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INSTANTANEOUS HYDROLYSIS OF PET BOTTLES: AN EFFICIENT PATHWAY TO THE CHEMICAL RECYCLING OF CONDENSATION POLYMERS

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ABSTRACT

Restoring the environmental balance that was disturbed by the rise of plastic commodities is a must for researchers and the wider community. It is imperative that the increasing amount of plastic waste and that the high amount of petrochemical resources consumed during the constant replacement of single-use plastics is reduced. Poly(ethylene terephthalate) (PET) is one of the most commonly produced single-use polymers in the world, and its mechanical recycling is challenging due to the loss of properties during reprocessing. Chemical recycling is a feasible alternative to reclaim the monomers, however, its viability relies on establishing a straightforward, fast, and inexpensive procedure to turn the end-of-use polymer into new pure monomers. This work reports on the fastest known procedure for PET chemical recycling to produce terephthalic acid and ethylene glycol in an efficient and straightforward manner, thanks to microwave-assisted heating that permitted 100 % PET conversion into TPA in just 1 minute at 120ºC. The depolymerization kinetics of this new procedure were studied and its improved efficiency over other reported hydrolyses procedures was attributed to a thicker shrinking layer. This new procedure may form a major breakthrough in chemical depolymerization. Evidence pointing to the higher reactivity of free OH species, enabled us also to obtain dimethyl terephthalate (DMT) through the use of an anhydrous depolymerization system that is able to convert PET into DMT in 4 min at 80 °C, but requiring careful humidity control. The activation energy for the proposed depolymerization system was estimated in 120 kJ/mol. An additional advantage of the proposed process is the production of potassium sulfate as a side-product, a valuable fertilizer with high market value. This product compensates for the lack of recoverability of the catalyst. Our KOH-in-Methanol Hydrolysis (KMH) process has the potential to become a widely used depolymerization solution for a wide range of (heterogeneous) condensation polymers, which is currently under study by our research group.

Keywords: Hydrolysis, PET, Terephthalic acid, Microwaves

1. Introduction

Poly(ethylene terephthalate) is one of the most consumed polymers in the world. While leading to a large reduction in CO_2 emissions from manufacturing and weight reduction during transport over glass, its use has also led to significant, and growing, environmental issues coming to the fore. Contamination of marine and land ecosystems by micro and macro plastics is an urgent threat, as it has been reported that microplastics are present in at least 12 species of fish in the North Sea, of which at least 3 % is PET[1]. Not only animals are affected by micro-plastics in the ecosystem, drinking water can also be affected as demonstrated recently.[2] These problems arise from inadequate disposal of plastic waste, to a significant extent caused by poorly managed recycling. Currently, a magnifying effect is the accelerated increase of single-use plastics consumption for personal protection, caused by the COVID-19 pandemic.[3] Despite increased awareness about selective collection of plastics and the availability of a growing number of biodegradable plastics,[4] the reduction of the environmental impact of plastics usage in society remains an important challenge. Different ways in which plastics can be recycled include re-use, mechanical recycling (re-processing), energy recovery (burning the plastics to use the energy), or chemical recycling (reclaiming the original components of the polymer). Mechanical recycling is the traditional pathway for plastics recycling, however, it tends to involve significant loss of properties, triggered by chain scission or degradation during re-melting, and removal of additives may be complex or not cost-effective. Reduction in mechanical performance makes it necessary to incorporate fresh feedstock in order to reach the desired properties for new fabricated products from recycled polymer.[5] Chemical recycling of polymers breaks the polymer back into its constituents (or other precursors), making it possible to separate the monomers and remove additives by traditional separation techniques, after which a new polymer can be produced, indistinguishable from non-recycled polymer.

Chemical recycling of PET can be performed via a nucleophilic or an electrophilic attack on the carbonyl by several different agents. This kind of process can render monomers for PET production or terephtalamides (for synthesis of other high added-value materials). The advantages of chemical recycling include the reduction in oil feedstock consumption, along with its versatility to produce high added-value materials, the possibility of producing new polymers with the same properties of the ones produced using petrochemical feedstock, and relative ease of removal of cumbersome additives and colorants. Life Cycle assessments have previously demonstrated that chemical recycling of plastics offer high potential for reducing CO_2 emissions compared to mechanical recycling, based on the quality of the obtained products that can directly be used to produce virgin-like materials, while mechanical recycling offers, most of the time, downgraded pellets that underperform the original materials, making a constant input of new petroleum-based monomers necessary. Furthermore, it is expected that a chemical recycling process involving low or zero organic solvents, will increase the energy economy of the process and consequently diminish the environmental impact of a recycling plant.[6]

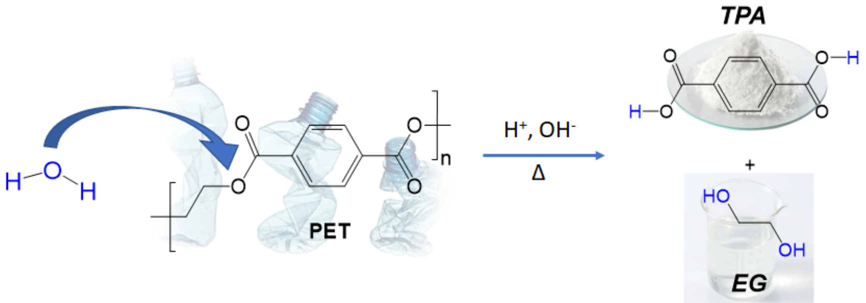

Figure 1 Illustration of chemical depolymerization of PET via hydrolysis of ester bond by acid or basic catalysts

Hydrolysis is the chemical reaction that produces chain scission in the PET chain, producing terephthalic acid (TPA) and ethylene glycol (EG) as final products **(Figure 1**). This reaction can be achieved either by acidic or basic aqueous processes. Many reports exist in the literature, reporting on a wide variety of different depolymerization conditions, covering inorganic acids to alkaline hydroxides, phase transfer catalysts, as well as microwave heating and ultrasound. **Table 1** summarizes a selection of important works and conditions found in literature for the hydrolysis of PET[7], including the values of environmental factors calculated following the description in section 2.2.1. One can see that on average, using aqueous solutions of alkaline hydroxides or concentrated acids, 100 % PET conversion is only possible at temperatures above 100°C and for several hours (which can be reduced down to 1-2 h by incorporation of a phase transfer catalyst).

Table 1. Summary of the most outstanding PET hydrolysis processes found in literature for complete depolymerization of PET

Ref	Catalyst	Co-catalyst/conditions	T (°C)	Reaction time (min)	E factor (a.u)	ε ($°C^{*-1}min^{-1}$)	ξ (°C*min)
8	H_2SO_4 (aq)	N.R	135	300	8,87	2,22E-05	3,99E+05
9	HNO_3	DMSO Na_2SO_4	98	140	5,86	5,07E-05	1,16E+05
9	HNO_3	DMSO Na_2SO_4	110	140	5,33	4,97E-05	1,07E+05
9	HNO_3	DMSO Na_2SO_4	120	140	4,68	5,19E-05	9,01E+04
10	NaOH (aq)	TBAI	90	45	3,9	2,44E-04	1,60E+04
11	NaOH (aq)	EtOH:water 80:20	110	30	12,28	2,70E-04	4,55E+04
12	NaOH (aq)	Microwave	220	2	1,72	2,20E-03	7,80E+02
13	HNO_3	DMSO Na_2SO_4 H_3PO_4	140	160	5,6	4,37E-05	1,28E+05

The aqueous hydrolysis of PET is a heterogeneous reaction between two incompatible phases: a solid (PET) suspended in an aqueous phase. One of the biggest issues for hydrolysis in aqueous media is the incompatibility between the liquid phase and the polymer. Consequently, the incorporation of a phase transfer catalyst has proven to be an important strategy to improve the reaction efficiency, as observed by several research groups.[10,14] An alternative way to improve reaction efficiency includes the use of microwaves, which reduces the environmental energy impact by increasing heating efficiency, thereby diminishing reaction time[12]. The present work explores the combined use of microwave irradiation and a solution of potassium hydroxide in anhydrous alcohol to develop an energy efficient non-aqueous hydrolysis process. We believe that the *in-situ* formed potassium methoxide will have improved diffusivity into the polymer matrix further speeding up the depolymerization reaction. The viability of the proposed method is completed by the formation of potassium sulfate, the byproduct generated by neutralization of the reaction mixture. Potassium sulfate is an important fertilizer used to provide sulfur and potassium to soil.[15] Hence, the proposed process has two valuable outputs that have the potential to be a game changer in polymer recycling.

2 Materials and methods

2.1 Materials

Methanol (>99.9%) was provided by Fischer Scientific. Transparent PET bottles were cut in rectangular flakes of around 0.5 cm^2, washed with soap, distilled water, and dried under vacuum before reaction. Potassium and sodium hydroxide were provided by VWR chemicals (89.3 %).

2.2 Methods

2.2.1 Synthesis of terephthalic acid from PET waste

Approximately 0.5 g of the cut PET flakes were charged into a high-pressure vial along with 10 ml of the KOH-in-Methanol (KMH) solution. The vial was closed with a hermetically sealed metallic lid and placed into the microwave reactor (Initiator+ Microwave System, Biotage, Sweden). The power was supplied in pulses until a stable temperature response was achieved. The reaction time was taken from the moment the system reached 5 °C below the programmed temperature. The system was stirred magnetically at 600 rpm. After the reaction time, 10 ml of distilled water was added to dilute the "salted out" potassium methoxide that precipitated along with terephthalate salts. The insoluble unreacted PET was filtered off, washed with distilled water (200 ml), dried under vacuum at 80 °C, and weighed. Acid addition was stopped around pH 4. The white solid was filtered off, washed with distilled water (200 ml) and methanol, dried under vacuum, and weighed.

PET conversion was calculated following Equation 1, where $m_{un.PET}$ is the mass of unreacted polymer and m_{PET} is the mass of initial polymer. TPA yield was calculated using Equation 2, where

m_{TPA} is the mass of TPA obtained after the reaction. The 0.874 coefficient corresponds to the ratio of molar mass of TPA and the molar mass of PET-mere. The balance for mass determination of PET before and after the reaction, had a resolution of ± 0.0001 g.

$$PET\ conversion\ (\%) = \frac{m_{un.PET}}{m_{PET}} * 100 \qquad \textbf{(1)}$$

$$TPA\ yield\ (\%) = \frac{m_{TPA}}{m_{PET} * 0.874} * 100 \qquad \textbf{(2)}$$

2.2.2 Production of dimethyl terephthalate

In an oven-dried high-pressure vial, approximately 2.48 g of metallic sodium was left to react with methanol under an argon flux. Once the sodium was consumed, approximately 0.5 g of PET was added and the system was sealed and further taken to the microwave reactor. After the reaction time, 10 ml distilled water was added. The remaining white solid was filtered off, dried and weighed, while the remaining solution was neutralized to pH 4 and processed as described in 2.2.1.

2.2.3 Green chemistry calculations

The energy efficiency coefficient ε is a way in which the proposed method can directly be compared to others to verify its efficiency, and it is defined by Equation (3) where t is the reaction time (in minutes), T the reaction temperature in degrees Celsius, and Y is the yield of the main monomer in mass fraction[7]. The lower the temperature and the reaction time, the higher the relative value of Ɛ. The E factor is based on the environmental factor (E), proposed by Prof. Sheldon in 1992[16] which has been used in green chemistry metrics with success[17] and corresponds to a simple mathematical relation defining the amount of waste generated per unit product. In this work, we propose a modification of the E factor, considering that it has been established that 90 % of solvent can be recycled in industrial processes[18], leading to Equation (4), used to compare the E factor of different PET depolymerization works in the literature and the ones presented here. The environmental energy impact corresponds to the combined effect of the mass input and the energy economy as described in (5).

$$Ɛ = \frac{Y}{T \times t} \qquad \textbf{(3)}$$

$$E_{factor} = \frac{\left[0.1 * \left(\frac{solvent}{PET} ratio\right) + \left(\frac{cat}{PET} ratio\right) + \left(other \frac{subst}{PET} ratio\right)\right] * mPET}{Yield_{Product} * \frac{MM_{Product}}{MM_{PET\ MERE}} * m_{PET}} \qquad \textbf{(4)}$$

$$\xi = \frac{E_{factor}}{\varepsilon} \qquad \textbf{(5)}$$

2.2.3 Characterizations

2.2.3.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analyses were performed on an Alpha 1 spectrophotometer (Bruker) operated in Attenuated Total Reflection mode with single reflection on unreacted polymers and depolymerization products combining 24 scans between wavenumbers 450 and 4000 cm^{-1}.

2.2.3.2 Thermogravimetric analysis (TGA)

TGA was performed on a Netzsch Tarsus TG209F3 using platinum pans for the polymers and alumina pans for depolymerization product. The apparatus was equipped with a differential thermal accessory for determination of thermal transitions. Amounts ranging from 5-10 mg were loaded in the pans and the analyses were carried out using air as carrier gas and nitrogen as protective flow gas for the microbalance. A heating rate of 10 °C/min was used from 30 to 900 °C.

2.2.3.3 Differential Scanning Calorimetry (DSC)

DSC analyses were carried out on a DSCQ2000 (TA instruments) using aluminum Tzero pans. The analysis consisted in heating the polymer from room temperature to 280 °C, keeping the sample isothermal for 5 min followed by rapid quenching to -60 °C, aiming to amplify the signal for the amorphous region and to promote cold crystallization. After stabilization at -60 ºC, the sample was heated at 5 °C/min to 280 ºC to determine the glass transition temperature (Tg), cold crystallization temperature (Tcc), melting temperature (Tm) and enthalpies of cold crystallization and melting (ΔHcc and ΔHm). For the analysis of the depolymerization product, a single heating cycle from room temperature to 280 °C at 5 °C/min was applied.

2.2.3.4 Nuclear magnetic resonance (NMR) spectroscopy

The ^{1}H-NMR spectroscopy analyses were carried on a Spinsolve 60 Ultra (Magritek). The analyses were carried out on products at a concentration of 20 mg/ml in deuterated DMSO as the solvent.

3 Results and discussion

3.1 Depolymerization using Conventional heating

Following the work by other authors in previous studies of adding alcohol in basic hydrolysis media,[11,19,20] we performed a comparison of the depolymerization of PET by basic solutions of potassium hydroxide in methanol, ethanol, iso-propanol, and tert-butanol in the absence of water. The present method differs greatly from the approach of pre-soaking PET in organic solvents,[21] making the process more sustainable and straightforward as only alcohol and alkali are used. The product for all the reactions is TPA as demonstrated by FTIR spectroscopy shown in the inset image in Figure 2 (the details of the absorption band attribution can be found in Table S.1). No differences were found neither among the depolymerization products, nor the PET conversion or TPA yield for the alcohols studied. This indicates that the alcohol itself is not the reactive species but rather acts as a medium for the alkaline catalyst, which is reinforced by the fact that the amount of acid needed for neutralization of the reaction medium does not depend on the PET conversion. The efficiency of the alcoholic medium for the hydrolysis of PET under basic conditions would be a function of its capacity to dissolve the highest amount of base, since it is a known fact exposed in multiple studies that the reaction speed increased and highest conversions are reached when the base concentration increases.[10–12,14] Taking this into considering, further reactions were carried out in methanol, since it could dissolve the highest amount of base.

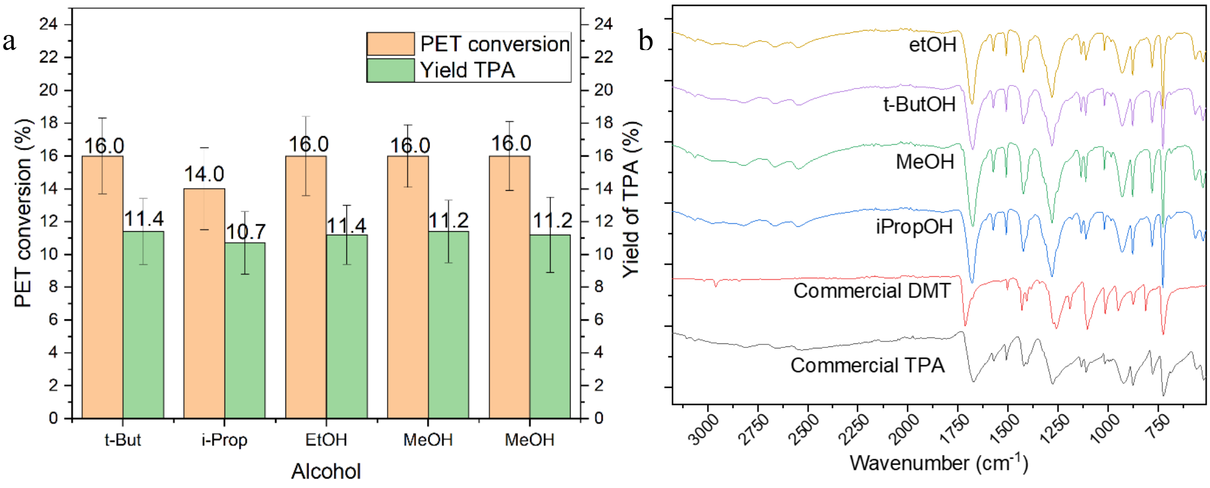

Figure 2 **a**. PET conversion and TPA yield as a function of the alcohol for a series of analogous reactions where the KOH solution was prepared in t-butanol, isopropanol, ethanol, and methanol. The reactions were performed under air atmosphere using a 0.25 M concentration of base (The experiment marked with * refers to a reaction under argon atmosphere). **b**. FITR spectra of the depolymerization products compared to commercial TPA and DMT.

The effect of the base cation was studied by comparing the performance of KOH and NaOH in methanol. Figure 3a shows the PET conversion as a function of reaction time for analogous reactions using NaOH and KOH keeping all the other variables constant. The reaction was significantly faster when KOH was employed, which could be attributed to the stability of the KMH solution compared to the low stability of NaOH in solution, a fact that is evidenced by the precipitation of NaOH at high concentrations in methanol, which is not observed in methanolic solutions of KOH.

We can compare the efficiency of the KMH solution process used here with the aqueous hydrolysis processes in published work:[10,11] The traditional aqueous hydrolysis method took 50 h at 110 °C to be completed without the incorporation of a phase transfer catalyst, while with use of 2 wt% of a phase transfer catalyst 100 % conversion of PET was achieved in 5 h. This comparison demonstrates the efficiency of the KMH system, which is faster and requires less energy than the aqueous approaches. The efficiency of the KMH system was also proven in a room temperature reaction (Figure 3c), as PET was fully depolymerized under stirring in 3 days. This performance of the KMH system performs beyond that of other depolymerization studies at room temperature irrespective of the solvent and catalyst system used.[22]

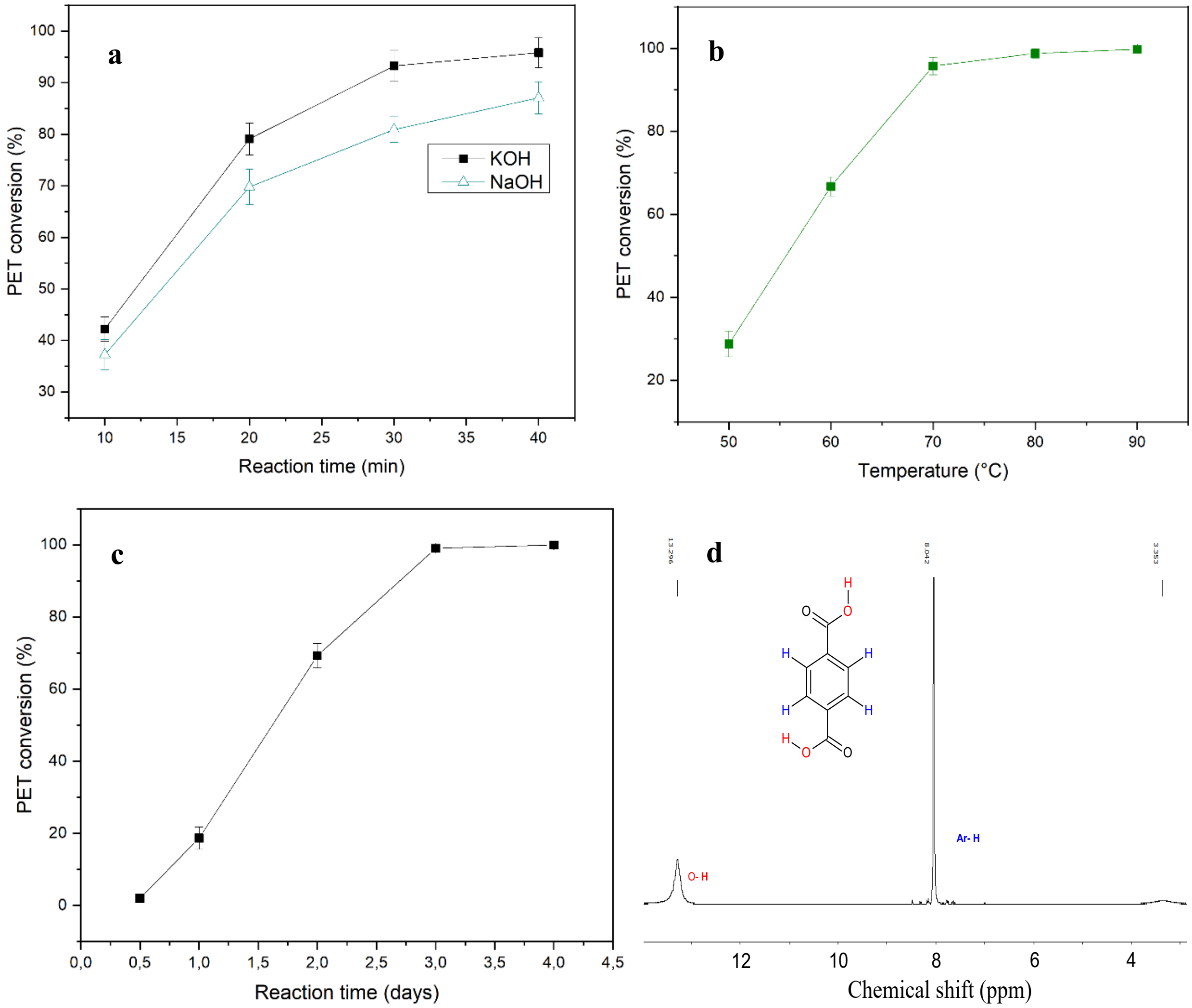

Figure 3 **a.** PET conversion as a function of reaction time in a 1.25 M solutions of KOH and NaOH in methanol (PET:Solution 1:20 g:ml) at 80 °C. **b.** PET conversion as a function of temperature for a 1.25 M KOH/MeOH solution (PET:Solution 1:20 g:ml). **c.** PET conversion (%) as a function of reaction time at room temperature (PET:Solution 1:20 g:ml). Representative NMR spectrum of obtained TPA solid.

3.2 Depolymerization using microwave reactor

PET conversion as a function of the base concentration was monitored in order to verify the optimal concentration at which microwave depolymerization could be performed with a maximum energy efficiency. Figure 4 shows the PET conversion as a function of molarity of the depolymerization solution for a reaction period of 3 min at 80 °C. The PET conversion increased with increasing KOH in MeOH concentration up to 1.25 mol/L, where it reached a plateau. Increasing the KOH concentration further did not lead to a further increase in PET conversion; PET conversion even showed a tendency to decrease. This behavior suggests an active participation of KOH in the reaction mechanism, yet, it was verified that KOH is not consumed during the reaction, as the amount of acid required for neutralizing the reaction mixture remains unaltered regardless the PET conversion. The behavior of PET conversion as a function of molarity of KOH in the depolymerization solution can be explained by the saturation of the solution with the formed potassium terephthalate. The produced salt requires more methanol molecules to be solvated, as a result, the remaining methanol is unable to solvate all the solute, which causes the base to salt out of the solution along with terephthalate, leading to an actual decrease of base concentration in the liquid phase with PET conversion, decelerating the reaction and thus, causing the plateau observed in Figure 4. We confirmed this by modifying the procedure described in 2.2.1, adding a filtration step of the reaction mixture after the reaction period, which permitted to verify that the basicity of filtered solution diminished along with PET conversion. This finding does not mean that KOH is actually consumed, it means that it leaves the liquid phase, causing the observed deceleration of the reaction. Given the apparent maximum for PET conversion around 1.25 mol/L KOH in MeOH, further experiments were carried out with this concentration.

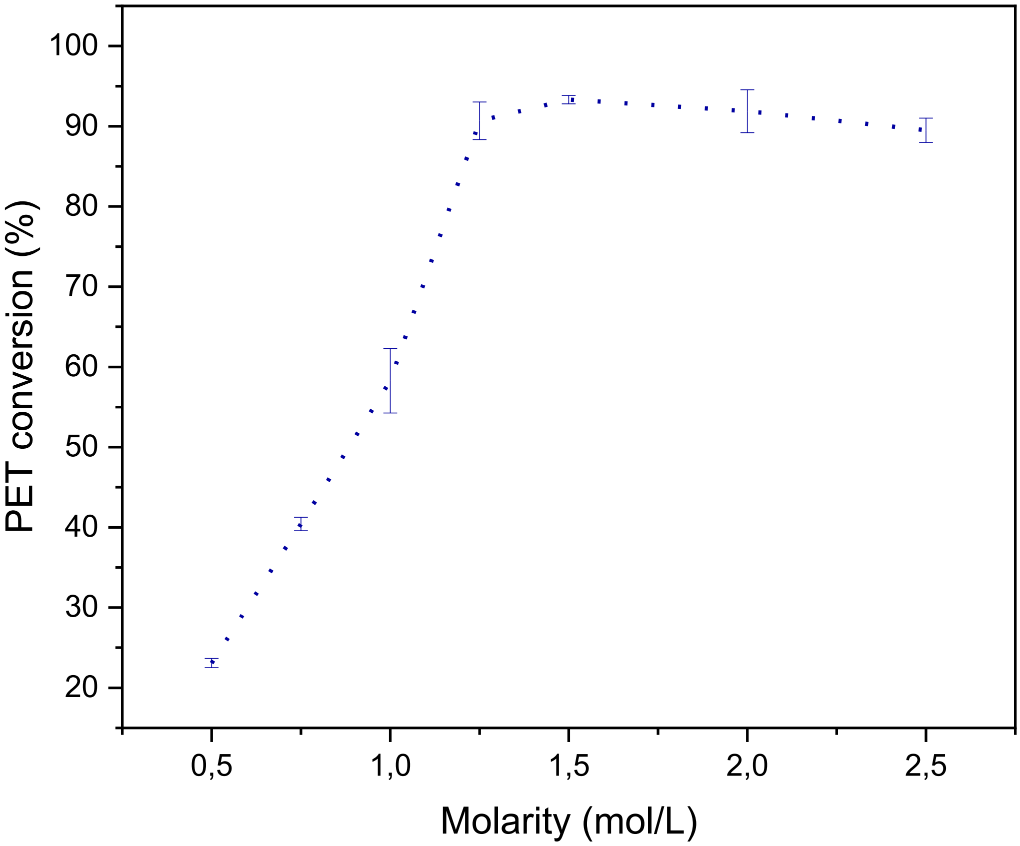

Figure 4 PET conversion as a function of molarity of KMH solution. Experiments were carried out at 80ºC for 3 min and PET:solution ratio of 0.5 g:10 ml.

Optimization of the reaction time for different temperatures is presented in Figure 5, where it is observed that PET conversion increased with reaction time for all investigated temperatures. Under microwave reactor conditions, all temperatures studied corresponded to an exponential increase of pressure, which is likely one of the factors responsible for the significant reduction in the required reaction time to attain 100 % PET conversion with increasing temperature. When the reaction temperature was set to 120 °C, only 1 min was required for complete PET conversion into soluble potassium terephthalate. Upon addition of water after one minute reaction time, a clear homogeneous solution was observed as precipitated base was dissolved. On the other hand, **Error! Reference source not found.** depicts the evolution of PET conversion as a function of temperature for different reaction times under the same reaction conditions as before. It was observed that the minimum temperature and time necessary for 100 % conversion of PET flakes are 4 min at 100 °C.

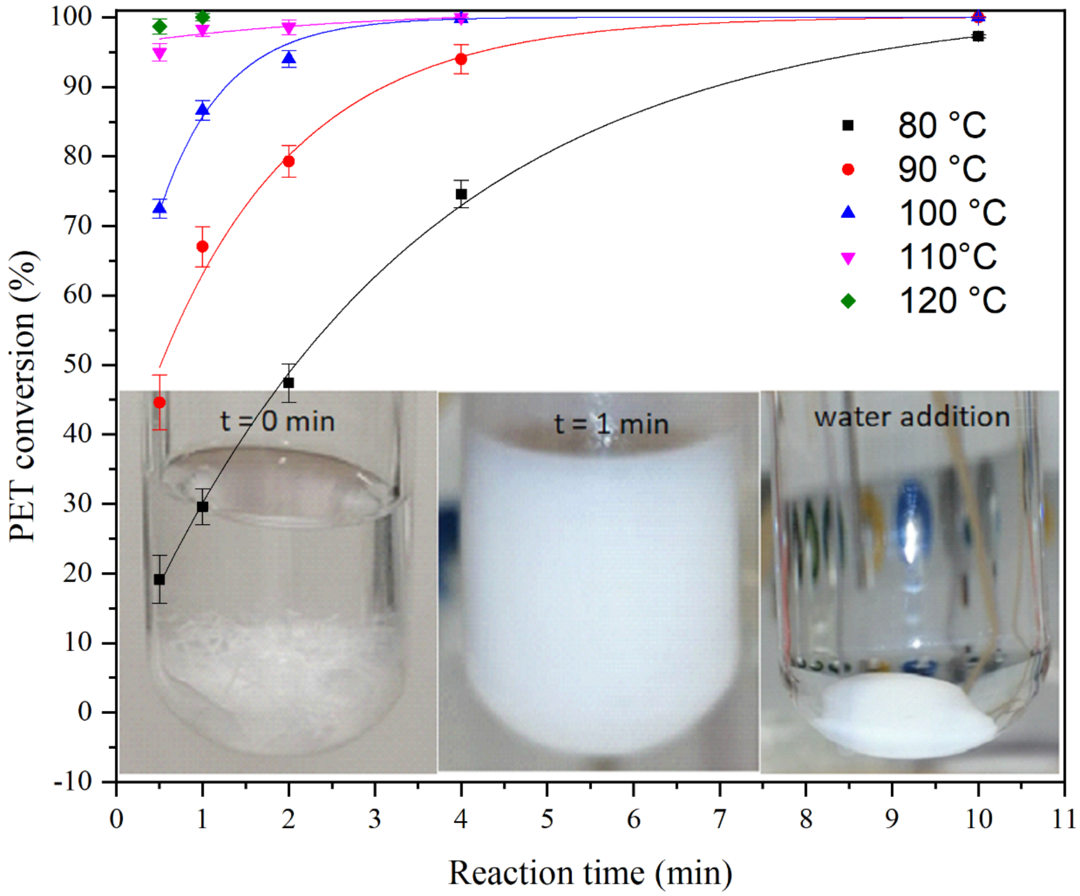

Figure 5 PET conversion as a function of reaction time for microwaves reactor with PET:Solution ratio of 0.5 g:10 ml and 1.25 M KOH in Methanol at different temperatures. Inset image shows the reaction progress for 1 min at 120 C: before reaction, showing the PET flakes; after 1 min reaction showing the "salted out" potassium methoxide and after water addition, where a transparent homogeneous mixture is observed.

3.4.3 Reaction kinetics

The activation energy for the depolymerization reaction of PET flakes was calculated by plotting the inverse of the concentration of poly(ethylene terephthalate) in the reaction system in (mol/L) as a function of reaction time. Working at four different temperatures (65, 80, 90 and 100 °C), four different slopes were obtained, which correspond to the reaction rates. Applying the Arrhenius equation (6), the activation energy for the depolymerization reaction of polyethylene terephthalate pellets using the developed KMH system was estimated to be 120.7 kJ/mol (**Error! Reference source not found.**B). This activation energy is in agreement with values reported for conventional hydrolysis systems, which indicates that the combination of microwaves and the developed of high pressure inside closed reaction vessels can be the cause of the outstanding performance of the proposed system.[23]

$$k = Ae^{-Ea/_{RT}} \qquad (6)$$

$$\ln(\ln(k) = -\frac{Ea}{R}(\frac{1}{T}) \qquad (7)$$

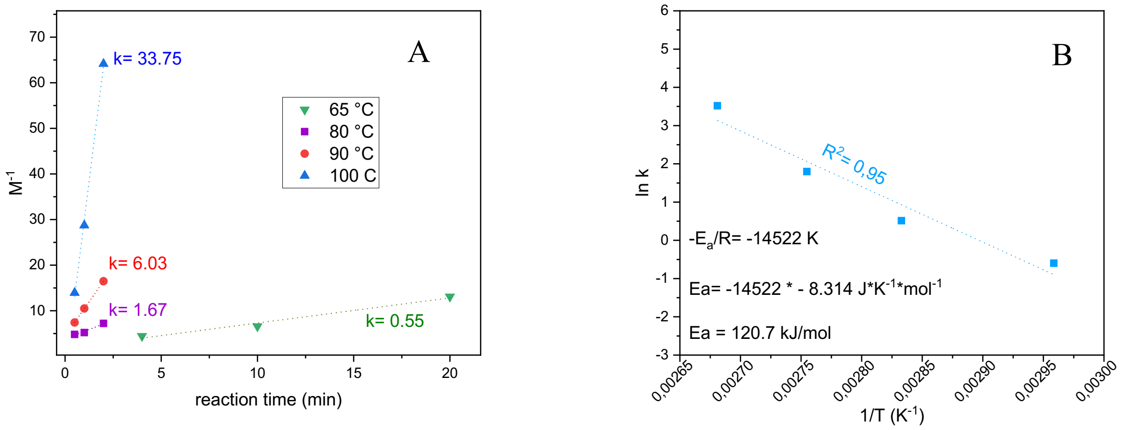

Figure 6. A. Reciprocal of concentration of polyethylene terephthalate as a function of reaction time at 65, 80, 90, and 100 °C. B. Arrhenius plot for the four temperatures studied in the depolymerization reaction of polyethylene terephthalate pellets using the KMH system.

3.4.4 Reaction mechanism

The outstanding results reported in this work require a deeper explanation of the chemistry involved in the reaction. Since the KOH-in-methanol solution produces potassium methoxide in an equilibrium reaction, it would be expected that dimethyl terephthalate would have been produced along with the terephthalic acid. However, the evidence showed that for all the temperatures studied, the depolymerization using KMH solution, produced exclusively TPA as the depolymerization product, which is a hydrolysis product, instead of DMT, which is the methanolysis product. DSC, FTIR and NMR, demonstrated that TPA is indeed the sole product of this depolymerization process without any DMT being formed. Figure 7 shows a comparison between the proposed mechanism for the depolymerization of PET by the KMH solution and the model study in which metallic sodium is dissolved in methanol, generating anhydrous sodium methoxide in situ. The depolymerization by Na^0/MeOH should lead exclusively to the methanolysis product: dimethyl terephthalate. We propose that the difference in reactivity for methanolysis and hydrolysis, is explained by the higher mobility of KOH compared to potassium methoxide, which makes this reaction temperature-driven (while methanolysis would be diffusion-driven). In order to prove this hypothesis, reactions of the Na^0/MeOH system were performed on PET pellets using 99.9% pure methanol for 5 min, keeping concentration and PET:solution proportion approximately constant (Figure 8). The experiments showed a clear competition between methanolysis and hydrolysis, where high temperatures clearly favor the hydrolysis over methanolysis, while there is a tendency for methanolysis prevalence at lower temperatures. This trend corroborates that the free OH, coming from the interaction of water traces in methanol and the atmosphere, has a high mobility and reacts preferentially at higher temperatures than the methoxide. Thus, the nucleophilic attack of the methoxide appears to be diffusion driven, while the hydroxide attack is temperature driven. In order to support this further, a reaction was carried out overnight at room temperature and it produced nearly 100 % DMT. The same system was tested at 80 °C using methanol pre-treated with molecular sieves, which produced DMT in more than 80 % yield. We believe that further control over the reaction conditions can lead to a near 100 % DMT yield.

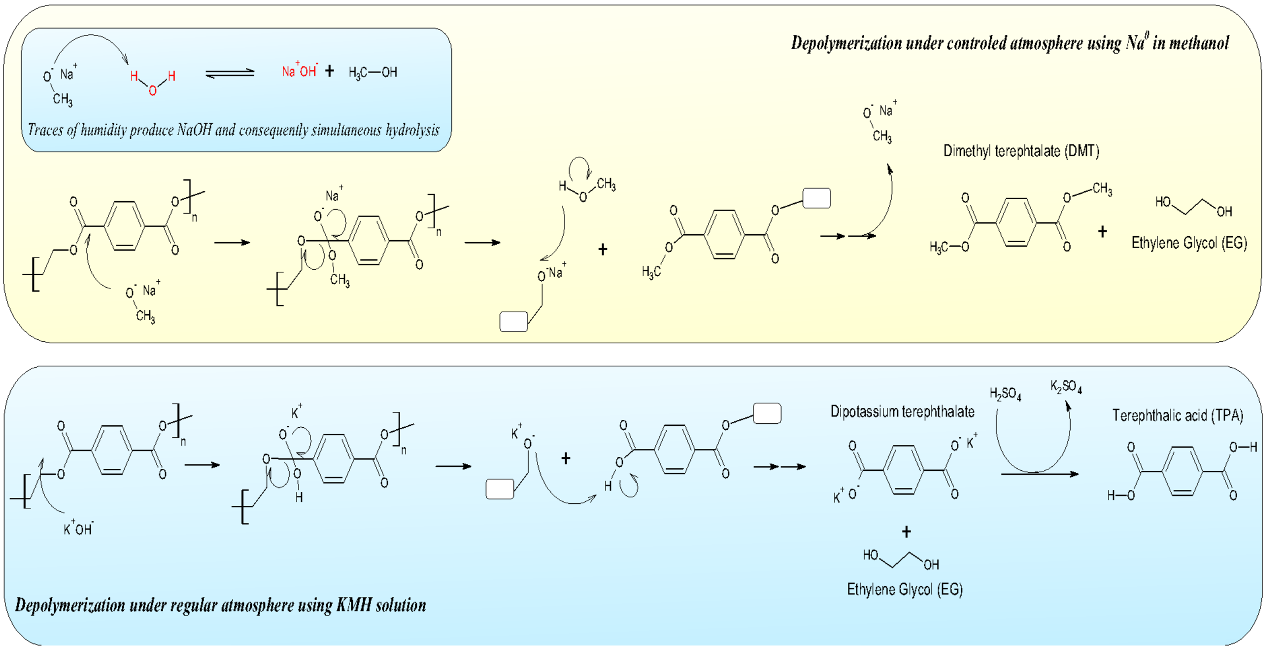

Figure 7. Proposed chemical reaction mechanism for the depolymerization of PET using the KMH solution and an analogous system using metallic sodium in methanol. The inset scheme shows the reaction of water traces present in the solvent and the in-situ formed

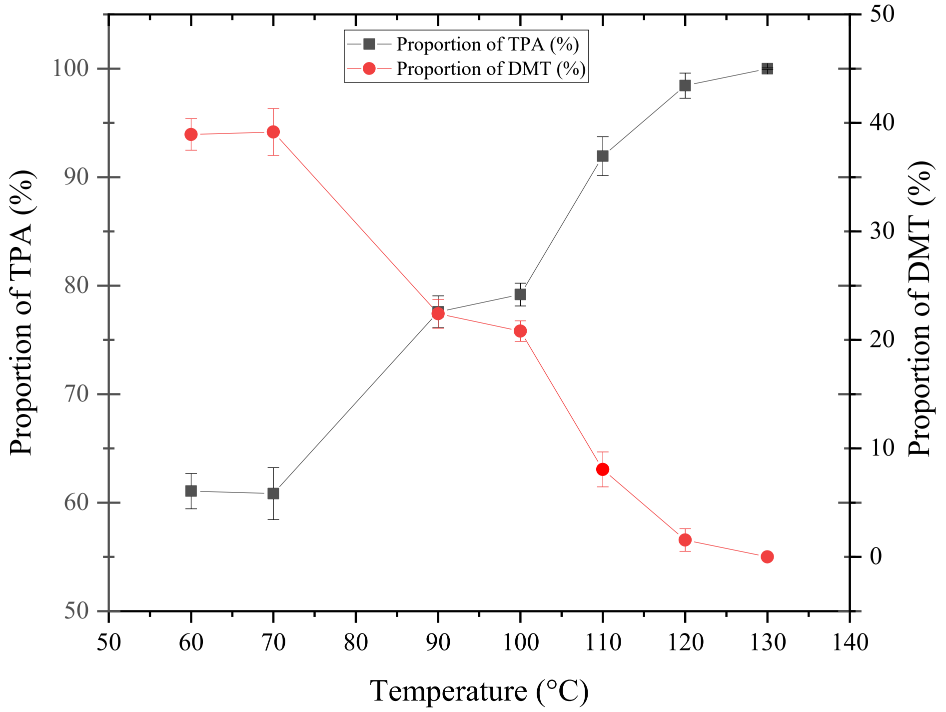

Figure 8. Proportion of produced TPA and DMT as a function of temperature for a competitive reaction of methanolysis-hydrolysis using the sodium/methanol system.

3.5 Interaction of phases and reaction velocity

The PET conversion and acid value of the obtained product as a function of the reaction time for the chosen KMH system (80 °C, 1.25 M, 0.5g:10 ml) is shown in Figure 9. The virtually constant acid value of the TPA produced throughout the length of the reaction, combined with the FTIR spectra (see Supporting Information), showed that the only soluble product derived from the process is the $TPAK_2$ salt. After the chain scission in the solid matrix, the shortened chains seem to remain in the solid state so that no other insoluble product is observed. This implies that there is a chain shortening and oligomers can be found at some point during the depolymerization process, however, the speed of the depolymerization is such, that the reactions proceeds almost instantaneously to the $TPAK_2$ salt. Consequently, what limits the reaction speed is the size and shape of the polymer fed to the reactor (additional experiments showed that big PET pellets take a longer time to fully depolymerize). The unreacted polymer, by the end of the reaction period, is affected only to a limited extent (*vide infra*), which results in a slight molar mass loss and increase in crystallinity, a consequence of the preferential attack of the depolymerization reaction in the amorphous regions. The only products are $TPAK_2$ (soluble) and unreacted PET (insoluble).

The core-shrinking model[24] was used as a basis to explain the high velocity observed in the depolymerization reactions studied here (Figure **10**). The comparative description of the aqueous and non-aqueous media points to the possible effect of the compatibility between the reactants and the reaction medium on the velocity of reaction. In the case of the non-aqueous system, the higher compatibility (translated in the higher solubility parameters encountered for PET/MeOH than for PET/water) promotes the formation of a wider shrinking layer which, as a result, enables a higher reaction rate in the reaction system, responsible for the outstanding results observed for the KMH under its ideal conditions. The conversion of PET into $TPAK_2$ salt is an irreversible process since the dipotassium salt cannot undergo an esterification reaction with EG, methanol or even the potassium methoxide as the carbonyl carbon is insufficiently electrophilic.[25] It is important to highlight that differences in solubility parameter are not the only factor that explain the outstanding results, but a combination of the compatibility (augmented by the presence of a base, which can interact with the carbonyls along polymer chain) and the basicity.

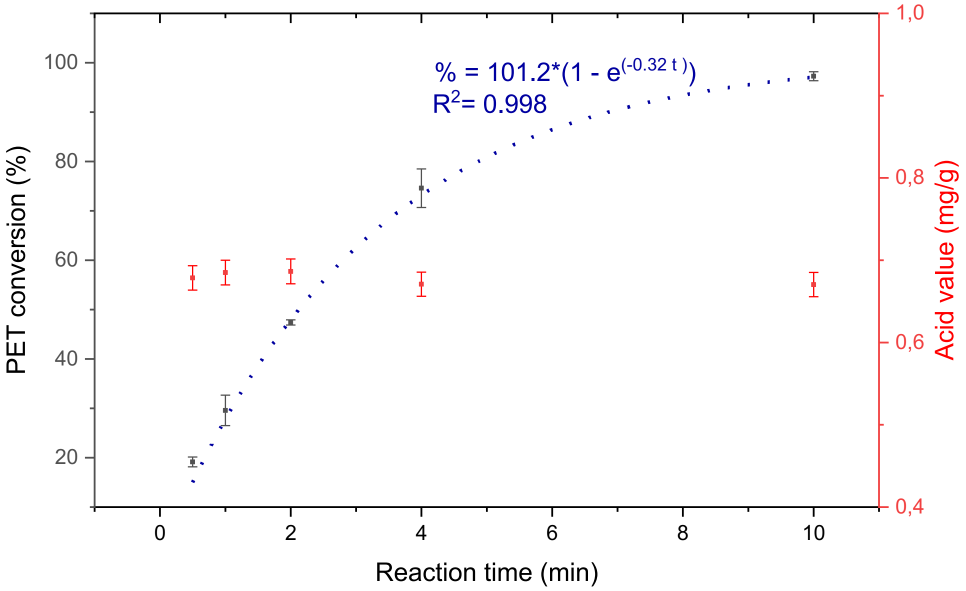

Figure 9 PET conversion and acid value of obtained TPA as a function of the reaction time for KMH depolymerization at 120 C, 1.25 M and 0.5g:10 ml PET:KMH ratio. The exponential equation that fits the experimental points of the curve is shown (R^2=0.998).

As observed by multiple researchers in previous work on the solvolytic depolymerization of PET,[26–29] the chain scission occurs preferentially in the amorphous regions of PET, as confirmed by the increase in melting enthalpies of unreacted PET with increasing reaction time (Figure **11**A). This indicates that the crystalline regions are retained longer than the amorphous ones, as the amorphous regions are more rapidly attacked and converted into soluble products. The DSC plots also show another particular fact: the marked inhibition of cold crystallization at around 30 s reaction time, attributed to chain shortening that occurs at low reaction times. This is corroborated by differential thermogravimetric analysis (Figure **11**B) showing a constant shift of the T_{max} of the main degradation step to higher temperatures. Hence, the more crystalline regions (with higher degradation temperature) become more prevalent inside the matrix as the reaction time increases.

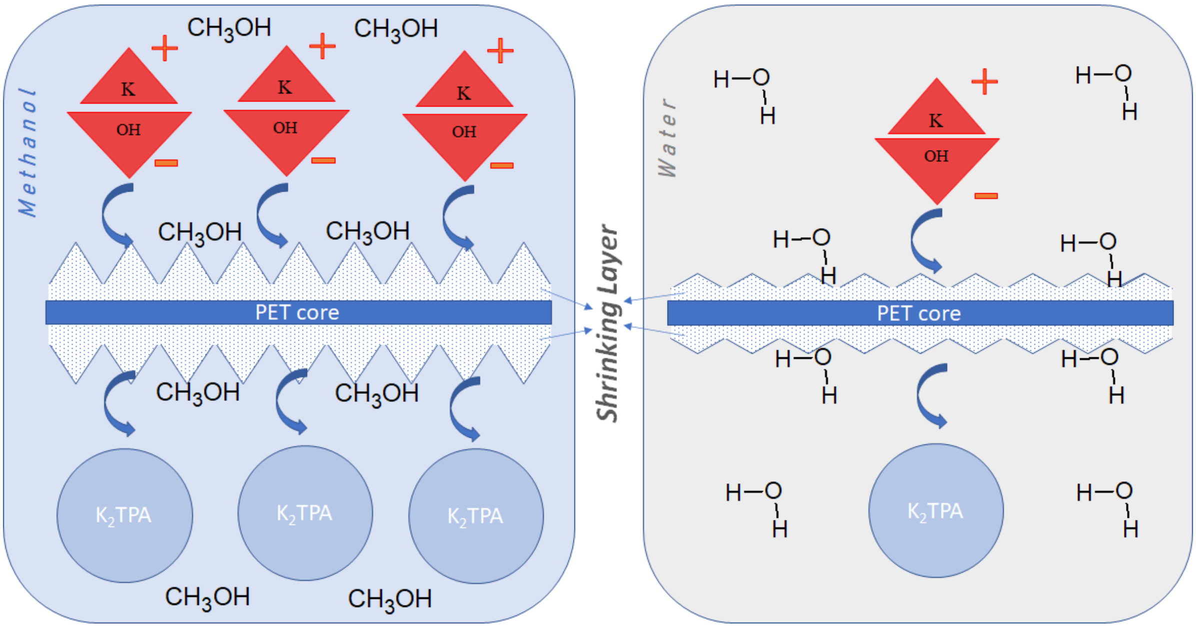

Figure 10. Interpretation of the differences observed between reaction in aqueous and methanolic media, based on the core-shrinking model of the MKH depolymerization system over PET flakes

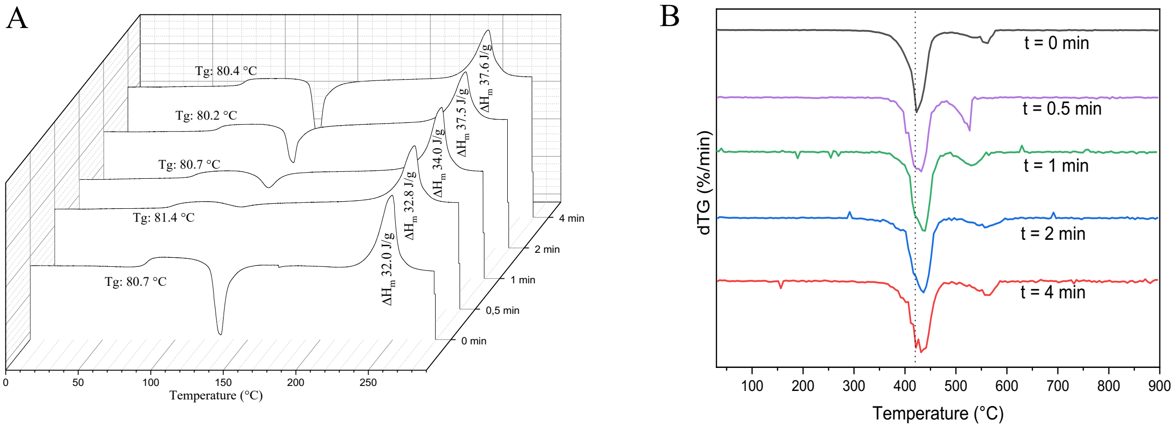

Figure 11. **A**. DSC plots of unreacted PET submitted to MKH depolymerization at 80 °C for different reaction times ranging from 0 to 4 min in the microwave reactor, keeping the PET:KMH solution ratio at 0.5 g:10 ml, 1.25 M. DSC analysis was performed at a heating rate of 5 °C/min. Only the second heating cycle after quenching at -80 °C is shown. **B**. Differential thermogravimetric analysis for unreacted PET submitted to MKH depolymerization at 80 °C for different reaction times ranging from 0 to 4 min in the microwave reactor, keeping the PET:KMH solution ratio at 0.5 g:10 ml, 1.25 M.

3.4.6 Effect of water on reaction efficiency

The presence of additional water in the reaction system has a negative impact on the performance of the KMH solution. When increasing the water content up to 2.5% in the KMH solution under ideal conditions to achieve 100 % PET conversion (1 min, 120°C), it was seen that PET conversion decreased when the water content surpassed 1% (Figure **12**). Therefore, it is important to use pure methanol and limit the water content to below 1% in the KMH solution. Similar results were found by Pham and Cho (2021),[30] investigating methanolysis of PET catalyzed by potassium carbonate. They determined that excessive water (molar ratio H_2O:PET around 0.8) was able to noticeably decrease PET conversion and even promote the competition between methanolysis and hydrolysis. In the present work, as previously explained, the competition is favorable to the hydrolysis product, obtaining exclusively TPA after work up.

The effect of water can be thus be explained using the aforementioned core shrinking model; increasing water content affects the solubilization of the outer layers and causes a reduction of the reactive shell volume thereby diminishing the reaction velocity and thus the PET conversion for water concentrations above 1%.

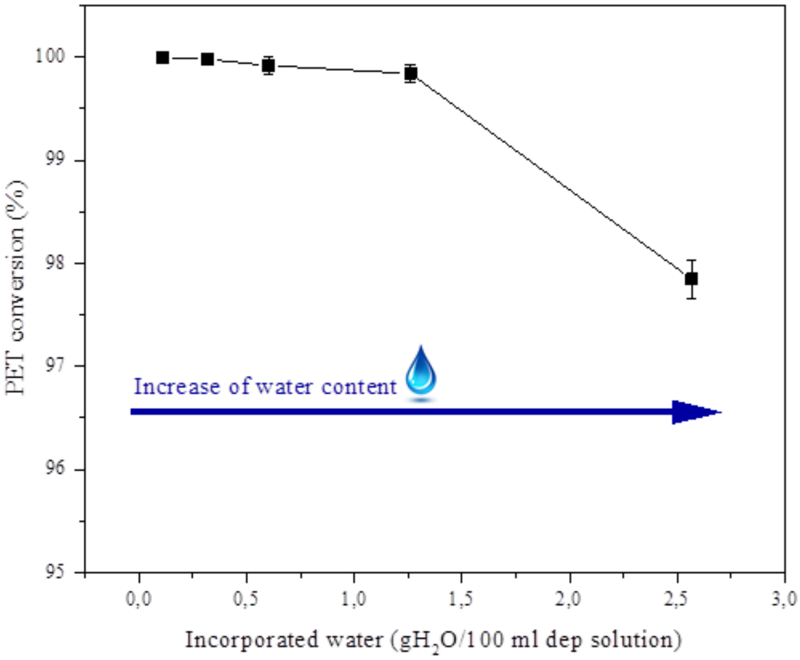

Figure 12 PET conversion as a function of the water content of the KMH solution in a reaction mixture containing 0.5 g:10 ml PET:KMH (molarity of KMH solution: 1.25 mol/L at 120oC for 2 min).

3.5 Industrial feasibility and green chemistry metrics

Five g of PET flakes were then reacted to verify the inputs and outputs for a hypothetical industrial process of PET depolymerization with the KMH system as illustrated in Figure **13**, where all the in- and outputs are displayed as a projection based on the results obtained in this work (the yields are expected to be significantly higher on an industrial scale due to reduced losses during purification). Potassium sulfate is a commonly used salt in fertilizers, providing sulfur and potassium to the soil. Therefore, the present process is able to produce two useful products out of PET waste. The yield of terephthalic acid was 93.8 % and its purity was confirmed by DSC, FTIR, TGA, and NMR spectroscopy (see Supporting Information). The TPA yield obtained in this work was used for the calculation of the green chemistry metrics as defined in section 2.2.2. Figure **14** presents a comparison among the three green chemistry parameters, namely E, ε and ξ for different literature reports dealing with PET depolymerization using microwaves. A great difference in ε factor is observed for the present work, which exceeds by at least 6 times the best work found in literature. Paliwal and

Mugray[10] used significantly higher temperatures and employed a phase transfer catalyst, a drawback in terms of green chemistry metrics. On the other hand, Căta and co-workers[12] employed significantly higher temperatures than the ones employed in the present study, which is also reflected in the green chemistry metrics. The positive chemistry metrics for the KMH systems is a decisive step forward towards the application of a feasible industrial process for chemical recycling of PET, since it is fast, straightforward and energetically favorable.

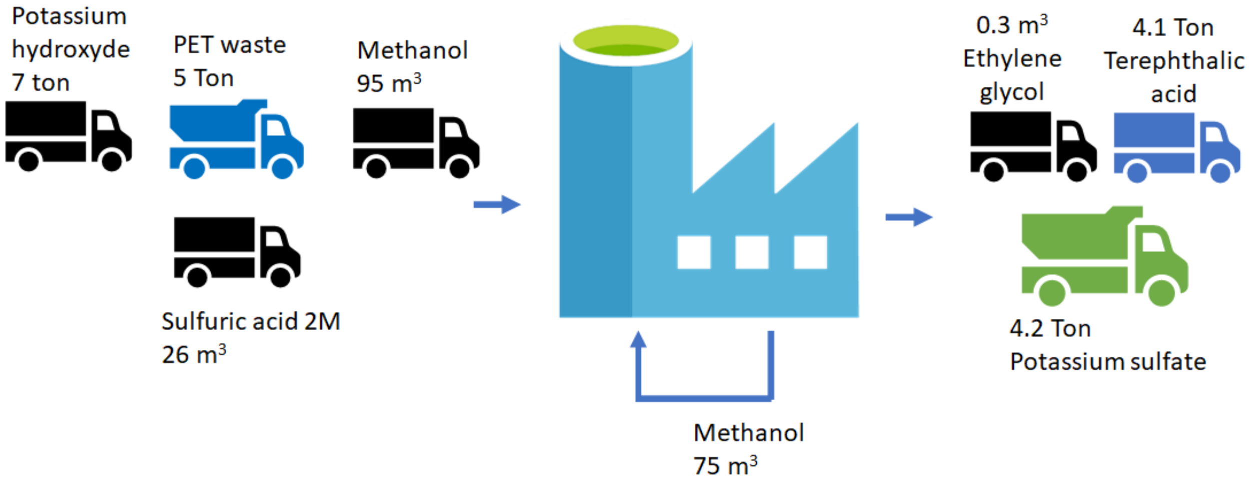

Figure 13 Upscaling of PET depolymerization by KMH system and the inputs of a hypothetical industrial process

Other work in the literature claims that the use of heterogeneous catalysts is a decisive factor for the implementation of chemical recycling, given the possibility of easy catalyst recovery.[31,32]. However, in our work, the catalyst is converted into potassium sulfate, a valuable byproduct in its own right that could cover the lack of catalysts recovery. The ease of the current process is such that it has the potential to be applied directly in small factories close to waste generating communities. One evident environmental advantage that should make a decisive change in current chemical recycling processes is the avoidance of organic solvents such as chloroform, dichloromethane or tetrahydrofuran, making the KMH solution not only less energetically demanding, but also less harmful to the environment. This could be especially beneficial in places with environmental plastic waste problems, such as Karachi, Pakistan, a city with a serious environmental issue related to the high amount of plastics in rivers and beaches, directly affecting the quality of the drinking water and the soil.[33,34] The development of recycling opportunities that can be implemented within local communities and use local plastic waste as the resource could lead to successful management of the local environmental issue while also providing economic benefits.

Since plastic waste is normally heterogeneous, the present process presents important advantages with respect to mechanical recycling, since the solubility of most plasticizers will permit a straightforward separation of contaminants from the desired monomers, while in a mechanical recycling process, the issue of molar mass loss will be accompanied by the presence of residual contaminants. Currently, our group works in a straightforward process that uses the KMH for mixed streams of polycondensation plastics.

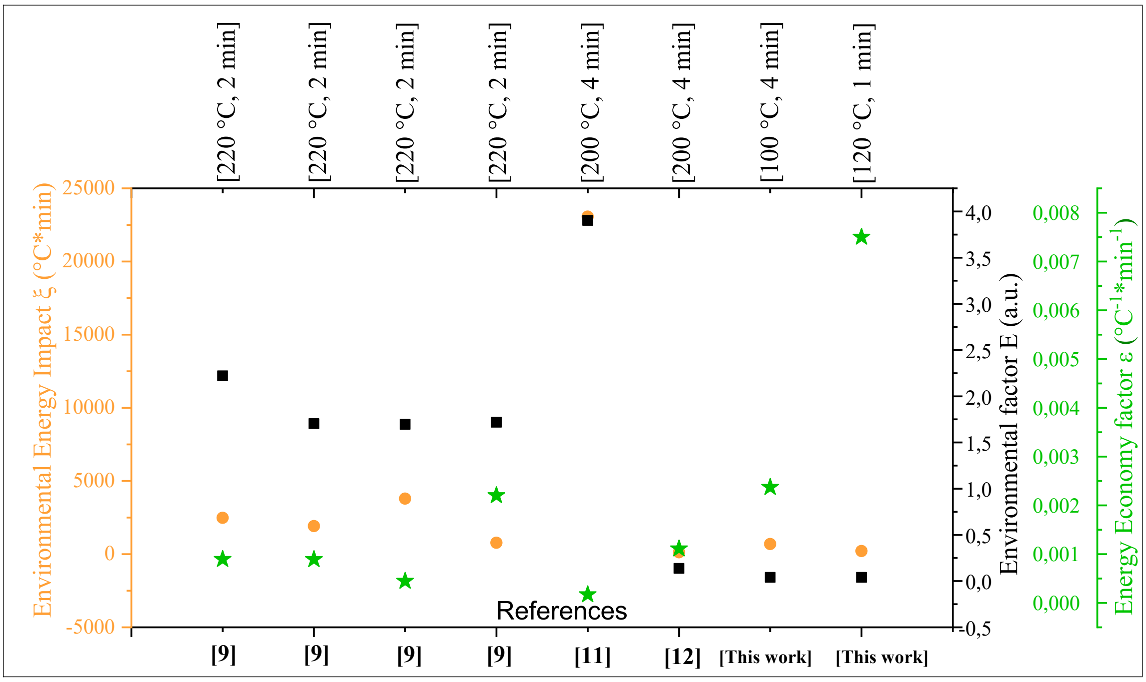

Figure 14. Green chemistry metrics for PET depolymerization processes found in literature using microwaves. In black, the environmental factor, in green the energy economy factor, in orange the environmental energy impact

Outlook and conclusions

The present work gives an insight in the properties of the KMH system for almost instantaneous depolymerization of PET. The lowest time required for complete depolymerization was 1 min at 120 °C, while the minimum temperature at which complete depolymerization was achieved was 100 °C for a 4 min reaction time. Both results are breakthroughs compared to the state of the art and represent a feasible option for implementation in recycling plants around the world, due to the simplicity and energy efficiency of the process, as well as the production of a fertilizer as by-product. A swollen shrinking layer in a core shrinking model was proposed to explain the high velocity of the reactions carried out using the KMH system. The higher compatibility between PET matrix and depolymerization solution is believed to create a wider reactive layer, which favors the rapid interaction between the base and the polymer. It was verified that amorphous regions are more susceptible to reaction than the crystalline ones as verified by DSC and DTGA. The activation energy for the depolymerization reaction was estimated in 120,7 kJ/mol. The effect of water on the depolymerization reaction was evaluated and revealed that the system performs well up to 1%, after which, PET conversion suffers a significant decrease, believed to be due to a reduced solubilization of the reactive outer layer and consequently the velocity of depolymerization.

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