

**MASTER**

**Chemical recycling of aromatic polyesters  
a study of the chemical recycling of polyethylene terephthalate and a PET-analogue**

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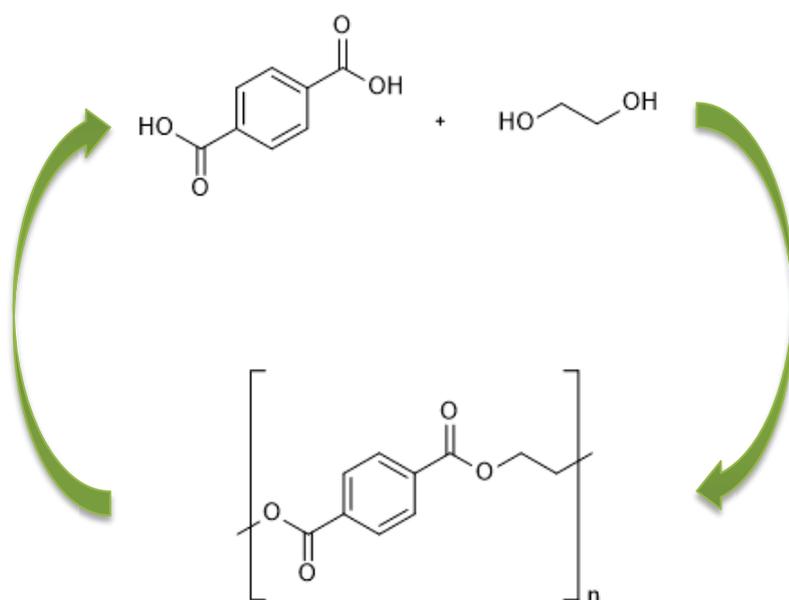
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# Chemical recycling of aromatic polyesters

A study of the chemical recycling of polyethylene terephthalate and a PET-analogue. This study deals with the kinetics and technological aspects of the depolymerization.



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## Summary

This report deals with the chemical recycling processes of aromatic polyesters. The chemical recycling of poly(ethylene terephthalate) (PET) and poly(dihydro coumaric acid) (Poly-H) has been investigated. Depolymerization of these polyesters has been carried out in a neutral reaction medium as well as by acid and alkaline catalyzed hydrolysis at three temperatures, *i.e.* 298, 323 and 353 Kelvin.

It has been found that after 48 hours of reaction in a 1M aqueous sodium hydroxide reaction medium, at 353 Kelvin, the conversion of virgin, *i.e.* purchased at DSM (Arnitel<sup>®</sup>), PET particles was 40%. The depolymerization of PET particles in a 1M aqueous sulfuric acid and in a neutral reaction medium did not result in any depolymerization of PET after 48 hours of reaction.

After reaction, the monomers, terephthalic acid and ethylene glycol have been recovered. By acidification terephthalic acid was precipitated and could be separated by filtration. Ethylene glycol was recovered by first removing the water by distillation. Because of the acidification NaCl salt was formed, which was separated from ethylene glycol by filtration. After separation the yield of the monomers terephthalic acid and ethylene glycol was respectively 38% and 28% and the selectivity was respectively 95% and 70%.

The global kinetics of the alkaline catalyzed depolymerization has been determined by a shrinking core model. It has been found that reaction rate increases by increasing the temperature. It has also been demonstrated that the resistance against mass transfer of sodium hydroxide is much lower than the resistance against reaction at the non-porous particle surface.

The conversion of Poly-H particles was 98% after 6 hours of reaction at 353 Kelvin in a 1M aqueous sulfuric acid reaction medium. Reaction rate constants of the depolymerization of Poly-H were about 30 times higher than for PET. This can be attributed to the fact that the ester group in Poly-H is aliphatic.

The advantage of acid catalyzed hydrolysis compared to alkaline catalyzed hydrolysis is that no acidification is needed after reaction and so there are no problems with salt formation during recovering the monomer. For Poly-H the isolation of the monomer still needs to be further investigated.

Because the hydrolysis of PET particles is slow, other chemical recycling methods have been investigated, like alkaline catalyzed hydrolysis carried out in alkanols and the aminolysis of PET particles. The results of both methods showed that conversions about 100% could be reached after one hour of reaction. To determine the reaction conversion in time of the aminolysis reactions, a High Performance Liquid Chromatography method has been developed.

## Table of Contents

1. Introduction.....	5
2. Theory.....	6
2.1 Reaction mechanisms.....	6
2.2 Kinetics .....	8
2.3 Mass transfer.....	9
2.4 Heat transfer .....	12
3. Experimental part.....	13
3.1 Materials and equipment.....	13
3.2 Hydrolysis PET and Poly H .....	14
3.3 Hydrolysis PET in alkanols .....	15
3.4 Aminolysis PET.....	15
3.5 Analysis.....	15
3.5.1 Sample pretreatment.....	15
3.5.2 High-performance liquid chromatography.....	15
3.5.3 UV-VIS analysis .....	16
4. Results .....	16
4.1 Hydrolysis PET .....	18
4.2 Scaling up the hydrolysis of PET .....	21
4.3 Hydrolysis Poly-H.....	23
4.4 Hydrolysis of PET in alkanols .....	25
4.5 Aminolysis of PET.....	27
5. Conclusion .....	28
6. Recommendations.....	29
References.....	31
Appendix.....	33
1. From lignin to Poly H .....	33
2. Reaction mechanisms.....	35
3. Development of HPLC method for BHETA analysis.....	37
4. Possible formation of quinone during alkaline hydrolysis Poly-H.....	39
5. Details on the calculations of the just-suspended stirrer speed.....	40
6. Details on the calculations of the heat transfer coefficient.....	42

## List of symbols

$B$	= solid-to-liquid ratio
$C_A$	= number of moles repeating units present per unit volume of the particle ( $mol\ m_s^{-3}$ )
$C_B$	= concentration of the catalyst ( $mol\ m^{-3}$ )
$c_p$	= specific heat capacity ( $J\ kg^{-1}\ K^{-1}$ )
$d_p$	= diameter of the particle ( $m$ )
$D$	= molecular diffusion coefficient ( $m^2\ s^{-1}$ )
$D_R$	= diameter of the reactor ( $m$ )
$D_i$	= diameter of the impeller ( $m$ )
$g$	= gravitational constant ( $m\ s^{-2}$ )
$h_r$	= partial heat transfer coefficient in the reactor ( $W\ m^{-2}\ K^{-1}$ )
$k$	= thermal conductivity ( $W\ m^{-1}\ K^{-1}$ )
$k_{LS}$	= mass transfer coefficient from the bulk liquid phase to the solid particle ( $m\ s^{-1}$ )
$k_r$	= reaction rate constant ( $m_i^3\ m_s^{-2}\ s^{-1}$ )
$N$	= impeller speed ( $rps$ )
$N_A$	= number of moles of the polymer repeating units
$N_{JS}$	= just-suspended stirrer speed ( $rps$ )
$N_p$	= power number (-)
$P$	= Power consumption ( $W$ )
$Pr$	= Prandtl number ( $\frac{\eta\ c_p}{k}$ )
$Q$	= heat flux ( $W\ m^{-2}$ )
$Re_T$	= impeller Reynolds number ( $\frac{\rho\ N\ D_i^2}{\eta}$ )
$S$	= shape factor (-)
$Sc$	= Schmidt number ( $V/D$ )
$S_c$	= surface area of unreacted core ( $m^2$ )
$t$	= time ( $s$ )
$T$	= temperature ( $K$ )
$U$	= overall heat transfer coefficient ( $W\ m^{-2}\ K^{-1}$ )
$V$	= volume ( $m^3$ )
$V_p$	= volume of the solid particle ( $m_s^3$ )
$W$	= weight ( $kg$ )
$X$	= conversion
$\emptyset$	= volume fraction
$\varepsilon$	= energy dissipation ( $m^2\ s^{-3}$ )
$\eta$	= dynamic viscosity ( $Pa\ s$ )
$\nu$	= kinematic viscosity ( $m^2\ s^{-1}$ )
$\rho$	= density ( $kg\ m^{-3}$ )

### Subscripts

0	= initial value
l	= liquid
m	= mixture
s	= solid

## 1. Introduction

Poly(ethylene terephthalate) (PET) is a widely used polymer worldwide. The polyester PET is well-known in the packaging industry, e.g. from soda bottles, but it finds its major application in textile industry. PET is produced from its monomers ethylene glycol (EG) and terephthalic acid (TPA), see Figure 1, or from ethylene glycol and dimethyl terephthalate by respectively an esterification or transesterification reaction.

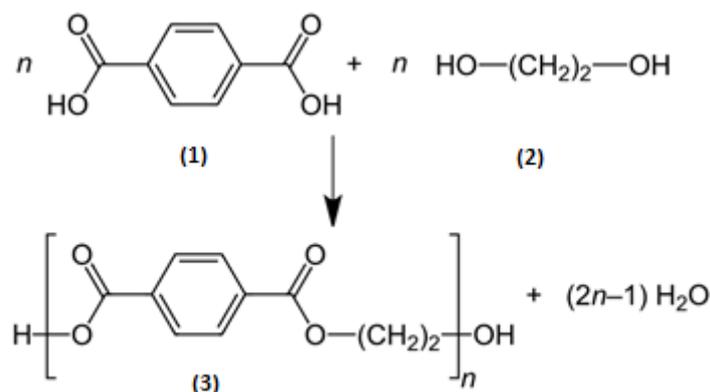


Figure 1: Production of poly(ethylene terephthalate) (3) from its monomers terephthalic acid (1) and ethylene glycol (2)

The monomers TPA and EG are derived from petrochemical feedstocks. In a world where the dependence of oil increased tremendously in the last century, the drive to reduce the use of petrochemical feedstocks grows. Therefore, investigation to recycle PET or to recover the building blocks (i.e. the monomers) remains interesting. Recycling the polymers can be carried out by thermal and/or mechanical methods. Recovering the monomers can be done by either biological and/or chemical procedures. From a sustainable point of view, chemical recovering is the most acceptable technique<sup>[1]</sup>.

On the other hand, to reduce the amount of required petrochemical feedstock, it is possible to use other sources to produce polyesters. Biomass is a promising alternative source for the production of polymers, because it consists of carbohydrates, fatty acids, fats, proteins and lignin. Lignin is, after cellulose, the most common organic polymer in the world. Lignin is a cross-linked polymer consisting of the following monolignols, see Figure 2: p-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol. In earlier research (PhD research J. van Schijndel) it has already been demonstrated that it is possible to synthesize polymers from these monolignols, see Appendix 1. These polymers could be an interesting alternative for polyethylene terephthalate (PET) polymers, because the building blocks of these polymers also contain an aromatic ring.

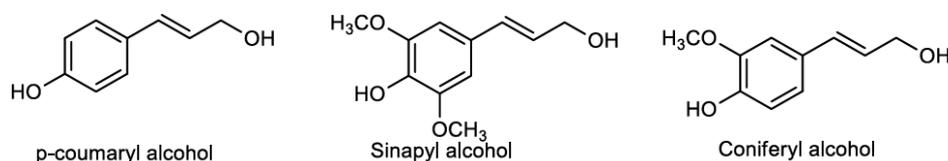


Figure 2: The three monolignols of lignin

In this research project the chemical recycling of PET **(3)** and poly(dihydro coumaric acid) **(5)** has been investigated. Depolymerization is carried out in a neutral reaction medium as well as by acid and alkaline catalyzed hydrolysis. The global kinetics of hydrolysis reactions have been determined. After depolymerization the monomers needed to be recovered. When it is possible to recover the monomer with a high purity (>98%) it can be polymerized again and so a closed cycle is realized, see Figure 3. This report deals with the chemical recycling processes of PET and poly(dihydro coumaric acid).

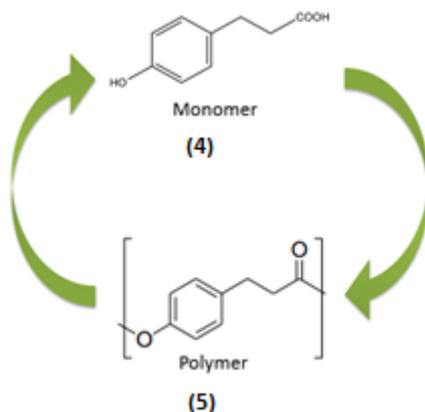


Figure 3: Chemical recycling process for poly(dihydro coumaric acid) **(5)**. Its monomer dihydro coumaric acid **(4)** is derived from lignin (see Appendix 1 for more information)

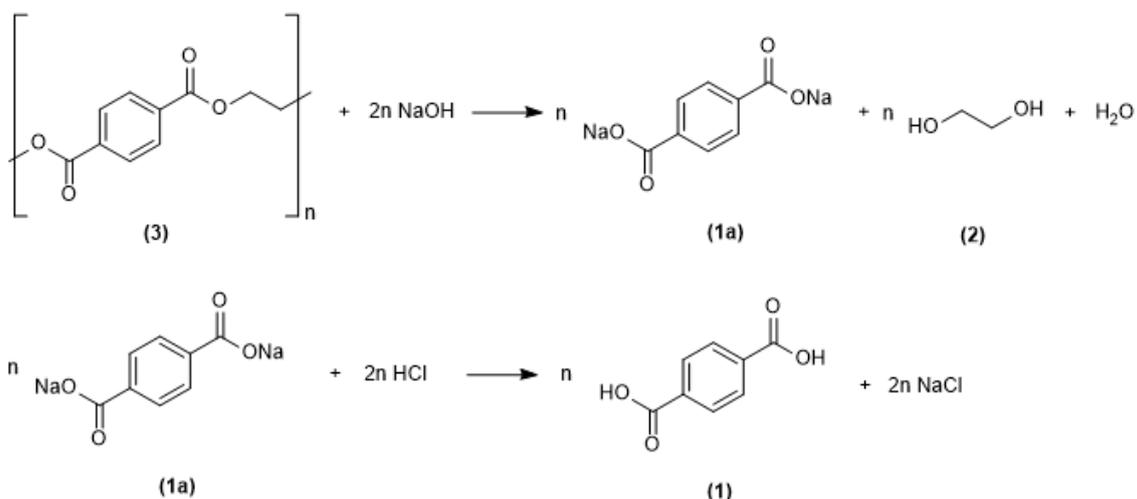
This report starts with describing the theory that is relevant for this research. First, the reaction mechanisms of all depolymerization reactions are given. Next, the balances as well as rate equations for kinetics and correlations for mass and heat transfer, relevant for this system, are presented. After the theory, the experimental part is described in chapter 3. Chapter 4, 'Results and Discussion', will start with an overview of the experimental results of the depolymerization reactions and separation steps. Next, a proposal for scaling-up is presented, taking into account the reaction kinetics, mass and heat transfer. This report will end with the conclusion and recommendations.

## 2. Theory

### 2.1 Reaction mechanisms

Depolymerization of the polymers will be carried out by neutral as well as acid and alkaline catalyzed hydrolysis. The reaction schemes for the acid and alkaline hydrolysis of PET and Poly-H are given in respectively Figure 4 and Figure 5. As can be seen, alkaline catalyzed depolymerization requires an extra acidification step to end-up with the monomer. For that reason an acid catalyzed depolymerization is preferred. However, it is expected that the rate of alkaline hydrolysis will be higher than the rate of acid hydrolysis, due to the fact that sodium hydroxide can directly break the ester linkage. This can be seen in the mechanisms given in Appendix 2.

Alkaline hydrolysis of poly(ethylene terephthalate):



Acid hydrolysis of poly(ethylene terephthalate):

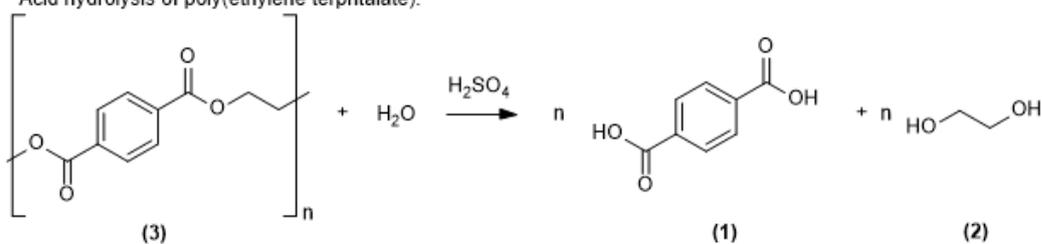
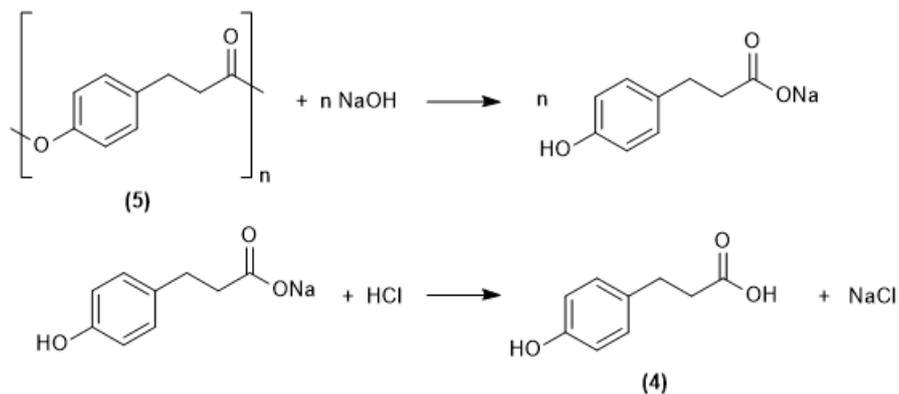


Figure 4: Reaction scheme of the depolymerization of PET **(3)** carried out by alkaline or acid hydrolysis, yielding the monomers terephthalic acid **(1)** and ethylene glycol **(2)**

Alkaline hydrolysis of poly(dihydrocoumaric acid):



Acid hydrolysis of poly(dihydrocoumaric acid):

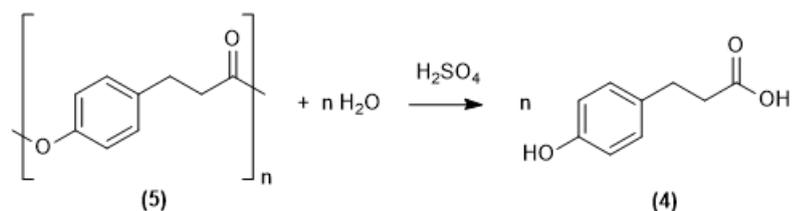


Figure 5: Reaction scheme of the depolymerization of Poly-H **(5)** carried out by acid or alkaline hydrolysis, yielding the monomer dihydro coumaric acid **(4)**

Given the reaction schemes for both PET and Poly-H, it is expected that the rate of hydrolysis of Poly-H will be higher than the rate of hydrolysis of PET. This rate difference is due to the fact that the ester group in Poly-H is aliphatic. Also Poly-H is (probably) a more amorphous polyester (according to DSC data, see Appendix 1), which is easier to depolymerize [2]. Experimental results will reveal if these expectations are true.

## 2.2 Kinetics

On forehand, it is assumed that all depolymerization reactions take place at the surface of the solid particle. During reaction the solid particle will shrink, because the polymer is depolymerized into its monomer(s). Therefore a shrinking core model is developed to describe the kinetics of depolymerization, taking into account the following assumptions:

- depolymerization of the polymer takes place at the surface of the solid polymer particle;
- the solid polymer particles are nonporous particles;
- the depolymerization of the polymer is slow and so the overall hydrolysis reaction is kinetically controlled;
- the polymer particles are assumed to be spheres and all have the same diameter, which is equal to the weighted average diameter of the fraction;
- solid particles are ideally mixed with the liquid phase;
- no reversible reaction takes place;
- catalyst (acid or base) concentration remains constant during reaction and is equal to the bulk concentration;
- reaction is first order to the polymer concentration (which is represented by the surface area of the polymer particle) [3] [4] and pseudo-first order to the acid or alkali concentration;
- reaction volume remains constant during hydrolysis process.

The depolymerization can be described by the following molar balance for one particle:

$$\frac{dN_A}{dt} = -k_r S_c C_B \quad (1),$$

where  $N_A$  is the number of moles of the polymer repeating units for one particle,  $k_r$  the reaction rate constant,  $S_c$  the surface area of the unreacted core and  $C_B$  the concentration of the catalyst (sodium hydroxide or sulfuric acid).

Eq. 1 can be written as:

$$\frac{dC_A V_p}{dt} = -k_r S_c C_B \quad (2),$$

and according to the shrinking core model:

$$C_A \frac{d\left(\frac{\pi}{6} d_p^3\right)}{dt} = -k_r \pi d_p^2 C_B \quad (3),$$

$$\frac{d(d_p)}{dt} = -\frac{2k_r C_B}{C_A} \quad (4),$$

where  $d_p$  is the diameter of the particle and  $C_A$  is the number of moles repeating units present per unit volume of the particle.

The conversion of the polymer can be described as:

$$X = 1 - \frac{V_p}{V_{p,0}} = 1 - \frac{\frac{\pi}{6} d_p^3}{\frac{\pi}{6} d_{p,0}^3} \quad (5),$$

$$d_p = (1 - X)^{1/3} d_{p,0} \quad (6),$$

when substituting Eq. 6 to Eq. 4 and after rearranging Eq. 7 is obtained:

$$\frac{d(1 - X)}{dt} = -\frac{2k_r C_B}{C_A d_{p,0}} (1 - X)^{2/3} \quad (7).$$

Integration yields:

$$(1 - X)^{1/3} - 1 = -k_{obs} t \quad (8),$$

where  $k_{obs}$  is equal to  $\frac{2k_r C_B}{3C_A d_{p,0}}$  in  $1/s$ .

## 2.3 Mass transfer

For kinetic modeling it is assumed that mass transfer limitations are negligible relative to the reaction rate (i.e.  $k_{LS} \gg k_r$ ). Nevertheless, mass transfer plays an important role in solid-liquid reactions. Agitation in heterogeneous systems is required to limit/avoid mass transfer limitations, therefore tank and impeller geometry can (positively) affect mass transfer.

Of course, the optimal tank depends on the specific process, but, based on experience <sup>[5]</sup>, it has been found that for turbulent mixing, for low viscosity fluids, the standard geometry shown in Figure 6 can be used. Here  $T$  is the diameter of the tank,  $H$  is the liquid height,  $D$  is the impeller diameter,  $W$  the impeller blade width,  $C$  the clearance of the impeller from the tank bottom and  $B$  is the baffle width. The standard tank is defined with four baffles placed 90° apart. The optimal ratios between e.g. tank and impeller diameter are also given in Figure 6.

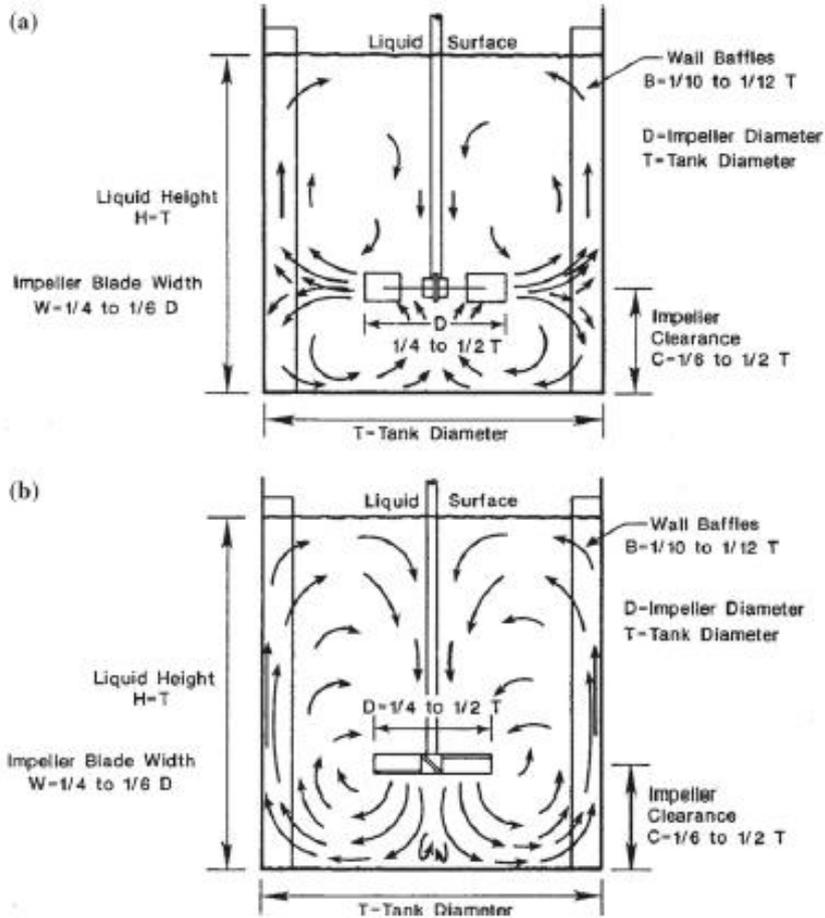


Figure 6: Turbulent flow impellers. The flow pattern produced in a standard tank geometry by a) a radial impeller and b) an axial impeller<sup>[5]</sup>

As can be seen in Figure 6, the impeller type can influence the flow pattern and therefore also mixing. For solid-liquid systems an axial flow is desired. Figure 7 shows typical axial flow impellers.

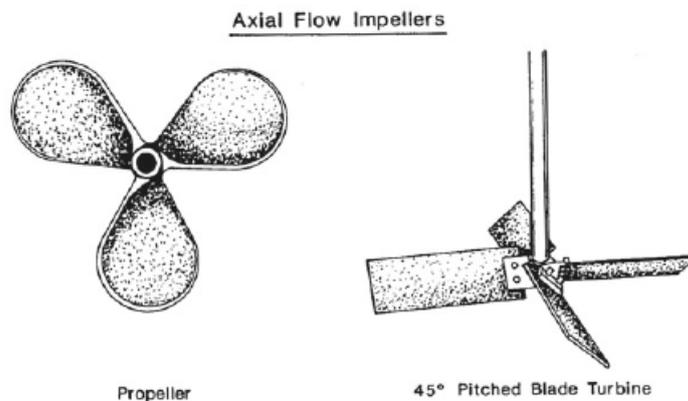


Figure 7: Typical axial flow impellers<sup>[5]</sup>

Next to the design of the tank and the type of impeller, also stirring itself is important. When the impeller speed is not high enough, particles could remain at the bottom of the reactor,

which can lead to an undesired effect on the observed reaction rate. Higher impeller speeds often only lead to a great increase in power consumption, since

$$P = N_p \rho_m N^3 D_i^5 \quad (9),$$

where  $P$  is the power consumption,  $N_p$  the power number,  $\rho_m$  the viscosity of the mixture,  $N$  the impeller speed and  $D_i$  the diameter of the stirrer. Therefore the lowest impeller speed, just sufficient for complete suspension, is defined according to the Zwietering suspension principle<sup>[6]</sup>.

Zwietering has developed a correlation that describes the lowest impeller speed that is required to prevent particles from remaining at the bottom of the tank. Zwietering used sand and sodium chloride as solid particles in his experiments and suspended them in liquids such as water, acetone and carbon tetrachloride. Five different type of impellers were used (2 types of paddle stirrers, a six bladed turbine, a vaned disk and a propeller). Zwietering has found the following correlation for the just-suspended stirrer speed ( $N_{JS}$ ):

$$N_{JS} = S \left( \frac{\eta_m}{\rho_m} \right)^{0.1} d_p^{0.2} \left( g \left( \frac{\rho_s - \rho_l}{\rho_l} \right) \right)^{0.45} (100B)^{0.13} D_i^{-0.85} \quad (10),$$

where  $S$  stands for the shape factor of the impeller,  $\eta_m$  for the viscosity of the suspension,  $\rho_m$  the density of the suspension,  $d_p$  the diameter of the solid particles,  $\rho_s$  viscosity of the solid,  $\rho_l$  viscosity of the liquid,  $B$  the solid-to-liquid ratio and  $D_i$  the diameter of the stirrer.

$N_{JS}$  is defined as the speed at which the system obeys the so-called “off-bottom” criterion. This criterion is met if all particles will remain at the bottom of the tank for no longer than two seconds before they will mix up into the bulk<sup>[7]</sup>. The correlation of Zwietering will be used when scaling up the depolymerization process.

To justify the assumption that the reaction is kinetically limited and mass transfer limitations can be neglected, it is relevant to determine the liquid-to-solid mass transfer coefficient ( $k_{LS}$ ). A lot of research has already been done on determining  $k_{LS}$  in agitated vessels. Sano et. al.<sup>[8]</sup> reported a correlation where  $k_{LS}$  can be estimated by:

$$\frac{k_{LS} d_p}{D} = \left[ 2 + 0,4 \left( \frac{\varepsilon d_p^4}{\nu_l^3} \right)^{\frac{1}{4}} Sc^{\frac{1}{3}} \right] \quad (11),$$

where  $k_{LS}$ ,  $d_p$ ,  $D$ ,  $\varepsilon$ ,  $\nu$  and  $Sc$  are defined as respectively the mass transfer coefficient from the bulk liquid phase to the surface of the solid particle, the particle diameter, the molecular diffusion coefficient of the substance to be transferred in the liquid phase, the energy supplied to the liquid flow, the kinematic viscosity of the liquid and the dimensionless Schmidt number (which is equal to  $\nu/D$ ).

The energy supplied to the liquid flow,  $\varepsilon$ , for agitated vessels, can be calculated by

$$\varepsilon = \frac{N_p N^3 D_i^5}{V_m} \quad (12),$$

where  $N_p$  is the power number,  $N$  the impeller speed,  $D_i$  the diameter of the impeller and  $V_m$  the volume of the suspension. The power number will be determined according to Bates' results. Bates<sup>[9]</sup> supposed that the power number  $N_p$  is a function of the impeller Reynolds number  $Re_T$ .

## 2.4 Heat transfer

Knowledge of the heat transfer in this depolymerization process is essential to control the reaction rate and reaction temperature. A change in reaction temperature can affect the rate, since the rate of reaction will (probably) strongly depend on the temperature (according to Arrhenius' law). When scaling up this process its necessary to know what the heat flux through the reactor wall will be, to design a proper heat exchange process. The heat transfer in agitated vessels depends on the geometry of the tank and the impeller, but also on the properties of the reaction mixture, as can be seen in Eq. (13) – (17).

The heat flux through the wall is given by

$$Q = U(T - T_{jacket}) \quad (13),$$

where  $U$  is the overall heat transfer coefficient,  $T$  is the temperature inside the reactor (i.e. of the reaction mixture) and  $T_{jacket}$  is the temperature of the heating/cooling medium.  $U$  can be determined by several resistances in series<sup>[10]</sup>. However for this heterogeneous system it is assumed that the total resistance is present in the reaction mixture and therefore

$$\frac{1}{U} = \frac{1}{h_r} \quad (14),$$

where  $h_r$  is the partial heat transfer coefficient in the vessel at the reaction mixture side. The partial heat transfer coefficient can be determined using the following relation for the Nusselt number<sup>[10]</sup>:

$$Nu = \frac{h_r D_R}{k_m} = 0,75 Re_T^{2/3} Pr^{1/3} \left( \frac{\eta_m}{\eta_{wall}} \right)^{0,14} \quad (15),$$

where

$$Re_T = \frac{\rho_m N D_i^2}{\eta_m} \quad (16),$$

$$Pr_m = \frac{\eta_m c_{p,m}}{k_m} \quad (17).$$

To scale up this process, the partial heat transfer coefficient of lab scale experiments ( $h_{r,lab}$ ) can be related to the partial heat transfer coefficient on plant scale ( $h_{r,plant}$ ) using<sup>[10]</sup>:

$$\frac{h_{r,plant}}{h_{r,lab}} = \left(\frac{D_{i,plant}}{D_{i,lab}}\right)^{1/3} \left(\frac{N_{plant}}{N_{lab}}\right)^{2/3} \left(\frac{\eta_{wall,plant}}{\eta_{wall,lab}}\right)^{0,14} \quad (18).$$

### 3. Experimental part

#### 3.1 Materials and equipment

Virgin PET granules were purchased at DSM (Arnitel®) and used without any further purification. PET waste bottles were cut into smaller pieces. These flakes were washed with demineralized water and dried in a vacuum oven for 4 hours at 40°C. The PET granules and PET waste bottles were grounded with Polymix PX-MFC 90D grinding equipment. The grounded PET has been sieved with stainless steel sieves with different mesh sizes; 180, 250, 355 and 500 µm (according to ISO 3310-1).

To determine the average particle diameter, photomicrographs were taken with DigiMicro Lab 5.0 equipment. Each photo presented a representative amount of particles of the fraction. The average diameter of each fraction was calculated by analyzing the photographs with ImageJ® software package<sup>[11]</sup>. The size boundaries of the sieve fractions were set equal to the minimum and maximum size of the fraction according to the mesh size. Particles were treated as spheres.

An aqueous solution of sodium hydroxide (NaOH) has been prepared by dissolving 4 gram (0,1 mol) NaOH pellets in 100 mL demineralized water, to obtain a concentration of 1 mol/L NaOH solution. 5,6 mL of an aqueous solution (95% w/w) of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was slowly added to 94,4 mL demineralized water to obtain a solution with a concentration of 1 mol/L H<sub>2</sub>SO<sub>4</sub>. A 1M hydrochloric acid (HCl) solution has been prepared by slowly adding 8,2 mL of a 37% (w/w) aqueous HCl solution to 91,8 mL demineralized water.

Poly-dihydro coumaric acid (Poly-H) was synthesized at Avans Applied University according to the method described in Appendix 1.

The supplier, purity, chemical formula, molecular weight and density of all chemicals are listed in Table 1.

All reactions were carried out in a round bottom three-neck flask equipped with a mechanical stirrer (Lightnin A100 Propeller) and a reflux cooler. Heat was supplied using a hot plate (IKA® RCT basic) equipped with a DrySyn heating block (Stuart) and a Pt1000 temperature sensor (IKA®). A continuous nitrogen flow was used, which was passed over the reaction mixture.

Table 1: Details of all chemicals used in the experimental work.

Compound name	Supplier	Purity	Chemical formula	MW (g mol <sup>-1</sup> )	ρ (g cm <sup>-3</sup> )
2-amino-ethanol	TCI	>99%	C <sub>2</sub> H <sub>7</sub> NO	61,08	1,012
1-butanol	Across	99,5%	C <sub>4</sub> H <sub>10</sub> O	74,12	0,810
3-(4-hydroxyphenyl) propionic acid	TCI	>98%	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	166,18	
Ethanol	J.T. Baker	Absolute	C <sub>2</sub> H <sub>5</sub> OH	46,07	0,789
Ethylene glycol	Sigma Aldrich	99,8%	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	62,07	1,11
1-heptanol	Sigma Aldrich	>99%	C <sub>7</sub> H <sub>16</sub> O	116,20	0,819
Hydrochloric Acid (37% w/w)	Boom	37%	HCl	36,46	1,19
Methanol, Anhydrous	Macron	HPLC grade	CH <sub>3</sub> OH	32,04	0,791
1-octanol	Sigma Aldrich	>99%	C <sub>8</sub> H <sub>18</sub> O	130,23	0,830
1-pentanol	Sigma Aldrich	>99%	C <sub>5</sub> H <sub>12</sub> O	88,15	0,814
PET	DSM, Arnitel®		(C <sub>10</sub> H <sub>8</sub> O <sub>4</sub> ) <sub>n</sub>	M <sub>n</sub> = 40.000 n = 208	1,38
Poly-H	Synthesized at Avans Applied University		(C <sub>9</sub> H <sub>8</sub> O <sub>2</sub> ) <sub>n</sub>	M <sub>n</sub> = 5.200 n = 38	
Sodium Hydroxide	Boom		NaOH	40,00	2,13
Sulfuric Acid (95% w/w)	Boom	95%	H <sub>2</sub> SO <sub>4</sub>	98,08	1,84
Terephthalic acid	Sigma Aldrich	98%	C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>	166,13	1,522
Toluene	Macron	AR grade	C <sub>7</sub> H <sub>8</sub>	92,14	0,867
Zinc acetate	Sigma Aldrich	99,99%	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> Zn	183,48	1,84

### 3.2 Hydrolysis PET and Poly H

1 gram (respectively 5 mmol and 7 mmol based on the repeating unit of PET and Poly-H) PET and Poly-H particles were added to 20 mL demineralized water; 20 mL 1M H<sub>2</sub>SO<sub>4</sub> solution and 20 mL 1M NaOH solution. The reaction mixture was left, under continuous stirring, for 48 hours at three temperatures (25, 50 and 80°C ± 1°C). Samples of 100 μL were taken 1, 2, 4, 8, 16, 24 and 48 hours after the start of the reaction.

After hydrolysis the reaction mixture was filtered to separate the unreacted polymer. The unreacted polymer was dried in a vacuum oven at 40°C for 24 hours. The conversion of the reaction is defined as

$$X(\%) = \frac{W_{polymer,i} - W_{polymer,f}}{W_{polymer,i}} \quad (19),$$

and the yield of the products is defined as

$$Yield(\%) = \frac{W_{Product}}{W_{Product,theoretical}} \quad (20).$$

### 3.3 Hydrolysis PET in alkanols

1 gram (5 mmol based on the repeating unit) virgin PET and 0,4 gram (10 mmol) NaOH pellets were added to 10 mL alcohol (methanol, 1-butanol, 1-pentanol, 1-heptanol and 1-octanol). The reaction mixture was refluxed, under continuous stirring, for 60 minutes. Samples of 100  $\mu$ L were taken every 10 minutes.

### 3.4 Aminolysis PET

5 gram PET (26 mmol based on the repeating unit) was mixed with 12,6 mL 2-amino-ethanol (0,21 mol) and 0,05 gram zinc acetate (0,27 mmol, 1% w/w by weight of the polymer) was added to the mixture. Hereafter the solution was refluxed for 3 hours. Samples of 100  $\mu$ L were taken every 10 minutes.

## 3.5 Analysis

### 3.5.1 Sample pretreatment

To make sure that in every sample the correct substance should be measured at the same wavelength in the UV-VIS detector of the HPLC equipment, the samples needed to be pretreated to obtain a pH of 2. Samples taken from alkaline and neutral hydrolysis were acidified by slowly adding respectively 200 and 100  $\mu$ L 1M HCl. The pH was measured with a Metrohm 827 pH lab equipment. All samples were supplemented with water to obtain a 1 mL solution. 0,1 mL sample of this solution has been taken and diluted in 0,9 mL MeOH (containing 0,4% v/v toluene as internal standard). Next, these samples were filtered with a PTFE 0,45  $\mu$ m filter and analyzed using HPLC equipment, see section 3.5.2.

Poly-H hydrolysis samples have also been acidified to pH 2 according to the same method as described above. However, because these samples were measured using UV-VIS spectrophotometer equipment, a dilution of 200 times with demineralized water was required to obtain a solution which has an extinction between 0,1 and 1 at the UV-VIS spectrophotometer. After dilution the samples were filtered and measured at the spectrophotometer.

### 3.5.2 High-performance liquid chromatography

PET hydrolysis samples were analyzed using a Liquid Chromatographic system (Agilent 1100 series) with a diode array UV-VIS detector (Agilent 1200 series) and an auto sampler injector with a 20  $\mu$ L loop (Agilent 1100 series G1316A). The system was equipped with a Luna 5  $\mu$ m C18 column (250 mm  $\times$  4,6 mm) using methanol (solvent A) and 1% acetic acid in water (solvent B) as the mobile phase.

Elution was performed at a temperature of 20°C, a flow rate of 1 mL/min, with the following linear gradient:

Time (min)	Solvent A (%)	Solvent B (%)
0	40	60
6	40	60
15 <sup>1</sup>	100	0
20	100	0
22	40	60
28	40	60

The PET aminolysis samples were also analyzed using a Liquid Chromatographic system (Agilent 1100 series) with a diode array detector (Agilent 1200 series) and a 20  $\mu$ L loop (Agilent 1100 series G1316A), but with manual injection. This system was equipped with a Zorbax CN column (250 mm  $\times$  4.6 mm) using heptane (solvent A) and ethanol (solvent B) as the mobile phase. As a part of this research the HPLC method for the analysis of the aminolysis samples had to be developed. The results of this work are reported in Appendix 3.

Agilent's ChemStation Software was used for data analysis. The quantitative determination of components in the reaction mixtures was carried out using a calibration curve and was based on peak areas.

### 3.5.3 UV-VIS analysis

The Poly H hydrolysis samples were analyzed using a UV-VIS spectrophotometer (Jenway 6705). A quartz cuvette (Hellma<sup>®</sup>) with a path length of 10 mm was used. All samples were measured at a wavelength of 224 nm.

## 4. Results

When depolymerization takes place at the surface of the solid polymer particle, the particle size will be of great importance in these reactions, because of the effective surface area per unit reaction volume. To illustrate this, the hydrolysis of PET is carried out using particles with varying size. PET was grounded and sieved with sieves with different mesh sizes (180, 250, 355 and 500  $\mu$ m). In Table 2 the particle size distribution of the particles is displayed. The weight average diameter is calculated by Eq. (21), where  $W_i$  is the weight fraction,  $d_{p,i}$  is the diameter of the fraction and  $W_{total}$  is the total weight of the grounded particles.

$$\langle d_p \rangle = \frac{\sum_i (W_i d_{p,i})}{W_{total}} \quad (21)$$

In Figure 8 the distribution of the particles is visually displayed in a bin chart. Each of these fractions was used in the depolymerization of PET, which was carried out in 1-butanol and sodium hydroxide according to the method described in the experimental part.

<sup>1</sup> In 9 minutes the eluent has changed with a linear gradient of A:B 40:60 to A:B 100:0

Table 2: Particle size distribution of PET

Fraction ( $\mu\text{m}$ )	$\overline{d}_p$ ( $\mu\text{m}$ )	Weight %
<180	68	31,9
180-250	202	12,0
250-355	280	27,8
355-500	458	28,3

$\langle d_p \rangle = 253 \mu\text{m}$

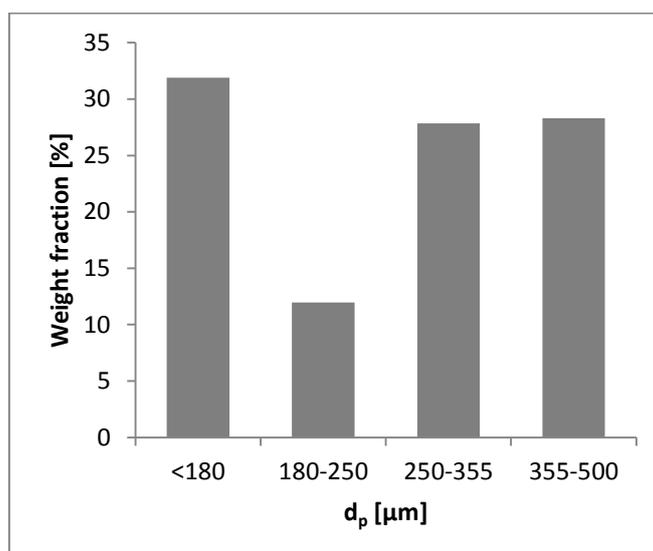


Figure 8: Bin chart of the particle size distribution of PET particles after grinding and sieving

Figure 9 shows that smaller particles lead to a decrease in reaction time. After 60 minutes reaction time a conversion of 76% is reached for the smallest fraction (<180  $\mu\text{m}$ ) against 51-57% for bigger particles (180-500  $\mu\text{m}$ ). The conversions of each reaction after one hour are collected in Table 3. It can also be seen in Figure 9 that conversion time histories for particle sizes above 180  $\mu\text{m}$  are not significantly different. To accelerate the depolymerization reaction its recommended that PET is grounded and sieved with sieves with mesh sizes below 180  $\mu\text{m}$ . In all further experiments only the fraction with particles <180  $\mu\text{m}$  has been used.

Table 3: Conversion after 1 hour depolymerization of PET at a temperature of 118°C in 1-butanol with 1M sodium hydroxide with varying particle size, solid content = 10% w/w

Fraction ( $\mu\text{m}$ )	Conversion (%)
<180	76
180-250	56
250-355	51
355-500	51

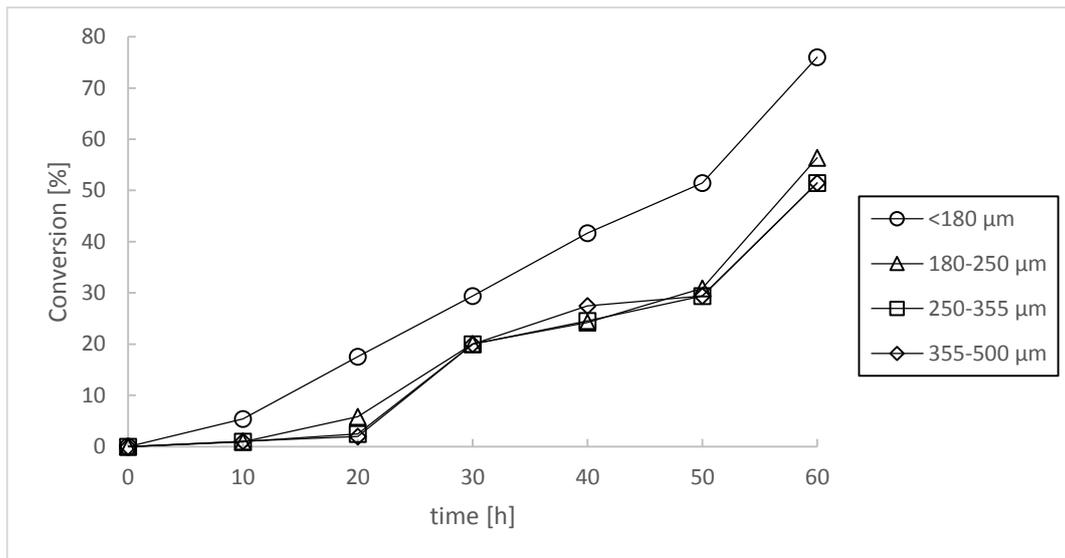


Figure 9: Conversion time history of the depolymerization of PET particles at a temperature of 118°C in 1-butanol and 1M sodium hydroxide with varying particle size, solid content = 10% w/w

#### 4.1 Hydrolysis PET

The hydrolysis of PET in demineralized water and 1M sulfuric acid did not result in any breakdown of PET. This was already expected due to the reaction mechanism as described in Appendix 2. It is possible to depolymerize PET by neutral or acid hydrolysis. However then higher temperatures <sup>[12], [13]</sup>, the use of catalysts <sup>[14]</sup> or higher acid concentrations <sup>[3], [15]</sup> are required.

The results of alkaline hydrolysis are given in Figure 10. After 48 hours of depolymerization the maximum conversion reached was 50% for PET waste particles at 353 Kelvin. An overview of conversions is given at the end of this chapter in Table 8. The conversions of virgin PET particles are lower, this can be attributed to the fact that PET waste bottles are in the amorphous state and that virgin PET is more crystalline. Also the additives in PET bottles could have influenced the rate of depolymerization.

It can also be pointed out that temperature has a large influence on the reaction time. A higher temperature leads to an increase in reaction rates, which is the case when a chemical reaction is the rate determining step.

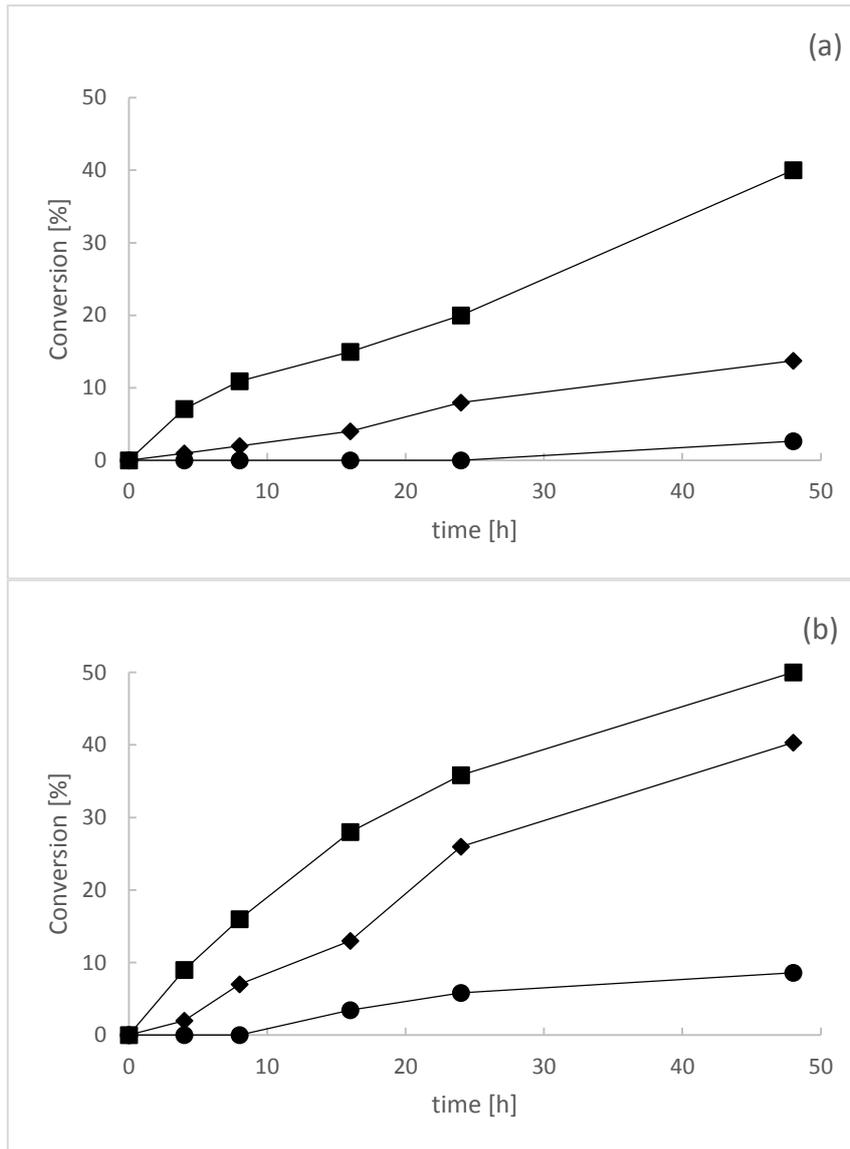


Figure 10: Conversion time history of the depolymerization of a) virgin PET and b) PET waste particles in 1M aqueous sodium hydroxide solution at ●: 298; ◆: 323 and ■: 353 Kelvin,  $d_{p,0} < 180 \mu\text{m}$ , solid content = 5% w/w.

The kinetic model described in Chapter 2 is applied to the experimental data of virgin PET. Because at a temperature of 298 Kelvin almost no conversion has occurred, this temperature has not been taken into account.

In Figure 11  $[1 - (1 - X)^{1/3}]$  has been plotted on the vertical axis against  $t$  on the horizontal axis. According to Eq. (8), the slope of the linear relation is equal to  $\frac{2k_r C_B}{3C_A d_{p,0}}$ . Table 4 shows the reaction rate constants ( $k_r$ ) at 323 and 353 Kelvin which have been found including their correlation coefficient ( $R^2$ ).

Table 4: Reaction rate constants for the alkaline catalyzed depolymerization of virgin PET at 323 and 353 Kelvin<sup>2</sup>

T [K]	$k_r [10^{-12} m_l^3 m_s^{-2} s^{-1}]$	$R^2 [-]$
323	6,36	0,988
353	19,1	0,979

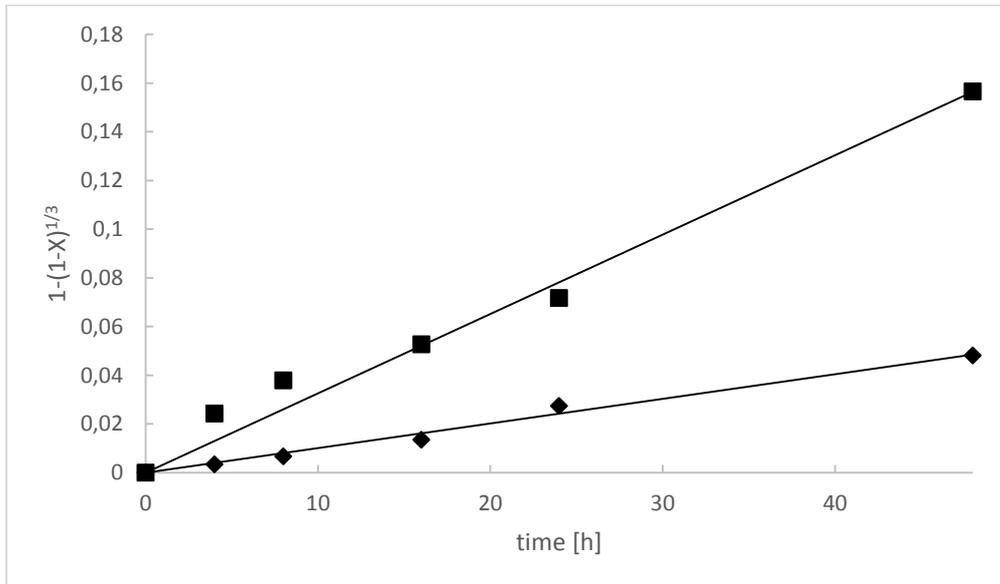


Figure 11: Evaluation of the kinetics of alkaline catalyzed depolymerization of virgin PET particles according to Eq.(8). ♦: 323 and ■: 353 Kelvin,  $d_{p,0} < 180 \mu\text{m}$ .

After hydrolysis, the monomers needed to be separated. First, the unreacted PET was separated by filtration. The remaining solution contains disodium terephthalate (TPA-Na) and ethylene glycol (EG). To end-up with terephthalic acid (TPA), instead of TPA-Na, the solution was acidified by titration to pH 3 with 7,5 mL of an aqueous 2M HCl solution. TPA precipitates and was separated by filtration. After drying, the yield of the monomer TPA was 38% for hydrolysis reaction of virgin PET at 353 Kelvin. The selectivity, after isolation, was calculated to be 95% towards TPA.

The remaining filtrate contains ethylene glycol (EG), water and salt (NaCl). This separation step has to deal with the difficulty of removing the salt. EG ( $T_B=197,3^\circ\text{C}$ ) and water can be easily separated by distillation. However, the salt then remains in the EG fraction. In this research project the salt was removed by filtration, which led to a yield of 28% of EG, so some improvement on this separation technique is required (see Chapter 6 Recommendations). The selectivity, after isolation, was calculated to be 70% towards EG.

<sup>2</sup>  $C_A = 208$  moles repeating units per unit volume of the particle,  $C_B = 1000 \text{ mol/m}^3$  and  $d_{p,0} = 68 \mu\text{m}$

## 4.2 Scaling up the hydrolysis of PET

In laboratory experiments the solid mass fraction was 5%, however, when scaling up this process, a higher solid mass fraction (~30%) would be required to increase the amount of polymer that can be degraded in the same time. At higher solid fractions, stirring becomes even more important. To check if the correlation of Zwietering holds for this polyester-water system, some scale up tests have been done in a reactor with the dimensions given in Table 5. The calculated value for  $N_{JS}$  has been compared with the experimental results.

First of all, during experiments, it gets clear that a solid mass fraction of 30% could not be reached in this reactor. It was not possible to get all the particles mixed up in the bulk. Therefore a mass fraction of 25% has been used. The impellers that have been used are shown in Figure 12. Results are collected in Table 6. Here also the dimensionless shape factor  $S$  that has been used is given, based on the findings of Zwietering<sup>[6]</sup>, and the stirrer diameter. The viscosity of the mixture has been determined by the correlation of Batchelor<sup>[16]</sup> and turned out to be  $0,9 \cdot 10^{-3} Pa s$  at  $50^{\circ}C$  and  $0,6 \cdot 10^{-3} Pa s$  at  $80^{\circ}C$ . Details on the calculations can be found in Appendix 5.

Table 5: Reactor dimensions

Reactor volume	[dm <sup>3</sup> ]	2
Diameter reactor	[cm]	10
Clearance	[cm]	1,8
Liquid level	[cm]	10
Number of baffles	[-]	4
Baffle width	[cm]	1

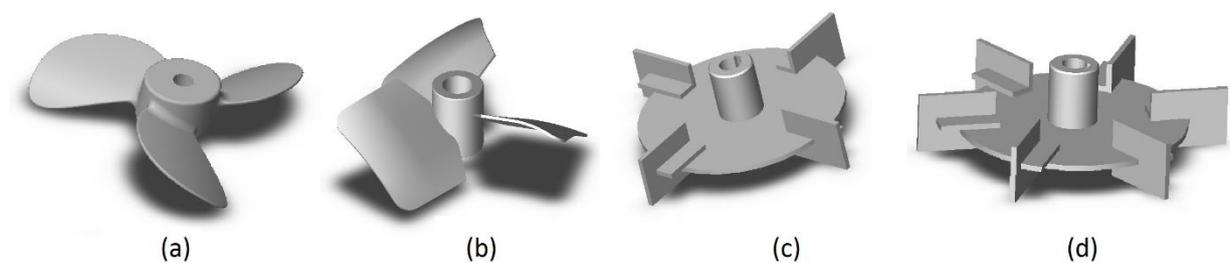


Figure 12: Types of impellers that have been used to determine the just-suspended impeller speed. a) Lightnin A100 b) Lightnin A320, c) RT4 – Rushton disc turbine with 4 blades, d) RT6 - Rushton disc turbine with 6 blades<sup>[17]</sup>

Table 6: Values of the just-suspended impeller speed. The calculated value based on the correlation of Zwietering (see details in Appendix 5) and the value observed by visual inspection in a 2 dm<sup>3</sup> reactor.

Impeller	S [-]	Stirrer diameter [cm]	T = 50°C		T = 80°C	
			N <sub>JS</sub> calculated [rpm]	N <sub>JS</sub> observed [rpm]	N <sub>JS</sub> calculated [rpm]	N <sub>JS</sub> observed [rpm]
<b>Propeller A100</b>	5	4,0	571	522	561	560
<b>Propeller A320</b>	6	4,5	620	580	609	586
<b>6-bladed turbine</b>	4	4,8	391	400	385	422
<b>4-bladed turbine</b>	4	4,6	406	641	399	673

The results in Table 6 demonstrate that the Zwietering correlation holds quite good for the propellers and the 6-bladed disc turbine impeller. For the 4-bladed disc turbine impeller a difference is found between the calculated and observed value.  $N_{JS}$  calculated is much lower than  $N_{JS}$  observed. This can be attributed to the fact that in the experimental work of Zwietering only solid mass fractions of 0,5 – 20,0%, reactor volumes of 3 – 170 dm<sup>3</sup> and stirrer diameters of 6 – 23 cm have been used [7]. These are significantly different from the reactor dimensions that are used in this work. Because the calculated value of  $N_{JS}$  for the 4-bladed disc turbine is lower than the one observed, presumably this type of impeller needs a higher impeller speed for solid mass fractions >20%. But it can also be affected to the fact that the stirrer diameter used in this experiments is too small (i.e. smaller than 6 cm. as used in the work of Zwietering).

However, when scaling up this process, it can be concluded that the Zwietering correlation can be used to determine the just-suspended impeller speed when propeller impellers are used. Besides, propeller types of impellers are also desired in this solid-liquid system, because they provide axial flow in the tank.

To justify the assumption that the reaction is kinetically controlled, the mass transfer coefficient has been determined according to Eq. (11). A molecular diffusion coefficient of sodium hydroxide in water of  $5 \cdot 10^{-9} \text{ m}^2/\text{s}$ , the observed stirrer speeds of Table 6 and the power numbers according to Bates [9] have been used. For each type of impeller the mass transfer coefficient has been determined and it turned out to be that  $k_{LS}$  has a value of  $0,4 \cdot 10^{-3} < k_{LS} < 0,6 \cdot 10^{-3} \text{ m/s}$  (depending on the impeller type). So it is justified that  $k_{LS} \gg k_r$  and when scaling up this process only the rate of reaction needs to be taken into account.

The heat transfer coefficient at the inner wall of the tank ( $h_r$ ) is determined according to Eq. (15) for each type of impeller and temperature. Details on the calculations are collected in Appendix 6. The values for the impeller Reynolds number  $Re_T$ , Prandtl number  $Pr$  and the heat transfer coefficient  $h_r$  are shown in Table 7. From these results it can be concluded that impeller geometry and the temperature both have a large impact at the heat transfer coefficient. The lowest value for  $h_r$  has been found for the impeller A100.

Table 7: Values of the Reynolds impeller number, Prandtl number of the mixture and the heat transfer coefficient for four types of impellers at 50 and 80°C. Calculated with Eq. (15) (details on the calculations can be found in Appendix 6), with  $D_R = 0,1\text{ m}$  and  $k_m = 0,5\text{ W}/(\text{m} \cdot \text{K})$

Impeller	T = 50°C			T = 80°C		
	Re <sub>τ</sub> [10 <sup>3</sup> -]	Pr <sub>m</sub> [-]	h <sub>r</sub> [10 <sup>3</sup> W/(m <sup>2</sup> ·K)]	Re <sub>τ</sub> [10 <sup>3</sup> -]	Pr <sub>m</sub> [-]	h <sub>r</sub> [10 <sup>3</sup> W/(m <sup>2</sup> ·K)]
<b>Propeller A100</b>	18	6	4,8	27	4	3,3
<b>Propeller A320</b>	25		5,9	37		4,1
<b>6-bladed turbine</b>	18		4,7	26		3,4
<b>4-bladed turbine</b>	27		6,2	42		4,2

### 4.3 Hydrolysis Poly-H

The hydrolysis of Poly-H in demineralized water did not result in any breakdown of the polymer after 48 hours reaction time at temperatures of 298, 323 and 353 Kelvin. This was also the case for PET. However, as can be seen in Figure 13, by acid catalyzed hydrolysis complete conversion of Poly-H was reached after 6 hours of reaction at 353 Kelvin. In contrast to PET, where no depolymerization took place in an aqueous sulfuric acid solution.

This validates the assumption that the reaction rate of acid catalyzed depolymerization of an aliphatic polyester, like Poly-H, is higher than the rate for the polyester PET.

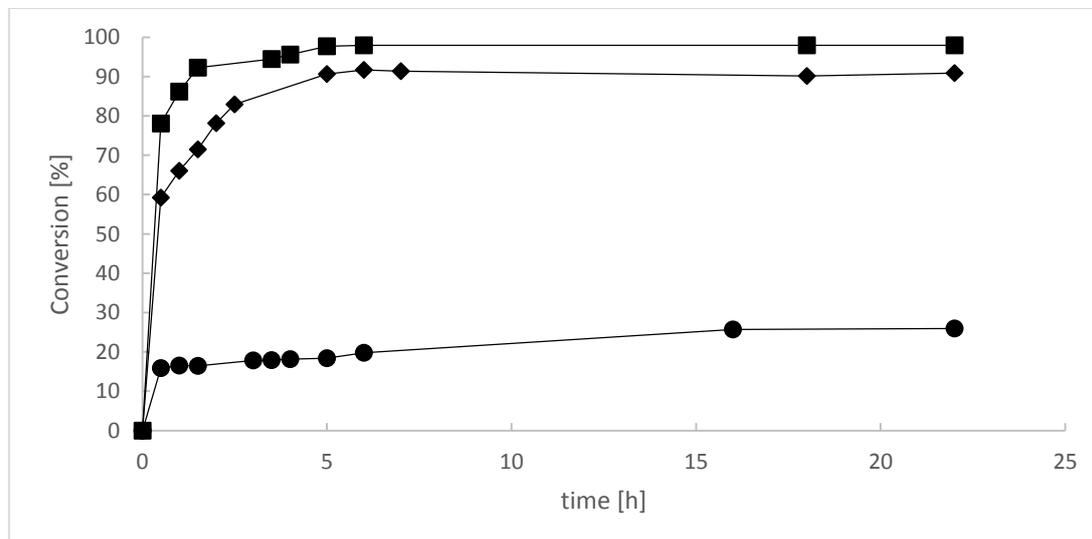


Figure 13: Conversion time history of the depolymerization of Poly-H particles in 1M aqueous sulfuric acid solution at ●: 298; ◆: 323 and ■: 353 Kelvin,  $d_{p,0} < 180\text{ }\mu\text{m}$ , solid fraction = 5% w/w.

Given the experimental results, it looks like the reaction time for complete depolymerization of Poly-H is much lower than the one for PET. However, it must be pointed out that the chain length and the crystallinity of the polymer can have a large influence on the rate of depolymerization. The chain length of Poly-H is 8 times lower than that for PET (respectively 5.200 against 40.000 g/mol). Therefore the shrinking core model (Chapter 2.2) has also been applied to the experimental data of hydrolysis of Poly-H. This model takes into account the

chain length of the polymer (i.e. number of moles repeating units ( $C_A$ ), and therefore a better comparison between the reaction rates of PET and Poly-H can be done. Table 5 shows the reaction rate constants for the depolymerization of Poly-H and Figure 14 the evaluation of the kinetics. Compared to the constants of PET (Table 4), the rate of depolymerization of Poly-H is  $\sim 40$  times higher than for PET.

Table 5: Reaction rate constants for the acid catalyzed depolymerization of Poly-H at 323 and 353 Kelvin<sup>3</sup>

T [K]	$k_r$ [ $10^{-9} m_w^3 m_s^{-2} s^{-1}$ ]	$R^2$ [-]
323	0,26	0,967
353	0,78	0,975

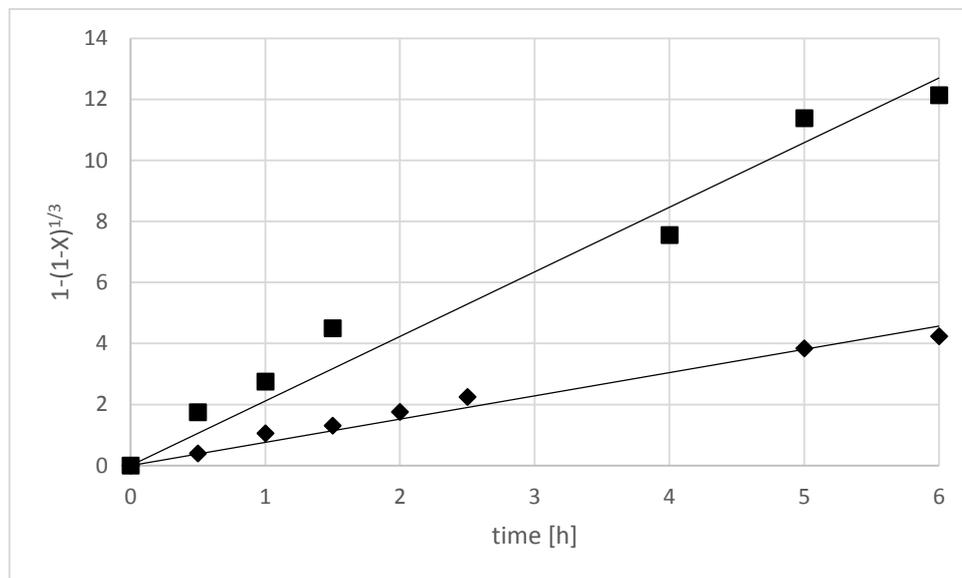


Figure 14: Evaluation of the kinetics of acid catalyzed depolymerization of Poly-H particles according to Eq.(8).  $\blacklozenge$ : 323 and  $\blacksquare$ : 353 Kelvin,  $d_{p,0} < 180 \mu m$ .

Also during alkaline catalyzed hydrolysis, complete conversion of Poly-H has been obtained. However, during analysis, it was noticed that after 30 minutes the amount of monomer (DHCA) produced decreases in time. It looks like the monomer undergoes a consecutive reaction. When analyzing these samples with HPLC, a peak with a higher absorption (300 nm) is increasing in time. Possibly this molecule is the quinone structure of DHCA. According to the reaction mechanism given in Appendix 4, it is possible that a quinone is formed during alkaline hydrolysis of Poly-H. This reaction is a redox reaction, after the quinone is formed it will not react back to DHCA without adding a reductor. Because too less is known about this mechanism, no further results of alkaline hydrolysis of Poly-H have been obtained.

<sup>3</sup>  $C_A = 38$  moles repeating units per unit volume of the particle,  $C_B = 1000 \text{ mol/m}^3$  and  $d_{p,0} = 68 \mu m$

The positive aspect of the successful depolymerization of Poly-H in an acidic reaction medium, is that no acidification is needed to obtain the monomer, as was the case at alkaline hydrolysis of PET. So salt formation does not occur.

Some first experiments on the separation of the monomer have been carried out. Because DHCA is fairly soluble in water (~50 g/L), extraction seems a good separation technique. Toluene, ethyl acetate, methyl-t-butyl-ether (MTBE), heptane and pentane are tested as solvents. Toluene, heptane and pentane are not suitable, because the monomer did not dissolve in any of these solvents. DHCA dissolves in Ethyl Acetate and MTBE, the partition coefficients determined for these two solvents were ~20. However, it must be pointed out that Ethyl Acetate and MTBE are also slightly soluble in water, so a ternary phase diagram is required here. This has not been taken into account in these first experiments. Also there is no knowledge yet about the activity coefficient of DHCA in water and ethyl acetate or MTBE, so further research on the separation of the monomer is required (see Recommendations).

#### 4.4 Hydrolysis of PET in alkanols

The reaction rate of hydrolysis of PET is very slow. To make this process economically feasible, higher conversions are necessary. From the experimental results it is clear that an increase in temperature could lead to higher conversions, however, at atmospheric pressure it is not possible to carry out the hydrolysis reaction in water above 373 Kelvin without evaporation of the solvent. By interpreting Figure 10 it is not expected that a temperature of 373 Kelvin would lead to a conversion towards 90% or higher. Therefore the use of other solvents with higher boiling points has been tested. When carrying out the alkaline depolymerization reaction in an alkanol with a high boiling point, possibly higher conversions could be reached.

Figure 15 shows the results of the depolymerization in various alkanols. Results show that after 60 minutes a conversion of 100% can be reached when the reaction is carried out in 1-heptanol or 1-octanol. Table 8 gives an overview of conversions and reaction temperatures. Also here, it can be seen that temperature strongly influences the reaction rate. Compared to hydrolysis in an aqueous reaction sodium hydroxide solution, much higher conversions can be reached in approximately one hour by carrying out the reaction with a higher alkanol as a solvent.

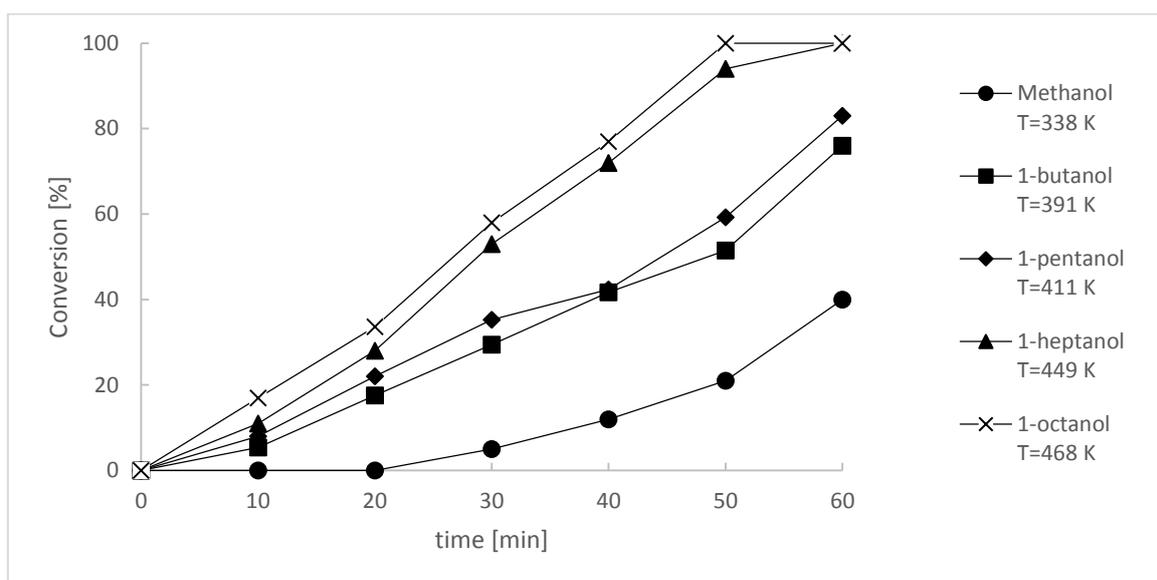


Figure 15: Conversion time history of depolymerization of virgin PET particles in different alkanols and 1M sodium hydroxide.  $d_{p,0} < 180 \mu\text{m}$ , solid content = 10% w/w

When choosing 1-octanol as solvent, the separation of the monomer TPA can be easily done by extraction. Octanol is slightly soluble in water (0,096 g/100 g) and by adding water to the reaction mixture two layers are formed. TPA will be in the aqueous layer. By adding 2M HCl to the aqueous layer, to obtain a pH of 3, TPA will precipitate and can be filtered off. After drying the TPA yield was measured to be 100%.

The separation of EG is facing the same problem as described in chapter 4.1. EG will probably be present in the aqueous and the organic layer. The partition coefficient of EG over 1-octanol and water is unknown and should be determined in further research. If the partition coefficient is known an extraction process can be developed. It is nevertheless assumed that the largest amount of EG will be present in the aqueous layer. Because the aqueous layer is acidified, NaCl salt is formed and NaCl can be separated by filtration, see chapter 4.1.

To determine the kinetics of the hydrolysis reaction in alkanols, the shrinking core model has been applied to the experimental data. However, this model does not fit the experimental data. This means another reaction mechanism holds for the hydrolysis of PET in alkanols. Because these reactions are carried out at higher temperatures (in most cases above the  $T_g$  of PET, which is  $80^\circ\text{C}$ ), probably this is not a surface reaction. Above the  $T_g$  the PET particles could undergo swelling. Or, because of the higher temperatures and the use of alkanols as solvent, PET particles will dissolve in the reaction medium and therefore another reaction mechanism will hold for these reactions.

## 4.5 Aminolysis of PET

Another method of chemical recycling is aminolysis, where PET is degraded by amines. The aminolysis of PET is also fast and will yield higher conversions as compared to hydrolysis in aqueous solutions<sup>[18]</sup>. Therefore also aminolysis has been investigated as a chemical recycling method. The results of the aminolysis of PET particles is shown in Figure 16.

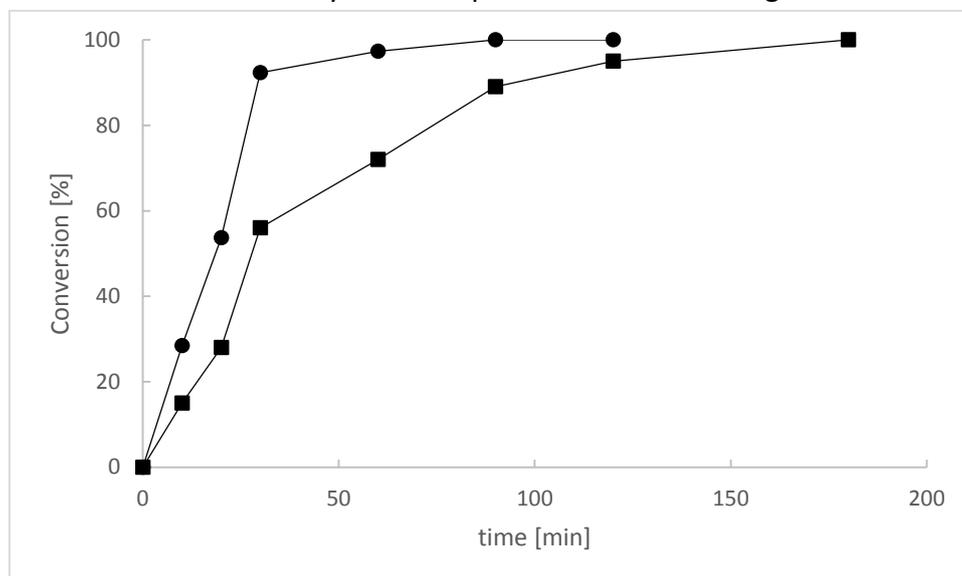


Figure 16: Conversion time history of aminolysis of ■: virgin PET and ●: PET waste particles in 2-amino-ethanol and 1% w/w Zinc Acetate. T=443 Kelvin,  $d_{p,0} < 180 \mu\text{m}$ , solid content = 40%

As can be seen complete depolymerization of PET waste is reached after 50 minutes reaction time. The yield of the product after separation was 78%. This method seems also very promising for the depolymerization of PET. The products of aminolytic depolymerization (e.g. with ethanolamine gives the product bis(2-hydroxy ethylene) terephthalamide, see figure 17) can be used as epoxy hardeners and nonionic polymeric surfactants. Or they can be further used for synthesis of bis-oxazolines, which have been used as monomers, chain extenders and crosslinkers in polymers<sup>[19]</sup>. Or, the building blocks of PET, TPA and EG, can be recovered when BHETA is hydrolyzed with an acid. This will yield TPA and the reactant 2-aminoethanol, which can be separated and reused in aminolysis. A first, qualitative, experiment on the acid catalyzed hydrolysis of BHETA has already been done and HPLC analysis showed that after 24 hours of reaction at 80°C TPA is formed.

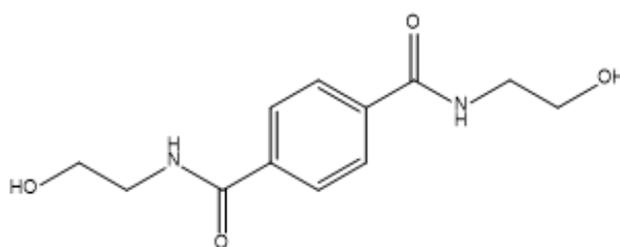


Figure 17: Structure of bis(2-hydroxy ethylene) terephthalamide (BHETA)

Table 8: An overview of all chemical recycling reactions with reaction conditions and conversion after a certain time.

Polymer type	Reaction medium	Catalyst	Temperature [K]	Reaction time [h]	Conversion [%]
PET virgin PET waste	Water	1M H <sub>2</sub> SO <sub>4</sub>	298, 323 and 353	48	0
PET virgin	Water	1M NaOH	298 323 353	48	3 14 40
PET waste	Water	1M NaOH	298 323 353	48	9 40 50
Poly-H	Water	1M H <sub>2</sub> SO <sub>4</sub>	298 323 353	6	20 92 98
Poly-H	Water	1M NaOH	298 323 353	6	100 100 100
PET virgin	Methanol 1-butanol 1-pentanol 1-heptanol 1-octanol	1M NaOH	338 391 411 449 468	1	40 76 80 100 100
PET virgin	2-amino ethanol	Zinc Acetate	443	3	100
PET waste	2-amino ethanol	Zinc Acetate	443	2	100

## 5. Conclusion

The chemical recycling of PET has been investigated. Hydrolysis of PET in an aqueous sulfuric acid medium is very slow, no depolymerization occurs after 48 hours of reaction. Alkaline catalyzed depolymerization leads to a conversion of virgin PET of 40% after 48 hours reaction at 353 Kelvin. The recovering of the monomer terephthalic acid can easily be carried out by acidification and precipitation, which leads to a yield of 38% TPA. The recovering of the monomer ethylene glycol has to deal with the problem of salt formation and only a yield of 28% was reached, so further research on the recovering of EG is required.

The reaction rate constants of alkaline depolymerization of PET have been determined by a Shrinking core model. They turned out to be 6,36 and 19,1  $10^{-12} \text{ m}^3_{\text{w}} \text{ m}^{-2}_{\text{s}} \text{ s}^{-1}$  for a reaction temperature of respectively 50°C and 80°C, so reaction rate increases with increasing temperature. It has been demonstrated that the resistance against mass transfer of OH<sup>-</sup> is much lower than the resistance against reaction at the particle surface.

Other chemical recycling methods have been tested, like hydrolysis by using an alcohol as solvent and aminolysis. These methods resulted to complete conversion of PET in 60 minutes reaction time, so these methods are promising techniques for the chemical recycling of PET.

Next to PET, the polyester Poly-H has also been hydrolyzed. This polyester was completely depolymerized in a 1M aqueous sulfuric acid solution after 6 hours at 353 Kelvin. It has been demonstrated that the rate of depolymerization of an aliphatic polyester, like Poly-H, is ~40 times higher than for PET. The advantage of acid depolymerization is that no acidification is needed after depolymerization and there will be no problems with salt formation. For Poly-H the recovering of the monomer still needed to be investigated further.

## 6. Recommendations

The yield of the recovered ethylene glycol needs to be improved. After alkaline hydrolysis there are problems with the salt that is formed after acidification. To end up with only EG, the salt and the water needed to be removed. Possible techniques are making use of membranes, like reversed osmosis. The salt can be removed by the membrane and next EG and water can be separated by distillation. Another possible separation technique is extraction with diethyl ether. In that case, separation of the water by distillation is not required. Probably all the salt will remain in the aqueous phase and ethylene glycol will be present in the organic phase. After extraction, diethyl ether can be evaporated to yield ethylene glycol. Evaporation of diethyl ether requires less energy compared to the distillation of water and ethylene glycol. Also the evaporated diethyl ether can be recycled in the extraction process. When developing this extraction method the partition coefficient of ethylene glycol in water and diethyl ether has to be known.

Also the partition coefficient of ethylene glycol in water and 1-octanol has to be determined, to design a proper separation process of ethylene glycol after the alkaline hydrolysis in 1-octanol.

The alkaline hydrolysis of Poly-H has to be investigated further. It has been found that the monomer that is formed reacts in a consecutive reaction, possibly to a quinone. Too little is known about this and more analysis should be done on this product. On the other hand, the question is, if it is worthwhile to collect more information about the alkaline hydrolysis of Poly-H. The reason for this is that acid catalyzed depolymerization looks very promising. Note that acid catalyzed depolymerization does not deal with the problems of salt during separation, so it is highly recommended to depolymerize Poly-H with acid catalyzed hydrolysis.

The depolymerization of Poly-H looks very promising. When the building block could be recovered with a high purity (>98%), the polymerization could be done again and so the closed cycle of chemical recycling is obtained. It is recommended to investigate the recovering of the monomer DHCA after the acidic catalyzed depolymerization. Extraction with ether (MTBE or diethyl ether) seems a good option, based on the preliminary tests on the partition coefficient

of DCHA in MTBE. However, note that in an acid reaction medium MTBE could react to tert-butyl alcohol and methanol<sup>[20]</sup>, so neutralization of the reaction medium before extraction is required. When the monomer is recovered it is interesting to polymerize it again to Poly-H with the method as described in Appendix 1.

The rate of hydrolysis of PET in alkanols is high. The shrinking core model does not fit to the experimental data obtained, so probably another mechanism will hold for these reactions. A kinetic model that describes the hydrolysis reaction of PET in alkanols should be developed. Probably the PET particles undergo swelling or dissolve in alkanols so these effects should be taken into account.

The aminolysis of PET yields BHETA as a product. Quantitative research on the acid hydrolysis of BHETA towards terephthalic acid and 2-amino-ethanol and the separation afterwards still has to be done. On the other hand, BHETA could also be used for synthesis of bis-oxazolines. From preliminary experiments (PhD. research J. van Schijndel) this seems possible and an interesting technique. In that case PET waste could be depolymerized fast by aminolysis to yield a product that can be used in other applications, e.g. as chain extender.

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## Appendix

### 1. From lignin to Poly H

By pyrolysis, lignin is degraded in various chemical compounds, including the three monolignols: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The starting material for this project is p-coumaryl alcohol. When p-coumaryl alcohol is oxidated and next hydrogenated, dihydro coumaric acid (DHCA) is obtained, as can be seen in Figure 18.

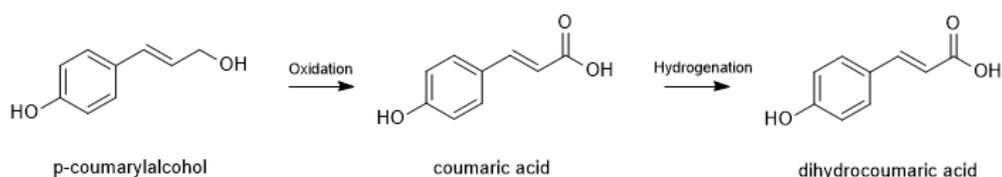
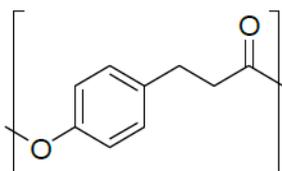


Figure 18: Reaction scheme of the monolignol p-coumaryl alcohol towards the monomer dihydrocoumaric acid

DHCA can be polymerized by polycondensation. The polymer obtained is called Poly-H (poly dihydro coumaric acid), its structure is given in Figure 19.



Poly-H is not (yet) commercially available, so at the start of this research project a trainee at Avans Hogeschool <sup>[21]</sup> produced a large amount of Poly-H. The polymerization was carried out by the following procedure:

Figure 19: Poly-H

DHCA (3-(4-hydroxyphenyl) propionic acid) (>98%) was purchased at TCI. The polycondensation was carried out in a 4560 mini Parr-reactor (100 mL) with a 4848 controller. The reactor was charged with 50 gram (300 mmol) DHCA and slowly heated to 130°C under a continuous nitrogen flow and a pressure of 500 mbar. Temperature was kept constant at 130°C for 2 hours. Next, 10% w/w (185 mmol) Zinc Chloride (Baker Analyzed, 97,0%) was added and the reactor content was further heated to 180°C. The temperature was kept constant at 180°C for 1 hour, still with a continuous nitrogen flow and a pressure of 500 mbar.

After polymerization the product was separated by a solvent/non-solvent method with methanol. The suspension was filtrated and the product was dried in a vacuum oven at 40°C. After drying the product was analyzed with Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC).

By GPC analysis the number molecular weight ( $M_n$ ) of Poly-H was found to be ~5.200 g/mol containing ~30 monomer repeating units. From DSC analysis, see Figure 20, it has been found that  $T_m=237^\circ\text{C}$ ,  $T_c=210^\circ\text{C}$  and  $T_g=77^\circ\text{C}$ . According to the method of PerkinElmer <sup>[22]</sup> the fraction crystalline material in the product was 0,05.

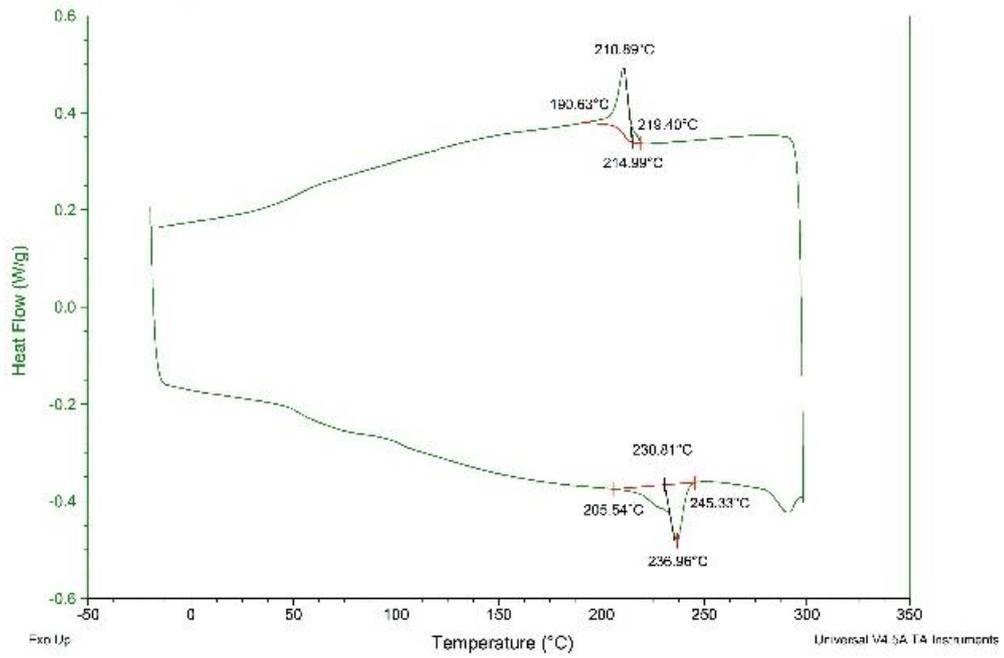


Figure 20: DSC of Poly-H

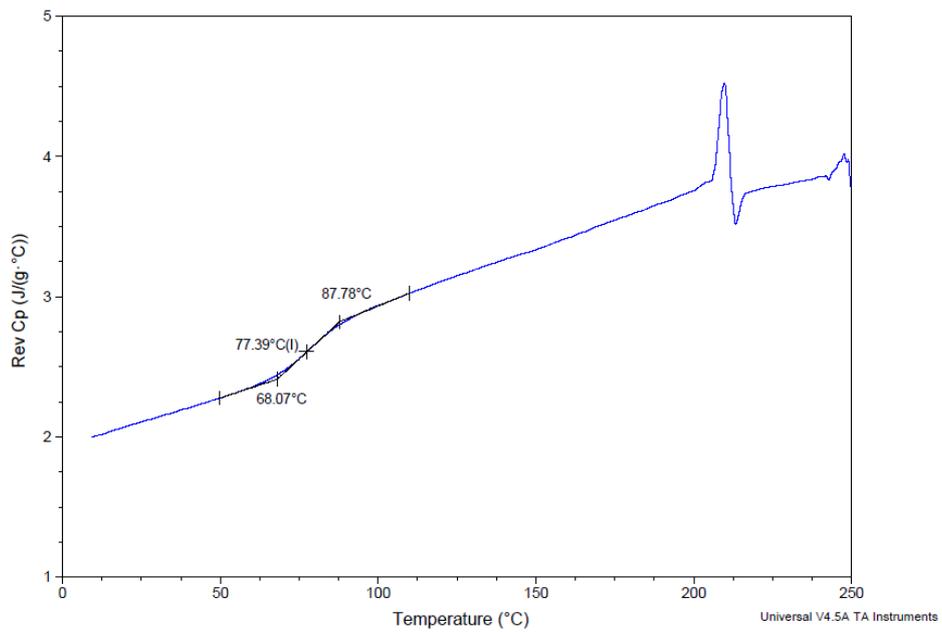


Figure 21: Modulated DSC of Poly-H to determine  $T_g$

## 2. Reaction mechanisms

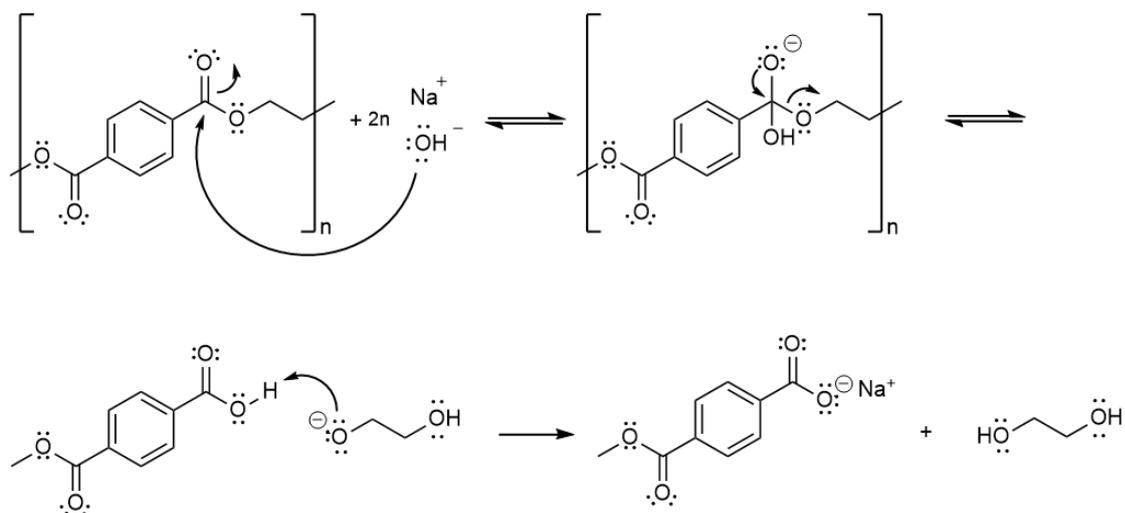


Figure 22: Mechanism of alkaline catalyzed depolymerization of PET

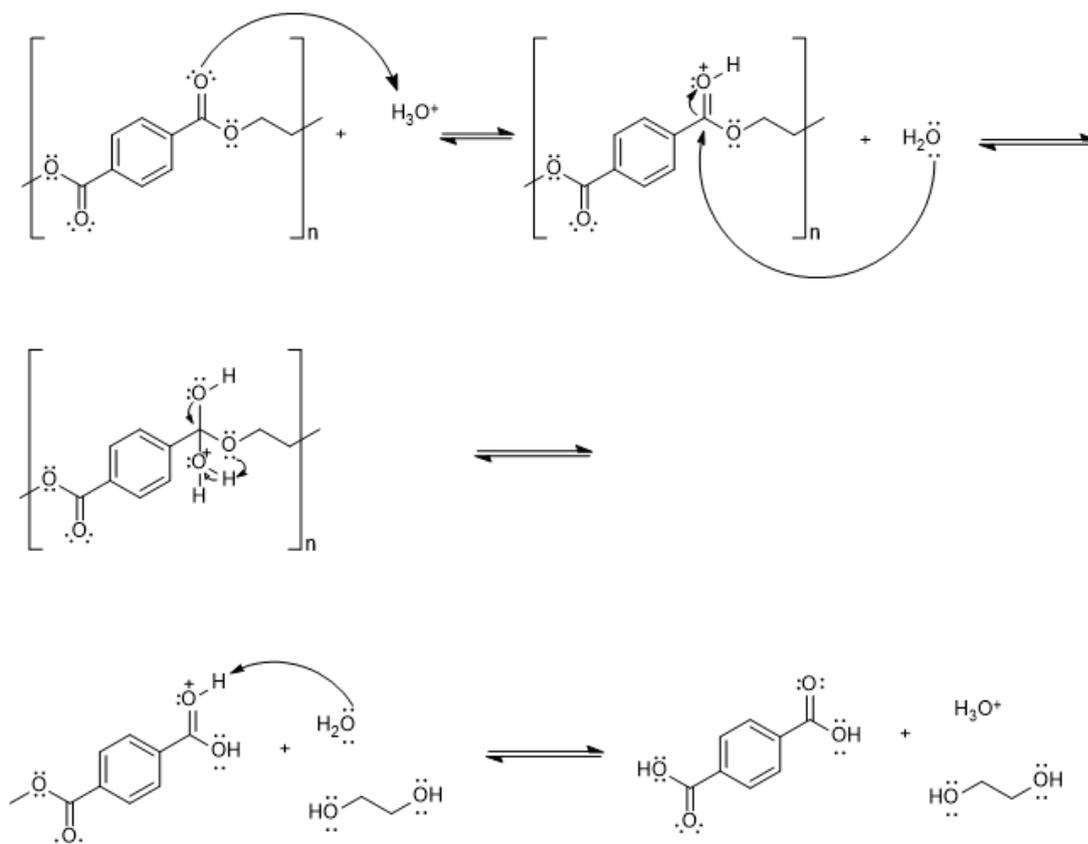


Figure 23: Mechanism of acid catalyzed depolymerization of PET

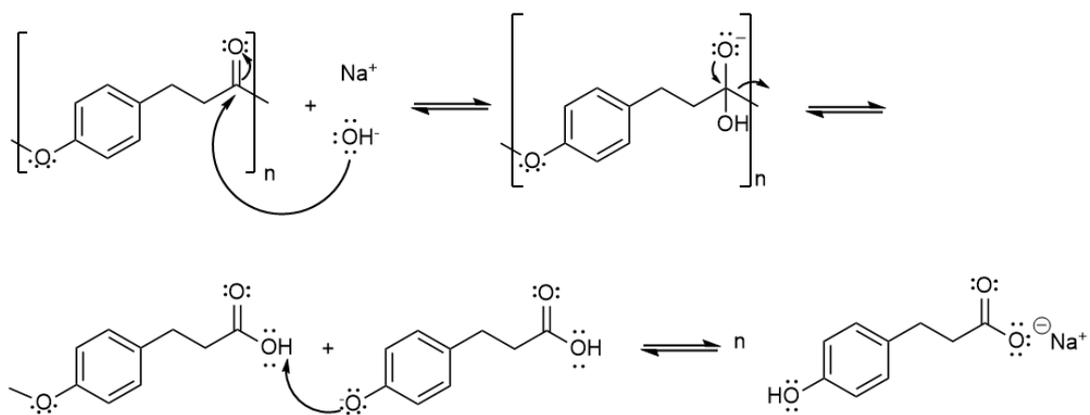


Figure 24: Mechanism of alkaline catalyzed depolymerization of Poly-H

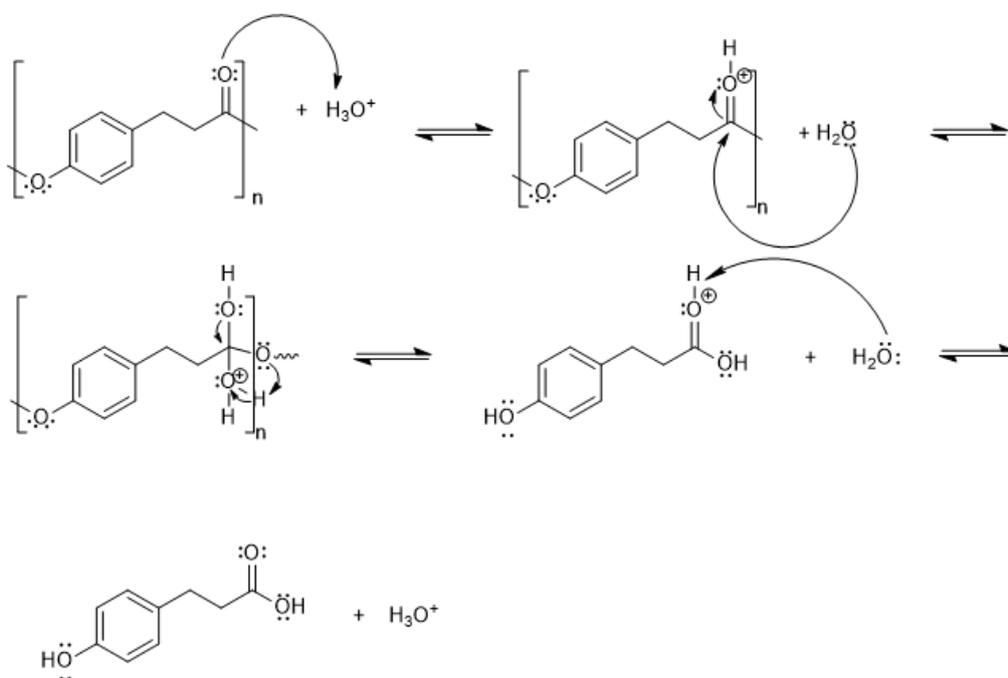


Figure 25: Mechanism of acid catalyzed depolymerization of Poly-H

### 3. Development of HPLC method for BHETA analysis

Concentration of all products from hydrolysis experiments could be measured at the nonpolar C18 column (reversed phase) with the method described in Chapter 3. However, the main product from aminolysis experiments (bis(2-hydroxyethyl) terephthalamide (BHETA)) is too polar and has no affinity with the C18 column. A (more) polar stationary phase would be better and therefore a new (normal phase) HPLC analysis method has been developed.

Available columns were Zorbax RX-SIL 150 x 4,6 mm and Zorbax CN 250 x 4,6 mm. For Thin Layer Chromatography (TLC) analysis the eluent used was ethanol:chloroform with a volume ratio of 1:9 [23] and 1:4 [24], so this was used as reference for choosing the eluent for HPLC.

The performance of the most polar column, Zorbax RX-SIL 150 x 4,6 mm, was investigated first. Different eluents have been tested in different ratios and with different gradients. But it looks like this column is too polar, as when a highly nonpolar solvent is used no peaks were obtained or a lot of tailing was observed, see Figure 26. Probably BHETA has too much affinity with this column and so the next column, Zorbax CN 250 x 4,6 mm has been used.

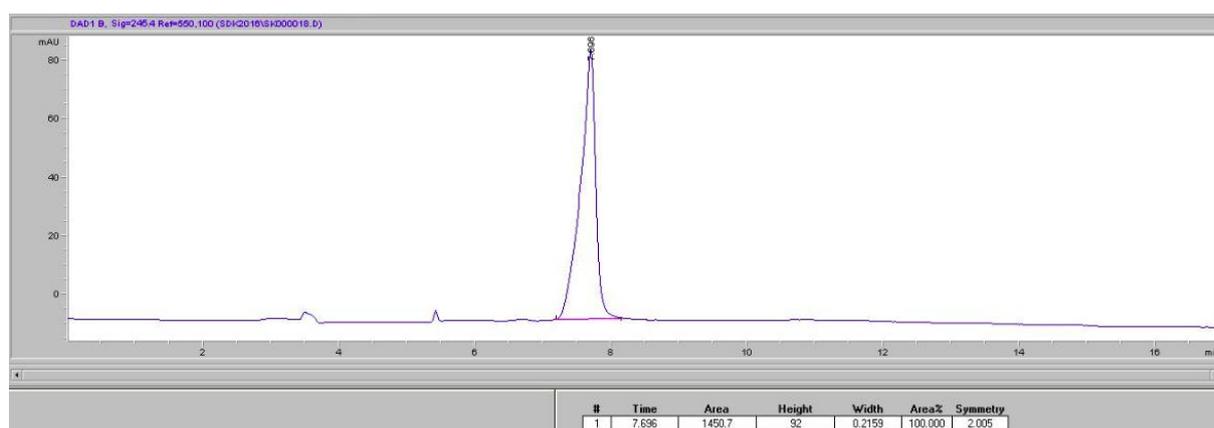


Figure 26: Chromatogram of BHETA analyzed with a Zorbax RX-SIL column, where tailing is observed. Symmetry = 2.005. UV detection at 245 nm

For this column, also a lot of different ratios of the eluent and gradients have been tested. Finally, the following method seemed to give good results: starting with 0% ethanol (solvent A) and 100% heptane (solvent B) as eluent, a linear gradient to 70:30 A:B in 12 min. and afterwards back to 0:100 A:B in 8 min. BHETA was eluted at a retention time of 11.2 min at 245 nm, see figure 27.

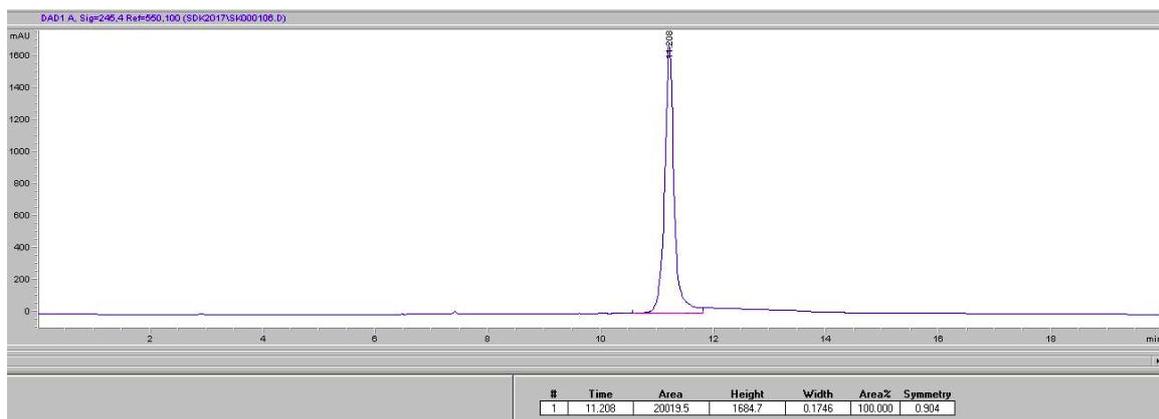


Figure 27: Chromatogram of BHETA analyzed at a Zorbax CN column. Symmetry=0.904. UV detection at 245 nm.

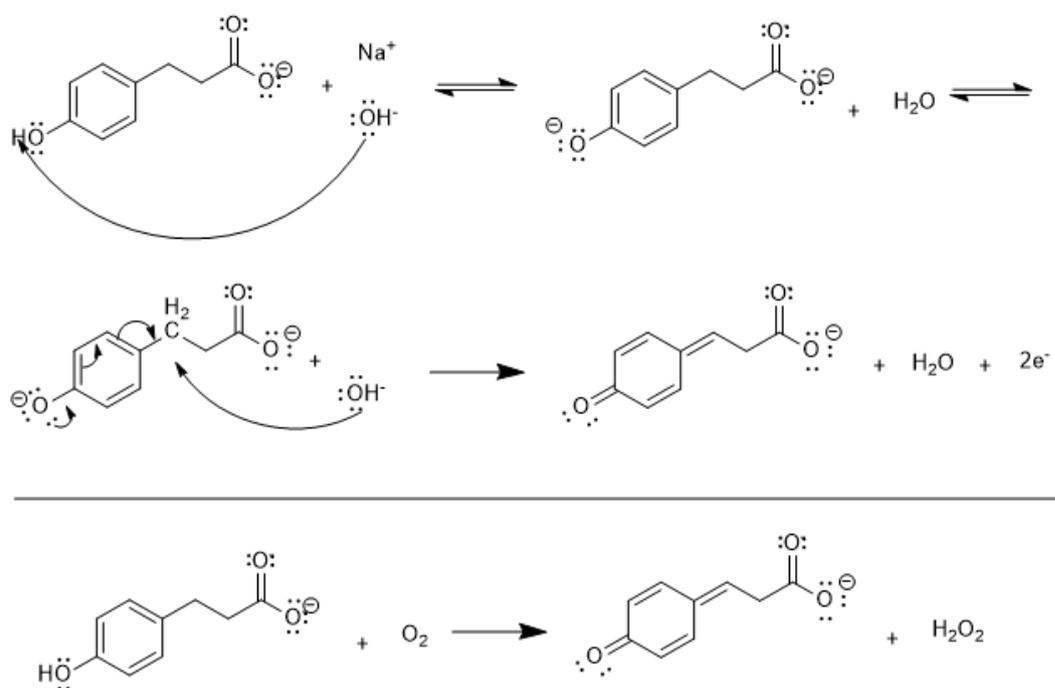
To determine the efficiency of this analysis, the number of theoretical plates ( $N$ ) and the height of one theoretical plate (HETP) were calculated for several measurements, according to respectively Eq. (22) and (23). The higher the plate number, the more efficient the analysis.

$$N = 5,545 \left( \frac{t_r}{w_{0.5}} \right)^2 \quad (22),$$

$$HETP = \frac{L}{N} \quad (23),$$

where  $t_r$  is the retention time (min.),  $w_{0.5}$  is the width of the peak at half the peak height (min.) and  $L$  is length of the column (m). The plate number is  $(25 \pm 4) \cdot 10^3$  and the plate height is  $10 \mu\text{m} (\pm 1,6)$ .

#### 4. Possible formation of quinone during alkaline hydrolysis Poly-H



## 5. Details on the calculations of the just-suspended stirrer speed

As described in section 2.3, Zwietering<sup>[6]</sup> has developed a correlation that describes the lowest impeller speed that is required to prevent particles from remaining at the bottom of the tank. Zwietering has found the following correlation (Eq. 10) for the just-suspended stirrer speed ( $N_{JS}$ ):

$$N_{JS} = S \left( \frac{\eta_m}{\rho_m} \right)^{0.1} d_p^{0.2} \left( g \left( \frac{\rho_s - \rho_l}{\rho_l} \right) \right)^{0.45} (100B)^{0.13} D_i^{-0.85} \quad (10).$$

The just-suspended stirrer speed has been determined by calculations, using above correlation, and experimental, by visual inspection (see section 4.2). The parameters that have been used for calculations are given in this appendix. Calculations were carried out for two temperatures: 50°C and 80°C.

$S$ ,  $d_p$ ,  $\rho_s$ ,  $g$ ,  $B$  and  $D_i$  are independent on temperature. The shape factor  $S$  and the impeller diameter  $D_i$  depend on the impeller type. Table 9 shows the values for the four types of impellers that have been used. The values for the shape factor  $S$  are based on the findings of Zwietering, who has found that the shape factor depends on the type of impeller, and the ratio of the vessel and stirrer diameter ( $T/D$ ) and the vessel diameter and the distance between the stirrer and the bottom of the tank ( $T/C$ )<sup>[6]</sup>.

Table 9: Values for the shape factor  $S$  and the impeller diameter  $D_i$  for the four types of impellers that have been used in this work

Impeller	S [-]	$D_i$ [cm]
Propeller A100	5	4,0
Propeller A320	6	4,5
6-bladed turbine	4	4,8
4-bladed turbine	4	4,6

The values that have been used for the particle diameter  $d_p$ , density of the solid PET particles  $\rho_s$ , gravitational constant  $g$  and solids fraction  $B$  are respectively  $180 \cdot 10^{-6} m$ ,  $1380 kg/m^3$ ,  $9,81 m/s^2$  and 0,25.

The viscosity and the density of the mixture,  $\eta_m$  and  $\rho_m$ , and the density of the liquid,  $\rho_l$ , depend on temperature. The density of the liquid (water) at 50 and 80°C is respectively 988 and  $972 kg/m^3$ . The density of the mixture has been taken as the weighted average of the density of the solid and the liquid phase and was calculated to be 1086 and  $1074 kg/m^3$  at respectively 50 and 80°C.

The viscosity of the mixture has been determined by the following correlation of Batchelor<sup>[16]</sup>:

$$\eta_m = \eta_l \left( 1 + \frac{5}{2} \phi + 5,2 \phi^2 \right) \quad (24),$$

where  $\eta_l$  is the viscosity of the liquid and  $\phi$  is the volume fraction of the solids in the suspension. At 50°C  $\eta_l$  is equal to  $0,55 \cdot 10^{-3} \text{ Pa s}$  and at 80°C  $0,355 \cdot 10^{-3} \text{ Pa s}$ . For each temperature  $\phi$  equals 0,1935. According to this correlation the viscosity of the mixture turned out to be  $0,9 \cdot 10^{-3} \text{ Pa s}$  at 50°C and  $0,6 \cdot 10^{-3} \text{ Pa s}$  at 80°C.

The values of the calculated  $N_{jS}$  are collected in table 6 in section 4.2.

## 6. Details on the calculations of the heat transfer coefficient

According to Eq. (15) the heat transfer coefficient can be calculated by

$$Nu = \frac{h_r D_R}{k_m} = 0,75 Re_T^{2/3} Pr^{1/3} \left( \frac{\eta_m}{\eta_{wall}} \right)^{0,14} \quad (15),$$

where

$$Re_T = \frac{\rho_m N D_i^2}{\eta_m} \quad (16),$$

$$Pr_m = \frac{\eta_m c_{p,m}}{k_m} \quad (17).$$

The following numbers have been used for the calculations of  $Re_T$ ,  $Pr_m$  and  $h_r$ :

		50°C	80°C
$\rho_m$	[kg/m <sup>3</sup> ]	1086	1074
$\eta_m$	[10 <sup>-3</sup> Pa s]	0,9	0,6
$c_{p,m}$	[J/(kg · K)]	3385 <sup>4</sup>	
$k_m$	[W/(m · K)]	0,5 <sup>3</sup>	
$D_R$	[m]	0,1	

The values used for the impeller speed  $N$  and the diameter of the impeller  $D_i$  are given in the table below. The impeller speeds are taken from the calculations of  $N_{JS}$  (table 6, section 4.2). Except for the 4-bladed disc turbine impeller the observed value is taken, because the deviation with the calculated value is too large.

Impeller	$D_i$ [cm]	$N_{50^\circ\text{C}}$ [rpm]	$N_{80^\circ\text{C}}$ [rpm]
Propeller A100	4,0	571	561
Propeller A320	4,5	620	609
6-bladed turbine	4,8	391	385
4-bladed turbine	4,6	641	673

The ratio of  $\frac{\eta_m}{\eta_{wall}}$  is assumed to be 1. The calculated values for  $Re_T$ ,  $Pr_m$  and  $h_r$  are given in table 7 in section 4.2.

<sup>4</sup> The values for  $c_{p,m}$  and  $k_m$  are estimated from the work of M.F. Kemmere<sup>[10]</sup>, where  $c_{p,m}$  and  $k_m$  values for a solid-liquid mixture of polystyrene in water have been used. The values are assumed to be constant over the temperature range 50 – 80 °C.