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# Process and Kinetic Study of PET Recycling Into PAT-Ac Ethanediol and PEAc by Hydrolysis Catalyzed by Excess Citric Acid Protonic Acid H+

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## Abstract

Recycling Polyethylene terephthalate (PET) by hydrolysis using excess citric acid molecules as catalysts to generate $H^+$ protonic acid sites had been undertaken. The products of this recycling process are PolyEster Citric Acid (PEAc), formed by the polyesterification of two citric acid molecules, Ethane Diol (ED) or ethylene glycol, and a new solid material called PAT-Ac, whose molecular formula is made up of one molecule of pure terephthalic acid (PAT) and two molecules of citric acid. Two procedures had been established, one for extracting the PEAc solution and the Ethane diol in acetone solution (AED-solution) using the usual organic solvents dichloromethane and acetone, and the second for extracting pure Ethane diol (ED) by vacuum evaporation using a rotavapor. This recycling was carried out in a laboratory glassware reactor, in a 1000ml cylindrical beaker covered by a funnel with a conical lid, capped but non-watertight, and therefore under atmospheric pressure at a temperature of 150°C. A kinetic study of this recycling process was carried out, using an acid-base assay with HF-0.0026N to follow the progress of the recycled TAP and deduce the evolution of PET conversion with reaction time; and an acid-base titration with NaOH-0.05N to quantify the $H^+$ protonic acid sites coming from the acid catalysts of the citric acid molecules and deduce the evolution of the citric acid quantity in the reaction medium. This latter assay also enabled the determination of the PAT-Ac molecular structure. A reaction mechanism for this recycling of PET by hydrolysis, using excess citric acid molecules as a catalyst source of $H^+$ proton active sites, is proposed and validated by the kinetic data collected during the various acid-base assays mentioned above. The maximum conversion of PET to PAT and ED recorded during the kinetic study is 34.49% after 20mn reaction time or $1.5114 \times 10^{-3}$ [moles of PAT regenerated per Gram of PET load], or $7.5572 \times 10^{-5}$ [moles of PAT regenerated per Gram of PET and per Minute]. In addition, the volume of ED collected is 17ml and the mass of PAT-Ac synthesized is 2.6 [g].

## Keywords

Recycling, Polyethylene Terephthalate (PET), Procedure, Kinetics, Mechanism, Pure Citric Terephthalic Acid (PAT-Ac), Ethane Diol (ED), Polyester Citric Acid (PEAc)

# 1. Introduction

This manuscript is subdivided into three main parts: the first part elaborates a bibliographical study on the physico-chemical characteristics of the raw materials and products of this PET recycling. It also presents the experimental conditions for PET recycling through the global hydrolysis reaction using the protonic H+ sites of acid catalysts, citric acid molecules. The second part is dedicated to the elaboration and description of the PET recycling procedure and the recovery procedures of the synthesized recycled products PAT-Ac followed by the extraction of the other recycled products ED and PEAc. In the third part, a mechanism for this PET recycling reaction is proposed; kinetic monitoring had been carried out and a comparison between the mechanism and these experimental results leads to validation of the mechanism and determination of the kinetic constants.

The laboratory materials used in this experimental study are: beaker 1000ml, funnel, stopper, beaker 250ml, graduated cylinder, flask heater, buret, filter paper, precision balance, pipette, magnetic stirrer, magnetic rod, dichloromethane, acetone, evaporator -rotavapor, separating funnel, flask 250ml, NaOH-0.05N, HF-0.0026N, helianthin, citric acid, distilled water, PET, iron slide and coverslip, grinder, kitchen sieve, 250 µm sieve, thermometer.

# 2. An Experimental Condition to Recycle Polyethylene Terephthalate – PET

## 2.1. The Polyethylene Terephthalate – PET

The polyethylene terephthalate (PET) is a polymer which monomer is synthesized by esterification between a molecule of pure terephthalic acid (PAT – figure 1) and a molecule of ethylene glycol also called ethane 1, 2-diol (figure 2). The polymerization of this monomer is made by oxygen link between the PAT-pure terephthalic acid's carboxylic acid organic function and the ethylene glycol's alcohol organic function. The monomer of the PET-polymer (figure 4) is represented on the Figure 3.
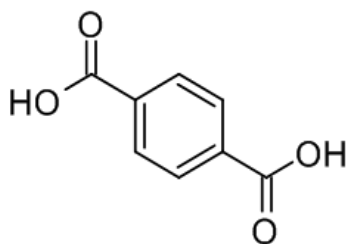


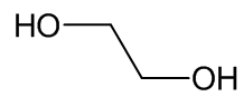*Figure 1. The molecule of Pure terephthalic acid (PTA) or benzene-1, 4-dicarboxylic acid.*



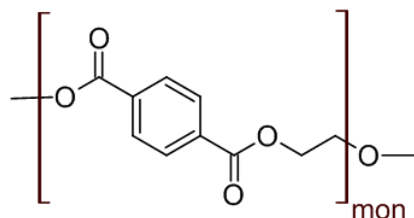*Figure 2. The molecule of ethylene glycol or ethane-1, 2-diol.*
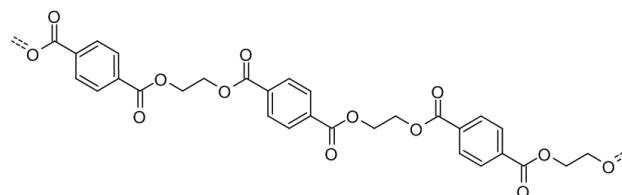


*Figure 3. The monomer of the PET.*



*Figure 4. The Polymer polyethylene terephthalate – PET.*

## 2.2. The PET – Polyethylene Terephthalate Recycling Conditions

There were many ways to recycle and to valorize the PET – polyethylene terephthalate but hydrolyzation is the only procedure to regenerate the molecules which composed its monomer such as the *Pure terephthalic acid (PTA) or benzene-1, 4-dicarboxylic acid* and the *ethylene glycol or ethane-1, 2-diol.* This recycling procedure could be catalyzed by protonic acid-H$^+$ catalysts – Bronsted acid or Lewis acid. The protonic acid-H$^+$ catalysts were generated by minerals or organic materials which structure contained protonic acid - H$^+$ functioning as a catalyst like citric acid which is a tricarboxylic acid (figure 5) generating protonic acid - H$^+$ according to the reactional pH [1, 2], like sulfuric acid molecule [3, 4] whereas the Lewis acid molecules contained vacant case like intermediary metals like iron and its derivatives used in different types of reactions such as citric acid polymerization [5], gas NOx reduction [6-9].

During the experimentations described in this manuscript, citric acid molecules were used as source of protonic acid catalyst to regenerate the PET-polyethylene terephthalate by hydrolysis. The solid PET used during the experimentations was the Malagasy water "eau vive" packaging. Seeing that the reactant and the catalyst citric acid was in liquid phase, we are in the case of heterogeneous catalysis. Also, it is noticed that in that case of PET recycling, the reactant citric

acid quantity was in excess in comparison to the PET with a weight ratio equals to 70.7591 (table 1). The citric acid 141,6032g was diluted completely in 200ml of distillated water and transferred in a beaker 1000ml. The PET 2.0012g was grinded until 57.79% have a size between [1mm, 2, 5mm] and 42,21% have a size less than 1mm, then they are transferred in the beaker with the reactant source of the catalyst protonic acid-H$^+$. The beaker was closed on top with a blocked reversed plastic funnel. The whole lot was taken into a balloon heater at temperature included between 141 ℃ and 200 ℃, at atmospheric pressure because the assembly funnel and beaker weren't completely watertight, steam could occasionally escape at the brim. So, the distillated water level decrease slowly with time reaction until 2.5cm from the bottom for which it must be taken back at maximally 6.5cm and minimally 3.5cm in order not to eject the funnel. The total duration of the hydrolysis reaction time is 11h 34mn.

**Table 1.** *The experimental conditions of the PET recycling.*

| Citric acid weight [g] | | 141.6032 |
|---|---|---|
| PET weight [g] | | 2.0012 |
| PET sizes [mm] | $1 \leq \emptyset \leq 2.5$ | 57,79% |
| | $\emptyset \leq 1$ | 42,21% |
| Distillated water volume [ml] | | 200 |
| Citric acid weight concentration [g/ml] (1) | | 708.016 |
| PET weight concentration [g/ml] (2) | | 10.006 |
| PET weight ratio (1)/(2) | | 70.7591 |
| Cylindric reactor with on top conical reversed block [cm$^3$] | | 148.4403 |
| Pressure | | Atmospheric |
| Temperature [℃] | | 141 ℃ to 200 ℃ |

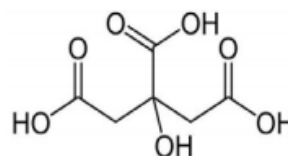| | |
|---|---|
| Hydrolysis duration [mn] | 694 |



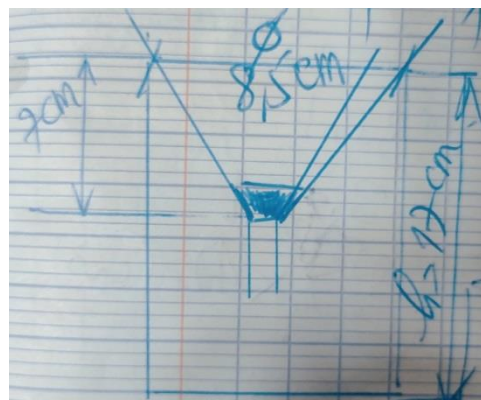**Figure 5.** *Citric acid molecule with their three carboxylic acids.*



**Figure 6.** *The laboratory cylindrical reactor conception*

## 2.3. The Elementary Fundamental Mechanism to Recycle PET by Hydrolysis

Usually recycling PET (Polyethylene Terephthalate) by hydrolysis pass principally through the part one of the reaction 1 and catalyzed by Lewis or Brönsted acid sites which conduct to the opening of the liaison on the oxygen atoms link and to the regeneration of the two organic molecules which composed the initial monomers of the PET such as the pure terephthalic acid – PAT and the ethylene glycol (reaction 1 – part 2).
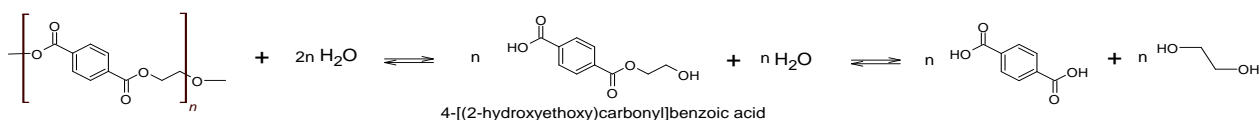


Equation 1. General reaction the PET composed with n monomers hydrolysis.

## 2.4. The Heterogeneous Protonic Catalytic Mechanism for Recycling PET by Hydrolysis
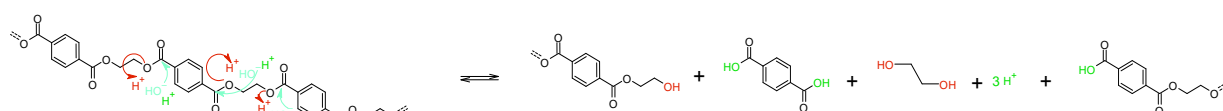


Equation 2. Mechanism of the PET hydrolysis catalyzed by protonic acid H$^+$ to regenerate the monomer compounds such as one molecule of PAT and one molecule of ethane-1, 2-diol.

In general, the hydrolysis of a PET polymer composed with n monomers (Figure 3) requires at least 2n moles of distilled water (Reaction 1) to form n moles of 4-[(2-hydroxyethoxy) carbonyl] benzoic acid as a possible intermediate, which by total hydrolysis with the remains of n moles of distilled water will form n moles of Pure Terephthalic Acid and n moles of ethylene glycol [10].

In practice, however, to increase the speed of this hydrolysis reaction, Lewis or Brönsted acid catalysts must be used [10]. In the test carried out and described in this manuscript, it is the $H^+$ protons of the carboxylic acid functions of the carboxylic acid molecules that catalyze the hydrolysis reaction. Thus, the $H^+$ protons of the acid functions of citric acid molecules are attracted by the electron doublets of the oxygen atom bridges to form an oxidanium bridge intermediate which is highly unstable causing a cleavage at its alpha position to form the acidic pure terephthalic product and a carbocation of the ketone function which is also highly unstable and will be joined and added with the hydronium ions of the water molecules to form the other ethylene glycol product with regeneration of the $H^+$ proton catalysts (Reaction 2).

## 2.5. The Experimental Process to Recycle the PET into PAT-Ac and Ethylene Glycol and Their Extractions

The following Figure 7 show the experimental process to recycle the PET-Polyethylene terephthalate.

After undertaking the hydrolysis described in paragraph §1, the 1000ml beaker is removed from the flask heater and left on the bench, covered with thick paper and in the open air, for a few minutes, sufficient not only to reduce the temperature without breaking the glassware, but also to decant the recycled solution and deposit the recycled product at the bottom of the beaker. After realizing the hydrolysis experimentation described on the paragraph 2.2, the beaker.

After decanting, the solution is filtered through a filter with an opening of between 0.5mm and 1mm; the retained material is a solid in the form of very brittle yellow-white crystals in the form of fine powder; some are even very fine in the solution and difficult to decant, which explains the need for sufficient time during the previous decanting. The material is then washed with cold or ice-cold water and stirred in a beaker for one minute, left to settle for a sufficient time, then filtered with filter paper. The retained material is air-dried at room temperature through a stream of hot air for two days. A white precipitate of PAT-Ac, i.e. a material whose unit molecule is made up of PAT and citric acid in a bonded form (cf. §2.6.). The water content of the PAT-Ac material is thus deduced. Its citric acid and PAT content is determined according to the dosing procedure described in §2.6., leading to the establishment of the fundamental structure of the PAT-Ac material and the positioning of its water molecules (cf. §2.6.). Subsequently, some of the washed material is taken and undergoes a second hydrolysis with excess water and intermittent heating at high temperature (141℃ - 200℃) to boiling point in an uncovered beaker. During the intermittent periods, the solution is stirred while an iron blade is placed against the flow of agitation. All this is done with the aim of obtaining finer and finer crystals, and the method proves effective. After decantation-filtration to room temperature and washing, the PAT-Ac material thus collected is dried-weighed and placed with those above, and the solution collected is of a transparent off-white color certainly containing ethane 1, 2-diol.

The solution collected after the first decantation-filtration is very transparent yellow in color, and undergoes a first extraction with dichloromethane (117ml volume), stirring softly for a few minutes in a 250ml beaker, then settling for 30 to 45 minutes. Two liquid phases and fine AC precipitates then appear: the yellow aqueous phase above is distilled water in which ethane diol and a yellow citric acid polyester solution are dissolved, and the organic phase below is dichloromethane in which any remaining citric acid molecules are dissolved. The upper liquid-aqueous phase is drawn off and quantified using a graduated pipette, while the lower liquid-organic phase is filtered through filter paper to retain any remaining PAT-Ac crystals, as well as citric acid polyester crystals and/or Ac crystals resulting from the hydrolysis-decomposition of citric acid polyester crystals; the liquid phase collected is a more or less viscous solution of citric acid yellow polyester dissolved in dichloromethane. After evaporating in the open air for a sufficiently long time, the dichloromethane solvent evaporates efficiently and very quickly, leaving only a viscous, odorless solution of citric acid yellow polyester to be quantified by volume.

Next, the water in the aqueous phase above is extracted with 200ml acetone in the 1000ml beaker. The whole is left to settle for two (2) days in the open air, which greatly reduces the quantity of acetone solvent by evaporation. To extract all the acetone solvent and water molecules and separate-recover the ethane 1, 2-diol, the remainder of the solution is vacuum-evaporated on the rotavapor at 45℃. Thus, the highly volatile acetone ethane 1, 2-diol solution is recovered in the outer flask by condensation in the vacuum circuit, while the heavier acetone-water solution condenses in the rotavapor condenser circuit itself and is recovered in the main flask. The only solution remaining in the evaporation flask is the pure water-free yellow polyester citric acid solution, which is quantified by volume (144ml) and added to the solution collected previously. The solution containing EDA is processed to recover separately all the pure solutions which characteristics are presented in paragraph §3.1.
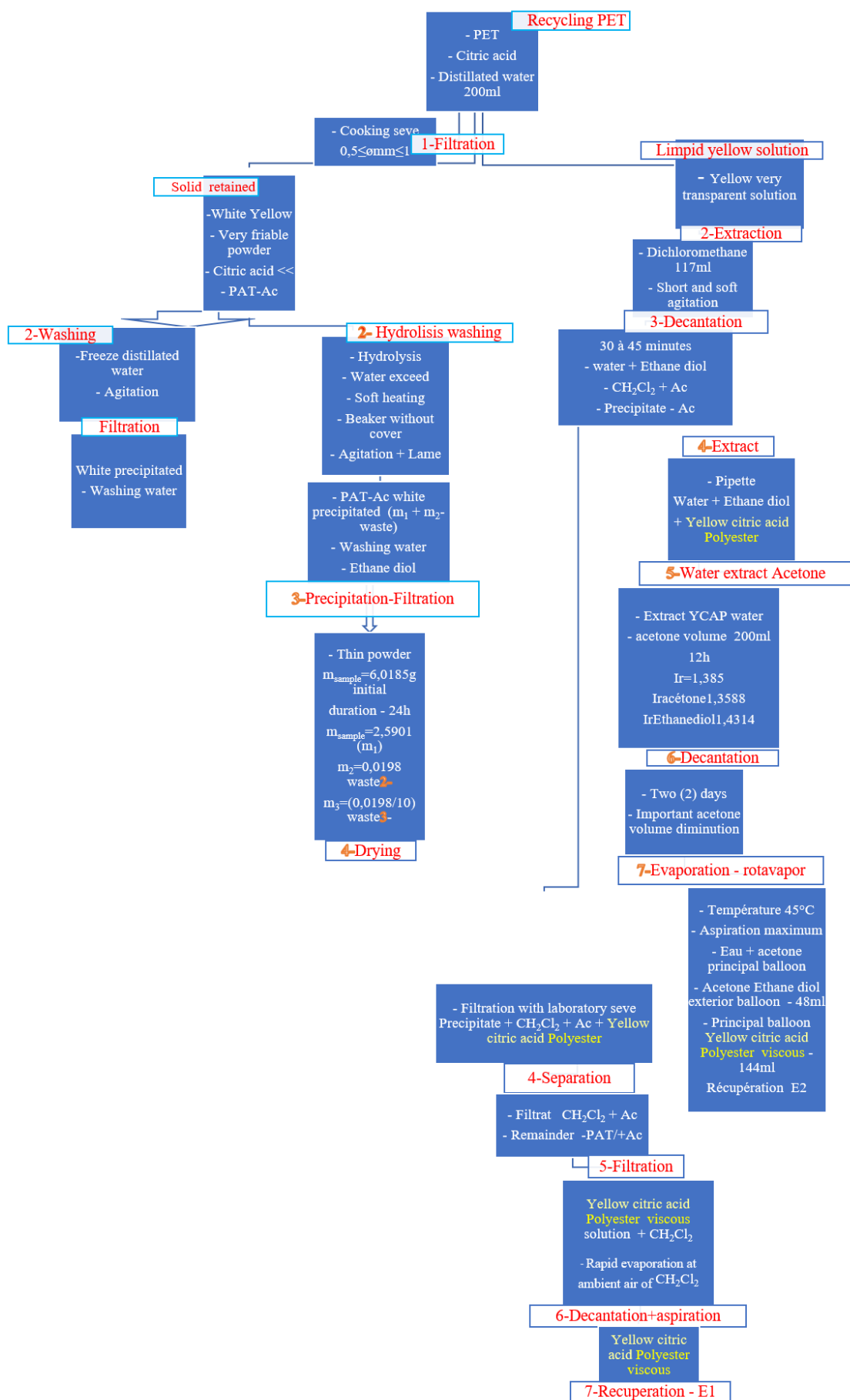
Recycling PET
- PET
- Citric acid
- Distillated water 200ml

1-Filtration
- Cooking seve 0,5≤ømm≤1

Limpid yellow solution
- Yellow very transparent solution

Solid retained
-White Yellow
- Very friable powder
- Citric acid <<
- PAT-Ac

2-Extraction
- Dichloromethane 117ml
- Short and soft agitation

2-Washing
-Freeze distilled water
- Agitation

2- Hydrolisis washing
- Hydrolysis
- Water exceed
- Soft heating
- Beaker without cover
- Agitation + Lame

3-Decantation
30 à 45 minutes
- water + Ethane diol
- $CH_2Cl_2$ + Ac
- Precipitate - Ac

Filtration
White precipitated
- Washing water

- PAT-Ac white precipitated $(m_1 + m_2$-waste)
- Washing water
- Ethane diol

4-Extract
- Pipette Water + Ethane diol + Yellow citric acid Polyester

3-Precipitation-Filtration

5-Water extract Acetone
- Extract YCAP water
- acetone volume 200ml
12h
Ir=1,385
Iracétone1,3588
IrEthanediol1,4314

- Thin powder
$m_{sample}$=6,0185g initial
duration - 24h
$m_{sample}$=2,5901 $(m_1)$
$m_2$=0,0198 waste2-
$m_3$=(0,0198/10) waste3-

6-Decantation
- Two (2) days
- Important acetone volume diminution

4-Drying

7-Evaporation - rotavapor
- Température 45°C
- Aspiration maximum
- Eau + acetone principal balloon
- Acetone Ethane diol exterior balloon - 48ml
- Principal balloon Yellow citric acid Polyester viscous - 144ml
Récupération E2

- Filtration with laboratory seve Precipitate + $CH_2Cl_2$ + Ac + Yellow citric acid Polyester

4-Separation
- Filtrat $CH_2Cl_2$ + Ac
- Remainder -PAT/+Ac

5-Filtration
Yellow citric acid Polyester viscous solution + $CH_2Cl_2$
- Rapid evaporation at ambient air of $CH_2Cl_2$

6-Decantation+aspiration
Yellow citric acid Polyester viscous

7-Recuperation - E1

*Figure 7. The experimental process for recycling the PET-Polyethylene terephthalate.*

The following Table 2 show the ratios between solvent used during the different extractions of this process.

| Citric acid/Solvents | Quantities | Molar ratios |
|---|---|---|
| Citric acid [g] | 141.6032 | 0.7370 moles |
| Dichloromethane [ml] | 117 | 1.8322 moles |
| Water [ml] | 200 | 11.1017 moles |
| Acetone [ml] | 200 | 2.7467 moles |
| Ratio Citric acid/CH$_2$Cl$_2$ | 1.21 [g/ml] | 0.4022 |
| Ratio Water/acetone | 1 [ml/ml] | 4.0418 |

## 2.6. PAT-Ac Formation

The dried white powder materials composed eventually with Pure Terephthalic Acid - PAT are all agglomerated particles with diameters strictly less than 0.5mm, some are even so very small as to be difficult to separate by decantation with the washing solution (distilled water). The total mass of PAT recovered is 2.61188g with apparent density and porosity equal to

$$d = \frac{0,4832}{2} = 0,2412 \left[\frac{g}{ml}\right].$$

This very low-density value shows that we have one of the agglomerated PAT grains which, macroscopically, formed a very porous solid. In addition, we know that since the beginning we have had to recycle 2.0012g of PET, whereas the mass of agglomerated PAT recovered is 2.6119g, with an increase of 0.61068g, which means that this PAT agglomerate still contains citric acid molecules esterified with the PATs in its structure. This new material formed by a PAT agglomerate with citric acid molecules in its structure will be referred to as PAT-Ac.

To confirm the formation of PAT-Ac and its dissociation into fine particles under hydrolysis, 1.0308g of PAT-Ac was subjected to hot hydrolysis with intermittent magnetic stirring in distilled water boiling at 100 ℃ or above. It was found that the use of a spoon as a stirring blade favored the formation of fine PAT particles and thus the reduction-hydrolysis of the PAT-Ac agglomerate. At the end of the hot hydrolysis, which lasted at least two (2) hours, it was seen that the diameter of the PAT-Ac agglomerates had decreased, with the formation of very fine particles that were difficult to separate under decantation. In addition, the solution became highly acidic, turning a bright yellow under the bromophenol blue indicator. A determination of the citric acid content of

the hydrolysis solution was carried out at the end of hydrolysis.

At the end of this experimentation to confirm the formation of PAT-Ac by hot hydrolysis accompanied with intermittent stirring using eventually a spoon as against flow stirring, the citric acid and the PAT in the hydrolysis solution was titrated successively with NaOH-0.05N. Indeed, Seeing that PAT are very fine particles that are not soluble in water, whereas citric acid molecules are in solution in water, even though the first two pKa of citric acid and TAP are very close, it is certainly the citric acid molecules in solution that are titrated first by the NaOH-0.05N sodium hydroxide titration solution, hence the formation of the first dark orange-yellow color marking the presence of the non-titrated TAP molecules. The following Table 3 shows the results of these determination of citric acid molecules and PAT in the hydrolysis solution.

| Titration characteristics | Values and results |
|---|---|
| Hydrolysis distilled water volume - ml | 150 |
| Sample volume - ml | 0,5 |
| Titration distilled water volume - ml | 15 |
| Helianthin indicator - drops | 3 |
| Titrated solution color | Rouge |
| Volume NaOH-0.05N until Dark orange-yellow color - ml | 0.3 |
| Volume NaOH-0,05N – Light orange-yellow color - ml | 06 |
| Results – Interpretations – NaOH-0.05N Citric acid-Ac titration | |
| Sample total H$^+$ quantities Dark orange-yellow color - moles | 1.5E-5 |
| Sample total H$^+$ quantities Light orange-yellow color -moles | 3.0E-5 |
| Total H$^+$ solution 150ml quantities Light orange-yellow color -moles | 9.0E-3 |
| H$^+$ - Ac -sample quantities - moles | 1.50E-05 |
| H$^+$ - Ac -Total - moles | 4.50E-03 |
| Total citric acid-Ac quantities- [moles] | 3.36E-03 |
| Total citric acid-Ac quantities - [g] (1) | 0.6453 |
| Results – Interpretations – NaOH-0.05N - Pure Terephthalic Acid - PAT titration | |
| Sample total H$^+$ quantities - PAT - moles | 1.50E-05 |
| Total H$^+$ quantities- PAT- moles | 4.50E-03 |

| Titration characteristics | Values and results |
|---|---|
| PAT-Total quantities – [moles] | 2.25E-03 |
| PAT-Total - quantities [g] (2) | 0.3738 |
| PAT–Ac ratios | |
| PAT-Ac -weight by titration [g] (1)+(2) | 1.0191 |
| purity of PAT-Ac | 98.86% |
| ratio PAT/Ac – moles | 0.67 |
| ratio Ac/PAT – moles | 1.5 |
| ratio Ac/WATER – moles | 4.90E-01 |
| ratio water/Ac – moles | 2.04E+00 |
| ratio water/PAT – moles | 3.04E+00 |

## 3. The Results of This PET Recycling Process

### 3.1. Characteristics of the PAT-Ac, AED and PEAc

During this PET recycling process, we synthesized a material composed of PAT and citric acid called PAT-Ac, whose ratios of PAT and citric acid, as well as the ratios of PAT and citric acid to water molecules (Table 3), were determined by dosing with NaOH-0.05N sodium hydroxide. The characteristics of the products recycled during this PET recycling process, namely Terephthalic Acid with citric acid (PAT-Ac), Ethane Diol conserved in a solution of acetone (AED) and Citric Acid Polyester solution (PEAc), are presented in the following Table 4:

*Table 4. Characteristics of the different products of PET recycling.*

| Characteristics | AED – solution Then ED-Ethane diol | PAT-Ac - solid | PEAc – Citric acid polyester |
|---|---|---|---|
| Refractive Index | 1356 - 1353 | - | 1414 |
| Odor | Acetone head odor no background odor After aeration and fairly long cooling, acetone evaporates and odorless liquid ethane diol is recovered. | Without odor | Oily |
| Color | Highly transparent, clear white | White | Transparent yellow |
| touch sensation | Liquid | Frittable | OIly |
| State | Liquid | granulate | Liquid |
| Viscosity | Non-viscous | - | non-viscous |
| Density – g/ml | 0.8954 – AED 1.1102 - ED | 0.24115 | 1.13009 |
| Citric acid content – moles/L | - | 2.24E-02 | Cf. ratio Table 3 |
| Auto-ignition temperature - ℃ | 398 ℃ - ED | > 300 ℃ | - |
| Characteristics | AED – solution | PAT - solide | PEAc |
| Melting point - ℃ | | 177 ℃ | |
| Boiling point - ℃ | - | - | 104.6 ℃ |
| Evaporation temperature | | | 123 ℃ |
| Water solubility – g/ml | water-miscible | Insoluble | soluble |
| Ethanol 90 ° solubility | - | - | 0.9417 [g/ml] |
| Porosity -% | - | 85.4 | - |

Based on the results of these physico-chemical character-istics, it is possible to consider the various.

possible ways of using recycled chemicals. Referring to the different ratios determined in Table 3, the figure of a PAT-Ac entity with the water molecules water molecules is shown in the following figure 8 to figure 10:
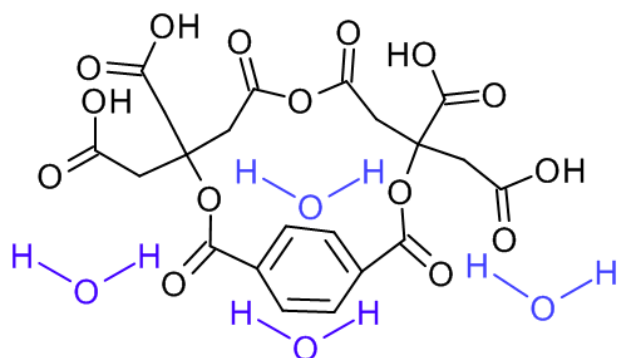


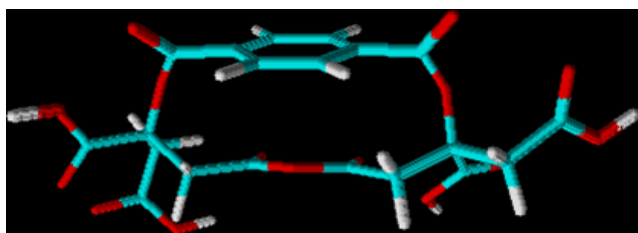*Figure 8. An entity of the PAT-Ac with their waters molecules.*
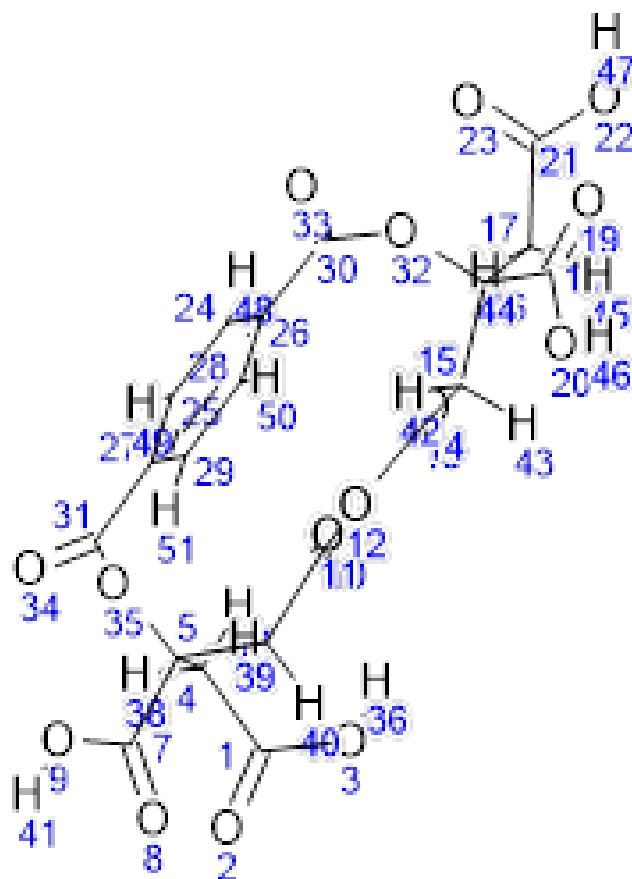


*Figure 9. 3D image of a PAT-Ac entity.*



*Figure 10. PAT-Ac entity atom numbers.*

Notice that the Ethane diol (ED) was extracted from the solution of acetone ethanediol (AED) according the process described in the following paragraph §3.2. 16.06 $\times$ $10^{-3}$ Pa s at 25 ℃-ED [11].
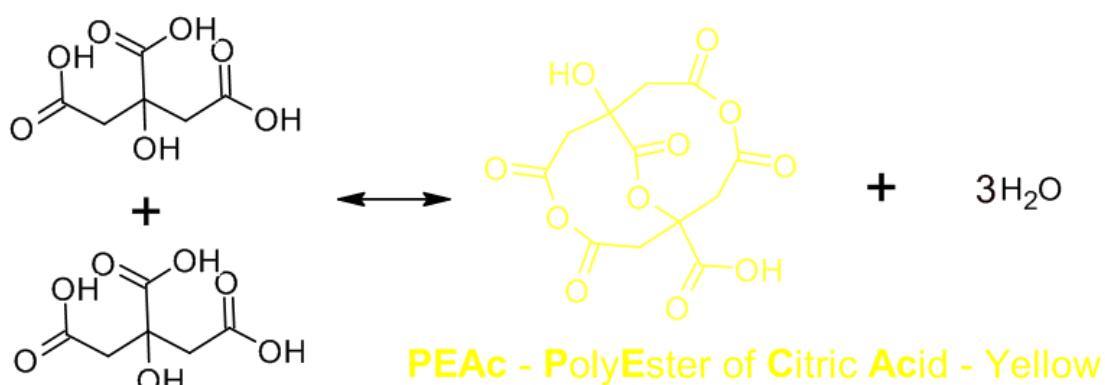


**PEAc - PolyEster of Citric Acid - Yellow**

*Figure 11. Structure of the PEAc.*

Using chemsketch free verion software, the evaluation of the porosity openings of a PAT-Ac entity is given in the following Table 5:

*Table 5. Evaluation by chemsketch free version of the porosity opening of a PAT-Ac entity.*

| Pore size evaluation | | |
| --- | --- | --- |
| **Atoms measured** | **Entity characteristics** | **Atoms distance - Å** |
| O35 – O32 | length | 7.183 |
| O12 – C28 | width | 3.145 |
| C5 – C30 | Axe1 | 7.291 |
| C16 – C31 | Axe2 | 7.109 |
| H50 – H42 | Space requirement per hydrogen | 2.35 |

## 3.2. Process of the Extraction of the ED from the Solution of AED

The following figure 12 presented the different process to extract the ED from the solution of AED.
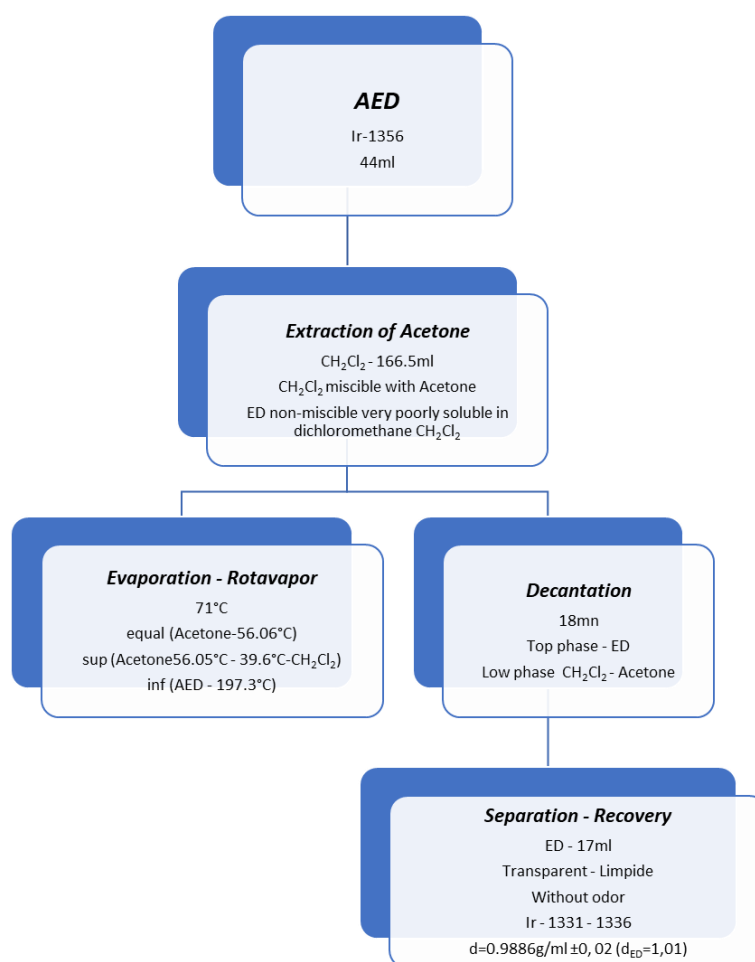


*Figure 12. Flow-sheet of the different process to extract the ED from the AED solution.*

After recovering the AED solution extracted using the procedure described in the previous paragraph, it is extracted from acetone using the solvent dichloromethane, which by its nature is miscible with acetone but only very slightly soluble with ED. This final solution can then undergo two pro-cesses to recover the ED solution: the first process consists in immediately passing the solution to evaporation under pressure on the evaporator-rotavapor at a temperature of 71 ℃, slightly higher than the boiling point of acetone and dichloromethane respective-ly 56.06 ℃ and 39.6 ℃ and well above that of ED-197.3 ℃. At the

end of evaporation, the pure ED solution is collected in the evaporation flask. The second procedure consists of leaving the ED-acetone and dichloromethane solution in a separating funnel for around 20 minutes, until two distinct, stable phases appear: the pure ED solution at the top, and the dichloromethane and acetone solution at the bottom. Recover the acetone and dichloromethane, which is the lower phase, then transfer the ED solution to a container. The density of the solution recovered 17ml, corresponding to 38.64%vol. in comparison to the initial AED volume, is 0.9886 g/ml which corresponds to the value of the ED's density in the bibliography (1.01g/ml), the solution is limpid, transparent and without odor. These characteristics confirm that the ED is recycled and extracted during this PET recycling process.

*Table 6. Characteristics and ratios of the ED extraction by dichloromethane.*

| | |
|---|---|
| Initial volume AED [ml] | 44 |
| Dichloromethane solvent $CH_2Cl_2$ volume [ml] | 166.5 |
| Ethane diol extracted [ml] | 17 |
| Voluminal ratio - $CH_2Cl_2/AED$ | 3.78 |
| extraction performance vol.% | 38.64 |

# 4. Study of the General PAT-Ac Formation-synthesis Mechanism

## 4.1. Global Kinetic Study of the PET Recycling Reaction Without Taking into Account the $H^+$-Citric Acid Catalyst

The global PET regeneration reaction without taking into account the $H^+$-Citric acid catalysts is:

$$PET + 2nH_2O + nAc \rightarrow nPAT - Ac + nEt - 2O \quad (3)$$

Thus, the global rate of this reaction as a function of the rate constant k is equal to

$$Vitesse - speed = k \times [H_2O]^\alpha \times [Ac]^\gamma \times [PET]^\beta \quad (4)$$

Seeing that the amount of water and citric acid (Ac) used in the recycling reactions is in excess of the amount of PET, we can estimate and apply another rate constant $k_{H_2O}$ such that

$$k_{H_2O-Ac} = k \times [[H_2O]^\alpha] \times [Ac]^\gamma \quad (5)$$

The rate expression became

$$Vitesse - speed = k_{H_2O-Ac} \times [PET]^\beta = -\frac{d[PET]}{dt} \quad (6)$$

By solving this differential equation (equation 6) with respect to PET concentration, it is possible to consider three cases:
1. If the global order with respect to PET is zero, then it is necessary and sufficient that the variation of the initial PET concentration $[PET]_O$ minus [PET] as a function of time is a straight line.
2. If the overall order with respect to PET is equal to one then it is necessary and sufficient that the variation of the initial PET concentration PET $\ln([PET]_O)$ minus $\ln([PET])$ as a function of time is a straight line.
3. If the global order with respect to PET is equal to two then it is necessary and sufficient that the variation of PET concentration PET $1/[PET]$ minus $1/[PET]_O$ as a function of time is a straight line.

The different values of these parameters are shown in the following Table 7.
$[PET]o = 10.17611808$ [g/L].

*Table 7. Results of global PET regeneration kinetic studies using H+ catalyst from citric acid carboxylic acid.*

| $H^+$ – Citric acid Reaction Time | Conversion into PAT and ED [wt%] | [PET] [g/L] | Order zéro $[PET]_0$ - [PET] | Order 1 LN$[PET]_0$ - LN[PET] | Order 2 1/[PET] - 1/$[PET]_0$ |
|---|---|---|---|---|---|
| 1mn | 23.93% | 7.4608E+00 | 1,7525E+00 | 1.9144E-01 | 2.0978E-02 |
| 3mn | 24.49% | 7.4875E+00 | 1,8142E+00 | 1.9635E-01 | 2.1320E-02 |
| 5mn | 27.99% | 7.1877E+00 | 2.0980E+00 | 2.2784E-01 | 2.4850E-02 |
| 7mn | 28.47% | 7.2200E+00 | 2.1597E+00 | 2.3225E-01 | 2.5087E-02 |
| 9mn | 30.05% | 7.1274E+00 | 2.3078E+00 | 2.4692E-01 | 2.6554E-02 |
| 11mn | 29.37% | 7.2939E+00 | 2.2831E+00 | 2.4058E-01 | 2.5472E-02 |
| 15mn | 33.91% | 6.9418E+00 | 2.7027E+00 | 2.8354E-01 | 2.9945E-02 |
| 20mn | 34.49% | 7.0975E+00 | 2.8385E+00 | 2.8915E-01 | 2.9660E-02 |

| H⁺ – Citric acid Reaction Time | Conversion into PAT and ED [wt%] | [PET] [g/L] | Order zéro [PET]₀ - [PET] | Order 1 LN[PET]₀ - LN[PET] | Order 2 1/[PET] - 1/[PET]₀ |
|---|---|---|---|---|---|
| 25mn | 33.95% | 7.4054E+00 | 2.8878E+00 | 2.8387E-01 | 2.8092E-02 |
| 30mn | 34.06% | 7.6484E+00 | 2.9989E+00 | 2.8501E-01 | 2.7270E-02 |
| 45mn | 32.01% | 8.8423E+00 | 3.1470E+00 | 2.6527E-01 | 2.2492E-02 |
| 60mn | 32.37% | 9.9530E+00 | 3.6036E+00 | 2.6870E-01 | 2.0156E-02 |
| 90mn | 27.47% | 1.4635E+01 | 4.1590E+00 | 2.2309E-01 | 1.2017E-02 |
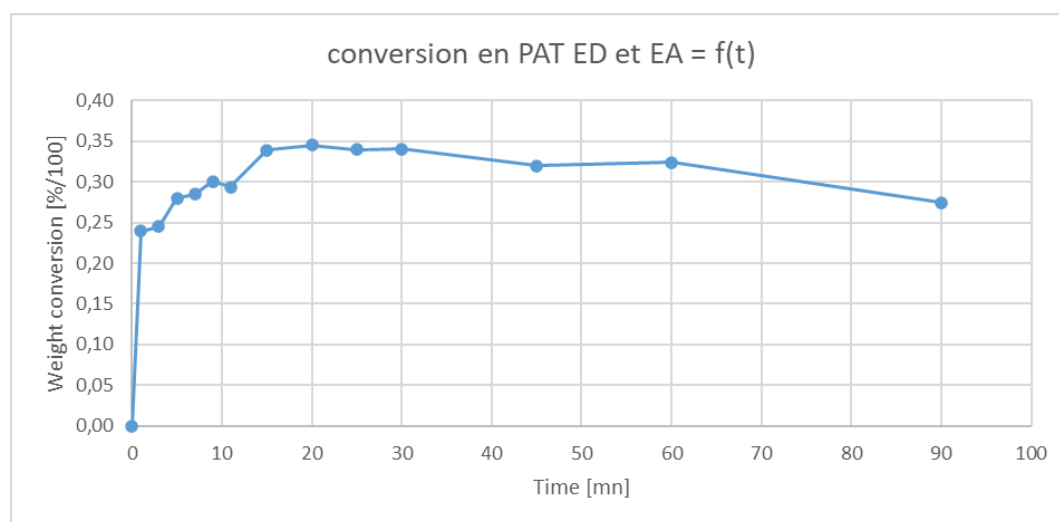


*Figure 13. Conversion into PAT and ED evolution with the reaction time.*

The PET conversion into PAT and ED (figure 13) increase initially but tend to be constant from 15mn to 30mn and decrease slowly from 30mn to 90mn. These evolutions seem normal because initially all protonic acid H⁺ catalytic sites are devoted to promote only the formation of the reactional intermediary $PET_n^+$ (Equation 7 – Equation 29) while after 15mn of reaction time these protonic acid H⁺ catalytic sites promote also the formation of the reactional intermediary $Ac^+$ (Equation 9 – Equation 31) which react with PAT to form the PAT-Ac molecules (Equation 10 – Equation 32); thus, their activities seems decreasing in long term. In addition, these protonic acid H⁺ catalytic sites are from the citric acid molecules' carboxylic acids which in long term participate to the formation of the PAT-Ac (Equation 10 – Equation 32) and PEAc (figure 11); thus, their quantities decrease along the time and in the same time their activities and the PET conversion into PAT and ED decrease also.

As said previously, the experimental results of this PET recycling (Table 7) were exploited in order to determine the kinetic constant partial order for the PET. The three principal orders for the PET such as zero order, first order and second order are tested seeing that the concentration of water and citric acid are in excess in comparison to the PET concentration. The results of the tests showed clearly that in general according to these experimental conditions, the partial order of the PET is zero (figure 14) that is to say the reaction speed is limited by the contact surface between the PET and the citric acid's protonic acid H⁺ catalytic sites, but initially it could be order 1 (figure 15) that is to say initially the reaction speed could be proportional with the PET concentration.

It's noticed that from 20mn, the curves representing the one and two orders decrease (figure 15, figure 16) indicating that from this time reaction the concentration of PET in the reactor increase. These results confirm that not only there is a few diminutions of water by evaporation during the reaction at atmospheric pressure but also the quantities of protonic acid H⁺ catalytic sites decrease and in the same time their activities decrease also.
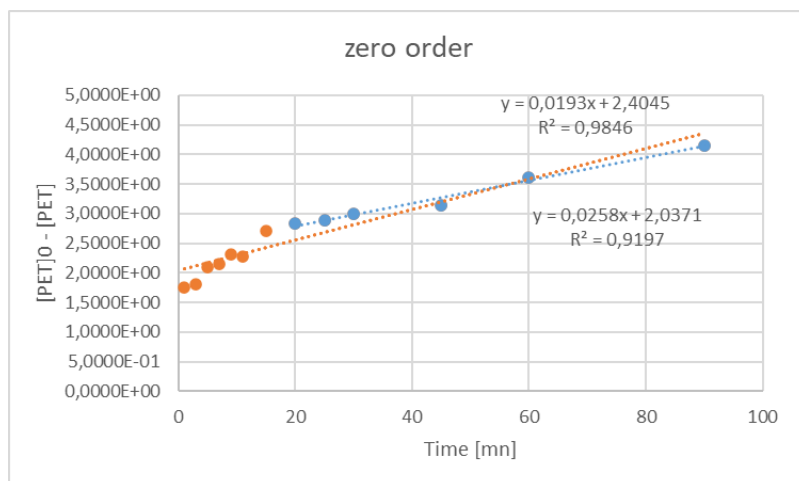
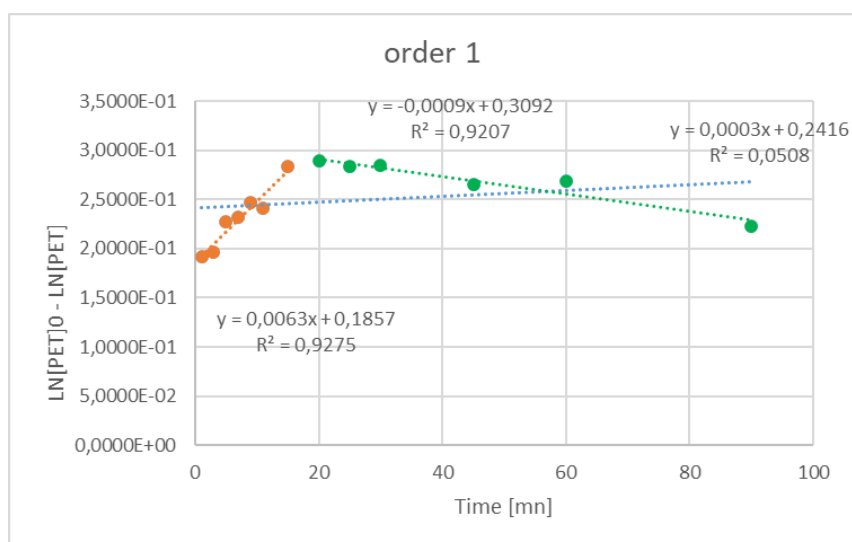***Figure 14.*** *Evolution of $[PET]_0$ - $[PET]$ with the reaction time.*



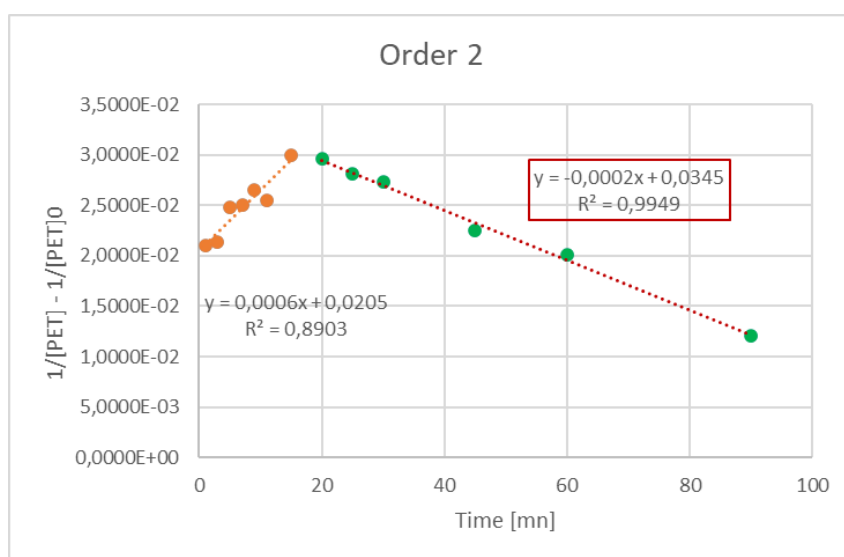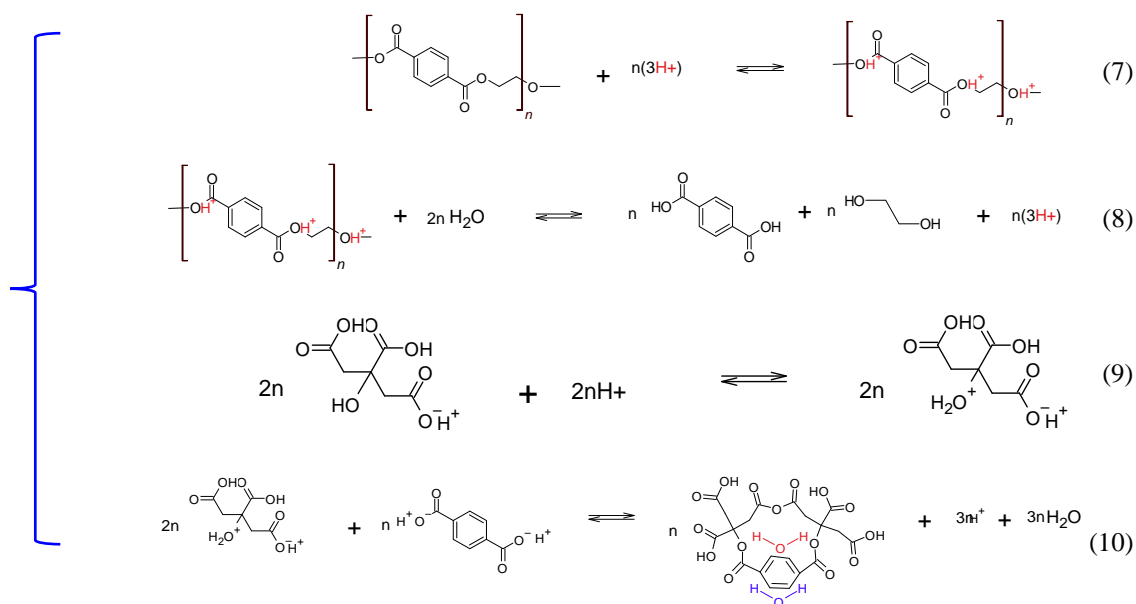***Figure 15.*** *Evolution of $(Ln[PET]_0$ - $Ln[PET])$ with the reaction time.*



***Figure 16.*** *Evolution of $1/[PET]$ - $1/[PET]_O$ with the reaction time.*

## 4.2. Global Kinetic Study of the PET Recycling Reaction Taking into Account the H⁺-citric Acid's Protonic Acid Sites Catalyst

The global mechanism of the PET recycling into PAT-Ac with taking into account the H⁺-Citric acid catalyst is:



Equation 11 – Linear Equation system of the global mechanism for the PET recycling.

This mechanism can be divided into two parts:

1. The first part is composed of the first two steps and consists of the formation of ethane diol and PAT from the PET molecules to be recycled and catalyzed by the protonic acids of the citric acid molecules. Thus, at the initial instants, normally, it is possible to establish a global velocity equation relating to the global mechanism (Equation 11).

$$PET + 2nH_2O + H^+ \rightarrow nPAT + nEt - 2OH + H^+ \quad (12)$$

$$v = -\frac{d[PET]}{dt} = k \times [PET]^\alpha \times [H_2O]^\beta \times [H^+]^\gamma \quad (13)$$

Such as: k - the speed constant, α - the partial order with respect to the PET to be recycled and β - the partial order with respect to the water, ϒ – the partial order with respect to the protonic acid H⁺.

Thus, it is possible to evaluate kinetic constants from kinetic monitoring at different instants, in particular at the initial instants of the evolution of water concentrations, and/or of the evolution of PET concentrations, and/or of the evolution of PAT concentrations and/or of the evolution of ethanediol concentrations. In our case, one of the first choices is to follow the reagents, in particular the weight of PET remaining over time, the initial and final quantity of water in the reactor, and then to evaluate the evolution of the quantity of water in the reactor during the reaction, assuming that it follows a linear decrease.

$$LnV = Lnk + \alpha Ln[PET] + \beta Ln[H_2O] + \gamma Ln[H^+] \quad (14)$$

To determine these partial orders and kinetics constants k, $\alpha, \beta$ and $\gamma$ of this first part of the mechanism the following linear equation system (Equation 18) from the previous equation 13 using the experimental values on table 8 must be resolved and the total PAT concentration must be determined by titrations with HF-0.0026N. (Rabeharitsara, Raherimandimby, Raobijaona, & Ratsimba, 2025).

*Table 8. Experimental values to resolve the linear equations system – Equation 14.*

| Time [mn] | V-speed$_{PAT}$ | [PET] - g.l⁻¹ | [H⁺] – g.l⁻¹ | [H₂O] g.l⁻¹ | K |
|-----------|-----------------|---------------|--------------|-------------|---|
| [0-1]     | 1.7525E+00      | 7.4608E+00    | 8.00E-01     | 2.3904E+02  |   |
| [1-3]     | 3.0853E-02      | 7.4875E+00    | 8.20E-01     | 2.3627E+02  |   |
| [3-5]     | 1.4192E-01      | 7.1877E+00    | 9.50E-01     | 2.3350E+02  |   |
| [5-7]     | 3.0853E-02      | 7.2200E+00    | 1.24E+00     | 2.3072E+02  |   |

| Time [mn] | V-speed$_{PAT}$ | [PET] - g.l$^{-1}$ | [H$^+$] – g.l$^{-1}$ | [H$_2$O] g.l$^{-1}$ | K |
|---|---|---|---|---|---|
| Time [mn] | Ln V | Ln [PET] - alpha -x1 | Ln [H+] - gamma-x2 | Ln [H2O] - bêta - x3 | Ln k - 1 |
| [0-1] | 0.5610 | 2.0097 | -0.2231 | 5.4766 | |
| [1-3] | -3.4785 | 2.0132 | -0.1985 | 5.4650 | |
| [3-5] | -1.9525 | 1.9724 | -0.0513 | 5.4532 | |
| [5-7] | -3.4785 | 1.9769 | 0.2151 | 5.4412 | |

$$\left[\begin{array}{l} 0.5610 = Lnk + 2.0097 \propto +5.4766\beta - 0.2231\gamma \quad (15) \\[6pt] -3.4785 = Lnk + 2.0132 \propto +5.4650\beta - 0.1985\gamma \quad (16) \\[6pt] -1.9525 = Lnk + 1.9724 \propto +5.4532\beta - 0.0513\gamma \quad (17) \\[6pt] -3.4785 = Lnk + 1.9769 \propto +5.4412\beta + 0.2151\gamma \quad (18) \end{array}\right.$$

Equation 19 - Linear equation system for determining the kinetics constants for first part.

Using the matrix calculator, the values are

$$lnk = (-1.69 \times 10^3); \propto = -97.5; \gamma = 11.4; \beta = 343$$

Seeing that for these values on table 8 which reaction times are less 20mn, the PET's partial order is equal to one in these conditions where water and citric acid are in excess (Figure 15).

That is to say,

The values of the speed constants are:

$$k = e^{-1.69 \times 10^3} = 1.3802 \times 10^{-745} [\text{g}^{-1} \times l \times \text{mn}^{-1}]$$

$$\propto = +1; \gamma = -0.1169 \approx \frac{3}{25}; \beta = -3.518 \approx \frac{-88}{25}$$

The partial order of H$^+$ is $\gamma = -0.1169 \approx \frac{3}{25}$ confirming that initially it is the essential entities to catalyze all reactions in this PET recycling.

Finally, the partial order of water H$_2$O is $\beta = -3.518 \approx \frac{-88}{25}$ indicating that water like the protonic acid in excess could be an inhibitor of the PET recycling.
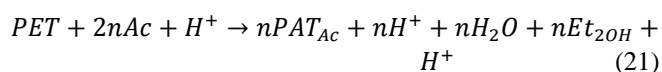
The lower value of the speed constant k confirms the slowness even if efficiency of this PET recycling process.

2. Seeing that the hydrolysis reaction (equation 8) take place slowly (table 7) but assuming that the steps of equation 9 and equation 10 could take place initially, it is interesting to follow both the total PAT concentration and the ethane diol concentration with reaction time by titrations with HF-0.0026N (Rabeharitsara, Raherimandimby, Raobijaona, & Ratsimba, 2025) in order to valid the previous proposed mechanism (Equation 11). In consequence, the global reaction of the PAT-Ac formation on this second part of the mechanism 16 is

$$PET + 2nH_2O + 2nAc + 2nH^+ \rightarrow nPAT_{Ac} + 3nH^+ + 3nH_2O \quad (20)$$
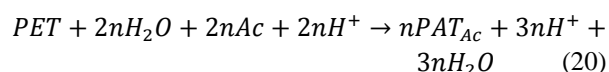
This equation 20 is equivalent to

$$PET + 2nAc + H^+ \rightarrow nPAT_{Ac} + nH^+ + nH_2O + nEt_{2OH} + H^+ \quad (21)$$

From this equation 21, the following equation 20 and equation 21 are deduced by using neperian logarithmic

$$v = -\frac{d[PET]}{dt} = k \times [PET]^\propto \times [Ac]^\beta \times [H^+]^\gamma \quad (22)$$

$$LnV = Lnk + \alpha Ln[PET] + \beta Ln[Ac] + \gamma Ln[H^+] \quad (23)$$

For determining these kinetics constants, the following linear equation system (Equation 28) from the previous equation 23 using the experimental values on table 9 must be resolved.

*Table 9. Experimental values to resolve the linear equations system – Equation 14.*

| Time [mn] | V-speed$_{PAT}$ | [PET] - g.l$^{-1}$ | [H$^+$] – g.l$^{-1}$ | [H$_2$O] g.l$^{-1}$ | k |
|---|---|---|---|---|---|
| {25-30} | 9.8730E-03 | 7.4054E+00 | 2.25E+00 | 5.85E+01 | |
| {30-45} | 7.4047E-03 | 7.6484E+00 | 2.34E+00 | 6.08E+01 | |

| Time [mn] | V-speed$_{PAT}$ | [PET] - g.l$^{-1}$ | [H$^+$] – g.l$^{-1}$ | [H$_2$O] g.l$^{-1}$ | k |
|---|---|---|---|---|---|
| [45-60] | 9.8730E-03 | 8.8423E+00 | 2.53E+00 | 6.58E+01 | |
| [60-90] | 1.5221E-02 | 9.9530E+00 | 3.52E+00 | 9.15E+01 | |

| Time [mn] | Ln V | Ln [PET] - alpha -x1 | Ln [H+] - gamma-x2 | Ln [H$_2$O] - b êta - x3 | Ln k - 1 |
|---|---|---|---|---|---|
| {25-30] | -4.6180E+00 | 2,0022E+00 | 0.8109E+00 | 4.0691E+00 | |
| {30-45] | -4,9056E+00 | 2,0345E+00 | 0.8502E+00 | 4.1083E+00 | |
| [45-60] | -4,6180E+00 | 2.1796E+00 | 0.9282E+00 | 4.1864E+00 | |
| [60-90] | -4.1851E+00 | 2,2979E+00 | 1.2585E+00 | 4.5166E+00 | |

$$-4.6180 = Lnk + 2.0022 \propto +4.0691\beta + 0.8109\gamma \quad (24)$$

$$-4.9056 = Lnk + 2.0345 \propto +4.1083\beta + 0.8502\gamma \quad (25)$$

$$-4.6180 = Lnk + 2.1796 \propto +4.1864\beta + 0.9282\gamma \quad (26)$$

$$-4.1851 = Lnk + 2.2979 \propto +4.5166\beta + 1.25851\gamma \quad (27)$$

Equation 28 – Linear equation system for determining the kinetics constants for second part.

Using the matrix calculator, the values are

$$lnk = (-1.12 \times 10^4); \propto = -2.03; \gamma = (-2,43 \times 10^3);$$

$$\beta = (3,43 \times 10^3)$$

Seeing that for these values on table 9 which reaction times are more than 20mn, the PET's partial order is equal to zero in these conditions where water and citric acid are in excess (Figure 14).

That is to say, $k = e^{-1.12 \times 10^4}$ [g$^{-1}$ ×l ×mn$^{-1}$]

The partial order of PET $\propto = \frac{2.03}{10^3} \approx +0$ confirm its global partial order equals to zero (Figure 14).
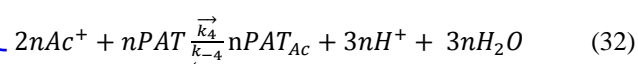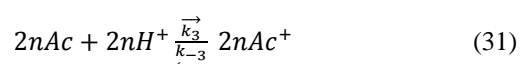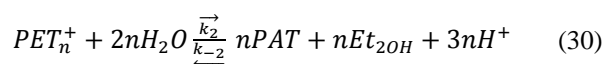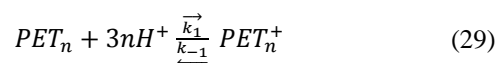
The partial order of H$^+$ is $\gamma = +2.43$ confirming that it is the essential entities to catalyze all reactions in this PET recycling and its quantities decrease for the benefit of the PEAc formation which is an important valuable by-product of this process.

Finally, the partial order of Citric acid - Ac is $\beta = (-3,43)$ indicating that water in excess could be an inhibitor of the PET recycling.

The lower value of the speed constant k confirms the slowness even if efficiency of this PET recycling process.

## 4.3. Establishment of the Mechanism (Equation 11) Speed and its Validation by Linear Curve

To make easier the establishment of the speed for the linear equation system (Equation 11), let's take it in other abbreviations representing each reacted and produced molecule. Thus, the following linear equation system (Equation 33) is attained

$$PET_n + 3nH^+ \underset{k_{-1}}{\overset{\vec{k_1}}{\rightleftharpoons}} PET_n^+ \quad (29)$$

$$PET_n^+ + 2nH_2O \underset{k_{-2}}{\overset{\vec{k_2}}{\rightleftharpoons}} nPAT + nEt_{2OH} + 3nH^+ \quad (30)$$

$$2nAc + 2nH^+ \underset{k_{-3}}{\overset{\vec{k_3}}{\rightleftharpoons}} 2nAc^+ \quad (31)$$

$$2nAc^+ + nPAT \underset{k_{-4}}{\overset{\vec{k_4}}{\rightleftharpoons}} nPAT_{Ac} + 3nH^+ + 3nH_2O \quad (32)$$

Equation 33 – Equation system of the global mechanism for the PET recycling (same as equation 11 but using abbreviations).

In this case of reactional system, the PET is in solid phase and the protonic acid-H$^+$ catalyst is in liquid phase, and it's a heterogeneous catalyst. The entities with plus signed are the intermediary reactional for this mechanism. Thus, the limit ante steps is the equation 30 corresponding to its hydrolysis and the speed of this PET recycling mechanism is:

$$V_{speed-reaction} = V_2 = (k_2 \times [PET_n^+] \times [H_2O]^{2n}) - (k_{-2} \times [PAT]^n \times [Et_{2OH}]^n \times [H^+]^{3n}) \quad (34)$$

In consequence, the over steps are in equilibrium and

$$V_1 = k_1 \times ([PET_n] \times [H^+]^{3n}) - (k_{-1} \times [PET_n^+]) = 0 \quad (35)$$

$$V_3 = k_3 \times ([Ac]^{2n} \times [H^+]^{2n}) - (k_{-3} \times [Ac^+]^{2n}) = 0 \quad (36)$$

$$V_4 = (k_4 \times [Ac^+]^{2n} \times [PAT]^n) - (k_{-4} \times [PAT_{Ac}]^n \times [H^+]^{3n} \times [H_2O]^{3n}) = 0 \tag{37}$$

The protonic acid H+ are the catalytic sites and

$$[H^+]_{total} = ([H^+] + 3[PET_n^+] + [Ac^+]) \tag{38}$$

Let's put

$$K_{PET} = \frac{k_1}{k_{-1}} \tag{39}$$

$$K_{Et_2OH} = \frac{k_{-2}}{k_2} \tag{40}$$

$$K_{Ac} = \frac{k_3}{k_{-3}} \tag{41}$$

$$\text{et } K_{PAT_{Ac}} = \frac{k_{-4}}{k_4} \tag{42}$$

From the equation 35 is deduced,

$$(k_{-1} \times [PET_n^+]) = k_1 \times ([PET_n] \times [H^+]^{3n}) \leftrightarrow [PET_n^+] = \frac{k_1}{k_{-1}} \times ([PET_n] \times [H^+]^{3n}) \tag{43}$$

$$[PET_n^+] = K_{PET} \times ([PET_n] \times [H^+]^{3n}) \tag{44}$$

From the equation 36 is deduced,

$$(k_{-3} \times [Ac^+]^{2n}) = k_3 \times ([Ac]^{2n} \times [H^+]^{2n}) \leftrightarrow [Ac^+]^{2n} = \frac{k_3}{k_{-3}} \times ([Ac]^{2n} \times [H^+]^{2n}) \tag{45}$$

$$[Ac^+]^{2n} = K_{Ac} \times ([Ac]^{2n} \times [H^+]^{2n}) \tag{46}$$

$$[Ac^+] = \sqrt[2n]{K_{Ac}} \times [Ac] \times [H^+] \tag{47}$$

Putting these letterals expressions on equation 44 and equation 47 into the expression equation 38, it's deduced

$$[H^+]_{total} = ([H^+] + 3K_{PET} \times ([PET_n] \times [H^+]^{3n}) + \sqrt[2n]{K_{Ac}} \times [Ac] \times [H^+] \tag{48}$$

$$[H^+]_{total} = [H^+] \times \left(1 + \sqrt[2n]{K_{Ac}} \times [Ac]\right) + 3K_{PET} \times ([PET_n] \times [H^+]^{3n}) \tag{49}$$

Taking into account that the limited development of $x^{3n}$ (as $[H^+]^{3n}$) until the order 1 in the vicinity of 0,03 which is the average protonic acid concentration of the solution is

$$f(x) = 0{,}03^{3n} + 3n \times 0{,}03^{3n-1}(x - 0{,}03) = 3n \times 0{,}03^{3n-1}x + 0{,}03^{3n} + 3n \times 0{,}03^{3n} \tag{50}$$

Such as n is the monomer number composing the PET to be recycled, thus when $n \to +\infty$ it is showed that $3n \times 0{,}03^{3n-1} \to 0$ then $f(x) \to 0$

Thus, the equation 49 became

$$[H^+]_{total} = [H^+] \times \left(1 + \sqrt[2n]{K_{Ac}} \times [Ac]\right) \tag{51}$$

Finally,

$$[H^+] = \frac{[H^+]_{total}}{\left(1 + \sqrt[2n]{K_{Ac}} \times [Ac]\right)} \tag{52}$$

From the equation 37, it could be deduced

$$(k_4 \times [Ac^+]^{2n} \times [PAT]^n) = (k_{-4} \times [PAT_{Ac}]^n \times [H^+]^{3n} \times [H_2O]^{3n}) \tag{53}$$

$$\leftrightarrow [PAT]^n = \frac{k_{-4}}{k_4} \times \frac{[PAT_{Ac}]^n \times [H^+]^{3n} \times [H_2O]^{3n}}{[Ac^+]^{2n}} \tag{54}$$

$$\leftrightarrow [PAT]^n = K_{PAT_{Ac}} \times \frac{[PAT_{Ac}]^n \times [H^+]^{3n} \times [H_2O]^{3n}}{K_{Ac} \times ([Ac]^{2n} \times [H^+]^{2n})} \tag{55}$$

$$\leftrightarrow [PAT]^n = \frac{K_{PAT_{Ac}}}{K_{Ac}} \times \frac{[PAT_{Ac}]^n \times [H_2O]^{3n} \times [H^+]^n}{[Ac]^{2n}} \tag{56}$$

Taking the expressions of the PAT concentration (equation 56) and the $PET_n^+$ (Equation 44) concentration in the speed expression (Equation 34) it is deduced:

$$\leftrightarrow V_{speed-réaction} = V_2 = (k_2 \times K_{PET} \times ([PET_n] \times [H^+]^{3n}) \times [H_2O]^{2n}) - \left(k_{-2} \times [Et_{2OH}]^n \times \frac{K_{PAT_{Ac}}}{K_{Ac}} \times \frac{[PAT_{Ac}]^n \times [H_2O]^{3n} \times [H^+]^n}{[Ac]^{2n}} \times [H^+]^{3n}\right) \tag{57}$$

$$\leftrightarrow V_{speed-réaction} = (k_2 \times K_{PET} \times ([PET_n] \times [H^+]^{3n}) \times [H_2O]^{2n}) - \left(\frac{k_{-2} \times K_{PAT_{Ac}}}{K_{Ac}} \times \frac{[PAT_{Ac}]^n \times [Et_{2OH}]^n \times [H_2O]^{3n}}{[Ac]^{2n}} \times [H^+]^{4n}\right) \tag{58}$$

$$\leftrightarrow V_{speed-réaction} = ([H^+]^{3n} \times [H_2O]^{2n}) \times \left\{(k_2 \times K_{PET} \times [PET_n]) - \left(\frac{k_{-2} \times K_{PAT_{Ac}}}{K_{Ac}} \times \frac{[PAT_{Ac}]^n \times [Et_{2OH}]^n}{[Ac]^{2n}} \times [H_2O]^n \times [H^+]^n\right)\right\} \tag{59}$$

$$\leftrightarrow \frac{V_{speed-réaction}}{([H^+]^{3n} \times [H_2O]^{2n})} = (k_2 \times K_{PET}) \times [PET_n]) - \left(\frac{k_{-2} \times K_{PAT_{Ac}}}{K_{Ac}} \times \frac{[PAT_{Ac}]^n \times [Et_{2OH}]^n}{[Ac]^{2n}} \times [H_2O]^n \times [H^+]^n\right) \tag{60}$$

By plotting the first part of the egality as $Y = \frac{V_{speed-réaction}}{([H^+]^{3n} \times [H_2O]^{2n})}$ as a function of $[PET_n]$, the following Figure 17 is shown and it's deduced the value of $(k_2 \times K_{PET}) = 1 \times 10^{18}$

And $\left(\frac{k_{-2} \times K_{PAT_{Ac}}}{K_{Ac}} \times \frac{[PAT_{Ac}]^n \times [Et_{2OH}]^n}{[Ac]^{2n}} \times [H_2O]^n \times [H^+]^n\right) = 9 \times 10^{18}$
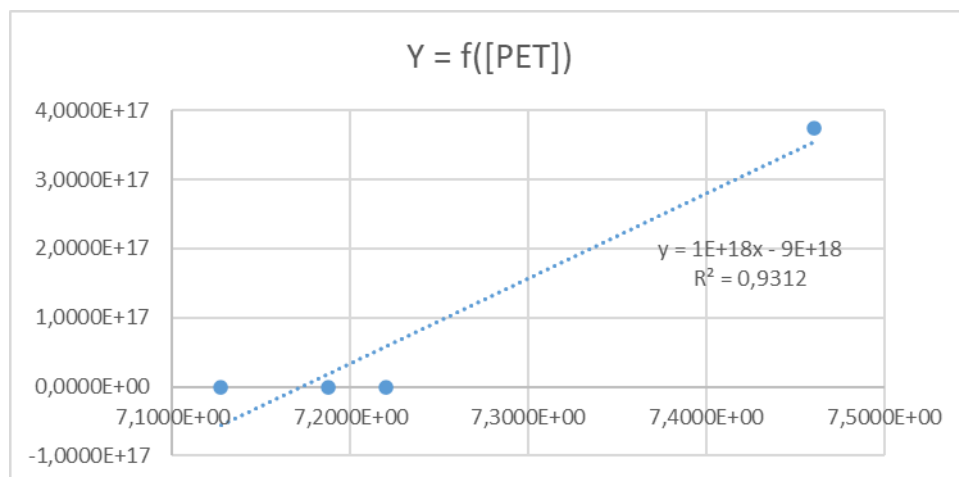
***Figure 17.*** *Stright line curve according to the Equation 60 confirming the validity of the proposed mechanism Equation 11 as Equation 33*

## 5. Conclusion

This experimental study confirms the efficiency and cost-effectiveness of recycling PET using citric acid in excess as a catalyst and source of H+ protonic acid sites. The process involves hydrolyzing PET using excess citric acid molecules. Three (3) reaction products quantified using acid-base assay procedures with NaOH-0.05N and HF-0. 0026N are recovered, in this case a new material, PAT-Ac, whose molecular formula is made up of one molecule of pure terephthalic acid (PAT) and two molecules of citric acid, Ethane diol (ED) and PolyEster Citric Acid (PEAc), which is a very clear, yellow, water-free liquid, all three of which are recoverable in various applications. The reactor used is a non-watertight covered reactor under atmospheric pressure at a temperature of 150 ℃, whose water content can be added easily depending on the reaction time and its water level.

A reaction mechanism relating to this experiment was validated by a kinetic study lasting 90 minutes without the addition of water. The efficiency of this PET recycling process was demonstrated, with a yield of PAT and ED of just 34.49% after 20 min of reaction time. This experimental study also made it possible to determine various kinetic constants and to realize the very important roles and effects of water and citric acid in this new PET recycling process. With a total duration of 11h 34mn, recycling 2.0012g of PET recovers 2.6g of PAT-Ac, 17ml of ED and 144ml of PEAc.

## Abbreviations

| | |
|---|---|
| PET | Polyethylene Terephthalate |
| PAT | Pure Terephthalic Acid |
| PAT-Ac | Pure Terephthalic Acid with Citric Acid |
| PEAc | PolyEster Citric Acid |
| ED | Ethane Diol, Ethylene Glycol |
| ech (echantillon) | Sample |
| Ln - ln | Neperian Logarithm |

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## Conflicts of Interest

The authors declare no conflicts of interest.

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