Article

Catalytic Pyrolysis of Waste Polyethylene Terephthalate over Waste Concrete

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Abstract

The feasibility of waste concrete as a catalyst for the effective pyrolysis of polyethylene terephthalate (PET) was examined using thermogravimetric (TG) and pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS) analyses. TG analysis results indicated that the maximum decomposition temperature of PET is not altered by the use of waste concrete, showing similar values (407 ℃ and 408 ℃ at 5 ℃/min). Meanwhile, the volatile product distribution data obtained from the Py-GC/MS analysis revealed that the use of waste concrete promoted the deoxygenation reaction via converting the oxygen containing products such as benzoic acids, benzoates, and terephthalates to valuable deoxygenated aromatic hydrocarbons including benzene, toluene, ethylbenzene, and styrene. This suggests that the waste concrete can be used as a potential catalyst for the production of valuable aromatic hydrocarbons from PET pyrolysis.

Keywords: Polyethylene terephthalate, Aromatic hydrocarbons, Waste concrete, Py-GC/MS

1. Introduction

Owing to the various advantages of plastics, such as their low price, easy machining, smooth processing surface, excellent hardness, and high strength, their consumption has largely been increased in recent decades. Polyethylene terephthalate (PET) has excellent strength, heat resistance, weather resistance, and chemical resistance; therefore, widely used in many industrial processes[1]. Especially, increasing fast consumption of PET in drinking water, beverage and other food packaging industries let the amount of waste PET be increased largely. Although a large amount of PET waste can be recycled, considerable amount of PET waste is still difficult to be recycled by simple material recycling technologies[2] and other thermochemical conversion methods, such as pyrolysis[3], gasification[4], and so on[5], are being emphasized with the increased demand generation of resource recirculation.

Pyrolysis is a thermal conversion method widely applied to waste plastics for the production of liquid fuel, which can be used as a fuel or chemical feedstock. However, the direct use of PET pyrolysis oil is limited due to the high contents of acids, such as benzoic acid and terephthalic acid which can cause corrosion and clogging of pyrolysis plant[6]. Many researchers reported that the additional use of catalysts, such as CaO[7], acid zeolite[8], and metals[9], on the pyrolysis of PET could suppress the formation of acids together with the production of value-added aromatic hydrocarbons which can be used as fuels.

The use of CaO is desirable because of both the proper conversion

efficiency, converting pyrolyzates to aromatic hydrocarbons due to its strong basicity, and its regeneration ability[7]. Waste concrete also contains CaO as its main component and has to be properly recycled. Although the catalytic use of waste concrete to PET pyrolysis can be considered because of its high CaO content and low price, its actual use on the catalytic pyrolysis of PET was not attempted, yet. The use of waste concrete as a catalyst is also an attractive option not only on the environmental aspect but also the overall process costs down.

Therefore, the catalytic pyrolysis of PET over waste concrete was investigated using a thermogravimetric (TG) and pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS) analysis in this study. The proper reaction temperature was concluded based on the thermal and catalytic TG analysis result of PET. The amounts of aromatic hydrocarbons obtained from isothermal flash pyrolysis of PET at different temperatures were compared with those obtained from the catalytic pyrolysis of PET using a Py-GC/MS.

2. Materials and Methods

2.1. PET

PET was obtained from a waste PET plastic bottle used for drinking water containers. This PET was milled, dried at 80 ℃ for 12 h, and sieved to make its particle size below 250 μm. Proximate and ultimate analysis results of PET were performed using the same procedure already reported in our previous literature[10]. The contents of volatiles, fixed carbon, and ash of PET were 91.7, 8.2, and 0.1%, respectively, suggesting a large amount of gas or oil formation by applying the pyrolysis. The contents of carbon, oxygen, hydrogen, and nitrogen of PET were 61.5, 33.9, 4.4, and 0.2%, respectively, owing to PET structure polymerized by ethylene terephthalate monomer unit.

Table 1. Py-GC/MS Condition Applied in This Study

Instrument		Condition
Pyrolyzer	Furnace	500 and 600 ℃
	Interface	320 ℃
GC	Inlet	320 ℃, split ratio 300 : 1
	Carrier gas	He, 1 mL/min
	Oven	40 ℃ (2 min hold) → 20 ℃/min → 320 ℃ (4 min hold)
	Column	UA-5 (30 m length × 0.25 mm inner diameter × 0.25 film thickness)
MS		Scan range, m/z 15~600

Figure 1. Schematic diagram of Py-GC/MS.

2.2. Waste concrete

Waste concrete, emitted in the form of crushed waste from a build reconstruction site located in Gyeongsan-si of Korea, was milled to powder form, sieved to make its particle size below 250 μm, and calcined at 600 ℃ for 4 h prior to its use. The contents of SiO_2, CaO, Al_2O_3, and Fe_2O_3 in waste concrete, analyzed by X-ray fluorescence (XRF), were 38.9, 38.5, 8.3, and 2.7 wt.%, respectively.

2.3. TG analysis

The thermal and catalytic TG analysis of PET were performed by heating 1 mg of PET and 11 mg of PET/waste concrete mixture (PET/waste concrete: 1/10) from ambient temperature to 800 ℃ at three heating rates, 5, 10, and 20 ℃/min under 50 mL/min of nitrogen (N_2) in a TG analyzer (TGA 55, TA Instrument).

2.4. Py-GC/MS analysis

Thermal and catalytic Py-GC/MS analysis of PET over waste concrete were carried out using a micro-furnace type pyrolyzer (EGA/Py-3030D, Frontier Laboratories, Ltd.), which directly connected to a GC/MS (7890A/5975 inert, Agilent Technologies) shown in Figure 1. Detailed explanation for Py-GC/MS system[11] and operation procedure[12] used for the thermal and catalytic pyrolysis studies of polymeric materials were already reported in other literatures. The analytical condition of Py-GC/MS applied in this study was shown in Table 1. Briefly, 1 mg of PET in a deactivated metal cup was inserted to the pyrolyzer heater at different temperatures (500 and 600 ℃). In case of catalytic pyrolysis, 10 mg of waste concrete was additionally

mixed with 1 mg of PET in the sample cup and free-fallen to the pyrolyzer heater. The product vapor, emitted from the pyrolyzer via the thermal and catalytic pyrolysis of PET, was cryo-focused at a capillary column front part for 3 minutes. After 3 min of cryo-focusing time, the product chemicals were separated in the column and detected by MS analyzer. After the analysis, the identification and integration of all peaks on GC/MS chromatogram were performed by comparing the MS spectrum of all peaks with those in MS library (NIST 08th) and integrating each MS peak.

3. Results and Discussion

3.1. TG analysis

Figure 2 shows the non-catalytic TG, and derivative TG (DTG) curves of PET obtained from its TG analysis at different heating rates. PET was mainly decomposed in narrow temperature region, between 350 and 450 ℃, at 5 ℃/min, sharply. The maximum decomposition temperatures (T_{max}s) of PET obtained on its DTG curves at 5, 10, and 20 ℃/min were 406, 419, and 435 ℃, respectively.

Figure 3 revealed the catalytic TG and DTG curves of PET over waste concrete. Although waste concrete was used as the catalyst, the T_{max}s of the first DTG peak (Zone 1) on the catalytic DTG curve of PET at 5, 10, 20 ℃/min, 407, 423, and 436 ℃, respectively, were not different largely with those obtained from the non-catalytic pyrolysis of PET (Figure 2), suggesting no catalytic effect of waste concrete lowering its decomposition temperature. Interestingly, the additional DTG peaks at the higher temperature zones than 500 ℃, Zone 2 (at between 550 and 630 ℃) and Zone 3 (at between 630 and 730 ℃), were observed on the catalytic DTG curve of PET over waste concrete, suggesting the additional emission of chemicals from the mixture of PET and waste concrete. Zone 2 and 3 can be assigned as the decomposition of calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$), respectively[13,14]. Park et al.[10] also found that the large amount of $CaCO_3$, formed during the catalytic upgrading of acids, is decomposed to CaO and CO_2 at the higher temperature than 650 ℃.

3.2. Py-GC/MS

Figure 4 shows the total ion chromatograms (TICs) obtained from the non-catalytic Py-GC/MS analysis of PET at 500 and 600 ℃, respectively. The non-catalytic pyrolysis of PET at 500 ℃ produced benzoates, acids, and terephthalates, as the main pyrolyzates. Although
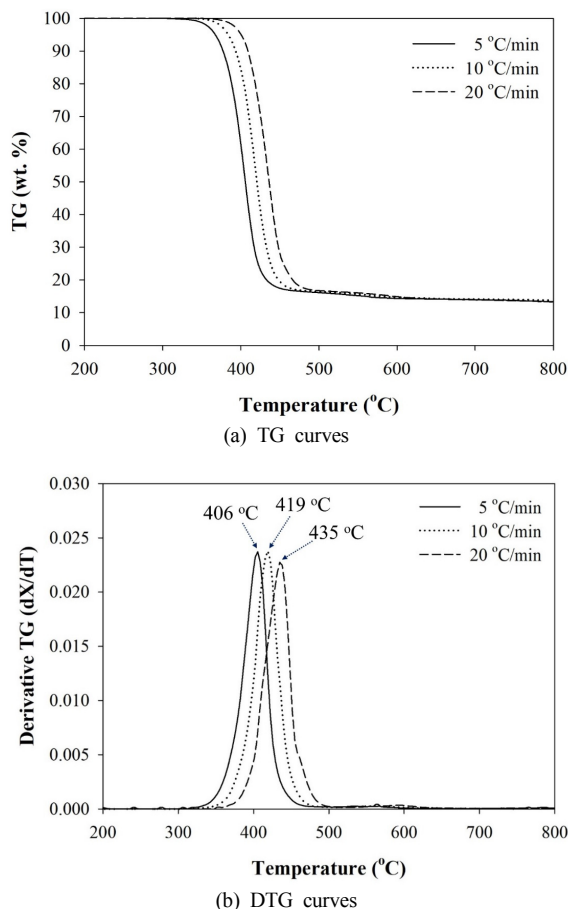
(a) TG curves

(b) DTG curves

Figure 2. Non-catalytic TG and DTG curves of PET at different heating rates.
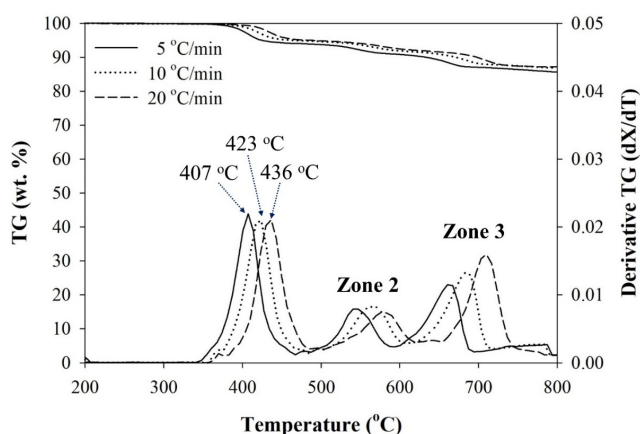

Figure 3. Catalytic TG and DTG curves of PET at 5, 10, and 20 ℃/min.

most of the pyrolyzates, detected on the PET pyrogram obtained at 500 ℃, were also monitored at 600 ℃, their peak intensities were different. The peak intensity of 4-(vinyloxycarbonyl) benzoic acid was decreased together with the increase of small molecular vinyl benzoate, suggesting the increased secondary cracking of PET pyrolyzates at the higher reaction temperature. The formation of aldehydes and acids can influence the pyrolysis process because these acidic pyrolyzates can

cause the corrosion of utility pipeline[15] and the high content of large molecular oxygenates in the pyrolysis oil is not proper to be used as fuel due to their instability[16]. Although stable aromatic hydrocarbons, such as benzene, toluene, and styrene, were also produced by elevating PET pyrolysis temperature to 600 ℃, Figure 4(b), their contents were very small compared to other oxygenates, proposing the necessity of additional catalyst use for the formation of stable aromatic hydrocarbons.

Figure 5 reveals the TICs obtained from the catalytic Py-GC/MS analysis of PET over waste concrete at 500 and 600 ℃. Compared to the non-catalytic pyrolysis of PET, its catalytic pyrolysis over waste concrete had the much larger amounts of aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and styrene. The peak intensities of acids, such as benzoic acid and 4-(vinyloxycarbonyl) benzoic acid, benzoates, and large molecular terephthalates on the TICs obtained from the catalytic pyrolysis of PET were much smaller than those from the non-catalytic pyrolysis. These indicate that the effective role of waste concrete converting acids, aldehydes, and terephthalates to mono aromatic hydrocarbons. Waste concrete has a large amount of CaO which can absorb acids due to its strong basicity[7]. These absorbed acids can produce large amounts of aromatic hydrocarbons via decarboxylation reaction of acids absorbed to CaO at the surface of waste concrete. CO_2 produced the decarboxylation of acids at the surface of waste concrete can convert the surface CaO to $CaCO_3$. $CaCO_3$ also can be decomposed to CaO and CO_2 at the higher temperature, as expected on the catalytic TG analysis of PET over waste concrete (Figure 3). The peak intensities of mono aromatic hydrocarbons produced from the catalytic Py-GC/MS over waste concrete were also increased by elevating the reaction temperature from 500 to 600 ℃. The production amount of aromatic hydrocarbons was also increased largely by applying the higher temperature. This suggests that the more effective formation of aromatic hydrocarbons via the catalytic decarboxylation of acids over CaO can be achieved at the higher reaction temperature. The increased catalytic effect of waste concrete on the formation of aromatic hydrocarbons at high temperatures can be explained with its high content of CaO which can provide the neutralization and catalytic cracking of acids over CaO. Park *et al.*[10] indicated that acids, phenols, and carbonyl compounds over CaO could be converted to ketones and stable aromatic hydrocarbons together with the formation of calcium carbonate ($CaCO_3$). $CaCO_3$ is decarbonated with the formation of CaO and CO_2 at higher temperatures[7]. This can confirm that the catalytic pyrolysis of PET over waste concrete at the higher temperature can lead not only additional production of aromatic hydrocarbons but also increase the overall lifetime of waste concrete as the catalyst.

The re-use of used waste concrete as the catalyst on the catalytic pyrolysis of PET can be considered; however, the low cost and abundance of waste concrete can lower the value of its catalytic re-use. The alternative utility of used waste concrete as a feedstock of cement also can be suggested because of the high content of $CaCO_3$, which can increase the strength of cement[17].
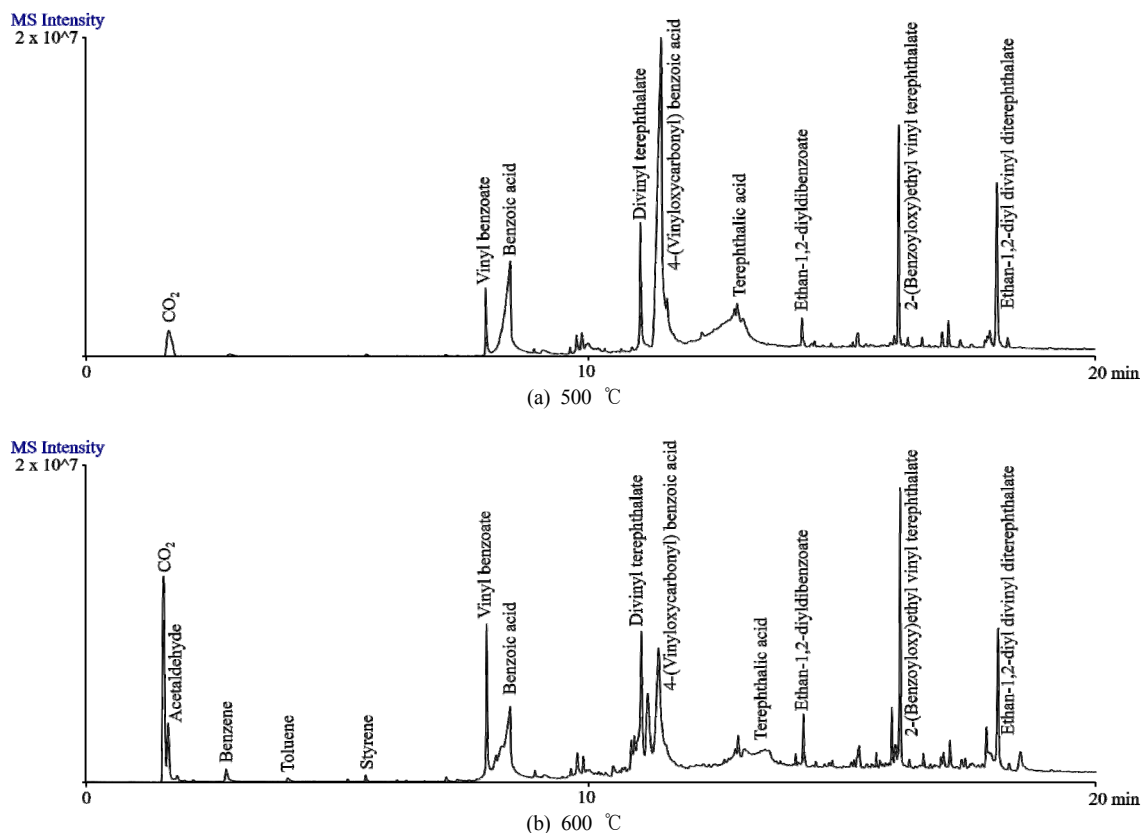
MS Intensity
2 x 10^7

(a) 500 ℃

MS Intensity
2 x 10^7

(b) 600 ℃

Figure 4. TICs obtained from the non-catalytic Py-GC/MS analysis of PET at 500 and 600 ℃.

MS Intensity
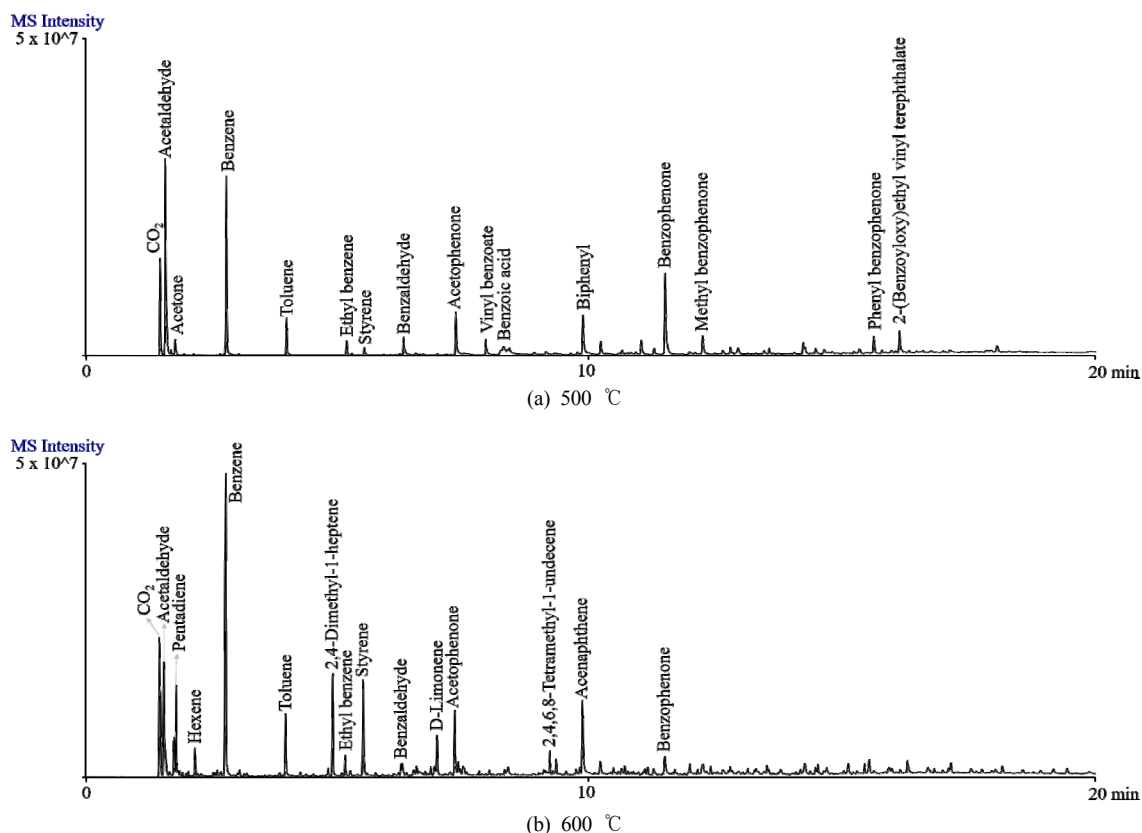5 x 10^7

(a) 500 ℃

MS Intensity
5 x 10^7

(b) 600 ℃

Figure 5. TICs obtained from the catalytic Py-GC/MS analysis of PET over waste concrete at 500 and 600 ℃.

4. Conclusion

In this study, waste concrete was applied as the catalyst to the catalytic pyrolysis of PET for the formation of stable aromatic hydrocarbons for the first time. Although the decomposition temperature of PET was not shifted to the lower temperature by the use of waste concrete, the formation amount of aromatic hydrocarbons on the catalytic pyrolysis of PET was increased via the use of waste concrete. The neutralization and catalytic decarboxylation of oxygenates over CaO were suggested as the main reaction on the additional production of aromatic hydrocarbons during the catalytic pyrolysis of PET over waste concrete.

Acknowledgements

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