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Effect of temperature management on the hydrolytic degradation of PET in a calcium oxide filled tube reactor

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ABSTRACT

Poly(ethylene terephthalate) (PET) was hydrolysed and decarboxylised, using a calcium oxide filled column under several thermal conditions, in order to obtain high yields of high purity benzene. The reactions of the hydrolysis of PET and the subsequent decarboxylation of the resulting terephthalic acid were successfully separated by a sophisticated temperature management. While hydrolysis proceeded well at temperatures below 500 °C, the decarboxylation proceeded with a sufficient velocity at about 500 °C. The yield and purity was strongly determined by the extent to which hydrolysis and decarboxylation were separated. At temperatures higher than the optimal temperature for hydrolysis, the resultant side reactions led to both a lower yield and purity of the product, while few by-products were observed when the hydrolysis was completed before the decarboxylation started. The best results were achieved at a heating rate of 2 $K\,min^{-1}$ between 300 °C and 500 °C, with a benzene yield of 74% and a purity of 97 wt.%.

1. Introduction

Poly(ethylene terephthalate) (PET) is the standard plastic with the highest growth in consumption. The demand in 2007 was 15 million tons worldwide. Until 2015, an annual growth-rate of about 7.5% is expected [1]. The majority of this PET is used in the packaging sector, especially for food applications, such as for beverage bottles and foils. Due to a combination of rising demand, limited resources and stricter legislations, the need for efficient recycling methods has become urgent. PET can be reused after mechanical recycling; however, these materials undergo unwanted degradation during processing, resulting in downgraded properties, and therefore, limited applications [2]. This makes it necessary to investigate the possibilities of chemical recycling.

The thermal decomposition of PET between 500 and 700 °C does not result in valuable products [3,4]. Little oil is obtained, and the discharge of carbonic acids like terephthalic acid and benzoic acid cause corrosion and blockages in the processing facilities. On the other hand, PET can be a valuable source of chemical materials. In recent years, a variety of chemical recycling processes have been developed to recover feedstocks for the chemical industry. Solvolysis processes using water, methanol and glycol can be used to gain terephthalic acid [5–9], dimethyl terephthalate (DMT) [10,11], bishydroxyethyl-terephthalate (BHET) [12–14] and glycol from bottle PET, which has a high purity. It may well prove possible to make use of ionic liquids as an alternative for the depolymerisation of PET [15]. Any of the products recovered can be employed in the production of new PET.

If PET contains foreign materials, such as fillers, additives, and other polymers, or is heavily contaminated other ways have to be found to make use of PET. Various catalysts can be employed to get different products from the monomers. Some studies have been focused on the liquefaction of PET. In the presence of a goethite catalyst, Masuda et al. [16] were able to produce a 56 wt.% oil at 500 °C with steam. The oil consisted of 46 wt.% acetophenone, 28 wt.% benzene, and 14 wt% phenol. Obuchi et al. [17] reported that a mixture of 15 wt.% PET and 85 wt.% polypropylene yielded 70 wt% of oil during thermal decomposition. The main products were aromatic and aliphatic hydrocarbons. Active carbon was also successfully obtained by the carbonization of PET using different chemical activators and conditions [18–20]. Surface areas between 100 $m^2\,g^{-1}$ and 2500 $m^2\,g^{-1}$ were achieved. Electro conductive carbon spheres with high hardness were obtained from waste PET under autogenic pressure at 700 °C [21].

Benzene is obtained in high yields from PET in the presence of $Ca(OH)_2$ at a temperature of 700 °C [22]. Other polyesters also release benzene in the same way under these conditions [23]. A mixture of CaO and NiO is an effective catalyst for the production of a synthesis gas [24]. The decomposition of PET can be divided into two steps. The first step, the hydrolysis of PET, proceeds also in the absence of a catalyst with the formation of high yields of terephthalic acid [25]. The second step, the decarboxylation of terephthalic acid, can only be efficiently achieved in the presence

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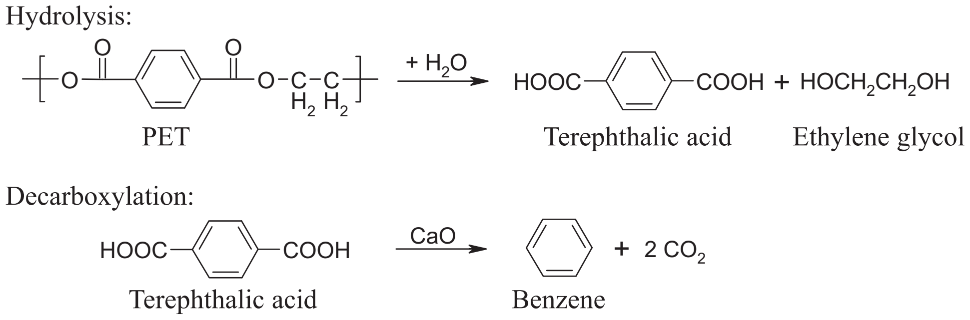


Scheme 1.

of a catalyst. The efficiency of calcium salts in the decarboxylation of organic acids has long been known [26].

Earlier research [22–24] showed promising results in the recovery of benzene using isothermal conditions. However, it became clear from the reaction mechanism (Scheme 1) that both sub steps occur at different optimal temperatures. Ethylene glycol decomposes under these conditions and cannot be recovered [25]. The thermal separation of hydrolysis and decarboxylation should lead to less side reactions and by-products. In contrast, higher benzene yields and purities can be expected. Therefore, the aim of this work is the development of a temperature program, allowing the hydrolysis of PET and the decarboxylation of terephthalic acid at different temperatures, and at the same time, minimizing side reactions.

2. Experimental

2.1. Materials

A commercial PET with a weight average of $M_w = 18{,}000$ g/mol (Aldrich) was used for these experiments. The PET-pellets (particle size: 3 mm) were grinded and sieved to obtain the 0.15–0.25 mm fraction used for these experiments. Common CaO was delivered by Okutama Co. and a grit size between 5 mm and 10 mm was used. Ethanol ($H_2O < 0.5\%$) and concentrated hydrochloric acid (35 wt.%) were distributed by Kanto Kagaku.

2.2. Decarboxylation experiments

The experiments were carried out in a tube reactor (length: 730 mm; inner diameter: 16 mm) (Fig. 1). The reactor was heated by two independently controlled 600 W heaters (Asahi-Rika ARF-40K). The upper heater was connected to a Chino DB1000 controller, making it possible not only to control the isothermal heating profiles but the heating rates as well. The lower heater was controlled by an Asahi-Rika AMF-S controller which only set the isothermal conditions. The temperature in the middle of reactor in height of the lower thermocouple was about 2 °C lower than the temperature of the thermocouple. The reactor was filled with 50 g of CaO resting on a punched plate at the level of the lower thermocouple, which controlled the isothermal maximum temperature of the reactor. The CaO column reached the level of the upper thermocouple, controlling the heating ramp of the upper heater. The top of the reactor was connected with a sample holder. A constant helium flow prevented the condensation of steam in sample holder.

The steam was produced at 170 °C in a steam generator consisting of a heated quartz tube filled with quartz glass wool. Water was pipelined by a silicon tube into the middle of the steam reactor, where it vaporized in contact with the glass wool layer. The dense layer prevented water drops from being entrained by the steam flow before the vaporization was completed. The pipe between the steam generator and reactor was heated by a ribbon heater to 200 °C ensuring that the steam did not condense between steam generator and reactor.

The PET sample was introduced into the tube reactor in one push after reaching the required temperature. Right after the introduction of the sample, marking the starting time of the experiment, the temperature program was started. The terephthalic acid released from the PET during the hydrolysis at the top of the CaO column was transported by the gas flow into the CaO bed, where it decarboxylized in contact with CaO under the formation of benzene and CO_2 (Scheme 1). The products were quickly removed from the hot reactor zone by the constant gas flow (steam: 89 vol.% (286 mg min^{-1}); helium: 11 vol.%) of 400 ml min^{-1} (at standard conditions). The liquid products were condensed in two ice-water cooled cooling traps, and the gas was collected in the gas bag attached. The cooling traps were changed every 30 min, then washed three times with a total of 50 ml of ethanol. The unified ethanol phase was filtered through a 1GP16 glass frit (Sibata) in order to remove residual solid materials.

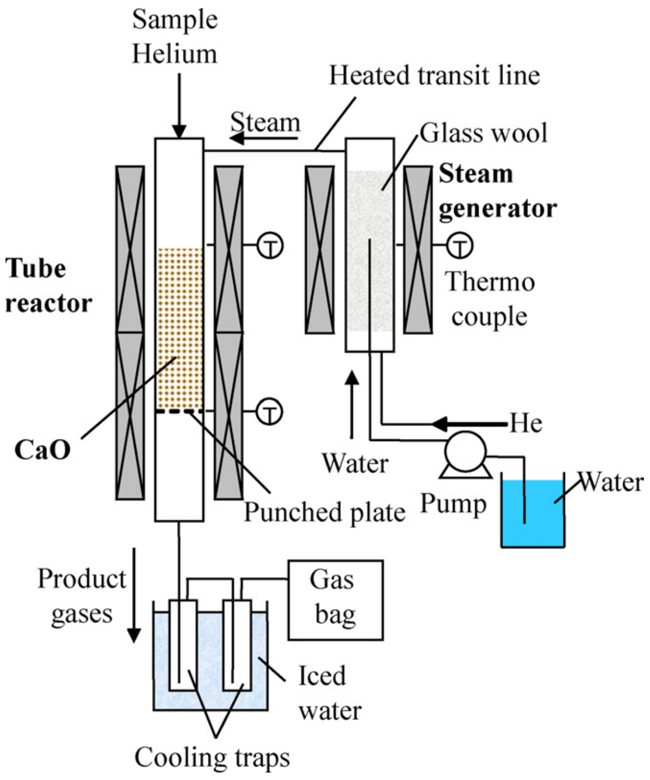


Fig. 1. Experimental setup.

2.3. Analytical methods

The gas composition was analysed by GC-TCD (GL-Science GC-323) with a packed column (Carboplot P7) (temperature program: 40 °C (3 min) → 10 K min^{-1} → 150 °C (5 min)). For the quantification of the gas, 5 ml of ethane standard gas (GL-Science) were added. The ethanolic solution of the condensed products was analysed qualitatively by GC-MS (GC: Hewlett Packard HP6890, MS: Hewlett Packard HP5973) with a GL-Science Inert Cap 5 capillary column (50 °C (5 min) → 10 K min^{-1} → 320 °C (3 min)). The analysis of the data was performed by a Hewlett Packard Standard Chemstation. The quantitative analysis was carried out by GC-FID (GL-Science GC-390) with a capillary column of the same type and the same temperature programme as used for the GC-MS. Naphthalene was used as a standard for the quantification of the different products by GC-FID. The calculation was conducted following the ECN-method [27].

For the determination of the CO_2 content in the CaO layer, 2 g of the homogenized CaO were treated with 10 ml of concentrated hydrochloric acid. The evolved gas was quantitatively transferred into a gas bag by a constant helium gas flow of 20 ml min^{-1}. The gas composition was analysed by GC-TCD as described above.

2.4. Calculated values

The weight fraction [wt.%] was defined as the ratio between the mass of one product or a group of products obtained and the mass of the PET input:

$$\text{weight fraction [wt.\%]} = 100 \times \frac{\text{mass of product [mg]}}{\text{mass of the PET input [mg]}}$$

Note that due to the reaction of PET with steam, the mass of the sum of all products might be higher than 100 wt.%.

The carbon fraction [C%] was defined as the ratio between the molar carbon content in one product or a group of products [mmol] and the carbon content in the PET input:

$$\text{carbon fraction [C\%]} = 100 \times \frac{\text{carbon content in the product [mmol]}}{\text{carbon content of PET input [mmol]}}$$

This value was mainly used for identifying the amount of residue in the reactor, since this value was not directly assessable. The use of the weight fraction did not lead to reliable information, since the product mass was altered by the reaction with steam.

The benzene yield [%] was defined as the ratio between the mass of benzene produced [mg] and the mass of benzene theoretically possible after the complete degradation of PET [mg] according to Scheme 1:

$$\text{benzene yield [\%]} = 100 \times \frac{\text{produced benzene mass [mg]}}{\text{theoretical benzene mass [mg]}}$$

The benzene purity [wt.%] was defined as the ratio between the benzene mass in the oil obtained from the degradation of PET [mg] and the oil weight [mg]:

$$\text{benzene purity [wt.\%]} = 100 \times \frac{\text{benzene mass [mg]}}{\text{oil mass [mg]}}$$

3. Results and discussion

3.1. Isothermal experiments

The isothermal experiments were carried out at 450 °C, 500 °C and 550 °C. After reaching the reaction temperature, the sample, consisting of 0.5 g of PET was introduced in one push into the reactor. The cooling traps and the gas bag were changed every 30 min in order to determine the time dependency of the reaction.

Table 1
Final product distribution under isothermal conditions. The values for wt.% refer to the initial PET mass.

	wt.%		
Temperature [°C]	**450**	**500**	**550**
Reaction time [min]	**540**	**180**	**90**
Liquids	**24**	**32**	**29**
Benzene	21	26	24
Toluene	0.5	1.0	1.4
Styrene	0.1	0.2	0.4
Biphenyl	1.8	2.5	1.7
Others	0.2	1.7	1.7
Gases	**11**	**8.9**	**9.2**
Hydrogen	1.1	0.9	1.0
Methane	1.1	3.1	2.3
Ethene	0.2	0.5	0.6
Carbon monoxide	1.0	0.7	0.4
Carbon dioxide	7.0	3.9	4.9
Sublime products[a]	–	–	–
Carbon dioxide as $CaCO_3$	**59**	**66**	**61**
Sum	**93**	**106**	**100**
Identified products [C%]	**64**	**82**	**75**
Benzene yield	**52**	**65**	**59**
Benzene purity	**89**	**83**	**82**

[a] Terephthalic acid and benzoic acid.

The reaction accelerated with increasing temperature (Fig. 2a). While at 450 °C products were still being released after 9 h, no products were observed after 90 min at 550 °C. At all the temperatures and time periods, benzene was the main product obtained. At 450 °C, the benzene production remained constant at about 5 wt.% h^{-1} for about 4 h, followed by a gradual and slight decrease over the next few hours. The reaction accelerated significantly at 500 °C and 550 °C, reaching degradation rates of 62 wt.% h^{-1} and 70 wt.% h^{-1}, respectively, in the first 30 min. After that, the product evolution decreased sharply to less than 0.5 wt.% h^{-1} after 180 min and 90 min at 500 °C and 550 °C, respectively.

The highest benzene yield (65%) was achieved at 500 °C (Table 1). Lower and higher temperatures resulted in lower benzene yields of 52% and 59% at 450 °C and 550 °C, respectively. Biphenyl and toluene were the by-products with the highest content in the oil. The biphenyl formation showed a correlation with the benzene evolution, resulting in a loss in the benzene yield between 5% and 10%. The slight decrease in biphenyl formation at 550 °C might be explained by the difference in the volume expansion of the gases at 450 °C and 550 °C, but it should be noted that more benzene was obtained at the higher temperature. The two notable effects of the expansion were the decrease in the residence time accompanied by a decrease in the volume concentration of benzene. This would explain the reduction of the biphenyl formation when it is assumed that biphenyl resulted from the condensation of two benzene molecules in the gas phase. Toluene was only observed in the first 30 min (500 °C and 550 °C) to 60 °min (450 °C) of the degradation. The formation of styrene increased with the temperature. Thus, the benzene content of the liquid product reached 89 wt.% at 450 °C, while it was slightly lower at 500 °C (83 wt.%) and 550 °C (82 wt.%). No sublime products, such as terephthalic acid and benzoic acid, were observed at any temperature.

The gas consisted mainly of hydrogen and CO_2 (Fig. 2b), due to decarboxylation of terephthalic acid (Scheme 1) and the degradation of ethylene glycol [25]:

$$HOCH_2CH_2OH + 2H_2O \rightarrow 2CO_2 + 4H_2$$

Most of the CO_2 does actually not appear in Fig. 2b due to the formation of $CaCO_3$. Between 26 C% (59 wt.% at 450 °C) and 29 C%

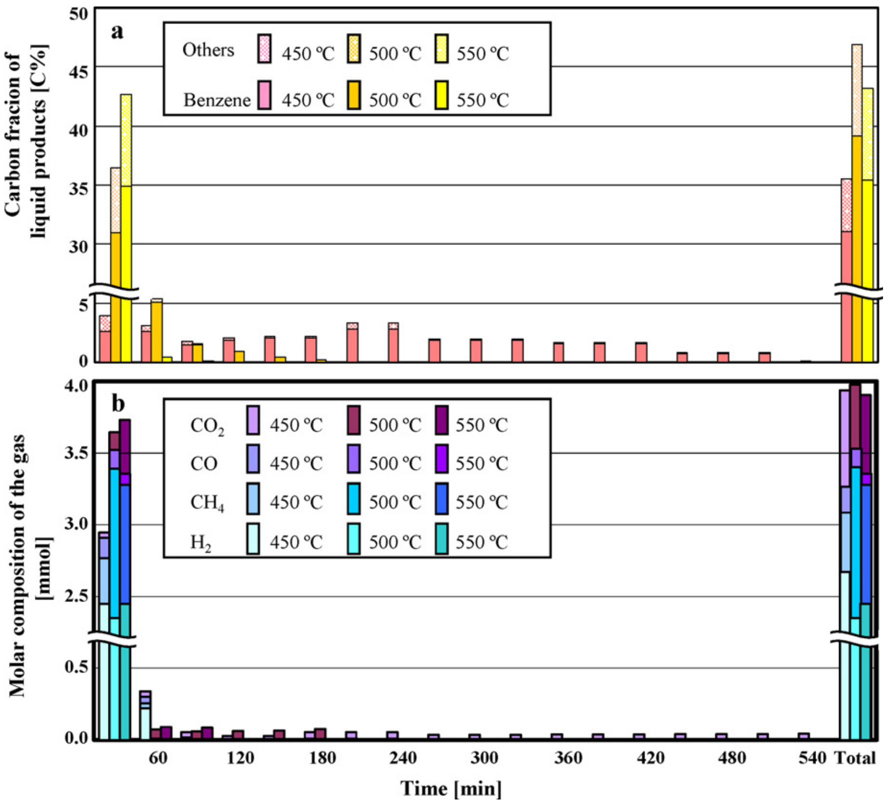


Fig. 2. Time dependence of the product distribution: (a) liquid products and (b) gaseous products. A carbon fraction of 60 C% for benzene would represent a benzene yield of 100%.

(66 wt.% at 500 °C) were fixed as carbonate. Another 1.7 C% (3.9 wt.% at 500 °C) to 3.1 C% (7.0 wt.% at 450 °C) were present in the evolved gases, resulting in about 30 C% released CO_2 from terephthalic acid carboxyl group and ethylene glycol (theory: 40 C%). Hydrogen was mainly formed by the oxidation of ethylene glycol by steam, resulting in a volume fraction of gas between 59% at 500 °C and 68% at 550 °C. Methane, ethene, and carbon monoxide were also present as by-products in the gas phase. The gas composition changed little with the temperature; only methane showed a significant rise at 500 °C. However, gas evolution took considerably less time with increasing temperature.

3.2. *Programmed temperature experiments*

In the previous experiments under isothermal conditions, it was found that the highest benzene yields were obtained at 500 °C. Lower temperatures led to a slower decarboxylation rate and some undecomposed terephthalic acid may have remained at the surface of the CaO particles. Even so, the benzene obtained at 450 °C had the highest purity. The accelerated decarboxylation of the terephthalic acid at 500 °C increased not only the benzene yield, but also amount of by-products, resulting in a reduction in benzene purity.

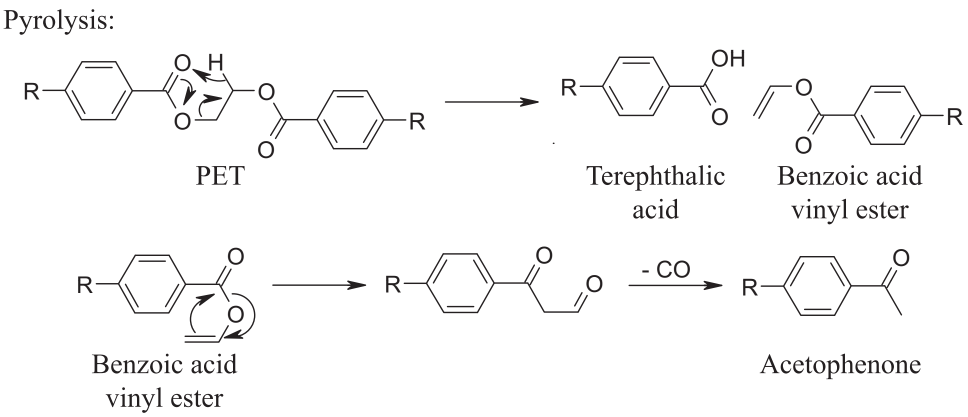
In order to find more accurate thermal conditions for the decarboxylation of the terephthalic acid obtained from the hydrolysis of PET, both a temperature gradient inside the tube and a heating rate were employed. The lower heater was set to 500 °C in order to assure the complete decarboxylation of the terephthalic acid and avoid excessive side reactions. The upper heater was set at first to 300 °C, a temperature at which little reaction was expected. After that, heating rates of 2 K min^{-1}, 5 K min^{-1}, and 10 K min^{-1} were employed in order to rise the temperature to 500 °C. After reaching 500 °C, the temperature was kept constant for another 90 min in order to ensure the completion of the reaction. Further, an experiment was conducted in which the temperature of the tube reactor was kept for 30 min at 400 °C and then heated rapidly to 500 °C for another 90 min. All experiments started with the introduction of 0.5 g of PET in the reactor after constant thermal conditions were reached.

The mild hydrolysis and decarboxylation of PET while using a heating rate resulted in significantly higher yields and benzene

Table 2
Final product distribution after the decomposition of PET employing heating rates of 2 K min^{-1}, 5 K min^{-1}, 10 K min^{-1}, and two isothermal steps (400/500 °C).

Heating rate [K min^{-1}]	[wt.%]			
	2	5	10	400/500 °C
Liquids	**31**	**33**	**32**	**31**
Benzene	30	30	29	28
Toluene	0.1	0.8	0.4	0.4
Styrene	–	–	–	0.1
Acetophenone	0.2	–	0.7	0.7
Biphenyl	0.6	0.9	0.8	0.8
Others	0.1	1.0	0.6	1.0
Gases	**8.6**	**7.7**	**13**	**12**
Hydrogen	1.0	0.6	0.8	0.8
Methane	0.6	0.7	0.7	0.8
Ethene	0.1	0.1	0.2	0.1
Carbon monoxide	0.5	0.6	8.4	4.9
Carbon dioxide	6.4	5.7	3.2	5.6
Sublime products[a]	–	–	–	–
Carbon dioxide as $CaCO_3$	**60**	**52**	**61**	**57**
Sum	**100**	**93**	**106**	**100**
Identified products [C%]	**76**	**75**	**82**	**79**
Benzene yield	**74**	**75**	**72**	**68**
Benzene purity	**97**	**92**	**92**	**90**

[a] Terephthalic acid and benzoic acid.



Scheme 2.

purities than the isothermal process (Table 2). At a slow heating rate of 2 K min^{-1}, a maximum benzene purity of 97 wt.% was obtained with a benzene yield of 74%. While an almost identical benzene yield was achieved 5 K min^{-1}, the benzene purity decreased. With a faster heating rate of 10 K min^{-1} both the benzene yield and purity reduced, reaching 72% and 92 wt.%, respectively. The by-products were mainly the same as those obtained during the isothermal process; however, products, such as biphenyl, toluene, and styrene, were significantly reduced. At a heating rate of 2 K min^{-1}, styrene was no longer observed and toluene reached values as low as 0.1 wt.% of the product composition. The biphenyl formation was reduced by two thirds compared with the results from the degradation at 450 °C (Table 1). On the other hand, acetophenone appeared as a new product, indicating the incomplete hydrolysis of PET. Bednas et al. [28] suggested a rearrangement of benzoic acid vinyl ester, which is formed in the primary step of the pyrolytic fission of PET, with a successive decarboxylation (Scheme 2). This reaction can only occur if two conditions are met: the temperature must be high enough for the formation of acetophenone and the hydrolysis of PET must still be in progress. The use of two isothermal steps at 400 °C and 500 °C resulted in both a lower purity (90 wt.%) and a lower yield (68%) of benzene than observed for any other heating rate. This is a clear indication of the importance of a sophisticated temperature control for this process.

The same conclusion can be drawn from Fig. 3. It is obviously that benzene is mainly obtained during the isothermal stage, independent of the heating rate. A slow heating rate promoted the formation of benzene in the first stage due to the long heating time before the final temperature of 500 °C was reached. Higher heating rates reduced the time for the formation of benzene before reaching a critical temperature range, in which by-products could be formed. When 400 °C was used as the isothermal stage, no benzene was formed during this first stage. It is obviously that the formation of benzene required higher temperatures, and more by-products were formed at 500 °C.

The gas production showed similar tendencies for the PET degradation. At a heating rate of 2 K min^{-1}, various gases were observed during the first stage, however, during the isothermal stage, only CO_2 was released. With increasing heating rate, other gases were also observed during the isothermal stage, indicating that PET hydrolysis was not completed when the temperature reached 500 °C at the end of the first stage. The only likely source of methane and ethane is ethylene glycol. Hydrogen was most likely produced during the degradation of ethylene glycol in the presence of steam [25]. Carbon monoxide can be seen as a product of the PET pyrolysis, resulting in acetophenone (Scheme 2) as well as other by products. Correspondingly, more aromatic by-products were obtained, thus reducing the benzene yield and purity.

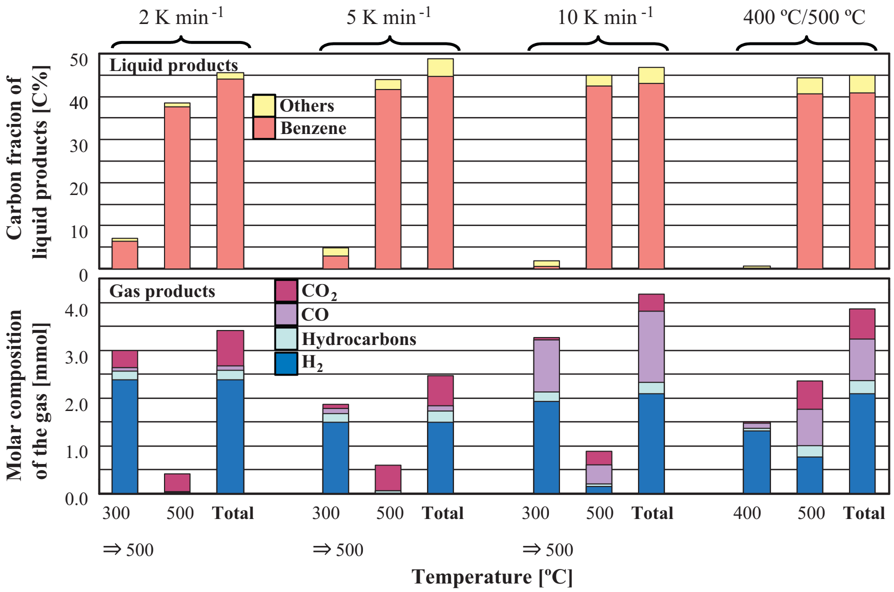


Fig. 3. Product evolution in different temperature ranges in dependence of the heating rate. A carbon fraction of 60 C% for benzene would represent a benzene yield of 100%.

4. Conclusion

It was shown in this work show that sophisticated temperature management makes it possible to recover high yields of high purity benzene. With a slow heating rate of $2\,\mathrm{K\,min^{-1}}$ between 300 °C and 500 °C, the most desirable separation of the hydrolysis and the decarboxylation reaction is achieved, resulting in benzene yields of about 75% and the purity of the resulting benzene is 97 wt.%. The purity of the products can be further improved by a fractionated condensation, since all the major by-products have a significantly higher boiling point than benzene.

These results can be used for the development of a new industrial process for the feedstock recycling of PET. Waste PET, especially recovered from used bottles, features still a high purity. Therefore, this advantage can be used to obtain products which also exhibit a high purity, thus reducing the effort and cost of purification.

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