Effect of Carbonization Temperature and Reaction Time on Non-Recyclable PET bottle for Char Formation

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Abstract
Carbonization experiments of non-recyclable PET bottles were carried out in using a 2.0 L autoclave reactor to determine the carbonization conditions on the yield of carbonization product. The effects of process variables; the operating temperature (320-480°C) and holding time (60-240 min) were investigated. The maximum yield of fixed-carbon of char 22.0 wt% was obtained at process conditions of 400-480°C and 240 min. The wax phase was also collected, and the characteristics were investigated using GC-MS analyzation, and quantified using HPLC. Results confirmed that wax was mostly made up of benzoic acid. The gaseous phase was quantified using GC-TCD and GC-FID analyzation. Results showed that the gaseous product was mostly made up of CO and CO_2 whereas a small trace of hydrocarbons such as methane and ethane were detected. In this study, it was clarified that high fixed-carbon yield char was obtained at 400-480ºC while only less than 10 C-wt% of CO_2 was emitted during carbonization. This makes the current method highly environmental and potentially commercial for processing non-recyclable PET bottles.

Keywords: Carbonization, PET bottles, Active carbon, Plastic waste, Carbon capture

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Introduction

In 2017, the US had reported only 21% of PET bottle recycling rate. Compared to the US, PET bottle recycling rate in Japan was reported to be 85% (The Council for PET Bottle Recycling, 2017). Although recycling rate seems high in Japan, still 15% of the total PET bottles collected are not recyclable. Here, non-recyclable PET bottles are referred to materials consisting of colored pigment, materials with impurities on surface and materials exposed to long-term UV degradation. These bottles usually lack mechanical strength and thermal stability due to additives and degradation that decrease the purity of polymer (Dutt, et al., 2013;). They have no value to be recycled into other materials and are still usually processed through thermal treatment. Thermal treatment of plastic materials is the least desired approach in waste management due to environmental and health concerns involving the emission of toxic PAHs (Saha, et al., 2005) and GHGs during the incineration of plastic wastes, especially when climate change is a serious global concern. There is still a need to improve the material value of non-recyclable PET bottles in order to mitigate the dependency on thermal treatment.

From all the above exposed, the aim of this research is to improve the material value of non-recyclable PET bottles. To achieve this, non-recyclable PET bottles were treated into char through carbonization. Carbonization is the thermal degradation of materials in the absence of oxygen to produce solid with high carbon content called char. (Ward, et al., 2014; Silva, et al., 2015) This method is widely used for solid waste treatment due to the temperature range sufficient for sterilization of waste, simplicity of the method, ease for bulk treatment and low energy input compared to thermal recycling. Carbonization of PET has advantages in terms of producing valuable precursor for activated carbon due to the high carbon content and absence of mineral matter. (Correa, et. al., 2017; Han, et al., 2019; Vilota, 2018) The aim of this research is to provide an alternative route to improve the material value of non-recyclable PET bottles for the enhancement of the PET bottle recycling cycle. In particular, we plan to treat the non-recyclable PET bottles into char through carbonization, followed by activation of the carbonized product into activated carbon.

In this study, we had conducted carbonization experiments using commercial PET bottles as model feedstock to give a better understanding on the factors in the carbonization of PET using a bench-scaled batch reactor to obtain high char yield. Current studies include the effects of operating temperature and reaction time on char, wax and gas yield.

Materials and Experimental Equipment

As shown in Figure 1, an autoclave reactor made of SUS316 with inner volume of 2.0 L was used in this experiment. The reactor was equipped with an inlet for N_2, an outlet for gaseous products, and a thermocouple to monitor the temperature inside the reactor. The outlet was connected to a heat exchanger followed by a gas-liquid separator, air filter, back pressure regulator (BPR) and finally to a gas bag for collection of gaseous products. φ90 ceramic crucible was placed inside the reactor and approximately 75 g of compressed PET bottles were packed for each experiment. PET bottles were prepared from commercial 500 mL bottles, which were dried overnight with their caps removed. Before each experiment, the reactor was purged with N_2 to remove O_2 from the system to prevent combustion of feedstock. Batch mode runs (Valve 1 and 2 closed) were initiated by heating the reactor from room temperature to set temperature under heating rate of 1ºC/min. After reaching the set temperature, the condition was kept constant until the predefined time. Note that reaction time is set to start when temperature reaches the set temperature. Detailed operating parameters are summarized in Table 1.

Char, wax and gaseous products were collected for analyzation. For char, calorific value, proximate and ultimate value were obtained; for wax, GC-MS analysis was used to identify the chemical compounds while HPLC analysis was used to quantify the compounds; for gas, components were quantified through GC-TCD and GC-FID analysis.

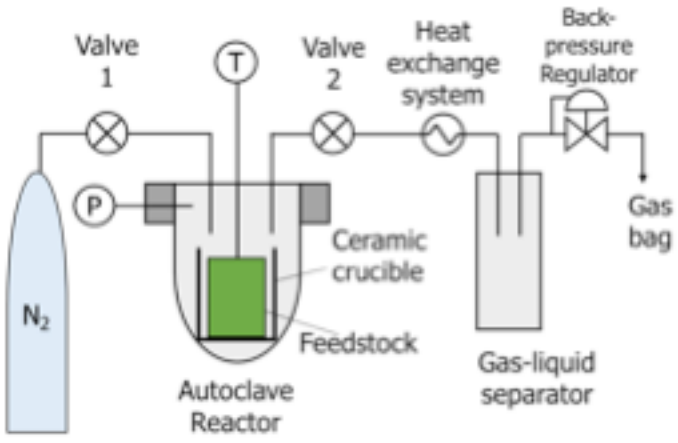

Figure 1: Experimental set-up of carbonization system.

Parameter	Value/Description
Feedstock Type	Clear waste bottle
Feedstock Loading [g]	65-75
Operating Medium	N_2
Operating Temperature [ºC]	320-400, 360-440, 400-480
Operating Pressure [MPa]	0.05
Holding Time [min]	30, 60, 120, 240

Table 1: Operating parameters of carbonization system.

Results and Discussion

Figure 2 shows the yield of char, wax and gas and yield of fixed carbon for operations under different temperature at constant holding time of 120 min; and operations under different holding time at constant temperature of 400-480°C.

In a series of temperature difference, char yield (y_{char}) was obtained as follows: 93 wt% in operating temperature 320-400°C, 37 wt% in operating temperature 360-440°C, 28 wt% in operating temperature 400-480°C; wax yield was obtained as follows: 6 wt% in operating temperature 320-400°C, 39 wt% in operating temperature 360-440°C, 38 wt% in operating temperature 400-480°C; and gas yield was obtained as follows: 1 wt% in operating temperature 320-400°C, 24 wt% in operating temperature 360-440°C, 34 wt% in operating temperature 400-480°C. Yield of fixed-carbon content increased rapidly compared to the raw PET material to give 12 wt% for Run 320-400°C, 16 wt% for Run 360-440°C and 21 wt% for Run 400-480°C. Although Run 320-400°C produced the highest char yield, further analyzation suggested that most of the char are composed of incompletely carbonized part. This explains the low mass fraction of fixed carbon of Run 320-400°C which was comparable to raw PET. The high fixed carbon of char from Run 400-480°C shows that high temperature is favored for the carbonization of PET to produce char with high fixed carbon yield. As a conclusion, the progression of carbonization was more favored under higher temperature.

On the other hand, in a series of different holding time, char yield was obtained as follows: 28 wt% in holding time 30 min, 30 wt% in holding time 60 min, 28 wt% in holding time 120 min and 28 wt% in holding time 240 min. Also, increasing the reaction time of operation had no significant effect on the fixed-carbon yield. This indicates that carbonization was complete at 30 min and increase of holding time did not affect the composition of product obtained.

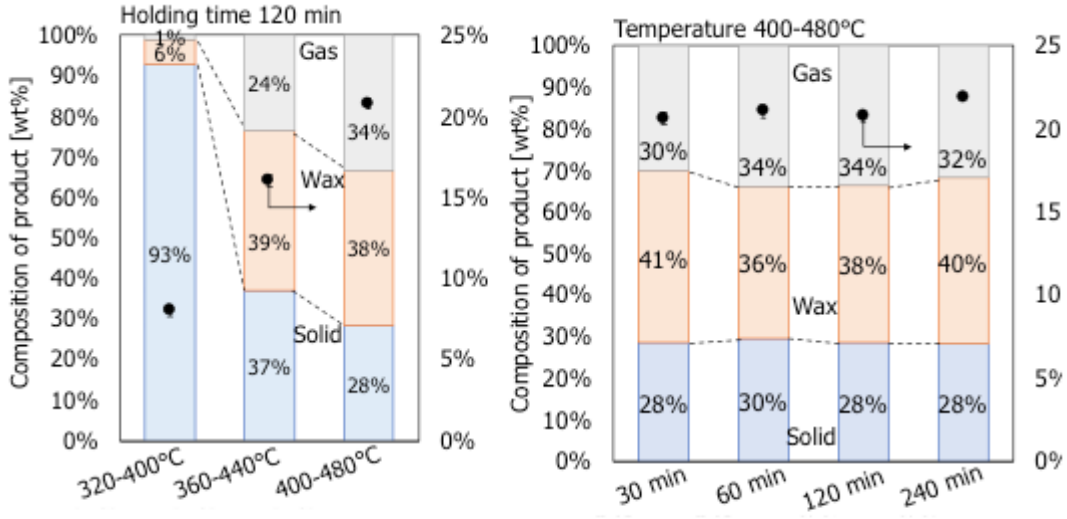

Figure 2: Yield of char, wax and gas and yield of fixed carbon for (Left) operations under different temperature at constant holding time of 120 min; and (Right) operations under different holding time, at constant temperature of 400-480°C.

Fixed-carbon yield (Nunoura, et al., 2006) was calculated by:

$$y_{fC} = y_{char}\left(\frac{\%Fixed\ Carbon}{100 - \%Feed\ Ash}\right)$$

Figure 3 shows the gas composition, wax composition and CHN composition of char obtained from operations under different temperature at constant holding time of 120 min. Results showed that, for wax composition, wax obtained was mainly composed of benzoic acid. For gas composition, gaseous product obtained was mainly composed of carbon monoxide (37 vol%) and carbon dioxide (43 vol%) with small traces of methane (13 vol%) and other hydrocarbons (7 vol%). For char, the carbon content increased while the oxygen content decreased at high operating temperature. As a summary, the composition of products for all phases are largely affected by the operating temperature.

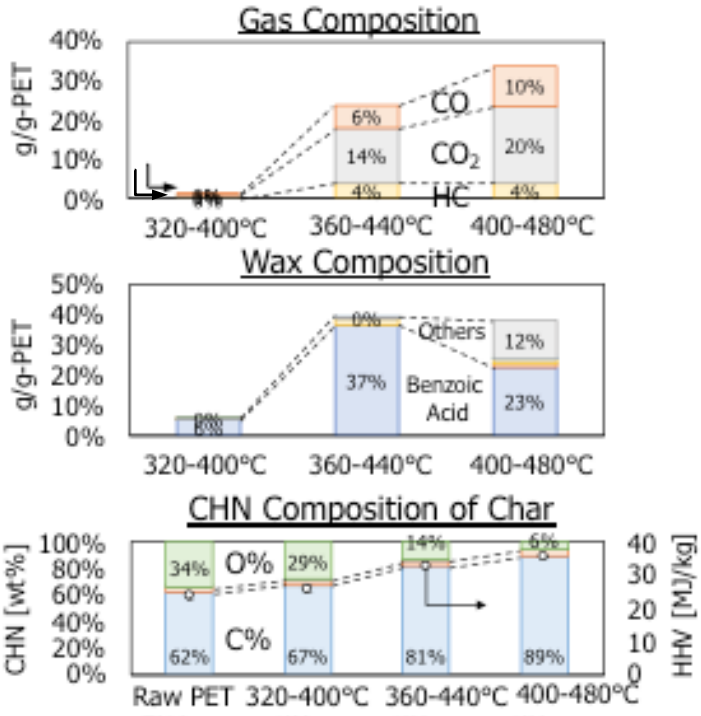

Figure 3: Gas composition, wax composition and CHN composition of char obtained from operations under different temperature at constant holding time of 120 min.

Conclusions

In this study, char obtained from 400-480ºC presents high fixed-carbon yield while only emitting less than 20 wt% of CO_2. This makes the current method highly environmental (less emission of greenhouse gas) and potentially commercial (achievable at 400-480ºC) for processing non-recyclable PET bottles. The carbonization of PET bottles may provide substitute materials for applications such as gas adsorbent. Trapping carbon from plastic waste as char may help reduce greenhouse gas emission and also solve limited landfill problems. Improving the material quality of end product of post-consumed PET bottle may also help enhance the sustainability of the PET bottle cycle.

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