

HYDROLYSIS OF POLYCARBONATE USING A FLUIDIZED BED REACTOR

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Abstract: The hydrolysis of polycarbonate was investigated to recycle the monomer of Bisphenol-A (BPA). Experiments were carried out with a laboratory scale sand bed fluidized by superheated steam. The yield and the selectivity of BPA were examined under various conditions such as bed materials, temperatures and feed rates. The production rate of BPA increased with increasing temperature whereas the selectivity of BPA decreased with increasing temperature. By using olivine sand as a bed material, the hydrolysis rate increased remarkably due to the catalytic effect by minerals in the sand. When the olivine sand was used, the yield of BPA increased with temperature up to 350 °C, and at the temperatures higher than 350 °C, the yield of BPA decreased due to the decomposition of BPA.

1. Introduction

Polycarbonate (PC) is one of the most widely used engineering plastics with high impact strength, strong heat resistance and excellent electrical and optical properties. Its production has been increasing in recent years, and this trend will continue. So, the developing of its effective recycling method is desirable for conserving natural resources. Until now, many studies about the degradation of PC have been reported. The examples include the decomposition by alcohol in a liquid phase[1], the degradation in super critical water[2,3] and the degradation by steam[4-6]. PC has the structure that BPAs are connecting through ester bond. This ester bond is easily broken by hydrolysis at high temperature, and the degradation is promoted by the presence of alkaline earth metals[4,6]. In this study, we performed the hydrolysis of PC with a fluidized sand bed as a reactor to recover the BPA effectively. The mixing of PC polymer with sand effectively increases the reaction surface of polymer with steam. Also, the minerals in the sand revealed a remarkable catalytic effect on the hydrolysis of PC. Therefore the reaction can occur with steam at atmospheric pressure without any organic solvent or expensive high-pressure vessel.

2. Experimental

2.1 Material

The Polycarbonate used in this experiment was PC pellet (CALIBRE™ 200-20, Sumitomo Dow Ltd.). The PC pellet was about 3 mm in size and was used without any preparation. The bed materials used were silica sand, river sand and olivine sand produced in Hokkaido prefecture.

2.2 Equipment and procedure

The experiments were carried out using a laboratory scale fluidized bed reactor with an inside diameter of 52 mm and a height of 600 mm (Fig.1). The reactor was heated to the programmed temperature from outside by an electric heater. Silica sand (130 g), river sand (135 g) and olivine sand(154g) were used as bed materials. Steam was generated by an electrical heating tube and was preheated up to about 500 °C. In order to prevent steam from flowing into a feeder unit, nitrogen gas was continuously sent into the feeder with a flow rate of 200 ml/min. PC pellets were continuously fed into the reactor for 15 min. The experimental parameters such as amount of the feed material and reaction temperature are listed in Tab. 1. The hydrolysis of PC occurs in the fluidized bed, and the vaporized product gas and steam mixture leave the reactor and condenses in a cooling trap chilled with iced water. After each experiment, the solid products were filtered from the condensed water and were dried in a vacuum for a whole day and night. The gas product was collected in a gasbag which was replaced at intervals of ten minutes.

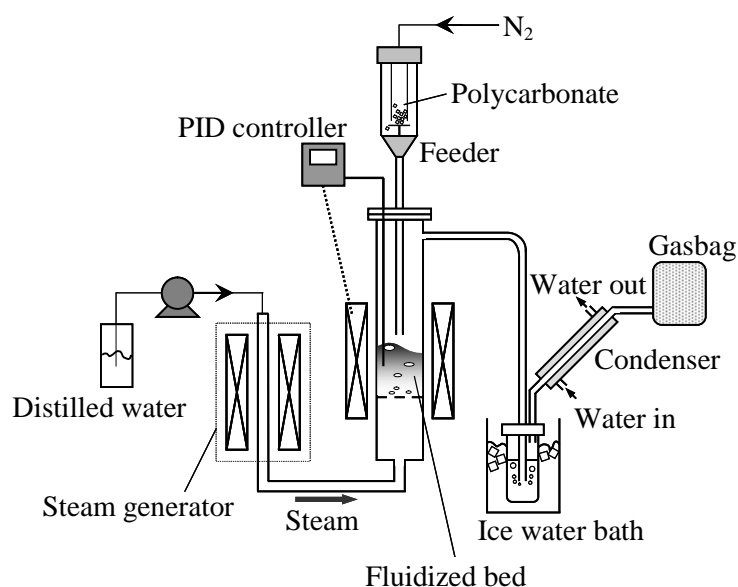


Fig.1 Schematic view of fluidized bed reactor

Tab. 1 Experimental conditions

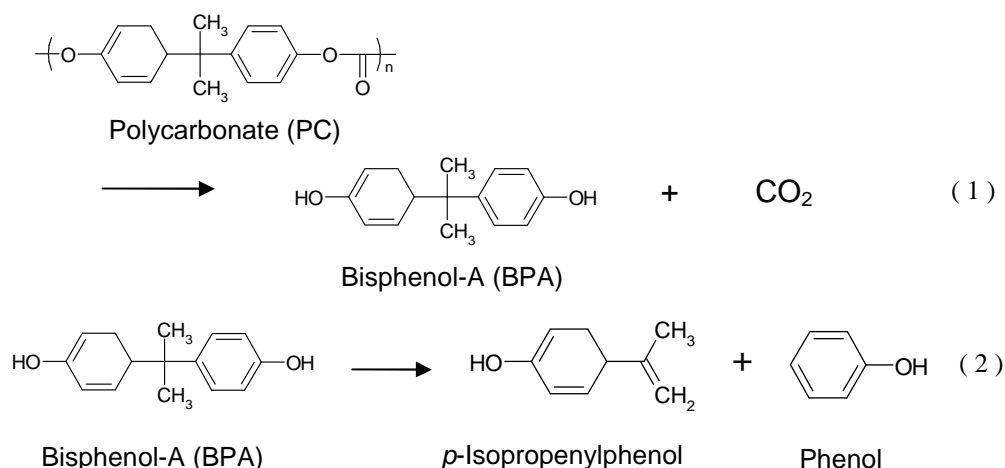
Experiment	Run 1	Run 2	Run 3
Fluidized bed temperature [°C]	400	400	400
Bed material	silica sand	olivine sand	river sand
Total weight of fed PC [g]	5.9	7.0	6.5
Feed rate [g / min]	0.39	0.46	0.44
Ratio of feed to bed material [h ⁻¹]	0.18	0.18	0.19
Water throughput [g / min]	10	9.4	9.3
Steam flow rate [l / min]	12	12	12

2.3 Analysis of reaction products

The solid products were classified into crystalline fraction and resinoid fraction that was a thick sticky liquid. Each of them was weighed by a balance and dissolved in 1-hexanol (Wako Pure Chemical Industries Ltd.). The products contained in the water were extracted with 1-hexanol. The 1-hexanol solutions were quantitatively analyzed by GC-FID (GC-17A, Shimadzu Ltd.) with a capillary column (ULBON HR-1, Shinwa Chemical Industries Ltd.). The qualitative analysis was carried out by GC-MS (GC: GC-17A, Shimadzu Ltd., MS: QP5000, Shimadzu Ltd.). The gas fraction was analyzed by GC-TCD (GC-9A, Shimadzu Ltd.). Residue was defined as the difference of all determined products to 100-wt%.

3. Results and Discussion

The experiments were conducted using three different bed materials. Fig.2 shows the sum of the yield of each component based on the total amounts of PC fed into the reactor. The main components are Bisphenol-A, Carbon dioxide, Phenol and *p*-Isopropenylphenol. Bisphenol-A was the largest composition (component?) in every experiment. Most of the gaseous product was carbon dioxide. Its yield ranged from 16 to 18 wt% and the bed materials did not make much difference. From the result of these products, primary reactions of the hydrolysis of PC were considered to be described by following two equations.



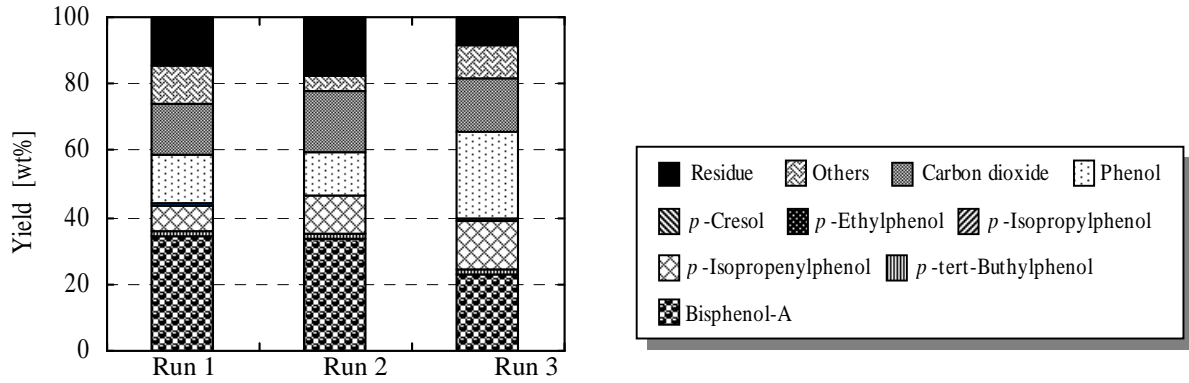


Fig.2 Product yield of the hydrolysis of PC (400 °C)

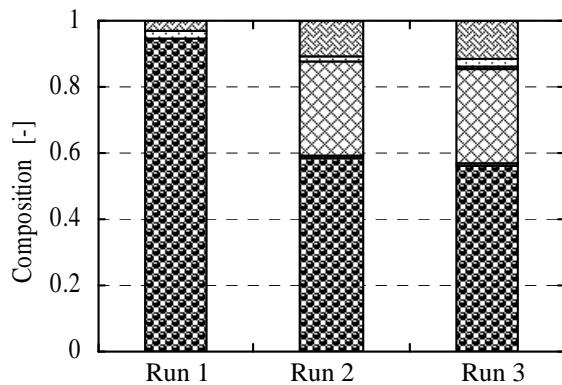


Fig.3 Composition of the crystalline solid

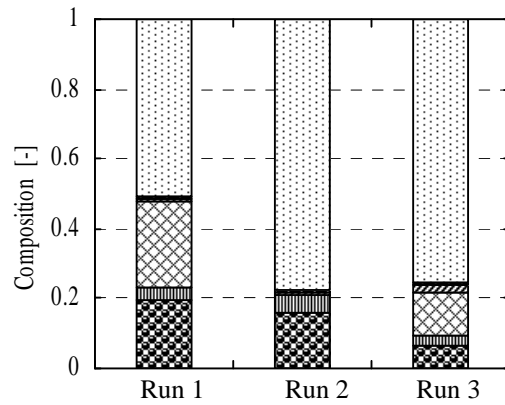


Fig.4 Composition of the water-soluble products

Among the solid product, the ratios of crystalline solid to resinoid solid were 0.45, 1, 0.62 for silica sand, olivine sand and river sand respectively. When the bed material was olivine sand (Run 2), the solid product was almost crystalline product. And it contained about 25wt% of *p*-Isopropenylphenol as shown in Fig. 5 whereas for the bed material of silica sand, the content of BPA was 94 %. As a result, the component yields for silica sand (RUN 1) and olivine sand (RUN2) were not so much different as shown in Fig. 2.

From the comparison of Run 1 and Run 3, the effect of river sand on the hydrolysis products was considered. In Run 3, both the ratio of *p*-isopropenylphenol in the crystalline solid and the ratio of phenol in the water increased. Though the reason for this is not clear, some minerals such as magnesium and calcium in river sand might have accelerated the degradation of BPA.

The main liquid product desolved in the water was phenol as shown in Fig.4. However, some amounts of *p*-cresol, *p*-ethylphenol, *p*-isopropylphenol, *p*-isopropenylphenol, *p*-tert-buthylphenol, BPA were also found to be desolved in the water.

Fig. 5 shows the curves of the production of carbon dioxide versus time. This figure shows that the production rate (Equation (1)) for the case of olivine sand is much larger than that for the case of silica sand or river sand. This may be due to the catalytic effect by the minerals contained in the olivine sand.

Both the hydrolysis reaction rate and the product component changed with temperature. When the olivine sand was used as a bed material, the yield of BPA increased with temperature up to 350 °C, however, at the temperatures higher than 350 °C, the yield of BPA decreased due to the decomposition of BPA as described in Equation (2). Therefore, the maximum yield of BPA was about 58 wt% at 350 °C .

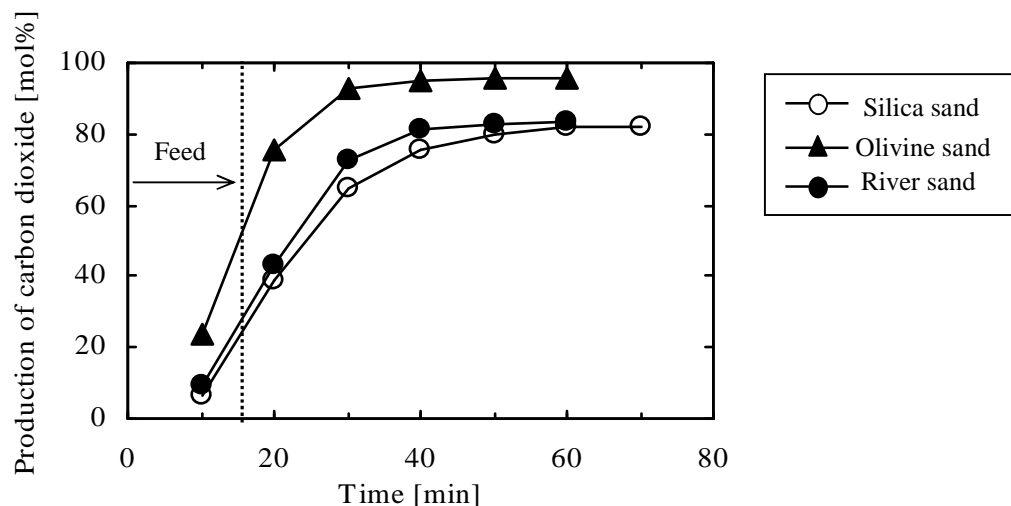


Fig.5 Production of carbon dioxide vs. time (350°C)

4. Conclusions

Polycarbonate (PC) was successfully hydrolyzed in the fluidized sand bed which is very effective to accelerate the reaction rate by increasing reaction surface. The hydrolysis reaction rate increased with temperature. However the selectivity of BPA decreased with increased temperature due to the degradation reaction (Equation (2)). The production rate and the selectivity were also strongly affected by the bed materials used. Especially olivine sand, which contains a large amount of magnesium and some other minerals, showed strong catalytic effect. The maximum yield of BPA was 58wt% in this experiment when the olivine sand was used as the bed material.

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