1-8 Benzene rich oil by the decarboxylation of PET

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1. Abstract

Benzene can be obtained by the hydrolysis and subsequent decarboxylation of PET. Since benzene is a valuable product (the prize increased by 300% in the last four years), it is desirable to obtain a pure product. Since it is possible to obtain pure PET for processing, benzene can be recovered in yields between 70 % and 75 % with a purity of 97 % employing a heating rate of 2 K/min between 300 °C and 500 °C in the presence of CaO in steam atmosphere. CaO accelerates the hydrolysis of PET and decarboxylates the resulting terephthalic acid. CO_2 is mainly absorbed by CaO.

2. Introduction

PET can be obtained as a pure material after use, especially from bottles. Due to this fact, it is possible to focus on the recovery of a single main product depending on the reaction conditions. Terephthalic acid [1] and benzene [2] were obtained in the past in different ways. Especially benzene can be achieved by the decarboxylation of PET in the presence of $Ca(OH)_2$ in high yields (88 %) and purity (79 wt%). But for the production of chemicals, a high purity is as important as a high yield, therefore, it reduces the number of purification steps. In this paper we describe a way of further purification during the pyrolysis of PET in the presence of CaO.

3. Experimental

In opposite to the one-step reactor used with $Ca(OH)_2$ [2], the reaction with CaO was carried out in a fixed bed reactor with two separate controlled heating zones (Figure 1). The sample consisting either of PET (0.40 g) and CaO (1.17 g at each position) or just PET was dropped into the upper heating zone in a semi batch process. The second heating zone was filled with CaO before the experiment was started. The hydrolysis took place in a steam atmosphere over a time of 30 min resulting in terephthalic acid. The hydrolysis products passed the CaO layer with the gas stream and the terephthalic acid was decarboxylized producing benzene. The products were condensed and analysed.

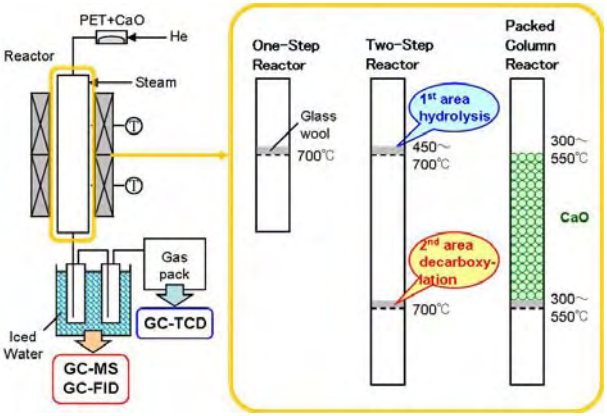

Figure 1 Experimental apparatus

In the packed column reactor, the reactor was filled with 50 g CaO and the sample of 0.50 g PET was added at once when the reactor reached a temperature of 300 °C. Then the temperature increased with heating rates from 2 to 10 K/min to a maximum temperature of 550 °C.

4. Results and Discussion

There were big differences in the product distribution depending on the position of the CaO bed (Figure 2). When CaO was placed in the upper position (450 °C), little benzene was produced. It was possible to double the benzene yield by the deposition of CaO in the lower position at 700 °C. The lack of benzene resulted in the formation of calcium terephthalate in the upper position. It can be seen that terephthalic acid was released slowly, while at this temperature terephthalic acid was little decarboxylated. The deposition of CaO in the lower position led to an effective reduction of terephthalic acid and benzoic acid. The benzene yield increased drastically, when PET was hydrolysed in the absence of CaO in the upper position. The terephthalic acid formed during the hydrolysis was transported unhindered to the lower CaO layer, where it was decarboxylised. The residue consisted mainly of CO_2 and unreacted PET in the upper position and char and CO_2 in the lower position.

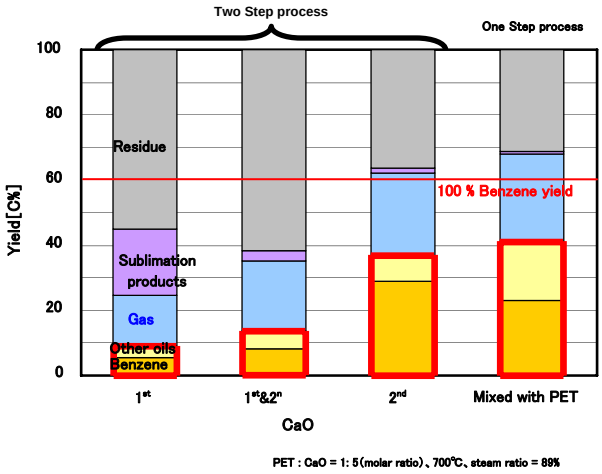

Figure 2 PET-degradation in one and two steps

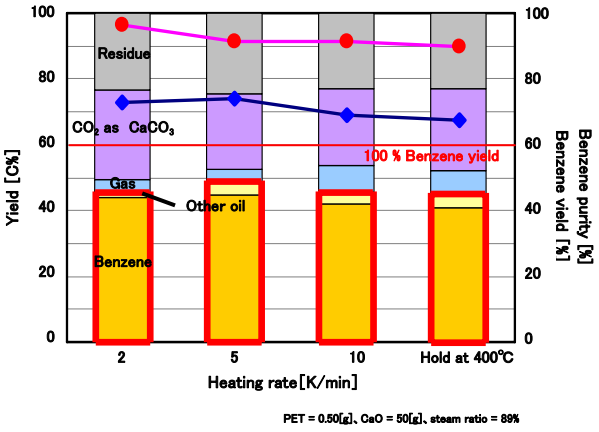

Figure 3 Product distribution at different heating rates

More effective as the two step reactor was the packed column reactor. The highest benzene yield was obtained at a heating rate of 5 K/min (75 %) with a purity of 92 wt%, but the highest purity (97 wt%) was reached at a heating rate of 2 K/min with a benzene yield of 74 %. The results for 10 K/min were similar to an experiment where the temperature was kept at 400 °C over the whole reaction time. The CO_2 was mainly absorbed in the CaO column. The residue might consist of unreacted PET and undecarboxylised terephthalic acid.

5. Conclusion

These experiments show that it is possible to obtain benzene from PET waste in high yields and purity. The best results were achieved with the packed column reactor at a heating rate of 2 K/min. A benzene yield of 74 % with a purity of 97 wt% was obtained. Instead of that, the two step reactor was little effective. Dependent on the CaO position, little benzene with poor purity was obtained. The high temperature of 700 °C in the lower CaO position promoted the formation of biphenyl and especially of char. The formation of char was avoided by the moderate temperature (<550 °C) used in the packed column reactor.

6. References

[1] G. Grause, W. Kaminsky, G. Fahrbach: *Polym. Degrad. Stab.* **85** (2004) 571-575

[2] T. Yoshioka, E. Kitagawa, T. Mizoguchi, A. Okuwaki: *Chem. Lett.* **33** (2004) 282-283