



Semi-continuous hydrothermal terephthalic acid recovery from poly(ethylene terephthalate)

János Béri^a, Mihály Hegyi^a, Alfréd Menyhárd^b, Edit Székely^{a,*}

^a Department of Chemical and Environmental Process Engineering, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary

^b Department of Physical Chemistry and Materials Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary

ARTICLE INFO

Keywords:

PET
TPA recovery
Semi-continuous
Decomposition
Chemical recycling
Residence time distribution

ABSTRACT

This research delves into the hydrothermal decomposition of PET [poly(ethylene terephthalate)] between 523 and 573 K temperature at 10 MPa pressure. PET was placed in a packed column, and a constant water flow was maintained with an average residence time of water between 403 and 430 s as it travelled from the reactor to the end of the system. Terephthalic acid (TPA) recovery ranged from 87 % to 94 %, increasing with the temperature. The time of full conversion of the 0.5 g PET by 1 g/min water flow rate reduced from 2500 to 1200 sec, with increasing temperature. To prevent premature precipitation of TPA during cooling, an alkaline quench stream was employed. Terephthalic acid isolation involved acidification-driven precipitation and subsequent filtration at atmospheric pressure. The solid dry TPA product underwent NMR analysis, showing structural conformity and DSC/TGA measurement, which presented a purity of 99.5 w/w%.

The fractional end-of-pipe sampling showed accelerating reaction rates at each temperature, which supports the autocatalytic nature of hydrothermal disintegration of the PET. Using the determined residence time distribution in the system, from the end-of-pipe data a crude Fourier transform-based backward calculation was carried out to map the variation of the TPA concentration in the high-temperature and –pressure reactor.

1. Introduction

1.1. Short overview of monomer recovery of PET

The cleavage of poly(ethylene terephthalate) (PET) ester bonds is a well-known phenomenon in the high-temperature and pressure literature [1–3]. Several solvolytic methods (e.g.: methanolysis, ethanolysis, glycolysis, aminolysis and alkali, acidic or neutral hydrolysis) have already been presented as viable options for selective PET ester cleavage in the last 40 years with a growing focus on waste polymer recycling [3–5]. The review of Geyer et al. [3] in 2016 presented > 150 studies on the subject, with glycol as the dominant medium. Side-by-side industrial patents (>10) were also granted—starting as early as the 1960s—for water-based chemical recycling processes of PET [6,7]. However, the “Plastics – the fast Facts 2023” EU document states that the EU and the world produce 58 million tons (Mt) and 400 Mt plastics yearly, respectively, where of only < 0.2 w/w% and < 0.1 w/w% respectively originates from a chemically recycled source. 39 % of

plastic production in the EU is packaging material, of which PET as a food-contact polymer represents a major fraction [8]. One of the main challenges is the fact that up-to-now available recycling processes either need high-quality PET waste (e.g.: Vacurema® process for industrial waste (strapping, skeleton) or bottle flakes [9]), or the product will not be on par with the pre-application quality [2]. Collaterally, the processes were also not designed to handle mixed and contaminated wastes. Regarding the policy of food-contact applications, the European Union strengthened its regulation in 2022, concerning both the chemical conversion processes and usage of recycled materials, especially in food-contact applications [10]. Therefore, growing interest arose in research regarding back-to-monomer chemical conversions techniques, which were robust enough to handle mixed polymer wastes [11–14] and are able to provide raw material for repolymerization. A European Chemical Industry Council commissioned short review [15] points out that fully circular monomer recovery results in –1 t CO₂ eq./t input compared to pyrolysis. Still, experimental results in batch systems are dominant, while examples of semi-batch/semi-continuous solutions are scarce

* Corresponding author.

E-mail address: edit.szekely@edu.bme.hu (E. Székely).

<https://doi.org/10.1016/j.cej.2024.154601>

Received 25 April 2024; Received in revised form 4 July 2024; Accepted 5 August 2024

Available online 6 August 2024

1385-8947/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC license (<http://creativecommons.org/licenses/by-nc/4.0/>).

[12] with respect to neutral hydrothermal terephthalic acid recovery. Development of (semi-)continuous processes would be an essential stepping stone towards continuous technology development, an inevitable necessity due to the scale of these waste streams.

1.2. Main motifs of neutral hydrothermal PET hydrolysis

Interestingly several patents exceeded scientific findings regarding aqueous decomposition [4] and several factors regarding the decomposition were already studied such as additives and catalysts of virgin polymer production. Transesterification (first stage of polymer synthesis) catalyst such as Mg-, Ca-, Zn-acetates showed accelerating effect on decomposition, however, the formation of oligomeric esters of glycol and terephthalic acid (TPA) was inevitable. Nevertheless, if pure TPA recovery is of interest, the oligomer formation could be kept to a minimum by fine tuning the conditions over a wide range of temperatures, between 490 to 693 K [16–19]. The main product TPA is practically insoluble in pure, ambient temperature water [20], which enables separation by filtration. Propagation of crystalline growth for easier separation can be achieved by slower cooling [21].

The kinetics of hydrothermal PET degradation reaction is still under debate. In case of molten state PET ($T > 518$ – 538 K), it was proposed that the hydrolysis behaves as an autocatalytic reaction [22] due to the liberation of carboxyl end-groups acting as H-donors. This was further supported [23] by showing that an autocatalytic half-order model fitted the results of hydrolysis (508–538 K, 10:1 water/PET mass ratio, up to 30 min reaction time) better than a second-order model. Autocatalysis is usually accompanied by a sigmoid S-like yield curve in batch systems [24]. On the other hand, it was suggested that the change of crystallinity and hydrophobicity during hydrolysis could similarly result in the observed behavior of the process as low as 373 K [25]. However, recent results [17,19,26] did not discuss the nature of the hydrolysis in case of molten PET and sigmoid curves were also not observed. This study was carried out to gain insight into formation of TPA from PET in a hydrothermal system, besides aiming for full conversion of PET with high yield and purity of isolated TPA at the same time. Applying a semi-continuous system where the emerging TPA is removed by constant water flow pressure provides experimental results regarding the behavior of the hydrothermal environment during the decomposition at various temperatures, compared to batch results where only post-reaction and cooled mixtures can be studied.

1.3. Interpretation of end-of-pipe data in changing density and flowrate systems

System response or residence time distribution (RTD) describes the molecular distribution inside any flow-type unit [27], in case of a single exit and single phase. Any non-reactive signal (e.g.: inert molecules) passing through the process without phase separation will be the convolution integral with the RTD. In case of reactive media the explicit time-dependent solution of the rate equation have to be incorporated into the signal [28]. This phenomenon is well-established and comprehensive models are available for tubular or tank reactors, for both reactive and unreactive flows [27]. However, most models require strict assumptions, such as constant density.

Flow systems of hydrothermal reactions usually incorporate several segments such as a pre-heater, a reactor, optional side-stream (quenching or stabilizing agent), and a cooling section. In the different sections even during an isobaric operation the temperature change induces the change of several properties e.g.: density, viscosity. This effect in constant mass-flow systems synergically effects the local velocity. Therefore, the well-established models describing the residence time distribution are inapplicable [27]. This change in density and viscosity is presented as an example on Fig. 1 to demonstrate the difference of the in/output and hydrothermal reactor conditions.

Therefore, end-of-pipe data are usually highly affected by the RTD

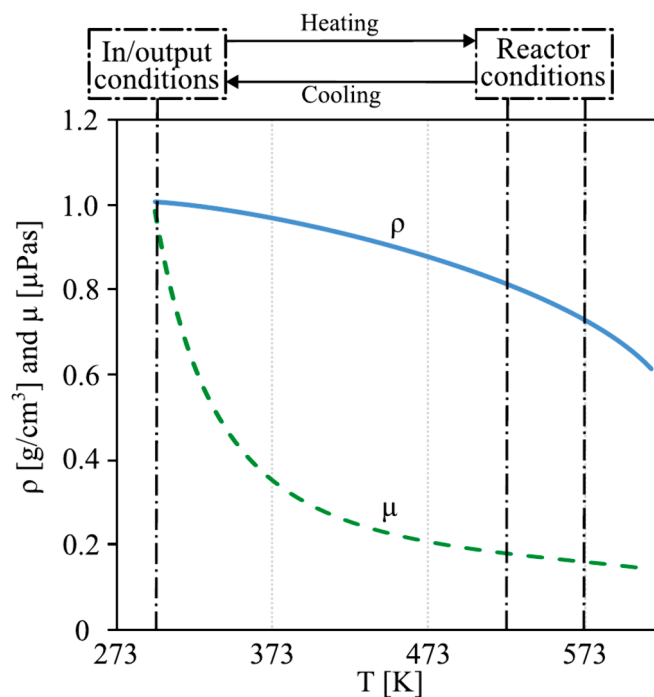


Fig. 1. Variation of density (solid line; blue) and viscosity (dashed line; green) at 10 MPa during operation in this study; vertical dashed lines indicate conditions in scope of current article, data calculated with IAPWS [33]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

from reactant inlet point to the exit point. This results in significant differences of measured concentration (or conversion) between batch and continuous systems for many reactions [29].

For this reason, a Fourier transformation-based [30] computation was carried out to approximate the concentration profile against time in the reactor. The shown method builds on the fact that TPA is practically unreactive in water at the conditions of the conducted experiments [17,31,32] and the single-phase criterion for TPA could be kept with a suitable quench line. Therefore, TPA acts an inert signal, only affected by the RTD. The resulting approximation is used to determine whether solubility limit is reached within the reactor.

2. Materials and methods

2.1. Materials

Commercially available virgin PET with the trademark name of Eastar MN211 was used (inherent viscosity: 0.75 ± 0.02 dl/g). Ultrapure water (UPW) was produced in-house with Purite HP700 ion-exchange column, after distillation of atmospheric tap water. The water conductivity was less than $0.1 \mu\text{S/cm}$. Solid dry NaOH (CAS: 1310-73-2; purity: 99 %) granule for the quench stream, NaCl (CAS: 7647-14-5; purity: 99.5 %) for RTD measurements, 37 % $\text{HCl}_{(\text{aq})}$ solution (CAS: 7647-01-0) for product precipitation, dichloromethane (CAS: 107-06-2; purity: min 99 w/w%) and ethyl-acetate (CAS: 141-78-6; purity: 99 %) for extraction were purchased from Molar Chemicals Ltd (Budapest, Hungary).

For analysis, methanol (CAS: 67-56-1; purity: ≥ 99.5 %) was supplied by Fischer Chemicals Ltd. Ammonium-acetate (CAS: 631-61-8, purity: 97 %), acetic acid (CAS: 64-19-7, purity: ≥ 96 %) and terephthalic acid (CAS: 100-21-0; purity: >99 %) were purchased from Molar Chemicals Ltd. (Budapest, Hungary).

2.2. Methods

2.2.1. Equipment

The schematic of the system can be seen on Fig. 2. Standard Swagelok® 316 stainless steel tubing and fittings were used.

UPW is supplied from (1) and measured on a tare scale (1a). The Jasco 4180 HPLC pump (2) was operated in a constant volumetric flow mode. The heated environment is a modified Carlo-Erba GC oven with 22–23 (K/min) heating rate with an endpoint tolerance of ± 1 K. The preheater (3) is made from 1/8" tubing and has a surface area of 0.06 m². Preheater performance was preliminary evaluated with an online temperature probe under 12 MPa liquid pressure. After preheating and start of flow the temperature of the liquid exiting the reactor reached 573 K within 1 min. The reactor (4a) is 1/4" tubing with 0.086 m length bent in a U-shape, capped with a 5 μ m filter fitting (4b). Room temperature 8 w/w NaOH_(aq) (8) is supplied by a Jasco 980 (9) HPLC pump, with equivalent volumetric flowrate to (2). A water cooler (5) is inserted to reach ambient temperature. The system pressure is maintained by a Jasco Back Pressure Regulator (BPR) (7) having ± 0.1 MPa regulating tolerance, located after the Swagelok® Tee-type filter (6).

2.2.2. Decomposition experiments

In each experiment a nominal mass of 0.5 g PET pellets were filled in the reactor as is under atmospheric conditions. After filling (4a), the reactor was filled and pressurized with ambient UPW. During the heat-up, the thermic expansion was compensated by the BPR. After reaching the desired temperature, (2) and (9) were started, set at 1 ml/min ambient flowrate, and the liquid exiting the BPR (end-of-pipe) was collected fractionally. The start of liquid flow is the zero time regarding the process, preheating is not included in time data. Each fraction collected was weighted on an analytical scale. A sampling profile was designed for each temperature based on preliminary experiments to achieve the highest resolution around steeper changes of the exiting TPA concentration. After finishing the experiment and cooling the system under pressure, the system was depressurized through the BPR.

2.2.3. Isolation and chemical analysis

A Jasco HPLC system was used for TPA content analysis—detailed description of the analytical procedure is given in the [Supplementary Material](#).

Solid TPA samples were prepared by HCl_(aq) addition to the alkaline crude until approx. pH=1 was achieved. The precipitate was filtered after 30 min crystal aging to facilitate filtration. The solid samples were dried in an oven (85 °C, 2–3 h), then approx. 30 mg of the crystals was dissolved in equimolar NaOH (assuming pure TPA) in D₂O and

measured with NMR for ¹H and ¹³C. This approach was chosen since this provides a similar medium as the crude product of the system, therefore all precipitated substances along with TPA will redissolve in the D₂O. The leftover dry precipitates were mixed in a mortar and the thermal decomposition temperature of this terephthalic acid mixture was studied using a simultaneous thermal analyser (Perkin Elmer STA6000). A sample of around 10 mg was placed in an open alumina crucible and heated from room temperature up to 700 °C at a heating rate of 5 °C/min. The sample was purged by pure nitrogen at a flow rate of 20 mL/min.

2.2.4. Residence time distribution measurement

The equipment was slightly modified for RTD measurements. (8) was swapped to UPW and the secondary supply chamber of the Jasco 4180 was connected with 1/16" tubing right before the reactor with a 1/16" orthogonal and 1/8" straight Tee. A 10 w/w% NaCl_(aq) solution—which is below its solubility limit at the whole temperature range [34]—was pre-filled up to the end of the 1/16" tubing. All other sections were pressurized by UPW filling. The equipment was heated up to the desired temperature and kept at constant pressure by the BPR. Then (2) and (9) were set to 1 ml/min flow rates. After (7) a Hannan Instruments HI-5521 conductometer was connected and the conductivity was measured every second as a proportional quantity to NaCl_(aq) concentration. After the continuous UPW flow set the baseline both (2) and (9) were stopped. A 5 sec 10 ml/min NaCl_(aq) signal was introduced to approximate impulse disturbance, then (2) and (9) were restarted. The experiments were conducted until conductivity returned approximately (± 10 %) to the baseline. The conductivity data, after baseline correction, was treated as linearly proportional to the concentration of NaCl. Profiles were numerically integrated and normalized to have an estimate of the normalized residence time distribution [27].

The measured RTD at 548 K was tested with a pre-programmed HPLC profile of NaCl_(aq) feed as well.

2.3. Calculations

2.3.1. End-of-pipe recovery

The fractional sample collection coupled with HPLC analysis provides the average TPA concentration of the fraction according to eq. (1):

$$\bar{c}_{i,TPA} = \frac{1}{t_i - t_{i-1}} \int_{t_{i-1}}^{t_i} c(t) dt \quad (1)$$

where $\bar{c}_{i,TPA}$ [mg/ml] is the HPLC measured value; $c(t)$ real value of the concentration at any t ; t_i time up to $i \in \mathbb{Z}^+$ fraction index. The box-method integration was chosen to avoid analysis error accumulation. The corresponding time for any $\bar{c}_i$ is given by eq. (2) as the best estimate of the actual t corresponding to $\bar{c}_i$.

$$\bar{c}_i \rightarrow t_{i-1} + \frac{t_i - t_{i-1}}{2} = \bar{t}_i \quad (2)$$

The TPA recovery is defined similar to as before in the literature [14] by eq. (3):

$$TPA_{recovery}(t_i) = \frac{\sum m_{TPA,i}}{0.86 \cdot m_{PET}} \quad (3)$$

where $TPA_{recovery}(t)$, cumulative TPA recovery [-] up to fraction i ; m_{PET} PET polymer weight [mg]; $m_{TPA,i}$ fractional TPA content [mg] in fraction i , calculated from HPLC results.

2.3.2. Calculation of the concentration profile in the reactor

Time-lapse and maxima of the concentration profile in the high pressure and high temperature reactor was calculated from the end-of-pipe concentration – time data using the residence time distribution of the setup from the reactor inlet to the end-of-pipe sample collection point. The method is based on the convolution theorem [30], that the convolution operation of two time-dependent functions (eq. (4) integral)

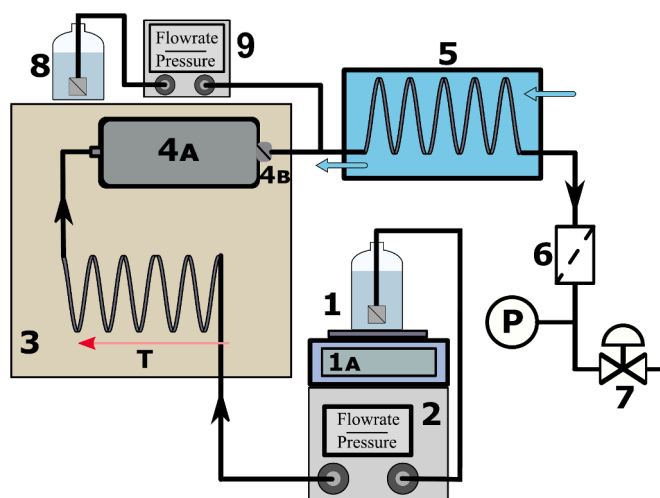


Fig. 2. Schematic equipment drawing; for notation see 2.2.1 Equipment.

is equivalent to the multiplication of the functions in the Fourier frequency domain (eq. (4) right side).

$$O(t) = \int_{-\infty}^{+\infty} I(t-\tau) \bullet RTD(\tau) d\tau = \mathcal{F}^{-1}\{\mathcal{F}\{I(t)\} \bullet \mathcal{F}\{RTD(t)\}\} \quad (4)$$

where t : time; τ : variable of integration with time dimension; $O(t)$: output signal; $I(t)$: input signal; $RTD(t)$: residence time distribution; $\mathcal{F}$, $\mathcal{F}^{-1}$: forward and inverse Fourier transform, respectively. In this work $O(t)$ is concentration–time data collected at the end-of-pipe point, while $I(t)$ is the concentration in the hydrothermal reactor. This is the general equation for calculating any non-reactive single-phase $O(t)$ if both the $I(t)$ and the $RTD(t)$ is known. However, in semi-batch studies the unknown function is $I(t)$ — since, only $RTD(t)$ and $O(t)$ can be directly measured. The nature of the integral in eq. (4) can be figuratively interpreted as the “smearing” of each individual point of $I(t)$ with a whole $RTD(t)$. Consequently, backward calculation of $I(t)$ from known $O(t)$ and $RTD(t)$ is only unambiguous if both $O(t)$ and $RTD(t)$ is error free and explicitly known as a continuous function.

However, in hydrothermal flow systems *in situ* online analysis is usually unfeasible (high engineering expectations of the instrumentation). Therefore, commonly, *ex situ* measurements are made through fractionally collected samples. These provide only sets of discrete datapoints.

The beneficial property of eq. (4) is that both forms (integral and Fourier multiplication) can be converted to a discrete version, by exchanging the original operations with finite sums of the whole dataset [35]. However, discretization of continuous functions inherently causes loss of information. Accordingly, only approximative techniques are possible, accuracy of which is highly dependent on the sampling rate. In this work, a higher sampling rate was used compared to batch studies [17,19,23,32] to minimize the effect of this drawback. An iterative solution was developed based on the Fast Fourier Transform (FFT) method to approximate $I(t)$, in this case the TPA concentration–time curve in the hydrothermal reactor. It should be noted that multiplication in the Fourier domain with FFT has a criterion for application: the two datasets need to have the same sampling rate and sample size.

Main steps of the developed routine are the following—for detailed version with an example see the [Supplementary Material](#):

1. The *ex-situ* experimental concentration–time data of TPA ($\bar{C}_i(\bar{t}_i)$) was linearly interpolated to achieve a dataset with 2048 points and 1 sec sampling rate — both values correspond to the configuration of the RTD measurement. A 15-sec moving average smoothing (MAS) was applied to eliminate sharp peak points in the dataset then the dataset was then normalized to integral one, henceforth denoted as $\bar{C}_i(\bar{t}_i)$.
2. A 15-sec MAS was applied to the measured $RTD(t)$ at the same reactor pressure and temperature as $\bar{C}_i(\bar{t}_i)$. This was done to minimize the stochastic error of the conductivity meter.
3. Arbitrary guess $I(t)$ was constructed with 2048 points, 1 sec sampling rate and an integral of one.
4. $\mathcal{F}\{I(t)\}$ and $\mathcal{F}\{RTD(t)\}$ were calculated, then multiplied point-by-point in the Fourier domain with the FFT module of the SciDAVis program. In the end, the result was transformed back to the time-domain yielding an $O(t)$ approximation.
5. The calculated $O(t)$ and $\bar{C}_i(\bar{t}_i)$ was compared and it was accepted if the residual square error on the rampant up-rising section was less than 5 %. Otherwise, the cycle returns to the third point. Main routes of improving the $I(t)$ was changing the first and second moments of the guess function (average residence time and sigma of the function, respectively).

If the $I(t)$ was accepted as a sufficient approximation then it was converted to concentration by using the IAPWS [33] equations for water properties, neglecting TPA in density calculations.

The method was validated to be an approximate solution through experiment. The distortion caused by both the error in the RTD measurements and discretization only allowed application of the routine to estimate the concentration maxima in the reactor at different temperatures.

3. Results and discussion

3.1. Disintegration of PET

The experimental setup described in sections 2.2.1 and 2.2.2 provided full conversion disintegration of PET at any temperatures in the studied 523 to 573 K temperature range at 10 MPa. In all cases after the measurement the high-pressure and –temperature reactor was cooled, depressurized and opened. It contained only colorless, clear water. Solid residues, separate liquid phases or any opalesque was never observed.

From the collected effluent, TPA was preparatively isolated and its purity was confirmed (see section 3.2). Effects of temperature on the total TPA recovery and time requirement is explained in section 3.1.2, followed by backward calculation results estimating TPA concentration in the high-pressure and –temperature semi-continuous reactor.

3.1.1. Preparative TPA isolation

The crude product is highly alkaline clear colourless liquid, the neutral form of TPA can be precipitated by acidification. $HCl_{(aq)}$ was chosen as acidification agent to guarantee efficient precipitation [36]. After precipitation and filtration, the dry product TPA recovery reached 1.00 in some cases (experiments at 573 K and 558 K). This is theorised to be a result of NaCl sorption on the surface of the crystals. The ^{13}C and 1H NMR spectra at three temperatures can be seen superimposed on Fig. 3.

The 1H spectra show some aromatic contaminants. However, the vast majority of the sample is the sodium salt of TPA. Comparing the contaminants to reference [38] only disodium isophthalate is identified in both 1H and ^{13}C spectra as minor impurity. The DSC-TGA shown in Fig. 4 also indicate high purity TPA precipitate. The melting process starts at 577.4 K, which is very close to the melting point of the pure TPA [40]. In addition, the mass change starts at the same temperature, since TPA sublimates at its melting point. The total mass loss is 99.5 w/w%, which also supports the high purity of this product. The sublimation of isophthalic acid contaminant at 620 K was not observed most probably because of its low concentration.

3.1.2. End-of-pipe results

The effects of temperature and pressure on the end-of-pipe concentration profiles and TPA recoveries were examined besides a reproducibility study. Three repeated experiments were carried out at 548 K and 20 MPa (see: [Supplementary Material Fig. S3](#)) resulting in an average 93.2 % TPA recovery with confidence interval of 1.7 % at 95 % probability level.

The results of the experiments at 10 MPa are shown in Fig. 5 and overall TPA recovery data in Table 1. Tabulated data is available in the [Supplementary Material Table S1](#). As TPA recovery at 548 K were the same at 10 MPa and 20 MPa system pressures, further pressure effect investigations were excluded.

All TPA recovery vs time curves (Fig. 5a) have inflection points, showing that the production rate of TPA is slow at first, by time it accelerates, and as the PET is consumed the production rate decreases again. This phenomenon seems to support the autocatalytic nature of the process and suggests an induction time. Unlike in batch setups [17,19,23,39], the water flow continuously extracts TPA increasing the driving force for soluble hydrolysis products towards the hydrothermal liquid phase. Besides, as the temperature is increased, the concentration profile changes from an apparent symmetric normal distribution to a skewed one (Fig. 5b).

The TPA recovery curves converge to a temperature-dependent limiting value (Fig. 5a and Table 1), independent of the fact that total

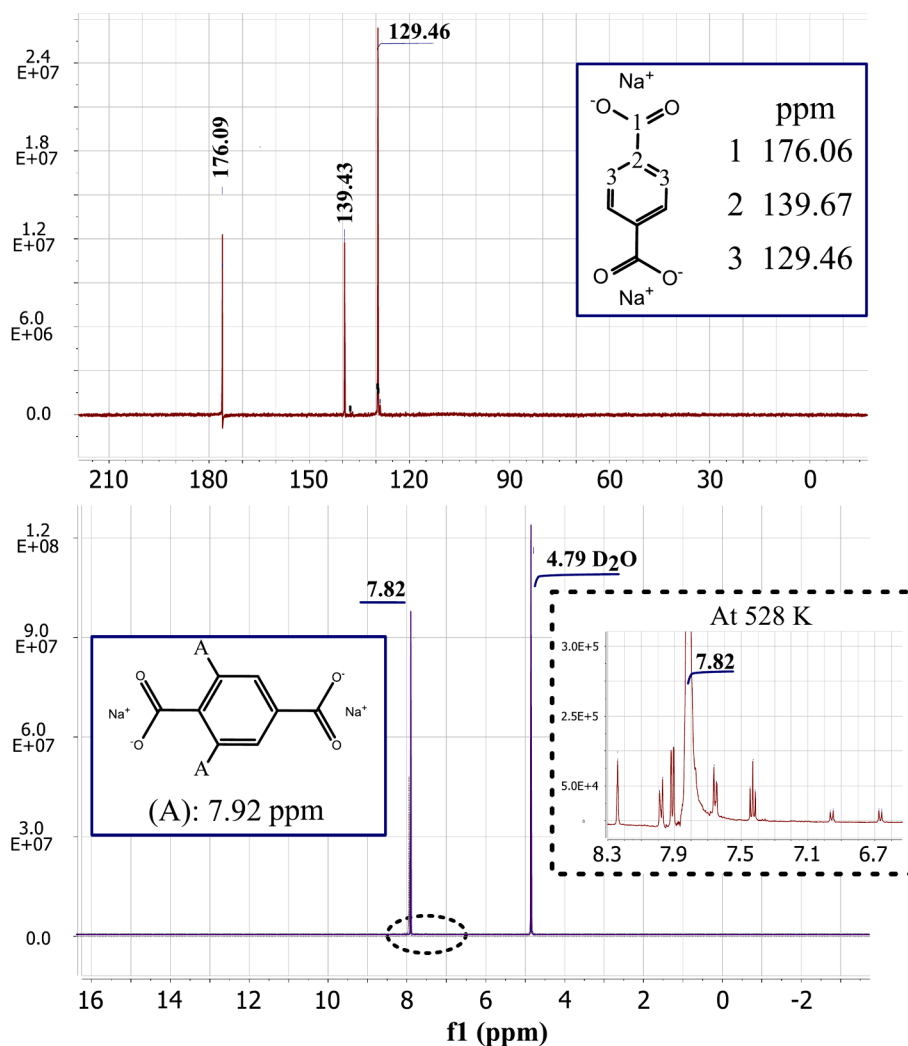


Fig. 3. Superimposed NMR spectra of HCl precipitated product of PET decomposition at 573, 548 and 523 K at 10 MPa; D₂O+TPA equimolar NaOH; dotted box in ¹H: exemplary contaminant profile in all samples. Reference data: SDBS [37].

conversion is achieved at all temperatures. Increasing temperature not only reduces the total time requirement and increases TPA recovery, but also results in higher TPA concentrations in the outlet (see Fig. 5b), which makes TPA isolation easier.

The variation of TPA recovery limit with temperature is most likely caused by a non-complete decomposition of mobilized oligomers at lower temperatures. This concept is formulated considering several additional experimental observations including that full conversion of PET was achieved in each case.

The alkaline crude product is a clear single-phase liquid. Therefore, all products beside TPA also have water solubility at alkaline pH. Moreover, after setting the pH to 1 for TPA precipitation these products still do not precipitate to a great extent (less than 0.5 w/w% impurity in the crystals according to DSC/TGA).

By-products can be either higher than TPA molecular weight sub-units or decomposition products, formed through random hydrolysis of PET chains, or decomposition products of TPA.

Lower molecular weight sub-units may be mono-, bis-(2-hydroxyethyl) terephthalate, which were reported to have ambient water solubility [19]. Therefore, these are most likely able to mobilize into the hydrothermal liquid phase meanwhile not precipitating during cooling.

At 523 K an additional experiment was carried out where the pH=1 filtered mother liquor was halved and individually extracted with dichloromethane and ethyl-acetate, right after the hydrolysis

experiment. The extracts were analysed with positive mode LC-MS screening. Above 600 *m/z* no signals were not detected apart from the baseline noise. Considering *z* = +2 presence of maximum size of six repeating unit PET oligomer is possible, but compared to LC-MS references of PET oligomers [40–42] the fragment patterns suggest that three-unit PET is most likely the largest. Besides, the presence of ethylene glycol and diethylene glycol is highly probable in the extracts according to the spectra, like in batch results [19]. Direct evidence for the presence of mono-, bis(2-hydroxyethyl) terephthalate is not present, but the fragments show evidence for chemically bound TPA (see Supplementary Material Figure S14).

Both explicit and implicit experimental observations suggest, that at lower temperature, the rate of sub-unit hydrolysis decreases inside the reactor and due to the limited time available, the hydrolysis to TPA was not completed. However, no higher than six-unit PET chains were present in the product. Therefore, if TPA recovery is the explicit goal, the system inherently hinders the liberation of non-target compounds, to a certain degree, by withholding the mobilization of larger molar mass fragments into the hydrothermal phase. Further control of these substances can be achieved through the control of the RTD.

The concentration curve is very similar to the respective RTD (Fig. 6, top) at 573 K suggesting, that the dissolved TPA was present inside the reactor at the start of the flow. This could be interpreted as the partial hydrolysis of PET and subsequent dissolution of some TPA, and smaller

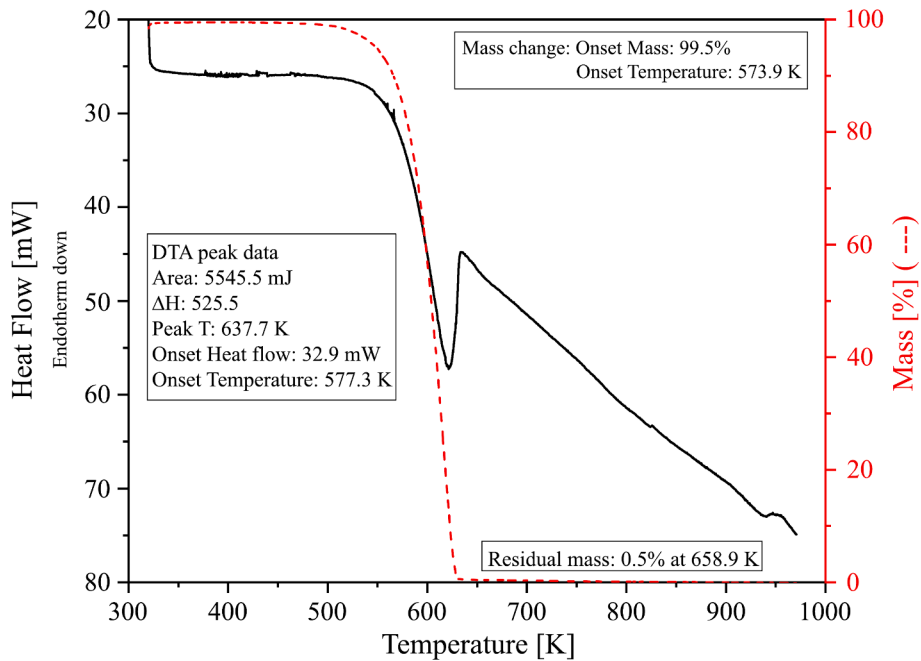


Fig. 4. DSC-TGA results of the average purity of precipitated TPA from decomposition at 573, 548 and 523 K at 10 MPa.

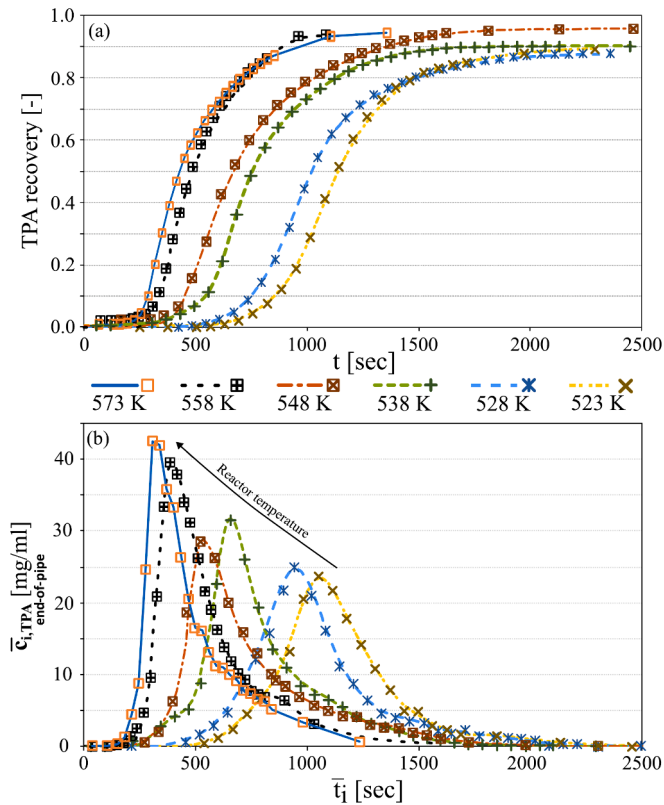


Fig. 5. End-of-pipe TPA recovery (a) and TPA concentration (b) at six temperatures and 10 MPa; subscript i: fraction index; curves are guide to the eye only.

Table 1
Maximal TPA recovery at each temperature.

Temperature [K]	523	528	538	548	558	573
TPA recovery limit [%]	87.2	87.7	90.0	93.2	93.6	94.0

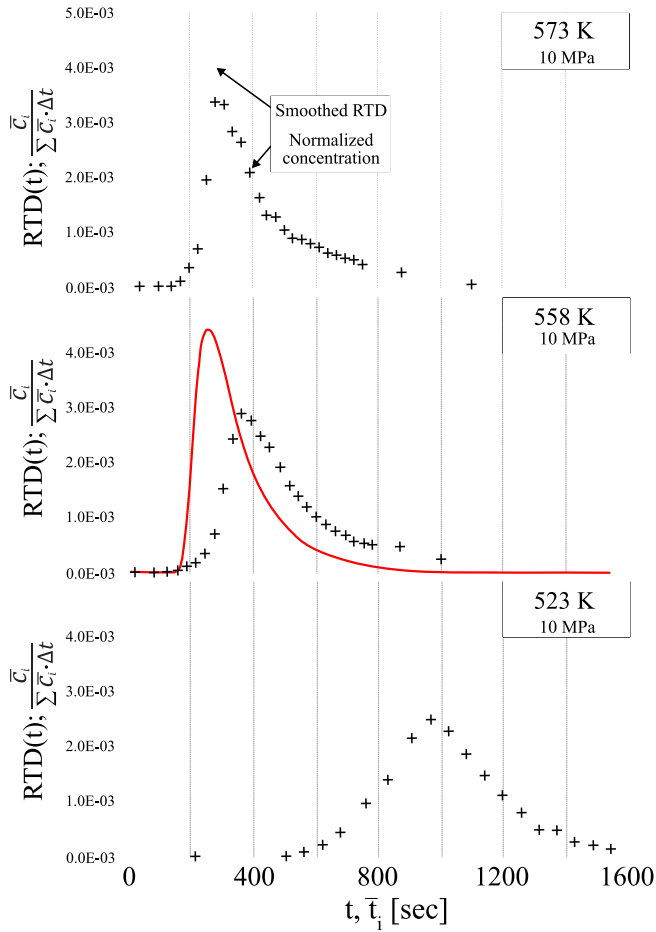


Fig. 6. Smoothed RTDs and normalized concentration profiles at 573–558–523 K and 10 MPa.

PET units started during heat-up in the hydrothermal media. However, at 558 K, the hydrolysis barely started before flow was started — significant TPA concentration increase was first recorded at the steep rise of the respective RTD (see Fig. 6 middle). However, the overall TPA recovery at 558 K was only 0.4 % less than at 573 K, which is insignificant. This high similarity in overall recovery suggests that the mobilized substances from PET spent enough time in the high temperature section to completely hydrolyse in an isothermal process even though the molar mass reduction of PET required longer induction time. The prolongation of the induction time with decreasing temperatures is visible in Fig. 6 middle and bottom.

3.2. Approximation of the TPA concentration in the reactor

The method of the residence time distribution measurements and calculations are described in sections 2.2.4 and 2.3.2, respectively and the untreated RTD results as well as the basic data treatment methodology are available in the Supplementary Material. The validation of the RTD was carried out by the comparison of a complex input profile and the convolution of the RTD with the known input. An example with the input profile at 548 K and 10 MPa can be seen on Fig. 7.

The RTD-based convolution results (known input → calculated output) show a wider spread than the measured distribution. The observed deviation arose from the RTD measurement technique. Dirac delta-function, which would provide the actual RTD, is usually unattainable (infinite slope accompanied by injection time (Δt) approaching zero). The approximation by a finite-length box-signal of $\text{NaCl}_{(\text{aq})}$ tracer yields deviation in calculations. Examples [43] in the literature for experimentally validated RTD and subsequent use for reactor input modelling in hydrothermal systems are scarce, and also show similar extent of deviations in the RTD(t) results. As demonstrated thus as an acceptable approximative tool, we deemed the method suitable with limitations.

Based on the above discussion, back-calculation of the concentration profile in the reactor (known output → calculated input) is expected to yield a curve with a smaller spread than the real concentration–time distribution, while conserving the total area under the curve. Therefore the maxima of the backward calculated curve is always an overestimate of the genuine concentration maximum—this is a general consequence of non-perfect Dirac delta “injection”.

The calculated maxima of TPA inputs converted to concentration can be seen on Fig. 8. Each fitted input profile is available in the

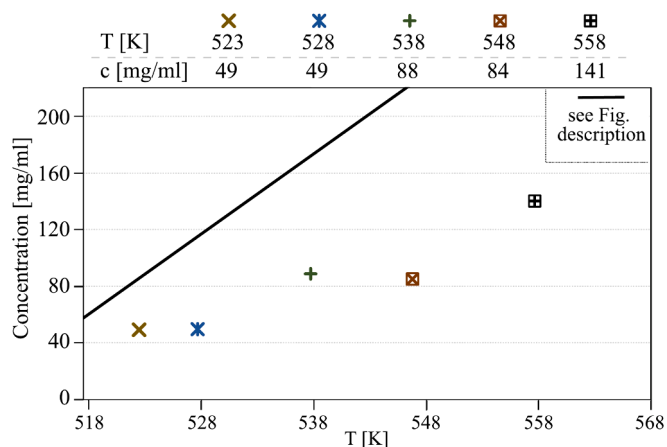


Fig. 8. Calculated input curve maxima converted to concentration. Solid line is the solubility of TPA as function of temperature [20] (validity up to 547 K) at 10 MPa in neat water.

Supplementary Material. The maxima of the measurement at 573 K is not plotted, because according to the routine a ca. 30 sec TPA box-signal with four times higher concentration than expected were calculated, according to the reference data extrapolation. This is however only the artificial result of the Fast Fourier Transform properties. FFT has a periodicity criteria, essentially handling a discrete data set as an infinite repetition of it, utilizing the achieved symmetry for computational cost reduction. Therefore, it cannot handle signals with data $t < 0$, consequently it will produce unreal results if the signal, even just partially, originates before the start of the flow. This result, implicitly further supports the validity of interpretation described in the previous section about the results at 573 K (see Fig. 6, top).

The calculated peak concentration of TPA in the reactor run under the available hydrothermal reference data [20], therefore the reaction was not limited by solubility at any temperature values.

4. Conclusions and outlook

State of the art industrial processes (e.g.: glycolysis) are unable to channel in mixed post-consumer plastic waste to food-contact packaging production even after rigorous sorting chains. The strict regulatory

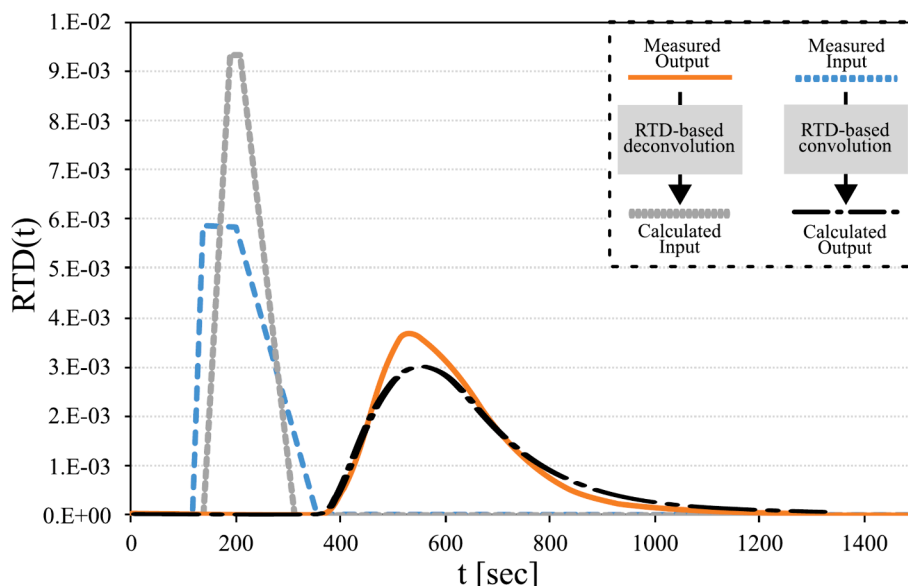


Fig. 7. Comparison of forward and backward convolution calculations to a known complex profile at 548 K and 10 MPa.

safety framework of said applications proves a so far unmanageable challenge for current technologies. For this reason, our study investigated the phenomenological understanding of pure PET melt decomposition in semi-continuous hydrothermal liquid media to further our understanding of the process with a future continuous monomer recovery application in mind.

Apart from the achieved total conversion of PET, the results show that the continuous removal of the product TPA accelerates the reaction. Meanwhile only lower molecular weight decomposition products are partially extracted, most of which are further hydrolysed in the hydrothermal section and provide high TPA recoveries TPA at higher temperatures. The time-scale changes of TPA concentration were accurately measured at the end of the system with a high sampling rate. An empirical deconvolution routine was implemented to gain insights on the TPA concentration–time curve inside the reactor. Due to the limitations of discrete data only the TPA maxima inside the reactor can be estimated with RTD measurements at each temperature. The data shows that further intensification is possible since the solubility limit is not reached inside the reactor.

The end-of-pipe alkaline liquid contained the monomer in high quantities with excellent recovery. Parallely, the alkaline quench provided simple preparative separation by acidification, which produced a clean, crystalline TPA product, with an above > 99 w/w% purity.

This simplified system showed that in case of PET the hydrothermal route might pose a viable opportunity for robust TPA recovery. However, it must be noted that establishing real industrial viability of the hydrothermal process compared to state of the art for PET recycling, conformity to the expectations of the FDA challenge tests or the EFSA guidelines must be presented [2], which is a future outlook of the authors.

CRedit authorship contribution statement

János Béri: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Mihály Hegyi:** Investigation, Data curation. **Alfréd Menyhárd:** Writing – review & editing, Investigation. **Edit Székely:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data has been included to the [Supplementary material](#).

Acknowledgements

The authors express their heartfelt gratitude to Prof. Blanka Tóth for her prompt assistance with excess chemical analysis and evaluation targeting minor components upon the request of the reviewers, and are grateful for the insightful questions and suggestions of the reviewers. The research was supported by the Ministry of Culture and Innovation of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-EGA funding scheme [grant no. TKP2021-EGA-02] and under the New National Excellence Program [grant no. ÚNKP-23-2-I-BME-256].

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2024.154601>.

References

- [1] D. Carta, G. Cao, C. D'Angeli, Chemical recycling of poly(ethylene terephthalate) (PET) by hydrolysis and glycolysis, *Environ. Sci. Pollut. Res.* 10 (2003) 390–394, <https://doi.org/10.1065/espr2001.12.104.8>.
- [2] M.J. Forrest, Recycling of polyethylene terephthalate, *De Gruyter* (2019), <https://doi.org/10.1515/9783110640304>.
- [3] B. Geyer, G. Lorenz, A. Kandelbauer, Recycling of poly(ethylene terephthalate) – a review focusing on chemical methods, *Express Polym. Lett.* 10 (2016) 559–586, <https://doi.org/10.3144/expresspolymlett.2016.53>.
- [4] D. Paszun, T. Spychaj, Chemical recycling of poly(ethylene terephthalate), *Ind. Eng. Chem. Res.* 36 (1997) 1373–1383, <https://doi.org/10.1021/ie960563c>.
- [5] V. Sinha, M.R. Patel, J.V. Patel, Pet waste management by chemical recycling: a review, *J. Polym. Environ.* 18 (2010) 8–25, <https://doi.org/10.1007/s10924-008-0106-7>.
- [6] J.W. Mandoki, Depolymerization of Condensation Polymers, US4,605,762, 1986.
- [7] T. Masuda, T. Kishino, S.R. Mukai, K. Hashimoto, S. Yoshida, Chemical recycling of mixture of waste plastics using a new reactor system with stirred heat medium particles in steam atmosphere, *Chem. Eng. J.* 82 (2001) 173–181, [https://doi.org/10.1016/S1385-8947\(00\)00347-8](https://doi.org/10.1016/S1385-8947(00)00347-8).
- [8] V. Janssens, M. Anne, Plastics the fast facts 2023: a review on plastic contributions to European economy, 2023. <https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2023/>.
- [9] M.S. Seshasayee, P.E. Savage, Oil from plastic via hydrothermal liquefaction: production and characterization, *Appl. Energy* 278 (2020) 115673, <https://doi.org/10.1016/j.apenergy.2020.115673>.
- [10] Regulation (EU) 2022/1616, Commission Regulation (EU) 2022/1616 of 15 September 2022 on recycled plastic materials and articles intended to come into contact with foods, and repealing Regulation (EC) No 282/2008, *Official Journal of the European Union*. 2006 (2022) 1–44.
- [11] P. Pereira, P.E. Savage, C.W. Pester, Acid catalyst screening for hydrolysis of post-consumer PET waste and exploration of acidolysis, *Green Chem.* 26 (2024) 1964–1974, <https://doi.org/10.1039/D3GC03906D>.
- [12] Q. Zheng, Y. Suga, H. Yamaguchi, M. Watanabe, Simultaneous material and chemical recycling of PET/PE multi-layer film using a semi-batch hydrothermal system, in: 19th European Meeting on Supercritical Fluids, 2023.
- [13] I. Agostini, B. Ciuffi, R. Gallorini, A.M. Rizzo, D. Chiaramonti, L. Rosi, Recovery of terephthalic acid from densified post-consumer plastic mix by HTL process, *Molecules* 27 (2022) 7112, <https://doi.org/10.3390/molecules27207112>.
- [14] P. Pereira, P.E. Savage, C.W. Pester, Neutral hydrolysis of post-consumer polyethylene terephthalate waste in different phases, *ACS Sustain. Chem. Eng.* 11 (2023) 7203–7209, <https://doi.org/10.1021/acssuschemeng.3c00946>.
- [15] Chemical Recycling: potential of an emerging waste management route, (2020). https://cefic.org/app/uploads/2020/12/CEFIC_Quantis_report_final.pdf.
- [16] M.L. Doerr, Process for minimizing formation of low molecular weight oligomers during hydrolytic depolymerization of condensation polymers, 4,578,510, 1986.
- [17] O. Sato, K. Arai, M. Shirai, Hydrolysis of poly(ethylene terephthalate) and poly(ethylene 2,6-naphthalene dicarboxylate) using water at high temperature: effect of proton on low ethylene glycol yield, *Catal. Today* 111 (2006) 297–301, <https://doi.org/10.1016/j.cattod.2005.10.040>.
- [18] T. Adschiri, O. Sato, K. Machida, N. Saito, K. Arai, Recovery of terephthalic acid by decomposition of PET in supercritical water, *Kagaku Kogaku Ronbunshu* 23 (1997) 505–511, <https://doi.org/10.1252/kakoronbunshu.23.505>.
- [19] A. Jaime-Azuara, T.H. Pedersen, R. Wimmer, Process optimization by NMR-assisted investigation of chemical pathways during depolymerization of PET in subcritical water, *Green Chem.* 25 (2023) 2711–2722, <https://doi.org/10.1039/d2gc04831k>.
- [20] Y. Takebayashi, K. Sue, S. Yoda, Y. Hakuta, T. Furuya, Solubility of terephthalic acid in subcritical water, *J. Chem. Eng. Data* 57 (2012) 1810–1816, <https://doi.org/10.1021/je300263z>.
- [21] R.F. Chambret, Production of terephthalic acid, 3,120,561, 1964.
- [22] D.A.S. Ravens, I.M. Ward, Chemical reactivity of polyethylene terephthalate, Hydrolysis and Esterification Reactions in the Solid Phase, *Transactions of the Faraday Society*. 57 (1961) 150, <https://doi.org/10.1039/tf9615700150>.
- [23] C.Y. Kao, B.Z. Wan, W.H. Cheng, Kinetics of hydrolytic depolymerization of melt poly(ethylene terephthalate), *Ind. Eng. Chem. Res.* 37 (1998) 1228–1234, <https://doi.org/10.1021/ie970543q>.
- [24] L.K. Doraiswamy, Organic Synthesis Engineering, in: *Organic Synthesis Engineering*, Oxford University Press, 2001, <https://doi.org/10.1093/oso/9780195096897.003.0031>.
- [25] A. Launay, F. Thominette, J. Verdu, Hydrolysis of poly(ethylene terephthalate): a kinetic study, *Polym. Degrad. Stab.* 46 (1994) 319–324, [https://doi.org/10.1016/0141-3910\(94\)90148-1](https://doi.org/10.1016/0141-3910(94)90148-1).
- [26] O. Sato, E. Mine, M. Osada, N. Hiyoshi, A. Yamaguchi, K.K. Bando, Y. Masuda, M. Shirai, Depolymerization of poly(ethylene terephthalate) to terephthalic acid and ethylene glycol in high-temperature liquid water, *Chem. Lett.* 38 (2009) 268–269, <https://doi.org/10.1246/cl.2009.268>.
- [27] O. Levenspiel, *Chemical Reaction Engineering*, 3rd ed., Wiley, 1998. <https://doi.org/10.1201/9781420087567-13>.
- [28] F.N. Madden, K.R. Godfrey, M.J. Chappell, R. Hovorka, R.A. Bates, A comparison of six deconvolution techniques, *J. Pharmacokinet. Biopharm.* 24 (1996) 283–299, <https://doi.org/10.1007/BF02353672>.
- [29] D.L. Kearns, F.S. Manning, Model simulation of adiabatic continuous flow stirred tank reactors, *AIChE J.* 15 (1969) 660–665, <https://doi.org/10.1002/aic.690150507>.

- [30] S.M. Riad, The Deconvolution Problem: An Overview, *Proceedings of the IEEE*. 74 (1986) 82–85. <https://doi.org/10.1109/PROC.1986.13407>.
- [31] J.B. Dunn, M.L. Burns, S.E. Hunter, P.E. Savage, Hydrothermal stability of aromatic carboxylic acids, *J. Supercrit. Fluids* 27 (2003) 263–274, [https://doi.org/10.1016/S0896-8446\(02\)00241-3](https://doi.org/10.1016/S0896-8446(02)00241-3).
- [32] M. Čolnik, D. Pečar, Ž. Knez, A. Goršek, M. Škerget, Kinetics study of hydrothermal degradation of pet waste into useful products, *Processes*. 10 (2022) 1–12, <https://doi.org/10.3390/pr10010024>.
- [33] W. Wagner, A. Pruß, The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use, *J. Phys. Chem. Ref. Data* 31 (2002) (1995) 387–535, <https://doi.org/10.1063/1.1461829>.
- [34] N.B. Kevvil, Vapor pressures of aqueous solutions at high temperatures, *J. Am. Chem. Soc.* 64 (1942) 841–850, <https://doi.org/10.1021/ja01256a030>.
- [35] K.B. Howell, *Principles of fourier analysis*, CRC Press (2001), <https://doi.org/10.1201/9781420036909>.
- [36] C. Müller, C.A. Heck, L. Stephan, M. Paschetag, S. Scholl, Precipitation of terephthalic acid from alkaline solution: influence of temperature and precipitation acid, *Ind. Eng. Chem. Res.* 62 (2023) 12029–12040, <https://doi.org/10.1021/acs.iecr.2c04451>.
- [37] SDBSWeb (National Institute of Advanced Industrial Science and Technology), (2023.09.11). <https://sdb.sdb.aist.go.jp>.
- [38] K. Qin, K. Holguin, M. Mohammadiroudbari, C. Luo, A conjugated tetracarboxylate anode for stable and sustainable Na-ion batteries, *Chem. Commun.* 57 (2021) 2360–2363, <https://doi.org/10.1039/d0cc08273b>.
- [39] J.R. Campanelli, M.R. Kamal, D.G. Cooper, A kinetic study of the hydrolytic degradation of polyethylene terephthalate at high temperatures, *J. Appl. Polym. Sci.* 48 (1993) 443–451, <https://doi.org/10.1002/app.1993.070480309>.
- [40] E.D. Tsochatzis, J. Alberto Lopes, O. Kappenstein, T. Tietz, E.J. Hoekstra, Quantification of PET cyclic and linear oligomers in teabags by a validated LC-MS method – In silico toxicity assessment and consumer's exposure, *Food Chemistry*. 317 (2020) 126427. <https://doi.org/10.1016/j.foodchem.2020.126427>.
- [41] D.J. Kim, K.T. Lee, Determination of monomers and oligomers in polyethylene terephthalate trays and bottles for food use by using high performance liquid chromatography- electrospray ionization-mass spectrometry, *Polym. Test.* 31 (2012) 490–499, <https://doi.org/10.1016/j.polymertesting.2012.02.001>.
- [42] S. Ubeda, M. Aznar, C. Nerín, Determination of oligomers in virgin and recycled polyethylene terephthalate (PET) samples by UPLC-MS-QTOF, *Anal. Bioanal. Chem.* 410 (2018) 2377–2384, <https://doi.org/10.1007/s00216-018-0902-4>.
- [43] J. Sierra-Pallares, T. Huddle, E. Alonso, F.A. Mato, J. García-Serna, M.J. Cocero, E. Lester, Prediction of residence time distributions in supercritical hydrothermal reactors working at low Reynolds numbers, *Chem. Eng. J.* 299 (2016) 373–385, <https://doi.org/10.1016/j.cej.2016.04.073>.