

Hydrolytic Degradation of Poly(ethylene terephthalate) in a Pyrolytic Two Step Process to Obtain Benzene Rich Oil

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ABSTRACT: Poly(ethylene terephthalate) (PET) was degraded in a two step process to obtain a valuable oil, consisting mainly of benzene. First, PET was hydrolyzed in a steam atmosphere at 450°C, and the resulting terephthalic acid was decarboxylized in the presence of CaO. By separating the two fundamental reactions of this degradation process, the hydrolysis reaction and decarboxylation, the amount of residue was reduced, and the amount of benzene obtained increased. It was found that the best results were obtained at a decarboxylation temperature of 700°C, with a yield of 48%

benzene. At lower temperatures, the terephthalic acid was adsorbed at the catalyst without decarboxylation; at higher temperatures, large amounts of char were formed due to pyrolytic reactions. Unlike solvolysis processes, no solvent is used in this process; in effect eliminating the expense of processing waste liquids. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3687–3694, 2011

Key words: recycling; degradation; catalysis; decarboxylation; calcium oxide

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a standard plastic, and has the highest growth in consumption among all plastics. The demand in 2007 was 15 million tons worldwide. The expected annual growth-rate over the next 5 years is expected to be about 7.5%.¹ The majority of this PET is used in the packaging sector, especially for food applications, in the form of beverage bottles and foils. Because of the rising demand, limited resources, and the introduction of stricter legislation, there is an urgent need for efficient recycling methods. PET can be reused after mechanical recycling; however, these materials tend to undergo unwanted degradation during processing, downgrading their properties, and therefore, limiting their applications.² The development of better alternative chemical recycling processes is a real and pressing necessity.

The thermal decomposition of PET between 500 and 700°C does not result in valuable products.³ Little oil is obtained, and the discharge of carbonic

acids like terephthalic acid and benzoic acid cause corrosion and problems with blockages in processing facilities. On the other hand, PET can be a valuable source of chemical materials. In recent years, a variety of different chemical recycling methods have been developed to recover feedstock for the chemical industry. Solvolysis processes using water, methanol, and glycol have been used to gain terephthalic acid,^{4–8} dimethyl terephthalate (DMT),^{9,10} bis(hydroxyethyl)-terephthalate (BHET),^{11–13} and glycol. All of these products can be employed in the production of new PET.

Another way is the use of catalysts to provide a product yield different from the monomers. Some researchers investigated the liquefaction of PET. Masuda et al.¹⁴ gained 56 wt % of oil at 500°C in the presence of steam and an FeOOH derived catalyst. The oil was rich in acetophenone (46 wt %), benzene (28 wt %), and phenol (14 wt %). Obuchi et al.¹⁵ obtained 70 wt % of oil containing aromatic and aliphatic hydrocarbons after the decomposition of a mixture of 15 wt % PET and 85 wt % polypropylene. Active carbon was also successfully obtained by carbonization of PET, using different chemical activators and conditions.^{16–18} Surface areas between 100 and 2500 m² g⁻¹ were achieved.

Very good benzene yields were obtained in the presence of Ca(OH)₂, reaching 88% with a purity of 79%.¹⁹ Other polyesters also release benzene and naphthalene in these conditions.²⁰ The use of Ca(OH)₂/Fe₂O₃ reduced the benzene yield, but improved the benzene purity.²¹ Masuda et al.¹⁴

Additional Supporting Information may be found in the online version of this article.

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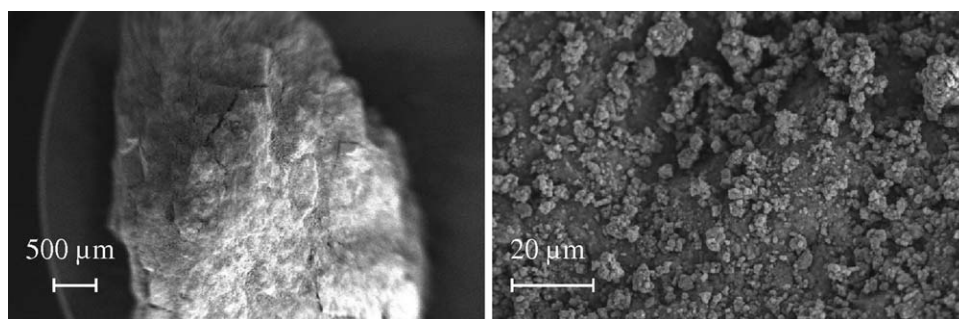


Figure 1 Scanning electro-microscope picture of one CaO particle used for the decarboxylation of PET.

carried out their experiments with the aim of obtaining oil without sublimating products, but without focusing on high benzene yields. The experiments reported by Yoshioka et al.^{19,21} were conducted at comparable conditions. Fine $\text{Ca}(\text{OH})_2$ powder was mixed with PET prior to the input, assuring good contact between the catalyst and the PET. Water was released by $\text{Ca}(\text{OH})_2$ directly at the spot of the PET degradation, resulting in high steam concentrations. This concept ensured high benzene yields; however it is not a suitable procedure for a continuous process, since $\text{Ca}(\text{OH})_2$ can release water only once. In contrast to these earlier papers, the focus of this article was our attempt to test a system that can be used for an extended period of time. This can be achieved by employing CaO instead of $\text{Ca}(\text{OH})_2$.

The decomposition of PET can be divided into two steps. The first step is the hydrolysis of PET, which proceeds without a catalyst and produces high yields of terephthalic acid.²² The second step is the decarboxylation of terephthalic acid, which can only be efficiently achieved in the presence of a catalyst. The efficiency of calcium salts in the decarboxylation of organic acids has long been known.²³

In this study, we investigated the effect of the spatial separation of these two steps, since hydrolysis and decarboxylation occur at different temperatures. The aim of this work is, therefore, to reduce the by-products while increasing both the benzene yield and the purity of the obtained oil with respect to the benzene content.

EXPERIMENTAL

Materials

A commercial PET with a mass average molecular weight of $M_w = 18,000 \text{ g mol}^{-1}$, (Aldrich) was used for these experiments. The PET-pellets (particle size: 3 mm) were grinded and sieved to obtain the 0.15- to 0.25-mm fraction used for these experiments. Since the hydrolysis rate most likely depends on the surface area of the PET melt, the degradation results are not expected to be affected even when the M_w of this PET sample is at the lower end of the range.

Ethanol ($\text{H}_2\text{O} < 0.5 \text{ wt } \%$), terephthalic acid, naphthalene, NaOH, hydrochloric acid, and CaO (Fig. 1) was distributed by Kanto Kagaku. With only one exception [Setup 4 Fig. 2(b)], CaO with a particle

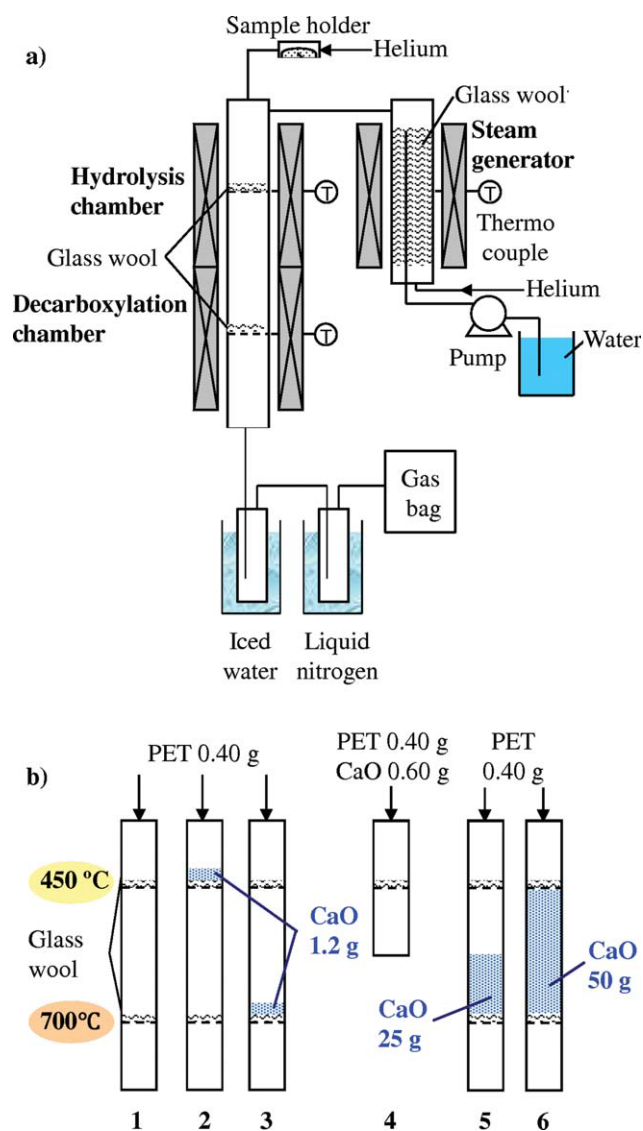


Figure 2 Experimental apparatus: (a) total view, (b) assigned setup for various CaO positions in the reactor. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

size of between 3.0 and 5 mm was used. For Setup 4, the CaO was a fine powder, able to pass through a 106- μm sieve. In all cases, the powders were used as obtained, without any modifications being made.

Pyrolysis experiments

The experiments were carried out in a combined hydrolysis/pyrolysis semibatch process [Fig. 2(a)]. A quartz glass reactor with a length of 730 mm and an inner diameter of 16 mm was heated electrically by two independently controlled 600-W furnaces (Asahi-Rika ARF-40K, Chiba, Japan), each with a length of 300 mm. The furnaces were controlled by two AMF-S controllers distributed by the same company. Two punched quartz glass plates were placed at the same height as the thermocouples controlling the furnaces. The upper plate was removable, allowing the CaO to fill the lower chamber. By placing glass wool at the top of each plate no solid material was able to pass the plates. The upper chamber was set to a temperature of 450°C and used for the hydrolysis of the PET sample. The lower chamber was filled with CaO, and served as the decarboxylation chamber at various temperatures between 600 and 800°C. After the PET sample entered the hydrolysis chamber from the top, the PET powder melted at the top of the glass wool and was hydrolyzed. The resulting terephthalic acid vaporized and was transported with the gas flow into the decarboxylation chamber, where it was decarboxylized in the presence of CaO. The products of the decarboxylation were quickly removed from the hot reactor zone by a constant gas flow (steam: 89 vol %, helium: 11 vol %, atmospheric pressure) of 400 mL min⁻¹ (at standard conditions). The steam was produced at 170°C in a steam generator consisting of an electric heated quartz tube filled with quartz wool. The pipe between the steam generator and reactor was heated by a ribbon heater to 200°C.

To evaluate the effect of CaO, several setups for CaO were tested [Fig. 2(b)]. For Setup 1, no CaO was used. For Setups 2 and 3, 1.2 g of CaO (column height: about 8 mm) was placed in the hydrolysis chamber and decarboxylation chamber, respectively. For Setups 5 and 6, the decarboxylation chamber was filled with 25 and 50 g of CaO, resulting in two columns 150 and 300 mm in height, respectively. For Setup 4, 0.4 g of PET was mixed with 0.6 g of CaO powder prior to the experiment. A smaller particle size was chosen, since the coarse CaO fraction did not pass the input tube without creating a blockage. Since the CaO powder tended to cause high pressure losses at column heights of more than ~ 20 mm, coarse material was used for all setups except of Setup 4.

After stable conditions were reached in both reaction chambers, 0.4 g of the ground PET was dropped in one push from the sample holder into the hydrolysis chamber. The products left the reactor with the gas flow downward. The steam and liquid products were condensed by a cooling trap, which was cooled with iced water. The gases then passed another cooling trap cooled by liquid nitrogen to condense the remaining volatile liquids. The gases were collected in a gas bag. After 30 min of reaction time, the steam was switched off, and the reactor was allowed to cool down. During that time, the reactor was quenched for another 10 min with helium gas to collect all the products formed. The nitrogen trap was defrosted in a constant flow of helium to transfer gases captured in the trap into the gas bag. Then, the reactor and the cooling traps were washed with 50 mL of ethanol. The unified ethanol phase was filtered through a 1GP16 glass frit (Sibata, Tokyo, Japan) to remove any remaining solid materials washed out of the reactor.

Each experiment was conducted twice to verify the results. There were no larger discrepancies observed between two runs under the same conditions.

The residence time of the gas in the CaO layer t_R was calculated by

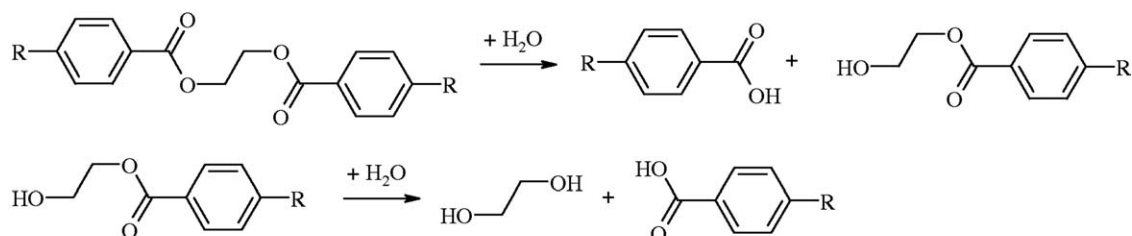
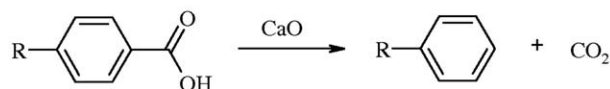
$$t_R = \frac{V_R - \frac{m_{\text{CaO}}}{\delta_{\text{CaO}}}}{\frac{\dot{V}_{\text{gas}, T_{\text{max}}} + \dot{V}_{\text{gas}, T_{\text{min}}}}{2}}$$

with the reactor volume filled with CaO V_R , the CaO mass m_{CaO} , the CaO density $\delta_{\text{CaO}} = 3.34$ g mL⁻¹, and $\dot{V}_{\text{gas}, T_{\text{min}}}$ and $\dot{V}_{\text{gas}, T_{\text{max}}}$ for the gas flow at the minimum and the maximum temperature at the top and the bottom of the CaO layer, respectively.

Analytical methods

The gas composition was analyzed by injecting 10 mL of product gas into a GC-TCD (gas chromatography-thermal conductivity detector) (GL-Science GC-323, Tokyo, Japan), equipped with a packed column (Carboplot P7) [injector temperature: 70°C, temperature program: 40°C (3 min) \rightarrow 10 K min⁻¹ \rightarrow 150°C (5 min), detector temperature: 100°C] using helium as carrier gas (50 mL min⁻¹). The analysis was repeated two times. A typical GC-TCD is given as Supporting Information.

The ethanolic solution of the condensed products was analyzed qualitatively by injecting 1 μL into the GC-MS (gas chromatography-mass spectroscopy) (GC: Hewlett-Packard HP6890, MS: Hewlett-Packard HP5973, Palo Alto, USA) equipped with a GL-Science Inert Cap 5 capillary column [injector: 270°C, temperature program: 50°C (5 min) \rightarrow 10 K min⁻¹

Hydrolysis**Decarboxylation**

Scheme 1 Degradation mechanism of the hydrolysis of PET and the decarboxylation of the resulting acid (R=COOH: terephthalic acid, R=H: benzoic acid).

→ 320°C (3 min), interface: 280°C, helium flow: 2.0 mL min⁻¹]. The mass-spectrometric analysis was carried out at energy of 70 eV in the range between 30 and 300 Da. The analysis of the data was performed by a Hewlett–Packard Standard Chemstation (library: Wiley275.L).

A quantitative analysis was carried out by injecting 1 μL of the ethanolic solution into the GC-FID (gas chromatography-flame ionisation detector) (GC-Science GC-390, Tokyo, Japan) equipped with a capillary column of the same type and set with same temperature program and conditions as those used during the GC-MS analysis. Naphthalene was used as an internal standard for the determination of the product weight. Response factors were calculated by the ECN-method.²⁴ The mass balance was calculated from the results of two consecutive runs. A typical GC-FID chromatogram is given as Supporting Information.

Terephthalic acid precipitated on the walls of the reactor tube in colder areas of the reactor. It was dissolved and removed with 1M NaOH solution. After precipitating with 5M HCl, the terephthalic acid was separated by a 1GP16 glass frit (Sibata, Tokyo, Japan) and balanced. The product was identified by Fourier transformed infrared spectroscopy (Win-IR 165, Bio-Rad, Hercules, USA).

In the discussion, two different values for the characterization of the product distribution and reaction efficiency are used. The weight fraction w given in wt % compares the mass of a certain compound or group of compounds m_c with the initial mass of the PET input m_{PET} :

$$w[\text{wt}\%] = \frac{m_c[\text{mg}]}{m_{\text{PET}}[\text{mg}]} * 100 [\text{wt}\%]$$

Since water is involved in the hydrolysis of the PET, the mass of all products is higher than the mass of

the PET input, resulting in a total mass fraction of more than 100 wt %, when high conversion is achieved.

The second value is the yield η of selected products, including benzene, terephthalic acid, and benzoic acid. The extent to which these products can be formed depends on the stoichiometry of the reaction. The yield η is given by comparing the mass of the compound c m_c with the theoretical mass m_{th} obtained by a complete conversion of the reactants:

$$\eta[\%] = \frac{m_c[\text{mg}]}{m_{\text{th}}[\text{mg}]} * 100 [\%]$$

The purity of benzene P was calculated by the comparison of the benzene mass m_{benzene} with the total mass of liquid products m_{oil} :

$$P[\%] = \frac{m_{\text{benzene}}[\text{mg}]}{m_{\text{oil}}[\text{mg}]} * 100 [\%]$$

RESULTS AND DISCUSSION

Quite unlike polymers, such as polystyrene, polymethyl methacrylate, and polytetrafluoroethylene, PET does not depolymerize by an unzip mechanism. Instead, PET undergoes a step reaction, in which each ester group is hydrolyzed independently (Scheme 1). Once hydrolysis has been completed, the decarboxylation of the resulting terephthalic acid occurs in the presence of CaO, and benzene is released. Ethylene glycol is not obtained as a product. Pyro-GC-MS investigations showed that ethylene glycol decomposes at temperatures higher than 400°C, releasing carbon oxides, formaldehyde, and ethene as products.²²

Hydrolysis and decarboxylation occur at different optimal temperatures, making the spatial separation

of these reactions desirable. It was found that in the fluidized bed, an efficient hydrolysis can be obtained at a temperature of about 450°C.²² The temperature range is limited to the bottom by the sublimation point of terephthalic acid near 400°C and to the top by the increasing pyrolysis temperatures to above 470°C, thus reducing the yield of terephthalic acid.

In contrast to earlier papers, the focus of this article was our attempt to test a system that can be used for an extended period of time. Therefore, we accepted the disadvantages of nonoptimal contact between the catalyst and substrate, and a larger particle size with a reduced surface area. To verify the efficiency of benzene recovery, we determined the following: the influence of the CaO position in the reactor, the reaction temperature of the decarboxylation, and the amount of CaO used.

Effect of the CaO position

These experiments were carried out at a decarboxylation temperature of 700°C. The CaO was placed either in the hydrolysis chamber or in the decarboxylation chamber. The results were compared with those obtained in the absence of CaO in any chamber, and with those obtained from the one step reactor, as described in earlier works.^{20,21}

In the absence of CaO, PET was hydrolyzed at 450°C, and the hydrolysis products passed the empty reactor tube of the decarboxylation chamber at 700°C. As was expected, the hydrolysis resulted mainly in terephthalic acid and benzoic acid, which underwent little degradation during their short residence time in the decarboxylation chamber. Under these conditions, terephthalic acid and benzoic acid yields of 17.4 and 23.3% (14.7 and 14.5 wt %), respectively, were obtained (Table I). Carbon oxides yielded 88% in respect to the PET carboxyl groups. However, it should be noted that ethylene glycol is not recovered, but decomposed, resulting also in carbon oxides.²² Besides the hydrolysis and decarboxylation of PET, pyrolysis took place in the absence of CaO. The most prominent pyrolysis products were benzoic acid (14.5 wt %) and acetophenone (4.6 wt %). Benzoic acid did probably not result from the decarboxylation of free terephthalic acid, since the gas flow would have removed terephthalic acid rapidly from the reactor. More likely, it was formed by the fission of the PET chain between the aromatic ring and the carboxyl group before hydrolysis took place. The hydrolysis of the other carboxyl group resulted in the release of benzoic acid, while the pyrolytic fission of this carboxyl group resulted in benzene (0.2 wt %). Acetophenone was probably formed in the high temperature range in the decarboxylation chamber due to the degradation of volatile oligomers released during the hydrolysis of PET.

TABLE I
Product Distribution After the Hydrolysis of PET and Yields of Important Products at a Hydrolysis Temperature of 450°C and a Decarboxylation Temperature of 700°C: (1) in the Absence of CaO, (2) CaO in the Hydrolysis Chamber, (3) CaO in the Decarboxylation Chamber, (4) Degradation in One Step at 700°C

CaO setup	1	2	3	4
Hydrolysis chamber		X		-
Decarboxylation chamber			X	-
Oil (wt %)	8.8	6.3	25.1	28.7
Benzene	0.2	3.8	19.6	15.6
Toluene	0.2	0.2	0.8	1.8
Styrene	-	-	-	0.8
Acetophenone	4.6	0.9	1.6	4.9
Biphenyl	1.0	0.7	1.8	1.9
Others	2.8	0.7	1.3	3.7
Gases (wt %)	36.4	24.4	49.8	29.3
Hydrogen	0.3	0.4	0.9	1.8
Methane	2.4	3.1	3.3	2.2
Ethene	1.4	0.5	0.4	0.7
Ethane	-	-	-	0.1
Carbon monoxide	13.8	9.9	6.5	17.7
Carbon dioxide	18.6	10.5	38.7	6.9
Solid products (wt %)	29.2	22.0	1.8	0.0
Terephthalic acid	14.7	22.0	1.8	-
Benzoic acid	14.5	-	-	-
Sum (identified products) (wt %)	74.4	52.6	76.7	58.0
Carbon yield (%)	63.7	44.8	63.8	74.4
Benzene yield (%)	0.5	9.4	48.2	38.4
Yields of solid products (%)	40.7	25.7	2.1	-
Yields of carbon oxides (%)	87.9	56.7	106.6	75.7

The CaO setup refers to Figure 2b. The carbon yield refers to the carbon, present in all products detected.
-: not detected.

The acceleration of PET hydrolysis when 1.2 g of CaO was added to the hydrolysis chamber was presumably due to the presence of basic sites. This higher hydrolysis rate reduced the reaction time necessary for the pyrolysis of PET, resulting in an increased terephthalic weight fraction (22.0 wt %) (Fig. 3) and a reduction of pyrolysis products. Most notably, benzoic acid was not observed under these conditions. It is also worth noting that acetophenone was reduced from 4.6 wt % in the absence to 0.9 wt % in the presence of CaO. Because of the slow decarboxylation at 450°C, little benzene (benzene yield: 9.4%, benzene fraction: 3.8 wt %) was obtained, and terephthalic acid yielded 25.7% (22.0 wt %). Compared with the hydrolysis in the absence of CaO, the carbon yield decreased from 63.7 to 44.8 wt %, indicating that organic material was fixed in the CaO layer. The absence of the black discoloration of the layer indicated that carbonization did not take place. It can be assumed that calcium terephthalate was formed, and this led to the reduced carbon yield. The low yield of carbon oxides (57%) underlined the finding that the decarboxylation took place on a limited scale.

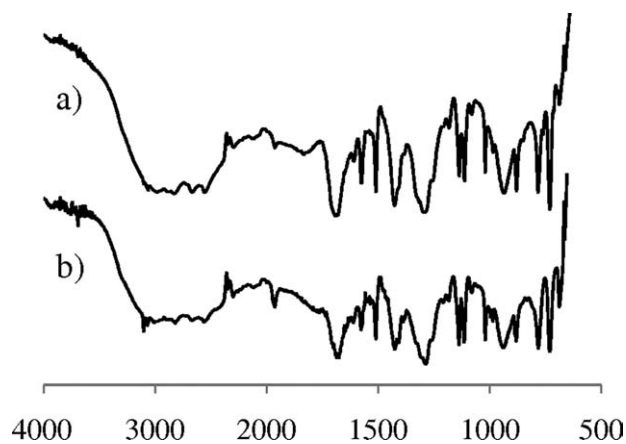


Figure 3 FT-IR spectra of (a) sublimation product, (b) commercial terephthalic acid.

When CaO was present in the decarboxylation chamber, the enhanced formation of benzene (19.6 wt %) was accompanied by a drastic increase in the production of oil. The purity of the benzene in the oil fraction reached 78 wt %. The efficient decarboxylation of the hydrolysis products was also visible in the almost complete decomposition of terephthalic acid and the high yields of carbon oxides, which reached more than 100%. This high yield was also the result of the complete decomposition of ethylene glycol, which was evident by its absence in all of the results. Fewer pyrolytic side products were formed than in the absence of CaO; however, slightly more pyrolysis products were found than in experiments using CaO in the hydrolysis chamber. The CaO in the hydrolysis chamber presumably prevented some of the hydrolysis products from reaching the decarboxylation chamber, where the pyrolysis products were mainly formed.

The results from the two step reactor were comparable with those from the one step reactor. However, the separation of hydrolysis and decarboxylation resulted in better decarboxylation efficiency, and therefore, in higher benzene yields. While the one step reactor yielded only 38.4%, 48.2% was obtained in the two step reactor. The formation of acetophenone in the one step reactor due to the expanded residence time in the 700°C hot temperature zone may explain this difference. Pyrolysis products, such as toluene, also increased in the one step reactor.

Effect of the decarboxylation temperature

Decarboxylation was performed at three different temperatures between 600 and 800°C. At the lowest temperature, 600°C, decarboxylation proceeded very slowly (Table II). Terephthalic acid was the main product, with a yield of about 42.6% (36.4 wt %), and the benzene yield was only 2.7% (1.1 wt %).

Comparable results for the oil composition were obtained when no CaO was used at all (Table I). The yields of solid products were also similar in both cases, with 40.7% in the absence of CaO and 42.6% during the decarboxylation at 600°C. It can be assumed that the decarboxylation rate was still low at this temperature. It may well have been that active catalytic sites were loaded with terephthalic acid and excessive terephthalic acid passed through the catalyst layer without reaction. Decarboxylation at 600°C also resulted in high amounts of pyrolytic by-products. Acetophenone and biphenyl were present to some extent due to the pyrolysis of PET in the hydrolysis chamber (Table I, CaO Setup 1); methane and ethane were observed as the degradation products of ethylene glycol. It can be concluded that the decarboxylation rate at 600°C was too slow to have a strong impact on the product distribution.

At 800°C, terephthalic acid was completely degraded; however, the yield of other aromatic products remained remarkably low. The benzene yield was only 7.5% (3.1 wt %). The main product obtained was carbon dioxide, with more than 50% of the carbon remaining in the decarboxylation chamber as carbonaceous residue.

These results show that this reaction has to be performed in a very narrow temperature range. At low

TABLE II
Product Distribution After the Hydrolysis of PET and Yields of Important Products at Different Decarboxylation Temperatures

Decarboxylation temperature (°C)	600	700	800
CaO setup	3	3	3
Oil (wt %)	6.6	25.1	7.4
Benzene	1.1	19.6	3.1
Toluene	0.2	0.8	0.5
Styrene	-	-	0.6
Acetophenone	3.1	1.6	-
Biphenyl	1.4	1.8	2.0
Others	0.8	1.3	1.2
Gases (wt %)	33.0	49.8	69.7
Hydrogen	0.6	0.9	-
Methane	2.2	3.3	5.4
Ethene	0.4	0.4	0.9
Ethane	3.9	-	-
Carbon monoxide	5.6	6.5	10.1
Carbon dioxide	20.3	38.7	52.2
Solid products (wt %)	36.4	1.8	-
Terephthalic acid	36.4	1.8	-
Benzoic acid	-	-	-
Sum (identified products) (wt %)	76.0	76.7	77.1
Carbon yield (%)	59.7	63.8	47.9
Benzene yield (%)	2.7	48.2	7.5
Yields of solid products (%)	42.6	2.1	-
Yields of carbon oxides (%)	63.5	106.6	148.5

The hydrolysis temperature was set to 450°C. The CaO setup refers to Figure 2b. The carbon yield refers to the carbon, present in all products detected.

-: not detected.

TABLE III
Product Distribution After the Hydrolysis of PET and Yields of Important Products, Using Different CaO Weights and Column Heights

CaO setup	3	5	6
CaO weight (g)	1.2	25	50
CaO column height (mm)	8	150	300
Residence time in the CaO layer (s)	0.06	1.1	2.4
Oil (wt %)	25.1	20.3	8.1
Benzene	19.6	16.4	4.4
Toluene	0.8	0.7	0.7
Styrene	-	-	-
Acetophenone	1.6	-	-
Biphenyl	1.8	2.4	1.9
Others	1.3	0.8	1.1
Gases (wt %)	49.8	55.1	23.6
Hydrogen	0.9	1.3	1.3
Methane	3.3	4.5	6.3
Ethene	0.4	0.3	0.1
Ethane	-	-	-
Carbon monoxide	6.5	0.5	-
Carbon dioxide	38.7	48.5	15.9
Solid products (wt %)	1.8	-	-
Terephthalic acid	1.8	-	-
Benzoic acid	-	-	-
Sum (identified products) (wt %)	76.7	75.4	31.7
Carbon yield (%)	63.8	57.0	26.6
Benzene yield (%)	48.2	40.4	10.8
Yields of solid products (%)	2.1	-	-
Yields of carbon oxides (%)	106.6	107.4	34.7

The CaO setup refers to Figure 2b. The carbon yield refers to the carbon, present in all products detected.

-: not detected.

temperatures, decarboxylation proceeds so slowly that, instead of benzene, terephthalic acid is formed. On the other hand, if the temperature is too high, the acceleration of radical reactions results in the formation of condensed aromatic compounds. The best result in terms of the recovery of benzene was obtained at 700°C, with a yield of almost 50% of the benzene originally present in the PET. Therefore, it can be concluded that temperature has a strong impact on the benzene yield, since a 100°C reductions and rise in the temperature caused the benzene yield to drop below 3 and 8%, respectively.

Effect of the CaO weight

The efficiency of the decarboxylation of terephthalic acid obtained from the hydrolysis of PET was demonstrated in the previous section: the maximum benzene yield of 48.2% was achieved at a decarboxylation temperature of 700°C. Even under these conditions, however, 1.8 wt % of terephthalic acid was observed. Thus, the height of the CaO layer was expanded to investigate the effect of longer residence times of the gas in the active catalytic layer (Table III). The results, however, are not only affected by the CaO weight and, therefore, the

change in the residence time, but also by the height of the CaO column, resulting in the change in the temperature at the top of the catalytic layer. The 1.2 g CaO used in the earlier experiments was about 8 mm high, and it was therefore in the hottest part of the reactor. The use of 25 and 50 g of CaO resulted in column heights of about 150 and 300 mm, respectively, so the columns reached the cooler sections of the reactor. Thus, 630 and 450°C were determined as the temperatures at the top of the CaO layers when 25 and 50 g of CaO, respectively, were used.

Neither terephthalic acid nor benzoic acid was detected at the end of the expanded CaO layers. In addition, the benzene yield dropped from 48.2% at 1.2 g slightly to 40.4% at 25 g, and more radically to 10.8% at 50 g. This is in agreement with the observation made earlier that at lower temperatures the terephthalic acid is adsorbed at the CaO surface, but not decarboxylated. Carbon oxides were also reduced with the length of the CaO column due to the formation of calcium carbonate. No organic products containing oxygen were observed when the amount of CaO expanded, while the amount of other pyrolysis products, such as toluene and biphenyl, were not affected by the amount of CaO. Thus, even though the benzene yield decreased, the purity of the benzene obtained rose from 78 wt % at 1.2 g CaO to 81 wt % at 25 g CaO.

Comparison with earlier results

The spatial separation of the hydrolysis of PET and the subsequent decarboxylation of the resulting terephthalic acid improves the properties of the oil obtained. The hydrolysis at 450°C and decarboxylation at 700°C in the presence of CaO leads to the best results with a benzene yield of 48% and a purity of 78 wt %. Decarboxylation shows high temperature sensitivity. At lower temperatures, the terephthalic acid is adsorbed on the CaO without decarboxylation, while at higher temperatures benzene is condensed due to the formation of

TABLE IV
Decarboxylation of PET Under Several Conditions

Catalyst	Temperature (°C)	Yield (%)	Purity (%)	Ref.
Ca(OH) ₂	700	88	79	19
FeOOH	500	41	29	14
Fe ₂ O ₃	700	37	79	21
Ca(OH) ₂ /Fe ₂ O ₃	700	67	90	21
CaO/H ₂ O (one step)	700	38	54	^a
CaO/H ₂ O (two step)	450/700	48	78	^a

Given is the benzene yield and purity.

^a This investigation.

carboneous residue. The expansion of the amount of CaO reduces the benzene yield, but improves the purity of the obtained benzene. It might be possible to improve the results using a more sophisticated temperature control.

It can be seen from the results in this article that the use of CaO leads to a reduced benzene yield compared with Ca(OH)₂ (Table IV). This result is probably related to the better contact between PET and Ca(OH)₂, since both were mixed prior to the experiment, and the higher steam concentration close to the PET, when Ca(OH)₂ released water in the hot reactor. However, the benzene purity reached comparable levels independent from the use of CaO or Ca(OH)₂.

CONCLUSIONS

This process makes it possible to achieve high quality oil from PET, which is a material that is difficult to recycle. Unlike solvolysis processes, it is not necessary to use solvents in this process. Fillers, other additives, and impurities tend to cause problems during the solvolysis.³ This combined hydrolysis/decarboxylation process, however, may be the key to being able to separate these impurities during hydrolysis, before the terephthalic acid is converted into oil. Therefore, this process might be especially suitable for the recycling of materials with a high content of fillers and other additives, i.e., X-ray films, audio, video tapes. CaO can be added to present calcination processes after use.

References

1. Available at: http://www.plasticseurope.org/DocShareNo-Frame/docs/2/FAHGBPNBMOLNEAEHFBBMDBCFAHGHPN19V95KBTVPDB3/PlasticsEurope/docs/DLS/PEMRG_DataCharts2007_FINAL_PuPuPublicVer20081112-20090129-003-EN-v1.pdf.
2. Krehula, L. K.; Hrnjak-Murgic, Z.; Andricic, B.; Jelencic, J. *ePolymers* 2008, 089.
3. Yoshioka, T.; Grause, G.; Eger, C.; Kaminsky, W.; Okuwaki, A. *Polym Degrad Stabil* 2004, 86, 499.
4. Campanelli, J. R.; Kamal, M. R.; Cooper, D. G. *J Appl Polym Sci* 1993, 48, 443.
5. Lopez-Fonseca, R.; Gonzales-Velasco, J. R.; Gutierrez-Ortiz, J. I. *Chem Eng J* 2009, 146, 287.
6. Yoshioka, T.; Sato, T.; Okuwaki, A. *J Appl Polym Sci* 1994, 52, 1353.
7. Yoshioka, T.; Okayama, N.; Okuwaki, A. *Ind Eng Chem Res* 1998, 37, 336.
8. Zenda, K.; Funazukuri, T. *J Chem Technol Biotechnol* 2008, 83, 1381.
9. Genta, M.; Iwaya, T.; Sasaki, M.; Goto, M. *Waste Manage* 2007, 27, 1167.
10. Kim, B. K.; Kim, D.; Cho, Y.; Han, M. *J Chem Eng Jpn* 2008, 41, 923.
11. Chen, J. W.; Chen, L. W.; Cheng, W. H. *Polym Int* 1999, 48, 885.
12. Shukla, S. R.; Palekar, V.; Pingale, N. *J Appl Polym Sci* 2008, 110, 501.
13. Troev, K.; Grancharov, G.; Tsevi, R.; Gitsov, I. A. *J Appl Polym Sci* 2003, 90, 1148.
14. Masuda, T.; Miwa, Y.; Hashimoto, K.; Ikeda, Y. *Polym Degrad Stabil* 1998, 61, 217.
15. Obuchi, E.; Suyama, M.; Nakano, K. *J Mater Cycle Waste Manage* 2001, 3, 88.
16. Marzec, M.; Tryba, B.; Kaleńczuk, R. J.; Morawski, A. W. *Polym Adv Technol* 1999, 10, 588.
17. Parra, J. B.; Ania, C. O.; Arenillas, A.; Rubiera, F.; Pis, J. J. *Appl Surf Sci* 2004, 238, 304.
18. Terakado, O.; Hirasawa, M. *J Anal Appl Pyrol* 2005, 73, 248.
19. Yoshioka, T.; Kitagawa, E.; Mizoguchi, T.; Okuwaki, A. *Chem Lett* 2004, 33, 282.
20. Yoshioka, T.; Grause, G.; Otani, S.; Okuwaki, A. *Polym Degrad Stabil* 2006, 91, 1002.
21. Yoshioka, T.; Handa, T.; Grause, G.; Lei, Z.; Inomata, H.; Mizoguchi, T. *J Anal Appl Pyrol* 2005, 73, 139.
22. Grause, G.; Kaminsky, W.; Fahrback, G. *Polym Degrad Stabil* 2004, 85, 571.
23. *Ann Chem Pharm* 1851, 80, 285.
24. Jorgensen, A. D.; Picel, K. C.; Stamoudis, V. C. *Anal Chem* 1990, 62, 683.