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The influence of reaction parameters on characteristics of pyrolysis oils from waste high impact polystyrene and acrylonitrile–butadiene–styrene using a fluidized bed reactor

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ABSTRACT

The aim of this study was to produce pyrolysis oils from waste high impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene (ABS) in a pyrolysis plant equipped with a fluidized bed reactor. The influence of various reaction parameters, such as temperature, feed rate and the kind of fluidizing medium, was investigated. The maximum oil yields were about 87 wt.% (474 °C) for the HIPS and 84 wt.% (525 °C) for the ABS. A higher feed rate and the use of product gas as a fluidizing medium were favorable for the oil production. The oils produced from the HIPS pyrolysis consisted chiefly of toluene, ethylbenzene, styrene, cumene, α-methylstyrene and styrene dimers and they appeared to be usable directly as a fuel or chemical source. Main compounds of the ABS pyrolysis oils were similar to those obtained from the HIPS, except for nitrogen-containing compounds. In the nitrogen mass balance of the ABS pyrolysis products, most of the nitrogen was concentrated in the oil with a content of 6.5–7.1 wt.%. The pyrolysis oil from the ABS seemed to require further treatment for its use as a fuel source.

1. Introduction

In Korea, the amount of waste electrical and electronic equipment (WEEE), such as televisions, mobile phones, printers, washing machines and personal computers, has steadily increased as the economy has grown [1]. High impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene (ABS) constitute the majority of WEEE plastics. Generally, the recycling of HIPS and ABS is conducted by pelletization using an extruder which produces low-grade end products, such as pipes, backyard furniture, plastic lumber and plastic/wood composites [2]. Recently, much research has been conducted to convert WEEE plastics into high-grade products. One approach investigated is the application of pyrolysis, a thermal degradation process in which organics are heated and cracked at moderately high temperatures in an inert atmosphere (oxygen-free). Pyrolysis of plastics produces three end-products: oil, gas and char. In particular, fast pyrolysis, which provides a high heating rate and short residence time of pyrolysis vapor, maximizes the oil yield [3]. The pyrolysis of HIPS and ABS containing brominated flame retardants has been extensively investigated. Hall and Williams carried out the pyrolysis of HIPS with decabromodiphenyl ether (deca-BDE) in a fluidized bed reactor and concluded that most of bromine was concentrated in the pyrolysis oil [4]. Bhaskar et al. pyrolyzed ABS with tetrabromobisphenol A (TBBPA) in a semi-batch reactor and reported that bromine was concentrated in carbon residue [5]. Bhaskar et al. also carried out the pyrolysis of HIPS containing decabromodiphenyl oxide (DDO) mixed with polyethylene terephthalate (PET) using catalysts (iron and calcium based) and reported that the bromine content in liquid fraction was reduced [6]. Other studies also focused on the removal of bromine [7–15]. However, there has been little research on the thermal degradation of HIPS without brominated flame retardants, whereas the thermal [15] or catalytic [16] pyrolysis of ABS has been investigated in a small glass reactor. Brebu et al. [15] conducted the thermal degradation of ABS and reported a maximum oil yield of 63 wt.% at 440 °C. They also concluded that the main nitrogen-containing compound in the oil fraction was benzenebutanenitrile, which accounted for about 16–19 wt.% of the oil.

Research on the pyrolysis of these two plastics (HIPS and ABS) in a fluidized bed reactor is scarce. A fluidized bed reactor, which offers high heat and mass transfer, shorter residence time of pyrolysis vapor, and constant reaction temperature, provides optimum conditions for fast pyrolysis. Consequently, pyrolysis using a fluidized bed reactor is an adequate technology that can produce fuel oil or chemical feedstock. In this study, two waste plastics (HIPS and ABS) were pyrolyzed in a bench-scale plant. The aim of the study was to determine the optimum reaction conditions (reaction temperature, feed rate and fluidizing medium) for the high yield of pyrolysis oil and to analyze the oil compositions qualitatively and quantitatively. In addition, the behavior of nitrogen in the ABS pyrolysis products (oil, char and distillation residue) was also investigated.

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2. Experiment

2.1. Feed material

Pellet-type waste HIPS and ABS were obtained from a local recycling center in Korea. HIPS is a graft copolymer consisting of a polystyrene backbone onto which chains of polybutadiene are grafted. The butadiene content generally lies between 5 and 10 wt.%. Meanwhile, ABS is a terpolymer whose monomers are acrylonitrile, butadiene and styrene. Prior to the pyrolysis experiments, the feed materials were sieved to obtain a desirable particle size of 2–3.35 mm to facilitate feeding into the pyrolysis reactor. The properties of the sieved materials are presented in Table 1. In the proximate analysis, the volatile matter contents of both feed materials were very high (>95 wt.%). The ash (3.5 wt.%) and nitrogen (6.3 wt.%) contents of the ABS were higher than those of the HIPS.

2.2. Pyrolysis plant

The pyrolysis experiments were carried out in a bench-scale pyrolysis plant that consisted chiefly of a feeding system, fluidized bed reactor, char removal system, quenching system and product gas circulating system. For quantitative feeding into the reactor, two screw feeders were used with variable feed rates (0–5 g/min). The fluidized bed reactor, which was indirectly heated by electricity, was made of a 310 SS tube with a length of 390 mm and an inner diameter of 110 mm. The reactor contained three thermocouples: one located in the freeboard, another in the middle and the other about 10 cm above the distributor. The reaction temperature was determined as the average of the temperature recorded by these three thermocouples. The standard deviation of temperatures of the three thermocouples in a typical experiment was approximately between 5 and 7. The distributor used in this work was a cap-tuyere type which could prevent the fluidized bed material from falling through the distributor plate. The char removal system was comprised of a cyclone and hot ceramic filter, which were designed to capture particles bigger than 10 and 2 μm, respectively. The char removal system was maintained above 400 °C to avoid condensation of pyrolysis vapor during the experiments. The quenching system consisted of one steel condenser, which was water-cooled at 20 °C, and two glass condensers, which were ethanol-cooled at −25 °C. The latter part of the quenching system was an electrostatic precipitator that could capture the aerosol phase of pyrolysis vapor. Non-condensable gas after the quenching system was circulated into the reactor through a pre-heater using a compressor (N0150ATE, KNF). Product gas was sampled using Teflon gas bags (2 L) at ten-minute intervals to analyze its compositions. The excess product gas was combusted via a gas flare to maintain a constant pressure during pyrolysis. A diagram of the pyrolysis plant is shown in Fig. 1.

2.3. Reaction conditions

Table 2 presents the reaction conditions of the experiments with the HIPS and ABS. In each experiment, 0.4 kg of feed material and 3.8 kg of fluidized bed material (quartz sand), the diameter of which was about 0.4 mm, were used. At initial phase of each experiment, the plant was purged with nitrogen gas at a flow rate of 20 NL/min for 2 h to remove any residual air, while the reactor was heated. When the reactor temperature maintained 30 °C above the aimed reaction temperature, the N_2 purging was stopped, and the N_2 in the plant was circulated by a compressor. About 10 min after N_2 circulation, the feeding of the plastics began. Runs 1 to 5 for both the HIPS and ABS were conducted to investigate the influence of reaction temperature on the pyrolysis products. Run 6 for each case was conducted to investigate the influence of feed rate. Runs 1–6 for both the HIPS and ABS were carried out with product gas as the fluidizing medium, while Run 7 used nitrogen. The comparison of Runs 3 and 7 for each case will reveal the effect of the kind of fluidizing medium. In all experiments, the flow rate of fluidizing gas was more than twice that of the minimum fluidizing velocity (u_{mf}), which was determined using the Ergun equation [17]. In each run, the flow rate was corrected with respect to reaction temperature to maintain a constant residence time of pyrolysis vapor in the reactor.

Table 1
Analyses of feed materials.

Proximate analysis	HIPS	ABS	Ultimate analysis[a]	HIPS	ABS
	wt.%			wt.%	
Moisture	0.1	0.4	C	92.2	86.1
Volatile matter	99.3	96.1	H	7.7	7.6
Fixed carbon[b]	0.0	0.0	N	0.1	6.3
Ash	0.6	3.5			

[a] Dry and ash free basis.
[b] By difference.

2.4. Mass balance

In each of the experiments, a mass balance of pyrolysis products was established. After each experiment, the weight of pyrolysis oil was determined by weighing. A homogenized sample of the pyrolysis oil was prepared by stirring it, and then the homogenized oil was distilled. After the distillation, the yields of light oil and distillation residue were measured by weight. The product gas yield was calculated by multiplying the volume of gas produced, which was measured using a gas meter, by the gas density calculated from the GC data. From the GC gas analysis, the portion of higher carbon number than C_4 in the gas fraction was assigned to the oil fraction. The char yield was determined from the difference between the amount of feed material and the sum of pyrolysis oil plus pyrolysis gas.

2.5. Analysis of the feed materials and products

A thermogravimetric analyzer (TGA Q50, TA Instruments) was used to determine the weight loss behavior for both the HIPS and ABS samples. A sample of 10–20 mg was loaded onto the platinum pan, which was then heated from 30 to 600 °C at heating rates of 10 and 20 °C/min. During the TGA experiments, N_2 as a purge gas was introduced into the balance and furnace with flow rates of 40 and 60 mL/min, respectively.

The pyrolysis oil obtained in each experiment was firstly distilled in a laboratory-scale apparatus under reduced pressure (210 °C, 13.3 kPa) to obtain a light fraction. The distillation conditions corresponded to the boiling point of 9H-fluorene. The original pyrolysis oil after distillation was divided into two fractions: a light oil fraction and viscous residue fraction. In this paper, the light oil and viscous residue fractions were designated as oil and distillation residue, respectively. The oil was analyzed using gas chromatography with a flame ionization detector (GC-FID; 7890A, Agilent Instruments) and gas chromatography–mass spectrometry (GC–MS; 5975C, Agilent Instruments). For quantitative analysis, the relative response factor of each component was calculated using the Kaiser equation [18] and then multiplied by the peak area of each component. The applied column used for both GC-FID and GC–MS was an HP-5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness), and helium was used as the carrier gas. For the analysis of oils using GC, the oven temperature was first kept at 40 °C for 10 min, followed by heating to 290 °C at a rate of 4 °C/min and then held for 10 min. The injector and detector temperatures for the GC were 290 and 250 °C respectively. The product gases sampled during the experiments were analyzed by two GC instruments (7890A, Agilent Instruments). One had a thermal conductivity detector (TCD) for the analysis of hydrogen, nitrogen, carbon monoxide, carbon dioxide and methane. The other had