operating conditions using a gas chromatography−flame ionization detector (GC−FID, 7890A, Agilent Instruments) and gas chromatography−−mass spectrometry (GC−MS, 5975C, Agilent Instruments). The response factor of each component was multiplied by the value of the measured area of each peak. Helium was used as a carrier gas, and the applied capillary column was a Petrocol (100 m × 0.25 mm × 0.5 μm). The contents of the metal and chlorine in the oil were analyzed with inductively coupled plasma−atomic emission spectrometry (ICP−AES, 138 Ultrace, Jobin Yvon) and a

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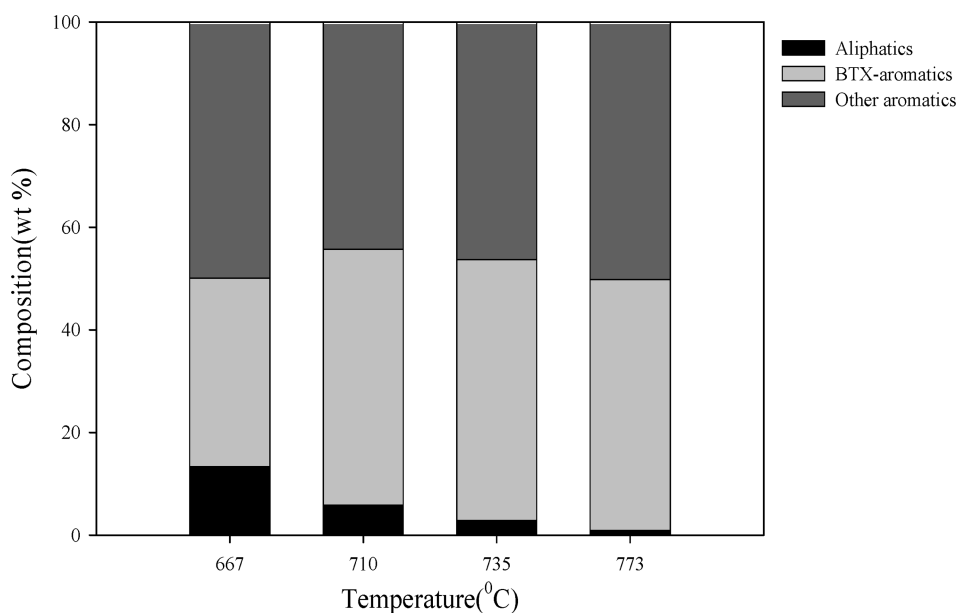
Trace chlorine analyzer (TCL-100, Mitsubishi). The calorific value of the oil was measured with a bomb calorimeter (1261, Parr). The water content of the pyrolysis oil was measured using the Karl Fischer titrator (Metrohm 787, KF Titrino), HYDRA-NAL Composite 5 K (Riedel-de Haen) as the titration reagent, and HYDRANAL Working Medium K (Riedel-de Haen) as the titration solvent. The gas product was analyzed with GCs (7890A, Agilent Instruments) using a thermal conductivity detector (TCD) and a FID, and argon was used as a carrier gas. The applied columns were a Carboxen 1000 (TCD) and a HP-plot Al_2O_3/KCl (FID). The element analysis of the oil, char, and distillation residue was conducted with an element analyzer (Flash 1112 series, CE Instruments).

3. Results and Discussion

3.1. Organic Mass Balance. To establish the organic mass balance in each experiment, the gas yield was calculated by multiplying the volume of the gas that was produced in the experiments and the gas density from the gas composition.
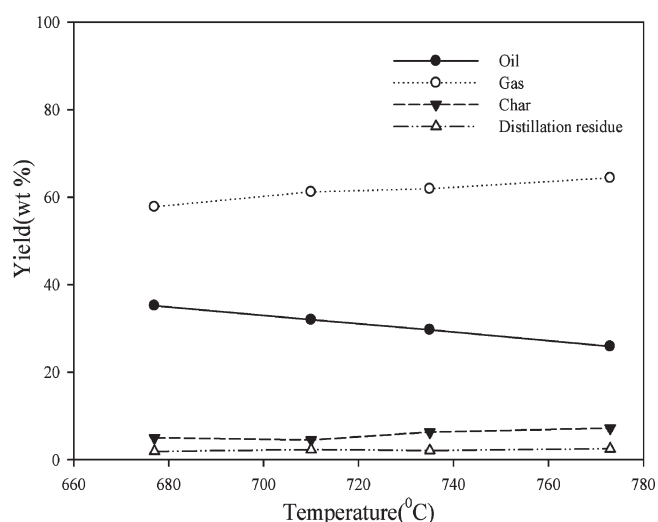
Figure 3. Product distribution, with respect to the reaction temperature.

The char yield was obtained via weighing after the pyrolysis. Finally, the oil yield was calculated from the difference, because of the difficulty in measuring the amount of high-boiling components condensed on the surface of the apparatus after experiments. Therefore, an error in oil yield can exist. The gas and pyrolysis oil are all organic. To determine the amount of organics in the char and the distillation residue, they were burnt at 850 °C in a muffle furnace. Figure 3 shows the product distribution with respect to the reaction temperature. The yields of the gas and the pyrolysis oil were about 58–65 and 26–35 wt %, respectively.

As the reaction temperature increased, the yield of the gas also increased because of the generation of thermodynamically stable gases. On the other hand, the yield of the pyrolysis oil decreased with the decrease in the reaction temperature. It was also shown that the reaction temperature did not strongly influence the char and distillation residue yields at the temperature range. In the experiments (runs 1–4), the maximum yield of the BTX aromatics was obtained at 735 °C. As the reaction temperature increased, the toluene and xylene contents sharply decreased. As a result, the yield of the BTX aromatics decreased at 773 °C. In run 8, which was carried out at 719 °C, the BTX aromatics made up 18 wt % of the total organic product, which was the maximum yield of the BTX in the experiments. The production of styrene seems to have been mainly due to the degradation of PS in the mixed plastics. A trace amount of oxygen compounds was also produced. The amount of the BTX aromatics in the experiments can be compared to that of an earlier experiment carried out in the Hamburg process with mixed waste plastics mainly composed of polyolefin (about 65%) and PS (about 14%).[8] The experiments in the Hamburg process produced the BTX aromatics up to about 20 wt % of the total input of organics. The difference between two experiments is mainly due to the difference in feed composition and reactor dimension.

Table 3 shows the organic mass balances of the pyrolysis products.

3.2. Product Gas. The gas product was composed mainly of methane, ethene, ethane, propene, butadiene, butane,

Figure 4. Development of the oil composition, with respect to the reaction temperature.

Table 3. Organic Mass Balance of the Pyrolysis Products

product	run 1 (677 °C)	run 2 (710 °C)	run 3 (735 °C)	run 4 (773 °C)	run 5 CaO (690 °C)	run 6 CaO (711 °C)	run 7 Ca(OH)$_2$	run 8 Ca(OH)$_2$	run 9 oyster shell	run 10 rice straw
gases (sum)	57.8	61.2	61.9	64.4	58.1	61.7	60.9	59.9	59.5	60.5
hydrogen	0.3	0.3	0.4	0.6	0.4	0.4	0.4	0.5	0.4	0.4
carbon monoxide	0.8	1.6	2.3	1.8	1.8	2.5	2.2	3	3.2	1.4
carbon dioxide	1.5	0.8	0.9	2	0.7	0.3	0.6	0.8	3.1	2.1
methane	17.5	21.7	25.8	31.6	18.4	20.9	21.4	22.5	20.6	23.7
ethene	13.2	15.9	17.1	18.2	14.6	16	15.8	15.3	14.7	15.7
ethane	6	5.7	4.8	3.7	6.3	5.6	5.5	5.1	4.8	5.1
propene	11	9.3	6.6	3.8	7.8	9.7	9.2	7.3	7.7	7.4
propane	0.8	0.6	0.3	0.2	0.9	0.6	0.6	0.4	0.5	0.4
butane	3.5	2.5	1.5	0.6	3.7	2.6	2.4	1.8	2.0	1.9
butadiene	1.4	1.4	1.2	1.1	1.5	1.5	1.4	1.2	1.3	1.3
others	1.8	1.4	1	0.8	2	1.5	1.4	1.9	1.2	1.1
oils (sum)	35.3	32	29.7	25.9	33.8	30.4	31.1	31.9	31.3	31.9
aliphatics (sum)	4.7	1.9	0.9	0.2	5.9	3	2.7	1.9	1.7	1.4
C$_4$–C$_{11}$	4.2	1.8	0.8	0.2	5.7	2.9	2.6	1.8	1.6	1.3
C$_{12}$–C$_{20}$	0.5	0.1	a	a	0.2	0.1	0.1	0.1	0.1	0.1
aromatics (sum)	30.6	30.1	28.8	25.7	27.9	27.4	28.4	30	29.6	30.5
benzene	5	8.1	8.5	8	7.5	8.5	8.6	9.9	8.7	8.7
toluene	5.9	6.2	5.4	3.8	6	5.7	5.9	6.5	6.2	6.1
xylenes	2	1.6	1.2	0.7	1.6	1.3	1.4	1.4	1.4	1.4
ethylbenzene	1	0.8	0.6	0.3	0.9	0.7	0.7	0.7	0.7	0.7
(1-methyl-2-cyclo propenyl)-benzene	0.7	0.5	0.4	0.2	0.5	0.4	0.4	0.4	0.4	0.5
styrene	4.8	4.3	4.5	3.5	3.9	3.6	3.9	3.7	4	4.3
indane	0.4	0.3	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2
indene	1.4	1.5	1.6	1.4	1	1.1	1.3	1.3	1.4	1.5
naphthalene	1.4	1.8	2.3	3.2	1.1	1.4	1.5	1.8	1.8	1.8
biphenyl	0.2	0.2	0.2	0.3	0.2	0.1	0.1	0.2	0.2	0.2
acenaphthen	0.2	0.1	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.1
fluorene	0.1	0.04	0.1	0.2	0.04	0.04	0.04	0.1	0.1	0.1
others	7.4	4.7	3.9	3.5	5	4.1	4.1	3.9	4.4	4.7
oxygenated compounds	0.04	0.01	a	a	0.02	0.01	0.01	0.01	0.01	0.01
distillation residue	1.9	2.3	2.1	2.5	2	1.8	1.7	2.3	2.0	1.9
char	5	4.5	6.3	7.2	6.1	6.1	6.3	5.9	7.2	5.7

^{a} Not detected.

Table 4. Composition of the Gas Product, with Respect to the Temperature

composition (wt %)	run 1 (677 °C)	run 2 (710 °C)	run 3 (735 °C)	run 4 (773 °C)
H$_2$	0.52	0.53	0.62	0.97
CO	1.42	2.58	3.71	2.75
CO$_2$	2.5	1.3	1.52	3.16
CH$_4$	30.31	35.42	41.72	49.05
C$_2$H$_4$	22.88	25.92	27.56	28.33
C$_2$H$_6$	10.35	9.26	7.75	5.7
C$_3$H$_6$	19.05	15.26	10.59	5.93
C$_4$H$_6$	2.37	2.36	1.98	1.77
C$_4$H$_{10}$	5.99	4.16	2.38	0.92
other C$_n$H$_m$	4.6	3.21	2.16	1.43
HHV (MJ/kg)	46.37	47.84	48.66	49.66

Table 5. Elemental Analysis of the Oils

element	run 1 (677 °C)	run 2 (710 °C)	run 3 (735 °C)	run 4 (773 °C)
C	88.2	88	89.9	90.4
H	8.6	7.9	7.9	7.4
C/H ratio	0.85	0.93	0.95	1.02
HHV (MJ/kg)	40.4	38.3	38.3	40.2

carbon monoxide, carbon dioxide, and hydrogen. Table 4 shows the development of the gas composition with respect to the reaction temperature. With the increase in the temperature, the amount of the gases with thermodynamically stable molecules, such as hydrogen and methane increased, whereas those of ethane, propene, and butane decreased. Carbon monoxide and carbon dioxide might have originated from oxygen-containing polymers, such as PET or polycarbonates. The gas product had a HHV of around 46–50 MJ/kg. Therefore, it seems that it could be used as a heat source for a pyrolysis plant or other fuel applications.

3.3. Pyrolysis Oil. The pyrolysis oils that were obtained after the distillation of the oil products were analyzed via a GC–FID and GC–MS. The water content of the pyrolysis oils was below 0.1 wt %. Figure 4 shows the composition of the pyrolysis oils that were obtained in the experiments (runs 1–4). The maximum BTX aromatics content of the pyrolysis oil was about 51 wt % at the reaction temperature of 735 °C. BTX aromatics can be formed under pyrolysis conditions via the Diels–Alder reaction and dehydrogenation.[13,14] The BTX aromatics increased up to 735 °C and then decreased at 773 °C, whereas the amount of the other aromatics, such as indene and naphthalene, increased at 710–773 °C. The results clearly showed that the monoaromatics, especially toluene and xylenes, which were formed at 735 °C, took part in the formation of polyaromatics at a higher temperature (773 °C). With rising temperatures, the aliphatics content sharply decreased.

Table 5 shows the results of the elemental analysis of the pyrolysis oils. With the increase in the reaction temperature, the C/H ratio of the pyrolysis oil also increased and the maximum C/H ratio of 1.02 was obtained at 773 °C. The C/H ratio indicates the characteristics of pyrolysis oil. Values above the C/H ratio of 1 mean that the oil has an aromatic characteristic.

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Table 6. Metal Content of the Pyrolysis Products

metal	feed material (ppm)	oil (ppm)				char (ppm)				distillation residue (ppm)			
		run 1 (677 °C)	run 2 (710 °C)	run 3 (735 °C)	run 4 (773 °C)	run 1 (677 °C)	run 2 (710 °C)	run 3 (735 °C)	run 4 (773 °C)	run 1 (677 °C)	run 2 (710 °C)	run 3 (735 °C)	run 4 (773 °C)
Al	7.5	2	2	2	2	254.6	548.6	701.7	586.2	2	2	2.7	2
Ba	219.6	1	1	1	1	1625	1375	1162	1603	5.8	3.2	5.4	21
Cr	10.9	1	1	1	1	268.3	560.3	692.7	587.4	1	1	4	3
Zn	53.1	0.04	0.03	0.18	0.14	573.9	396	200.9	482.8	5	5.2	12.2	24.3
Pb	26.3	0.02	0.04	0.01	0.01	633	488.5	241.7	644.8	4.6	4.4	9.7	21.5

Table 7. Elemental Analysis of the Char and Distillation Residue

element	char (wt %)				distillation residue (wt %)			
	run 1 (677 °C)	run 2 (710 °C)	run 3 (735 °C)	run 4 (773 °C)	run 1 (677 °C)	run 2 (710 °C)	run 3 (735 °C)	run 4 (773 °C)
C	23.7	24.3	14.8	22.2	94.1	93.7	81.5	91.7
H	0.9	0.9	0.6	0.8	3.1	2.6	3.1	2.6
inorganics[a]	75.4	74.8	84.6	77	2.8	3.7	15.4	5.7
C/H ratio	2.19	2.25	2.06	2.31	2.53	3	2.19	2.94

[a] By difference.

Table 8. Chlorine Content of the Pyrolysis Oil

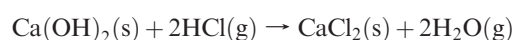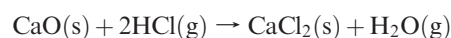| experiment	feed material	run 1 (677 °C)	run 2 (710 °C)	run 3 (735 °C)	run 4 (773 °C)	run 5 CaO (690 °C)	run 6 CaO (711 °C)	run 7 38−40 m^2/g Ca(OH)$_2$	run 8 11−15 m^2/g Ca(OH)$_2$	run 9 oyster shell	run 10 rice straw
		without additive									
chlorine (ppm)	11300	506	502	424	358	74	58	55	50	57	331

Table 6 represents the metal distribution in the pyrolysis products. Most of the metals that were liberated during the pyrolysis seemed to have been adsorbed by the char. As a result, the metal content of the oil was very small. Almost metal-free pyrolysis oils resulted from the efficient filtration by the char removal system of very fine particles. Because of the good performance of the char removal system, the distillation residues also had very low metal contents.

3.4. Char and Distillation Residue. Table 7 shows the results of the elemental analysis of the char and distillation residue. The char contained a high amount of inorganics that originated from the inorganics in the feed material and the sand particles that were used as fluidizing materials. The C/H ratios of the char and distillation residue were 2−2.3 and 2.2−3, respectively, which show a polyaromatic nature.

3.5. Hydrogen Chloride Removal. If the feed material has a chlorine element, chlorinated organic or inorganic compounds are formed during the pyrolysis. The generation of harmful compounds, such as polychlorinated dibenzo-dioxins and polychlorinated dibenzo-furans, is also possible if the feed material has chlorine and oxygen elements.[15] If HCl is generated during the pyrolysis, it may cause corrosion of the pipe and the device and may contribute to the occurrence of acid rain. The HCl content of pyrolysis oil also limits the applicability of the pyrolysis oil as a petrochemical feedstock or fuel oil, because for the processing of pyrolysis oil in existing petrochemical plants, its chlorine content should not exceed 10 ppm.[2] For this reason, the distribution of chlorine among the product fractions and the chlorine content of a single product fraction are very important in estimating the value of the target products and the usability of the byproduct.[16] In the experiments, the chlorine content of the

feed material was 11 300 ppm. It originated mainly from the chlorinated plastics, such as PVC. Table 8 shows the chlorine content of the pyrolysis oil.

For the pyrolysis oils that were obtained from the experiments without additives, the chlorine content was higher than 350 ppm, although it slightly differed depending upon the reaction temperature. Because no chlorinated organic compound was identified in the GC−MS analysis, the chlorine content seemed to have been mainly due to HCl. To absorb the HCl, four additives were applied to the feed material. The HCl that was generated during the pyrolysis reacted with the absorbents to produce solid salts. Calcium oxide, calcium hydroxide, and crushed oyster shells were added to the feed material thrice at stoichiometric amounts. Up to 3 wt % of the rice straw was added to the feed material. Some alkali and alkaline earth metals, such as K, Na, Ca, and Mg, can be found in high concentrations in biomass. For example, potassium is a macronutrient for plants, and it is a highly mobile element in plants, moves to younger and actively developing tissues, and exceeds 1% dry matter in annual growth tissue.[17] Alkali and alkaline earth metals have low melting points and densities and may be volatilized into the flue gas during pyrolysis, which would cause their adhesion to the wall of the reactor or the piping that would worsen the heat transmission. They can also react with halogens to form ionic salts. The additives that were applied in the experiments can be reacted with HCl as follows:[18]

$$CaO(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(g)$$

$$Ca(OH)_2(s) + 2HCl(g) \rightarrow CaCl_2(s) + 2H_2O(g)$$

$$CaCO_3(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(g) + CO_2(g)$$

Runs 5 and 6 were carried out to investigate the effect of the calcium oxide at different reaction temperatures.

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At higher temperatures (>600 °C), the reaction between CaO and HCl was first chemical and then was a combined chemical reaction and product layer diffusion. The binding capacity of CaO to HCl peaked at 500−600 °C in the fluidized bed.[19] Daoudi and Walters found out in their experiments that CaO conversion levels increased at lower temperatures. This is due to high-temperature sintering, which increases grain diffusion resistance.[20] The experimental results (runs 5 and 6), however, showed no greater difference in the chlorine removal efficiency, mainly because of the negligible difference between the reaction temperatures.

One important parameter that affects chlorine removal is the specific surface area. For effective heterogeneous reactions, additives should have higher specific surface areas. Runs 7 and 8 were performed to investigate the effect of calcium hydroxide with different specific surface areas. Calcium hydroxide that had a specific surface area of 38−40 m^2/g was used in run 7, and calcium hydroxide with a specific surface area of 11−15 m^2/g was used in run 8. The experimental results showed only a slightly enhanced effect with the calcium hydroxide that had a bigger specific surface. In the experiments, calcium hydroxide showed better results than calcium oxide. Run 9 was carried out with crushed oyster shells. Korea generates 0.3 million tons/year of oyster shells, approximately 0.15 million tons of which are continually disposed by dumping them on coasts.[21] Oyster shells are composed mainly of $CaCO_3$.[22] The results of the experiment with crushed oyster shells were similar to those in the experiment with $Ca(OH)_2$, which stimulates the reuse of waste oyster shells. Run 10 was performed to investigate the effect of alkali and alkaline earth metal species, such as Na, K, and Ca, in rice straw for chlorine removal. The contents of alkali and alkaline earth metals were found in a previous study.[23] The effect of chlorine removal in the experiment, however, was minor. The amount of rice straw that was added was limited to 5 wt %, because the pyrolysis of rice straw makes the total oil product heterogeneous and causes phase separation. With respect to the efficiency of the chlorine removal, however, the addition of more rice straw may reduce the chlorine content of pyrolysis oils.

Conclusions

In this study, the effect of the reaction temperature on the product spectrum was investigated. In addition, experiments were carried out to find the best additive for chlorine removal. To absorb the hydrogen chloride liberated from the degradation of PVC, additives (calcium oxide, calcium hydroxide, oyster shells, and rice straw) were added to the feed material. The oil products obtained from the experiments were composed of aliphatics and mono- and polyaromatic compounds. As the reaction temperature increased to 735 °C, the BTX aromatics content of the oil increased. The maximum yield of the BTX aromatics was obtained at 719 °C (run 8), with a value of 18 wt % of the organic product. The main compounds of the gas product were CH_4, C_2H_4, C_3H_6, C_4H_6, and C_4H_{10}, and the gas product had a HHV of about 50 MJ/kg. Because of its high caloric value, it can be used as a heat source for a pyrolysis plant or other fuel applications. The pyrolysis oil had almost no metal content. The metals were concentrated in the char. The cyclone and hot filter system almost perfectly removed the fine char particles. The amount of chlorine in the pyrolysis oils that were obtained without additives was above 350 ppm. To reduce the HCl that was liberated during the pyrolysis, various additives (calcium oxide, calcium hydroxide, crushed oyster shells, and rice straw) were added to the feed material. The calcium oxide, calcium hydroxide, and oyster shells significantly influenced the HCl removal to produce pyrolysis oils with a chlorine content of about 50 ppm. The application of oyster shells as absorbents of HCl presents the possibility of their reuse. The pyrolysis oils that were obtained by applying the additives can be mixed with fresh oil to dilute the HCl concentration, and the diluted oil can then be processed in petrochemical plants. To summarize, the liquid and gas products that were obtained from the experiments had good characteristics for use as petrochemical feedstock or fuel oil.

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