SIMULTANEOUS SILVER AND BENZENE RECOVERY FROM X-RAY FILM

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Abstract

X-ray film consisting of poly(ethylene terephthalate) (PET) was hydrolyzed at a temperature of 450 °C in a steam atmosphere resulting in terephthalic acid (TPA). It was found during earlier investigations that TPA is decarboxylated in the presence of calcium oxide (CaO), and benzene is selectively produced. In this work, silver was recovered during the thermal decomposition of X-ray film and the effect of CaO on the liquefaction of X-ray film was investigated. Benzene yield and purity were promoted in the presence of CaO, resulting in 42% and 78%, respectively. For the purpose of comparison, PET from one-way bottles was pyrolyzed under the same conditions with results showing a similar tendency. Furthermore, 95% of the silver content was recovered during the liquefaction of X-ray film. These results imply that this method can also be applied to other PET based materials containing inorganic substances, which cannot be recycled effectively otherwise.

Keywords: *Pyrolysis, PET, Calcium oxide, Metal recovery, Feedstock recycling*

1. Introduction

Thermal decomposition of waste PET is a feasible alternative for materials containing inorganic substances, which cannot be recycled mechanically. However, terephthalic acid (TPA) and benzoic acid (BA) are formed during the pyrolysis of PET, causing concerns for corrosion and blockage of pipes in the treatment facilities. From our previous work,[1-3] to prevent such negative effects, PET and TPA were pyrolyzed in the presence of calcium oxide (CaO), resulting in oil with a high benzene content and without sublimating substances such as TPA.

In this study, X-ray film consisting of PET and the remaining silver from the photosensitive layer of the film was converted into benzene. Simultaneously, silver was recovered, applying the previous developed process. The film was pyrolyzed in the presence and absence of CaO in order to investigate the effect of CaO on the liquefaction of PET containing silver as an additve. Furthermore, silver recovery yields were investigated. For the purpose of comparison, PET bottles were also pyrolyzed under the same conditions.

2. Materials and Methods

2.1. Materials

Cut PET bottles and X-ray film (2.8 mm × 2.8 mm) were used for pyrolysis experiments. Samples were prepared by the quartering method. CaO, with a particle sizes between 1.0 and 3.0 mm was used as a catalyst.

2.2. Pyrolysis experiments and analytical methods

The experiments were carried out in a quartz tube, embedded in two independently heated electric furnaces which separated the quartz tube in two heating zones: one assigned as “PET hydrolysis chamber” and one as “TPA decarboxylation chamber”, which was filled with CaO. The sample was kept in a perforated sample holder inside the hydrolysis chamber. The CaO bed was calcined prior to the experiment in the decarboxylation chamber for 1h at 900 °C in a He atmosphere in order to decompose potential calcium carbonate ($CaCO_3$). After calcination, the sample was hydrolyzed in the hydrolysis chamber at 450 °C in a steam flow of 327 mL min^{-1} (steam:88 vol%, He:12 vol%). Gaseous TPA from the PET hydrolysis was carried with other gases by the steam flow into the decarboxylation chamber, where it reacted with CaO at 700 °C. Liquid products were gathered in cooling traps cooled by ice and liquid nitrogen. Gaseous products were collected in a gas bag. Silver remained with carbonaceous residue in the sample bag.

For qualitative and quantitative analysis, gaseous products and liquid products were analyzed by gas chromatography (GC-FID, GC-TCD and GC-MS). Recovered silver was analyzed by XRD and ICP-AES. Spent CaO was analyzed by XRD.

All products were standardized on the basis of the sample weight (100 wt%).

3. Results and Discussion

Table 1 shows the elemental composition of PET bottles and X-ray film determined by elemental analysis. The CHO content of PET bottles and X-ray film used for the pyrolysis experiments was approximately the same. Differences to the theoretical composition of PET were negligible. X-ray film contained further silver and bromine from the photosensitive material, and nitrogen from gelatin.

The fractions of benzene, TPA and BA, as well as the benzene purity were slightly higher for PET bottles than

for X-ray film in the absence of CaO (Fig 1), since PET bottles have a higher PET content. However, the same pyrolysis products were observed from PET bottles and X-ray film. More carbonaceous residue was obtained from X-ray film than from PET bottles, since X-ray film might contain high molecular stabilizers.

Table 1. Elemental composition of PET bottles and X-ray film.

Element	PET (theoretical)	PET bottle	X-ray film
Carbon	62.5	61.9	61.5
Hydrogen	4.2	4.3	4.4
Oxygen	33.3	33.7	32.8
Nitrogen	-	-	0.4
Bromine	-	-	0.5
Silver	-	-	0.4

The pyrolysis of X-ray film in the presence of CaO resulted in a strongly increased benzene fraction of 16.9 wt% (yield: 42%) and purity of 78%, respectively. In accordance with the promotion of the benzene fraction, carbonaceous residue decreased. Furthermore, the CO_2 fraction increased, as well, since the decarboxylation of carboxyl groups from TPA was accelerated. The values from the present experiments are smaller than the maximum benzene yield of 74% and purity of 97%, reported in our previous work[2] due to the inefficient hydrolysis of PET.

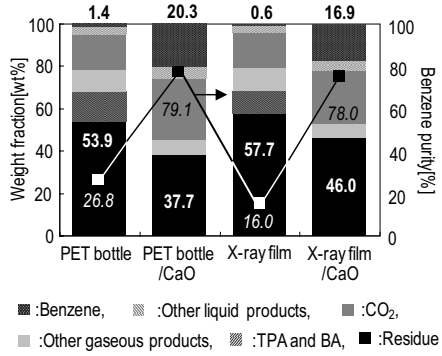
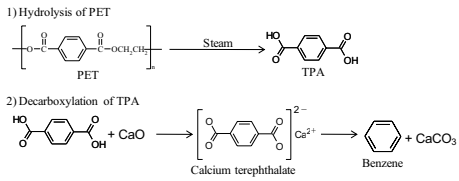


Fig. 1. Pyrolysis product distribution and benzene purity of the product oil.



Scheme 1. Reaction scheme of the degradation of PET in the presence of CaO.

Scheme 1 shows the reaction scheme of the degradation of PET in the presence of CaO. At first, PET is hydrolyzed in steam atmosphere resulting in TPA. The produced TPA is adsorbed at the CaO surface forming calcium terephthalate.[3] In a second step, the carboxyl group of TPA is decarboxylated, resulting in benzene and $CaCO_3$. $CaCO_3$ is decarbonated and CaO is regenerated, allowing readsorption of TPA.

Fig.2 shows XRD pattern of the recovered silver, incorporated in the carbonaceous residue from the hydrolysis chamber. The result indicates that the silver remained as metallic silver. An average of 95% silver was recovered from the initial silver content.

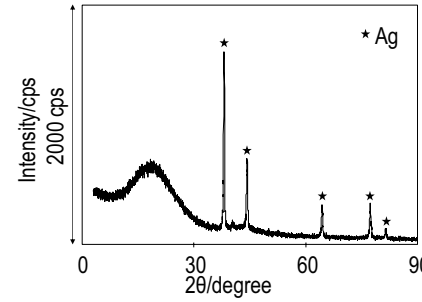


Fig.2. XRD pattern of silver and carbonaceous residue from the hydrolysis chamber.

4. Conclusions

The aim of this research was the investigation of the effect of CaO on the recovery rate of silver and benzene from PET containing X-ray film. From the elemental analysis, it was confirmed that PET bottles and X-ray film have a similar elemental composition. In addition, benzene yield and purity from the degradation of X-ray film were promoted in the presence of CaO, showing 42% and 78% respectively. Furthermore, an average of 95% of silver was recovered from the hydrolysis chamber. Hence, these results imply that the existing process of converting PET into benzene can be applied to X-ray film, and possibly also to PET materials containing other inorganic materials.

References

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