INSTITUTO SUPERIOR TÉCNICO
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# Purification of Isophthalic Acid. Product Quality Optimization and Identification of Impurities

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Dissertação para a obtenção do Grau de Mestre em

## Engenharia Química

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## Abstract

Isophthalic Acid's (IPA) demand is directly related to its applications in the productions of Polyethylene Terephthalate. The optimization of the purification process is an essential project for CEPSA QUIMICA, S.A. in order to keep its relevance on world market.

The main goal is to obtain a Purified Isophthalic Acid (PIPA) with a good colour (low *b value*). This work had three main sections, reactions of hydrogenations, colorimetry tests and influence of operational conditions on identified impurities.

The studies made at atmospheric pressures and semi-continuous were revealed to be unreproductible and the use of sodium hydroxide, as dissolvent, turn to be a bad choice because this dissolvent changed the characteristics of the system.

The impurities responsible for the yellow colour, and subsequently the *b value*, were identified using a study developed by the analysis' department of Centre of Research of CEPSA and the chromatograms obtained by high liquid pressure chromatography (HPLC). The main impurities were dicarboxylic fluorenones and tricarboxylic biphenyls.

To know the influence of some operational variables on these impurities and other compounds were made tests with different temperature, pressure and hydrogenation time. The variable that has more influence is the temperature. With the data from CEPSA QUIMICA was concluded that the b value decreases with the increase of temperature and pressure.

**Keywords:** *Isophthalic Acid, Purification, High Pressure Liquid Chromatography, Colorimetry, B value.*

## Resumo

A procura de ácido isoftálico (IPA) está directamente relacionada com a sua principal aplicação, polietileno de tereftalato. A optimização do processo de purificação é um projecto essencial para a CEPSA Química, S.A., com o objectivo de manter a sua posição no mercado mundial.

O principal objectivo é obter um ácido isoftálico purificado (PIPA) com um baixo *valor b*. Este trabalho teve três secções principais, reacções de hidrogenação, colorimetria e testes para verificar a influência das condições operacionais nas impurezas identificadas.

Os testes realizados a pressão atmosférica e em semi-contínuo revelaram ser não reprodutíveis e a utilização de hidróxido de sódio, como dissolvente, demonstrou ser uma má escolha, uma vez que este dissolvente alterava as características do sistema.

As impurezas responsáveis pela cor amarela, e subsequentemente pelo *valor b*, foram identificadas utilizando um estudo desenvolvido pelo Departamento de Análise do Centro de Investigação da CEPSA e os cromatogramas obtidos por Cromatografia Líquida de Alta Pressão (HPLC). As principais impurezas identificadas foram as fluorenonas dicarboxílicas e os bifenis tricarboxílicos.

Para conhecer a influência de algumas variáveis de operação sobre estas impurezas e outros compostos foram realizados testes a diferentes temperaturas, pressão e tempo de hidrogenação. A variável que tem maior influência é a temperatura. Com os dados fornecidos pela CEPSA QUIMICA foi possível concluir que o *valor b* diminui com o aumento da temperatura e pressão.



**Palavras-chave:** *Ácido Isoftálico, Purificação, Cromatografia Liquida de Alta Pressão, Colorimetria, Valor B.*

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# 1 Introduction

## *1.1 Benzene polycarboxylic acids*

There are twelve benzene carboxylic acids; one monobasic acid (benzoic acid), three dibasic acids (benzene-1,2-dicarboxylic (phthalic acid), benzene-1,3-dicarboxylic acid (isophthalic acid), and benzene-1,4-dicarboxylic (terephthalic acid)), three tribasic acid (benzene-1,2,3-tricarboxylic (hemimellitic), benzene-1,2,4-tricarboxylic (trimellitic acid), and benzene-1,3,5-tricarboxylic (trimesic acid)), three tetrabasic acids (benzene-1,2,3,4-tetracarboxylic (mellophanic acid), benzene-1,2,3,5-tetracarboxylic (prehnite acid) and benzene-1,2,4,5-tetracarboxylic (pyromellitic acid)), one pentabasic acid (benzene-pentacarboxylic acid), and one hexabasic acid (benzene-hexacarboxylic (mellitic) acid) [1].

The most produced benzenepolycarboxylic acids are the terephthalic acid and isophthalic acid, both $C_8H_6O_4$. They are produced by oxidation of the methyl groups on the corresponding *p*-xylene or *m*-xylene [2].

Terephthalic acid, and also dimethyl terephthalate, are used to make saturated polyesters with aliphatic diols as the comonomer. Isophthalic acid is used as feedstock for unsaturated polyesters as well as a comonomer in some saturated products. The molecular structures can be represented as following:

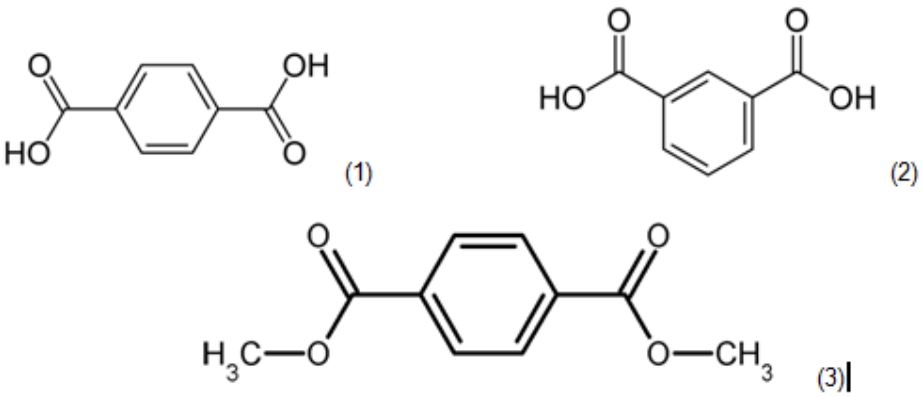



**Figure 1:** Structures of terephthalic acid (1), isophthalic acid (2) and dimethyl terephthalate (3).

### 1.1.1 Physical Properties

The physical properties of these acids are summarized in the Table 1 [3].

**Table 1:** Physical properties of few benzenepolycarboxylic acids.

| Common name | Formula weight | Melting point, ºC | $\Delta H_f^\circ$ at 25ºC kJ/mol | Solubility, g/100g water | |
|---|---|---|---|---|---|
| | | | | at 25ºC | at 100ºC |
| Phthalic | 166,14 | 211 | -782 | 0,7 | 19,0 |
| Isophthalic | 166,14 | 384 | -803 | 0,012 | 0,32 |
| Terephthalic | 166,14 | 402 | -816 | 0,0017 | 0,033 |

### 1.1.2 Chemical Properties

The chemistry of benzenepolycarboxylic acids generally is the same as of others carboxylic acids, which can be converted into esters, salts, acid chlorides, and anhydrides. Each carboxyl group can react separately, so that compounds in which carboxyl groups are converted into different derivates can be prepared. Because there are aromatic hydrogens available in most of these acids, they also undergo reactions characteristic of the benzene nucleus [3].

#### *1.1.2.1 Reactions of the Carboxyl Groups*

Carboxyl groups in the ortho position, like isophthalic acid, spontaneously form a strainless five-membered ring when heated to form salts.

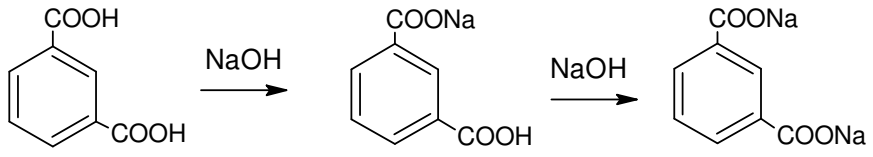



**Figure 2:** Reaction of isophthalic acid with NaOH to form a salt.

Acid chlorides can be formed by reaction with thionyl chloride:

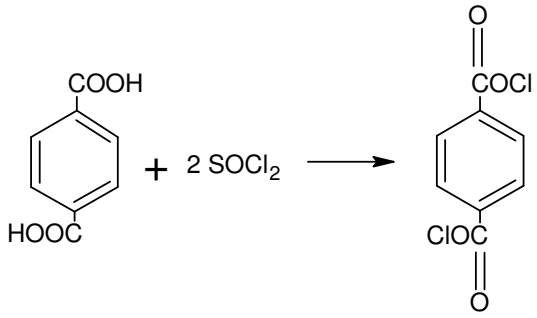



**Figure 3:** Reaction of terephthalic acid with thionyl chloride to form an acid chloride.

Condensation polymerization also occurs and essentially is the only reason for the commercial existence of the terephthalic acid:

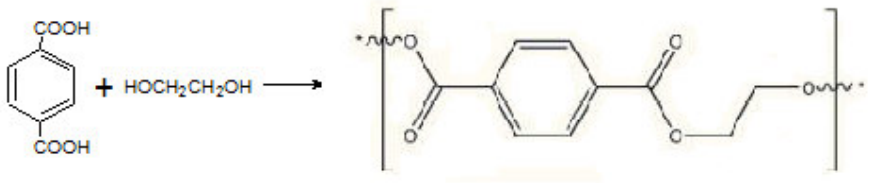



**Figure 4:** Reaction of polymerization from terephthalic acid.

Reactions of the Benzene Ring

The benzene rings of the benzenepolycarboxylic acids undergo halogenations:

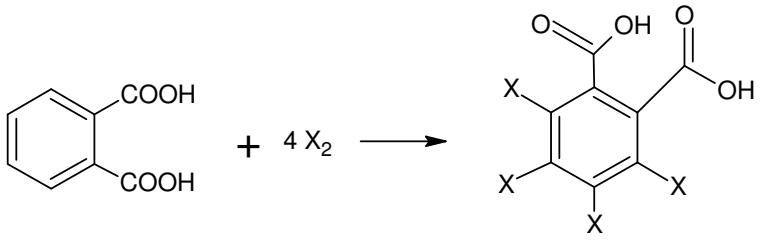



**Figure 5:** Halogenation of phthalic acid.

and sulfonation:

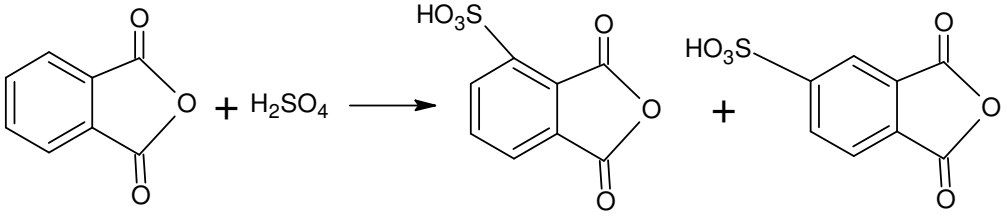



**Figure 6:** Sulfonation of trimellitic anhydride.

When mixed phthalic acids are converted to their dipotassium salts, they can be thermally or catalytically rearranged to the *para* isomer. This rearrangement is known as the Henkel reaction:

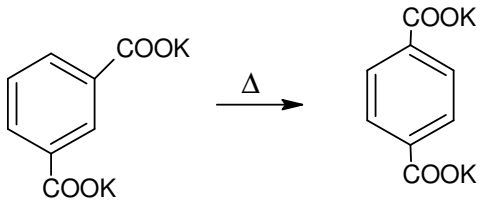



**Figure 7:** Henkel reaction.

## *1.2 Isophthalic Acid*

Isophthalic acid is used as a raw material in the production of polyesters. Much of the isophthalic acid is used for unsaturated polyesters, whereas terephthalic acid is used almost exclusively in saturated (thermoplastic) polyesters. However, a considerable amount of isophthalic acid is used as a minor comonomer in saturated polyesters, where the principal diacid is terephthalic acid. The production volume of isophthalic acid is less than 2% that of terephthalic. Isophthalic acid was formerly produced in technical or crude grades and only a small amount was purified. Now, however, it is all purified to a standard similar to that of terephthalic acid [3].

This benzene carboxylic acid is also used in aramid fibbers, as a component of co polyester resins and high-temperature polymers [4].

### 1.2.1 Physical and Chemical Properties

Some of the most important physical and chemical properties of isophthalic acid are shown in Table 2 and in Table 3.

**Table 2:** Physical Constants and Properties of Isophthalic Acid [3].

| Property | Value |
|---|---|
| Melting point (close tube), ºC | 345 – 348 |
| Vapour pressure, kPa | |
| at 100ºC | 0,009 |
| 125ºC | 0,08 |
| 230ºC | 0,23 |
| 260ºC | 1,03 |
| 290ºC | 3,98 |
| Specific gravity at 4ºC | 1,53 |
| Heat of combustion at 25ºC, kJ/mol | -3202 |
| Heat of formation at 25ºC, kJ/mol | -802 |
| Heat of sublimation at 25ºC, kJ/mol | 106,7 |

**Table 3:** Solubilities of Isophthalic Acid, g/100 g solvent [3].

| Solvent | Temperature, ºC | | | | |
|---|---|---|---|---|---|
| | 25ºC | 50ºC | 100ºC | 150ºC | 200ºC |
| Water | 0,012 | 0,035 | 0,32 | 2,8 | 25 |
| Acetic acid (glacial) | 0,23 | 0,41 | 1,3 | 4,3 | 11,1 |
| Methanol | 2,5 | 4,0 | —— | —— | —— |
| 1-Propanol | 1,7 | 2,7 | 7,0 | —— | —— |
| Dimethylformamide | 37 | —— | —— | —— | —— |
| Dimethyl sulfoxide | 64 | —— | —— | —— | —— |

### 1.2.2 Production

*p*-Xylene is the feedstock for terephthalic acid and dimethyl terephthalate production and *m*-xylene is used for isophthalic acid. Actually the oxidation catalyst and conditions leave the benzene ring virtually untouched. The catalyst is a combination of cobalt, manganese and bromide, or cobalt with a co-oxidant. Oxygen is the oxidant in all process and acetic acid the

reaction solvent. There is only one industrial oxidation process, with different variations, two separate purification processes, and one process which intermixes oxidation and esterification steps [5].

#### *1.2.2.1 Amoco Oxidation*

Amoco developed a commercial process, as Mitsui Petrochemical, now Mitsui Sekka did. Both Amoco and Mitsui participate in joint-venture companies, and both have licensed the process.

A soluble cobalt-manganese-bromide catalyst system is the centre of the process. This yields nearly quantitative oxidation of the *m*-xylene methyl groups with small xylene losses [6]. Acetic acid is the solvent, and oxygen in compressed air is the oxidant. Various salts of cobalt and manganese can be used, and bromine source can be HBr, NaBr, or tetrabromoethane among others. The highly corrosive bromine-acetic acid environment requires the use of titanium-lined equipment in some parts of the process.

A feed mixture of m-xylene, acetic acid, and catalyst is continuously fed to the oxidation reactor (Figure 8). The feed mixture also contains water, which is a by-product of the reaction. The reactor is operated at 175 – 225ºC and 1500-3000 kPa. Compressed air is added to the reactor in excess of stoichiometric requirements to provide measurable oxygen partial pressure and archive high *m*-xylene conversion. The reaction is highly exothermic and water is released. The reaction of 1 mol m-xylene with 3 mol dioxygen gives 1 mol terephthalic acid and 2 mols water. Only four hydrogen atoms, representing a small scale over 2 wt% of the m-xylene molecule, are not incorporated in the isophthalic acid.

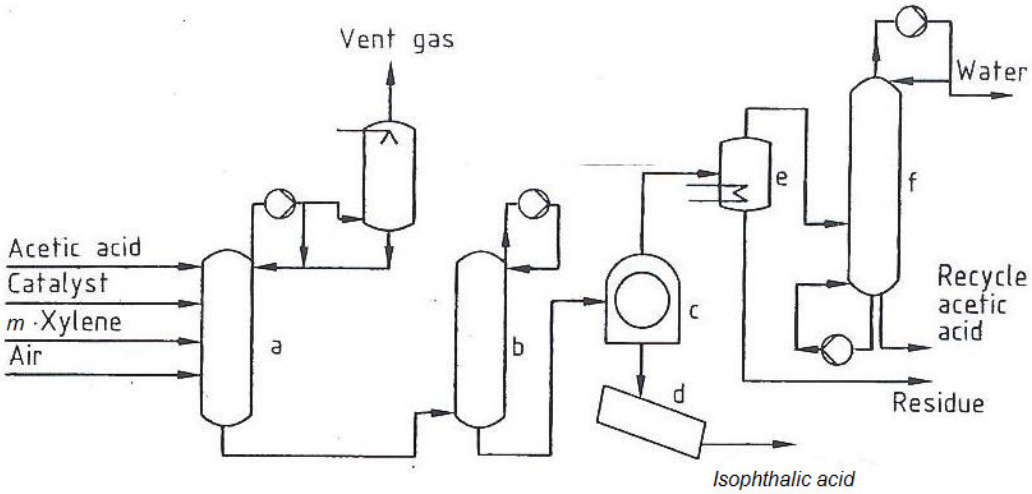



**Figure 8:** Catalytic, liquid-phase oxidation of m-xylene to isophthalic acid by the Amoco process. a) oxidation reactor; b) surge vessel; c) filter; d) dryer; e) residue still; f) dehydration column [3].

Due to low solubility of isophthalic acid in the solvent, most of it precipitates as it forms. This produces a three-phase system: solid isophthalic acid crystals; solvent with some dissolved isophthalic acid; and vapour consisting of nitrogen, acetic acid, water, and a small amount of oxygen. The heat of reaction is removed by solvent evaporation. Small amounts of m-xylene and acetic acid are lost, owing to complete oxidation to carbon oxides, and impurities such as oxidation intermediates are present in the effluent of the reactor.

The oxidation of the methyl groups occurs in steps, with two intermediates, m-toluic acid and 3-formylbenzoic acid. While 3-formylbenzoic acid is the IUPAC name of the intermediate, it is customarily referred to as 3-carboxybenzaldehyde (3-CBA).

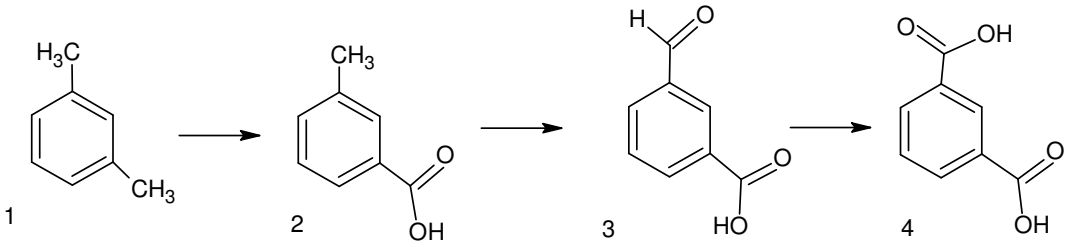



**Figure 9:** 1) m-xylene; 2) m-toluic acid; 3) 3-formyl-benzoic acid; 4) isophthalic acid.

3-Formylbenzoic acid is troublesome, due to its structural similarity to isophthalic acid. It co-crystallizes with isophthalic acid and becomes trapped and inaccessible for completion of the oxidation. The 3-formylbenzoic acid present necessitates a purification step to make the isophthalic suitable as a feedstock for polyesters production.

The slurry is passed to one or more surge vessels where the pressure is reduced. Solid isophthalic acid is then recovered by centrifugation, and the cake is dried and stored to purification.

Vapour from reactor is condensed in overhead heat exchangers, and the condensate is refluxed to the reactor. Steam is generated by condensation and is used as a heating source in other parts of the process. Similar to the reactor condensate, liquid from centrifuges is sent to solvent recovery. Since the centrifugate contains dissolved species, it is first sent to a residue still. Vapour from the still and other vents from the oxidation process are sent to a solvent dehydration tower. The tower removes the water formed in the reaction as the overhead stream, and acetic acid from the tower bottom is combined with fresh acetic acid to make up for process losses, and returned to the process.

### *1.2.2.2 Amoco Purification*

Crude isophthalic acid is inappropriate to polyesters, primarily owing to the 3-formylbenzoic acid impurity concentration. There are also yellow impurities and residual amounts of catalyst metals and bromine. This process removes 3-CBA and also gives a white powder from the slightly yellow feed.

To make all impurities available to reaction, isophthalic acid is slurried with water and heated until it dissolves entirely. The solution passes to a reactor where hydrogen is added. This solution is contacted with a carbon-supported palladium catalyst. Reactor pressure is held above the vapour pressure of water to maintain a liquid phase. The 3-formylbenzoic acid is converted to *m*-toluic acid in the reactor, and some coloured impurities are hydrogenated to colourless compounds (Figure 10).

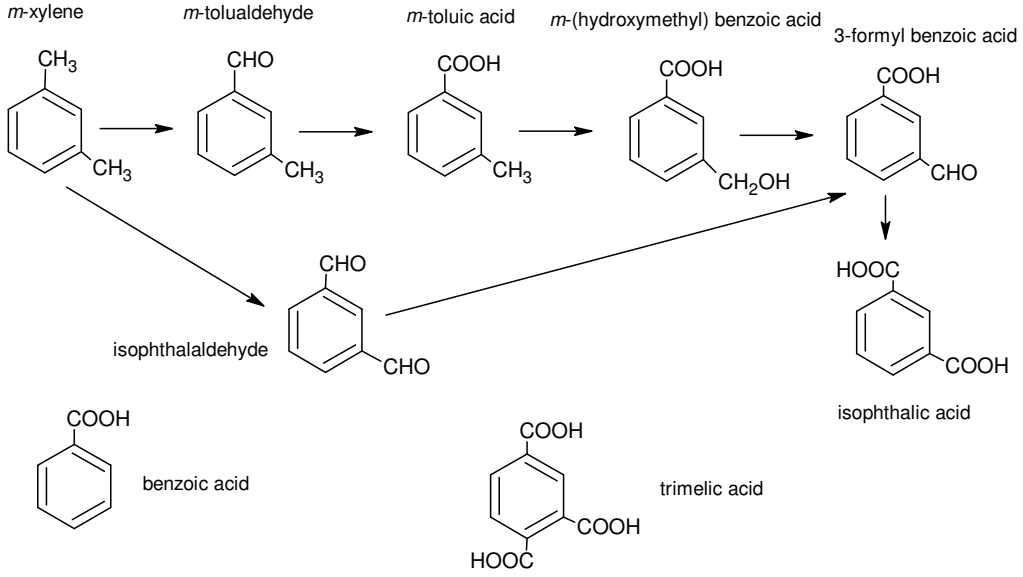



**Figure 10:** Scheme of the compounds present in the isophthalic acid process.

After this hydrogenation, the solution passes to a series of crystallizers where the pressure is sequentially decreased [7]. This results in a stepped temperature reduction, and crystallization of the isophthalic acid. The more soluble *m*-toluic acid formed in the reactor, and other impurities, remain in the mother liquor. After leaving the final crystallizer, the slurry undergoes centrifugation and filtration to yield a wet cake and the cake is dried to give a free-flowing isophthalic acid powder as the product. The product purified is named as purified isophthalic acid (PIPA).

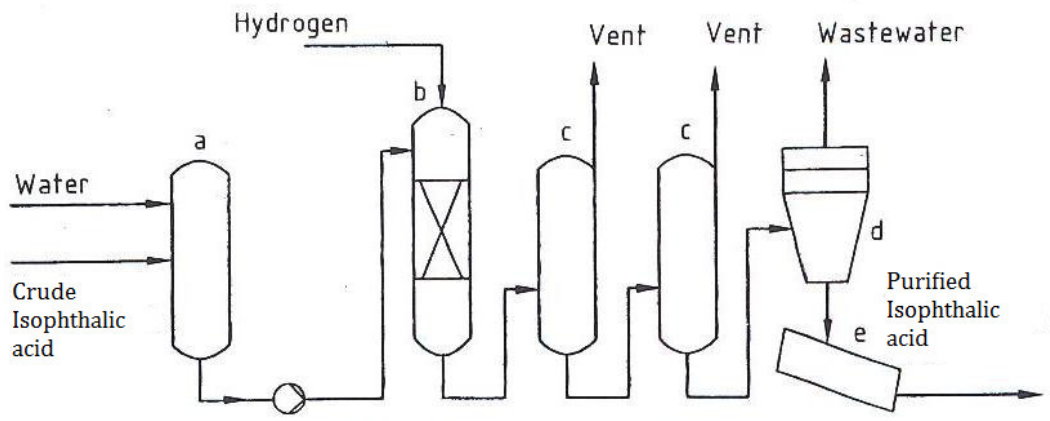



**Figure 11:** Purification of Isophthalic acid by the Amoco process. a) Slurry drum; b) Hydrogenation reactor; c) Crystallizers; d) Centrifuge; e) Dryer [3].

## *1.3 Polyethylene Terephthalate*

Polyethylene terephthalate (PET) is the most common thermoplastic polyester and is often called by “polyester”. PET is an engineering plastic with excellent processing characteristics and high strength. The most important properties are [8]:

- Extreme low water absorption, in particular comparison to Nylon;
- Exceptional dimensional stability, due to the low water absorption;
- Excellent electrical properties;
- Excellent resistance to chemical attack and high environmental stress crack resistance;
- Very good heat and heat ageing resistance;
- Very low creep, even at elevated temperatures;
- Very good colour stability;
- Excellent wear properties;

PET is used extensively in fibber and packaging industries. For most applications it is essential that the base polymer should exhibit only minor variations in physical/chemical properties, which results in uniform processability but additionally the optical properties luminance, yellowness and fluorescence must also be tightly controlled for aesthetic reasons and customer acceptance [9].

The first thermoplastically processible polyesters synthesized from adipic acid and ethylene glycol were described in 1932. Polyesters only became of industrial interest in 1941, with the

synthesis of high melting point products based on terephthalic acid. The fast industrial development of polyesters after World War II was initially restricted to polyester fibbers based on polyethylene terephthalate, polyoxy-1,2-ethanediyloxycarbonyl-1,4-phenylenecarbonyl.

Polyethylene terephthalate has recently become one of the most important and fastest growing plastic materials. Until 1960, only dimethyl terephthalate (DMT) was used as raw material for PET production, but later the purified terephthalic acid (PTA) process, jointly developed by Scientific Design and Amoco, rapidly became the preferred one [10].

Thermoplastic polyesters are generally produced from dicarboxylic acids, hydrocarboxylic acids and lactones and dihydric alcohols and bisphenols. Terephthalic acid is by far the most important dicarboxylic acid. This compound was previously difficult to obtain in sufficiently pure form, dimethyl esters and dicarboxylic acids were therefore mainly used as raw materials.

### 1.3.1 Production of polyethylene terephthalate from terephthalic acid

The direct esterification of terephthalic acid (TA) with ethylene glycol became important when economic processes were developed for producing fibber-grade TA. An important advance was made when the reaction times were reduced by performing esterification under pressure at temperatures above boiling point of ethylene glycol.

The TA process now yields products that are qualitatively competitive with the polyesters produced in the DMT process (see Table 4).

In new plants direct esterification is the main method of PET production. The advantages of direct esterification with TA compared with transesterification with DMT are:

- The higher reaction rate;
- The lower weight of TA compared DMT (storage costs);
- The use of water instead of methanol as condensation agent;
- No transesterification catalyst is required;
- Higher molecular masses are obtained.

**Table 4:** Quality specifications for additive-free PET used in film production.

| Specification | Raw material | |
|---|---|---|
| | DMT | TA |
| Intrinsic viscosity, $cm^3/g$ | 65 ± 0,015 | 65 ± 0,015 |
| Carboxyl terminal groups, mmol/kg | 20 – 30 | 20 – 30 |
| Ash content, wt% | < 0,04 | < 0,02 |
| Diethylene glycol content, wt% | 0,5 – 1,2 | 0,7 – 1,2 |
| Filter value (15µm filter braid), bar $cm^2/kg$ | < 30 | < 30 |

## *1.4 Isophthalic Acid in CEPSA*

The isophthalic acid industry is very concentrated, with only a handful of producers worldwide as of year-end 2005 – Flint Hills Resources LLC (United States of America), Eastman Chemical (United States of America), BP (Belgium), CEPSA QUIMICA (Spain), A.G. International Chemical Company (Japan), Kohap (Republic of Korea), Lonza (Singapore), Sinopec Beijing Yanshan (China), and Tuntex Petrochemicals (Taiwan) [4]. But only CEPSA QUIMICA is a subsidiary of CEPSA and is located at San Roque (Cadiz).

CEPSA QUIMICA is specialized in the manufacturing and sale of purified terephthalic acid (PTA – 450000 tons annually), dimethyl terephthalate (DMT – 90000 tons annually) and purified isophthalic acid (PIPA – 30000 tons annually) used as raw materials of different types of polyester for textile fibbers, powder paint and coatings, film, easily-recyclable PET bottles and containers and other applications.

The main reasons for eliminating the colour of PIPA, to CEPSA are:

- The bottles produced from PET have to be transparent, although the process admits small quantities of coloured compounds but the final product has to be the most transparent possible; Anyway, this question is a aesthetic related one, and it does not implies a low quality product;
- PIPA is employed for producing other products different from PET, such as saturated liquid and powder coating polyesters, alkyd resins, polyamides and adhesives, which are based in optical properties so it was impossible to have small quantities of coloured compounds because the final product would be affected;

- The final product, purified isophthalic acid, PIPA, produced by CEPSA has to compete with others, which have a lower yellow index.

# 2 Experimental Part

## *2.1 Reagents and Catalyst*

### 2.1.1 Reagents

During this all experience, the chemical reagent used for hydrogenation reactions are listed in the Table 5. Beside these products Millipore water was also used. This water was filter by a Millipack 4 filter with 0,22µm.

**Table 5:** Reagents applied in this project.

| Chemical Reagent | Chemical Formula | Purity | Trademark | Application |
|---|---|---|---|---|
| Isophthalic acid | $C_8H_6O_4$ | | CEPSA | Main product |
| Sodium hydroxide | NaOH | > 98% | Scharlau | pH adjustment and hydrogenation's reactions |
| Ammonia | $NH_3$ | | Scharlau | Hydrogenation's reactions |
| Hydrochloric acid | HCl | 37% | Scharlau | pH adjustment |
| Dimethyl sulfoxide | $C_2H_6OS$ | Extra pure | Scharlau | Solvent |
| Acetronitrile | $CH_3CN$ | > 99,9% | Merck | HPLC |
| Ortho-Phosphoric acid | $H_3PO_4$ | 58% | Scharlau | HPLC |
| N, N - Dimethylformamide | $H.CO.N(CH_3)_2$ | 99% | Scharlau | Preparation of PIPA after hydrogenation |

The main product used in this all experience is isophthalic acid, produced in CEPSA QUIMICA. Since the beginning of this project, sodium hydroxide is used as IPA's dissolvent for hydrogenation's reactions because of the lower solubility with other dissolvent at room

temperature, although the dissolvent applied in the process is water at high temperature. The amount of NaOH used to dissolve IPA is 7,2g of NaOH/ 15g IPA. Once the solution of NaOH prepared was necessary remove some impurities of IPA, as Cu and Co, because at a basic pH these metals form hydroxides which precipitate. Hydrochloric acid is used to turn IPA, which was in a salt basic form to an acid form and in solid form. Dimethyl sulfoxide (DMSO) was used as dissolvent of the samplings and acetronitile (ACN) and ortho-phosphoric acid were used as eluents of the HPLC.

### 2.1.2 Catalyst

The catalysts used in these tests were the same than those employed in the industrial process for purification stage. They are commercially available palladium supported (carbon from coconut peel) catalysts. The catalysts have codified names, A for fresh catalyst and B for used catalyst.

## *2.2 Equipment and experimental techniques*

### 2.2.1 Reactions of hydrogenation at atmospheric pressure

The first attempt to create one system to make hydrogenations was a very simple, because the reactions were made in an Erlenmeyer. In this Erlenmeyer was added the mass of catalyst and a magnetic stir bar. In the head of Erlenmeyer the hydrogen was introduced by a balloon, and the recirculation of hydrogen was provided to maintain the reaction (Figure 12).

The procedure used to this kind of system is written bellow:

1. Introduce the magnetic stir bar, catalyst and IPA in solution in NaOH in one Erlenmeyer.
2. Introduce a balloon with nitrogen in the head of the Erlenmeyer, and vacuum to the lateral exit, to remove all oxygen. The vacuum and the nitrogen are applied in an alternate.
3. Remove the balloon of nitrogen and replace by the hydrogen balloon.
4. Turn on the magnetic plate.
5. Cut the vacuum and open the stopcock valve to introduce the hydrogen to the system.

6. When the reaction finish, cut the entrance of hydrogen and replace again by the nitrogen balloon to clean the atmosphere.
7. Take off the Erlenmeyer, and turn off the magnetic plate.
8. Take off all the liquid from the Erlenmeyer to a beaker, and remove all catalyst for future analysis.
9. Make a vacuum filtration to remove all the trace off crushed catalyst.
10. Reduce the pH of the filtrate to 1, with the solution of HCl, and add some Millipore water to clean the pH probe and to turn the solution more aqueous.
11. Make other vacuum filtration to remove the mother waters, and after that put the solid in the vacuum oven at 60 degree to remove all the humidity.

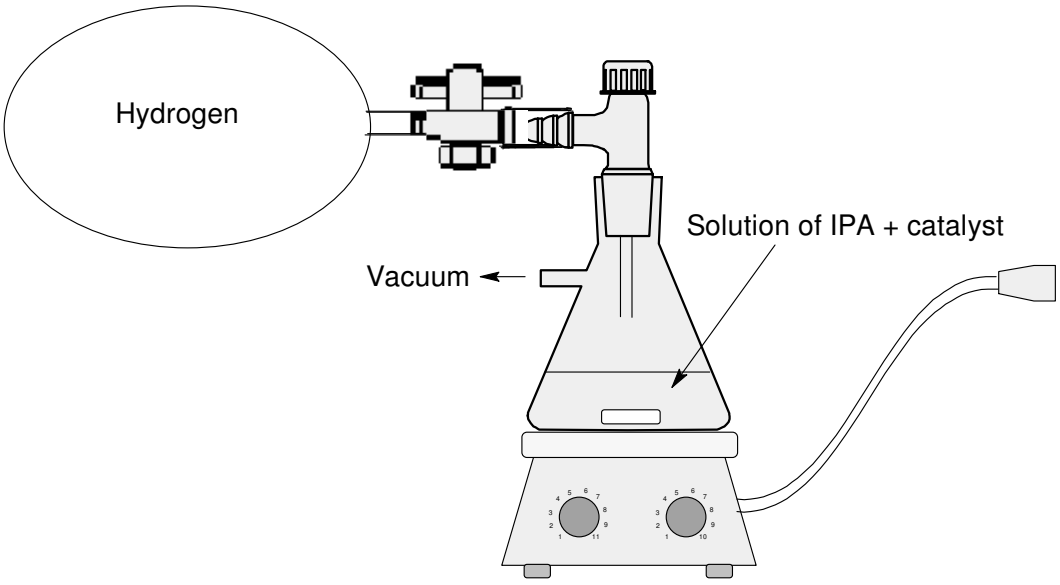



**Figure 12:** Scheme of hydrogenation at atmospheric pressure.

### 2.2.2 Hydrogenation at semi-continuous

This attempt of hydrogenation was made in a four-neck round-bottom flask. These exits allowed to control the entrance of gases (nitrogen and hydrogen), one exit provided the gases' extraction, other to take samples and the last one to thermometer, if it was necessary (Figure 13).

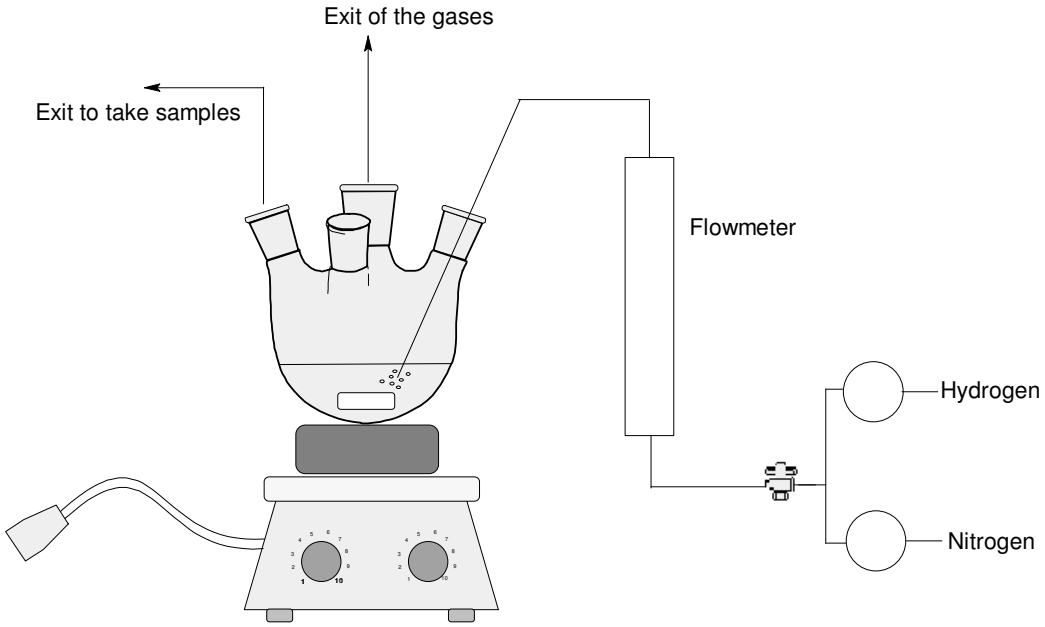



**Figure 13:** Scheme of hydrogenations at semi-continuous.

As it was possible to observe in the last figure, gases were introduced in the liquid in order to permit a best contact between hydrogen with the solution of IPA, to reduce the limitations to mass transfer.

This procedure it is very similar to the reactions of hydrogenation at atmospheric pressure because it was needed to remove all gases before the beginning of the reaction. This was made by cleaning the round-bottom flask with nitrogen and after entrance of hydrogen to start the reaction. The gases' flow was controlled by a flowmeter.

1. In a round-bottom flask with four exits introduce the magnetic stir bar, catalyst and the solution of IPA in NaOH.
2. Turn on the magnetic plate to guarantee the exact rotation.
3. Change hydrogen to nitrogen to stop the reaction.
4. Remove the round-bottom flask, the magnetic stir bar which was inside.
5. Remove all the liquid inside the flask with a pipet to a beaker.
6. Remove all the catalyst for a future analysis if it is needed.
7. Repeat the steps 9, 10 and 11 from the reaction of hydrogenation at atmospheric pressure to pass IPA to its acid form.

### 2.2.3 Hydrogenations in autoclave

These hydrogenations were made in order to recreate industrial conditions, temperature and pressure. The reactor and all pieces are made in stainless steel to avoid the corrosion of these materials.

This system (Figure 14) has a system of gases (Figure 15), hydrogen (line with red valves), nitrogen (line with black valves) and synthetic air (line with green valves), a reactor (Figure 16) and a furnace (Figure 17).

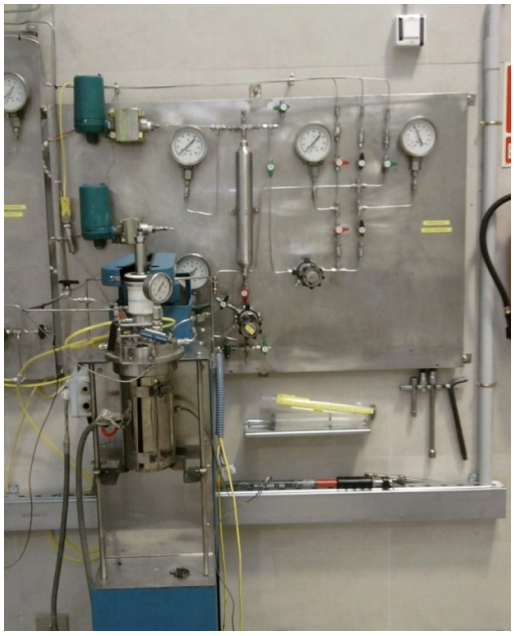


**Figure 14:** System of autoclave.

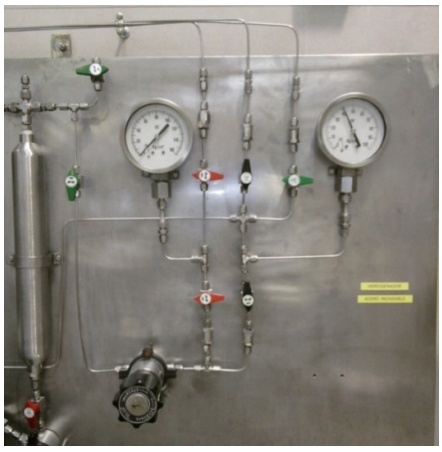


**Figure 15:** System of gases in autoclave's system.

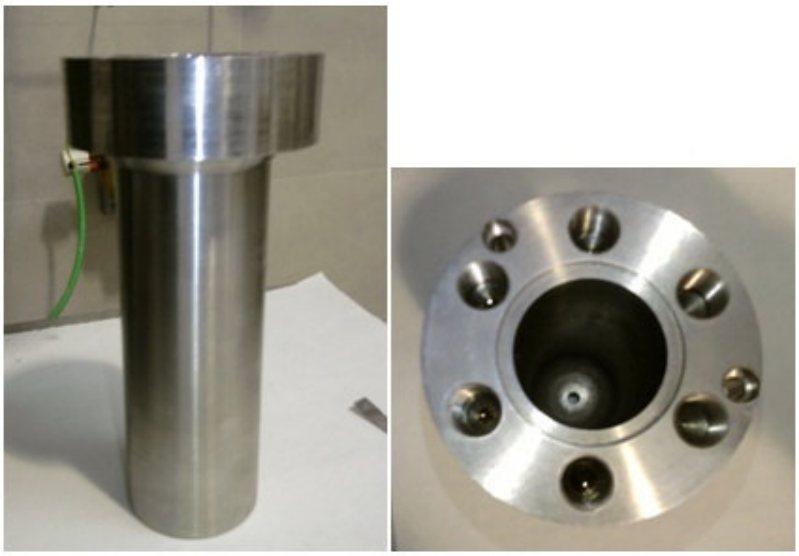


**Figure 16:** Autoclave reactor of hydrogenation.

**Figure 17:** Reactor with the furnace.

Inside the reactor was introduced a basket that contains the catalyst (Figure 18), a thermocouple type K, a baffle for breaking vortex (Figure 19) and two baskets with glass spheres (3mm) to create dead volume (Figure 20). The catalyst's basket and the impeller (Figure 21) were attached to a vertical axis, which allowed the rotation and subsequent agitation. This vertical axis has a system which allows dropping the catalyst basket when the temperature inside the reactor is at the desire conditions, so the contact between the solutions of IPA with the catalyst only occurs when the basket is bellow.

**Figure 18:** Catalyst's basket.

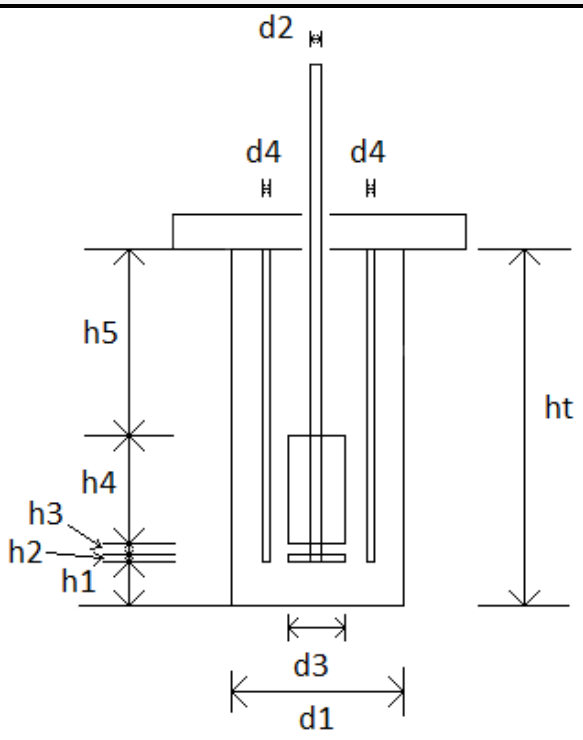
**Figure 19:** Baffle of the reactor.

**Figure 20:** Inside of the reactor - Catalyst's basket, thermocouple and basket with glass spheres.

**Figure 21:** Impeller from the hydrogenation reactor.

The autoclave reactor dimensions are in Table 6.

**Table 6:** Autoclave reactor's dimensions.

| Autoclave Reactor Scheme | Nomenclature | Dimensions, cm |
|---|---|---|
|  | $h_1$ | 1,5 |
| | $h_2$ | 2,0 |
| | $h_3$ | 0,5 |
| | $h_4$ | 7,5 |
| | $h_5$ | 12 |
| | $h_t$ | 23,5 |
| | $d_1$ | 7,5 |
| | $d_2$ | 1,5 |
| | $d_3$ | 3,3 |
| | $d_4$ | 1,0 |

The hydrogenations in this reactor had the following procedure:

1. Insert the catalyst in the catalyst's basket and close this basket with its cover and attach it to the vertical axis.
2. At the end of the vertical axis apply the impeller.
3. Insert clean glass spheres in the basket and attach them to the head of the reactor.
4. Introduce inside the reactor IPA and water and also the baffle.
5. Close the reactor with six screws, first in a cross and after in a circle with a tension of 40N.m.
6. Introduce the thermocouple in the head of the reactor and the furnace.
7. Clean the gases inside the reactor with nitrogen. This cleaning is made by opening the valve of nitrogen and closing the exit high pressure valve.
8. To start the heating, close the nitrogen valve, and let a pressure of 1 bar inside the reactor.
9. In the control room, turn on the agitation at 600 rpm and the heating.
10. When the temperature inside the reactor is at the desire conditions, the catalyst basket is dropped and the hydrogen valve is open to get the desire pressure inside.
11. Turn on the automatic control and after the time of hydrogenation reaction, turn off the heating, removing the furnace, and cut the inlet of hydrogen to get an internal pressure of 1 bar.
12. When the temperature inside the reactor is around 50ºC open the reactor, removing the screws.
13. Filter the effluent of the reactor with a vacuum filtration.
14. After all water is removed, the solid is maintained for 18 hours in an oven at 100ºC.

#### *2.2.3.1 Preparation of PIPA after hydrogenations in autoclave*

PIPA preparation was needed because sometimes the product from the reactor had some grey particles due to catalyst friction with itself and with the catalyst's basket. The procedure was based in the size of the particles. First was needed to find a good solvent that could dissolve PIPA at room temperature and had a low boiling point. For this treatment was used dimethylformamide, that requires a special care due to its carcinogenic characteristics. Consequently, the result mixture was centrifuged with a Centrifuge Beckman model J2-21M – induction drive centrifuge. To recover the PIPA was used a rotary evaporated to evaporate all the dimethylformamide. Others dissolvents were tested (see Table 3) but water and acetic acid had low solubility, methanol and 1-propanol, for being alcohols, react with the acid group of the isophthalic acid and form esters. The reason for the choice of dimethylformamide on detriment

of dimethyl sulfoxide was based in their boiling temperature, because the normal boiling point is 153ºC and 189ºC for dimethylformamide and dimethyl sulfoxide, respectively [3].

1. Take 40g from the PIPA produced in the autoclave and dissolve it in a beaker.
2. Add 120mL of dimethylformamide and a magnetic stir bar.
3. Wait till every PIPA is dissolved, and then put the solution in test tubes.
4. Close all test tubes with parafilm and put them in a centrifuge with 12000rpm during 10 minutes.
5. Remove all liquid, leaving the solid particles in the test tubes, and put it in round-bottom flask to rotary-evaporation.
6. Turn on the silicone bath at 147ºC, the vacuum pump, and the refrigeration water.
7. Connect the round-bottom flask to the rotary-evaporator (Figure 22).
8. Wait until all dissolvent had evaporated and remove the solid to mortar and keep it in a oven

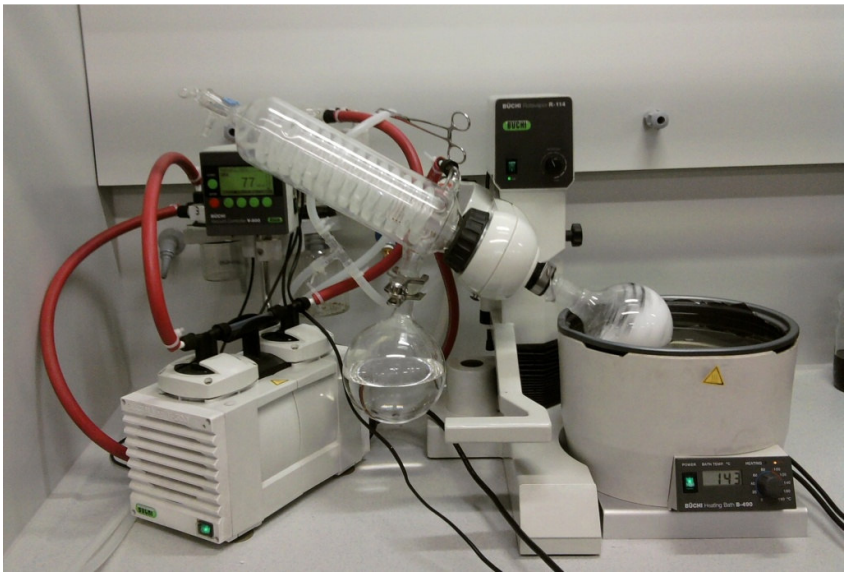


**Figure 22:** Rotary-evaporator used to recover PIPA from dimethylformamide.

## 2.3 Analysis Techniques

The analysis techniques applied to this work was essentially based in colour, because of the influence of this parameter in the isophthalic acid production. Other technique applied was high performance liquid chromatography, which was used to identify the compounds.

### 2.3.1 Optical Density Spectrophotometry's Analysis

This analysis measure the intensity of the sample as function of the colour. The samples were scanned in a 1 cm cell from 800 to 190 nm on a Lambda 900 UV/VIS/NIR (Perkin Elmer). Total concentration of the organic impurities was monitored by absorbance of an alkaline solution at a fixed wavelength of 340nm [9].

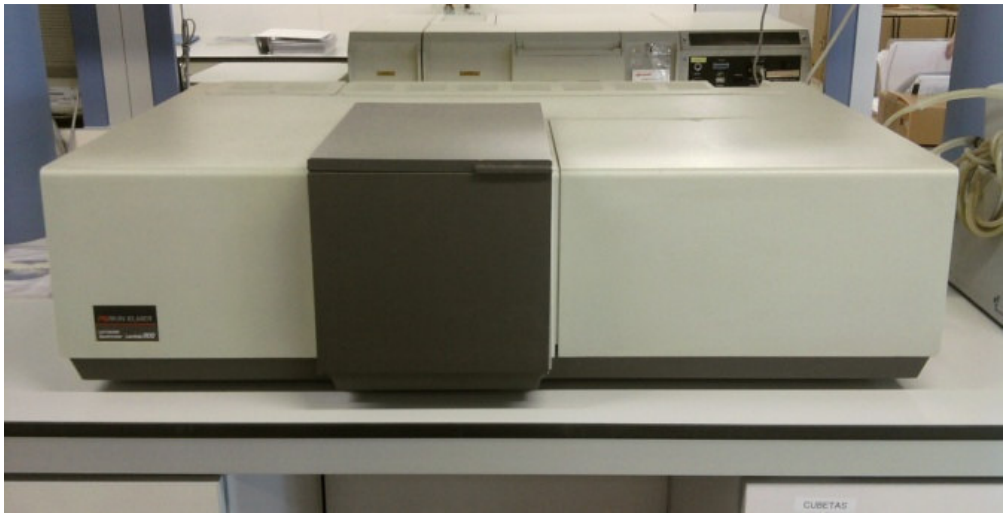


**Figure 23:** Optical Density Spectrophotometer – Lambda 900.

1. Weigh 3g of the solid sample and dissolve in 10mL with a 6M of NaOH solution.
2. Prepare a blank cell with NaOH, because it is the dissolvent.
3. Fill up the cells with samples.
4. Run the analysis method (*PIPA.MSC*[1]).
5. Make an *Autozero* to start the analysis.
6. Put the cells in their place and start the analysis method.
7. After the analysis took place, remove the cells and the results.

[1] This method was defined by the laboratory of CEPSA.

### 2.3.2 Colorimetry

This analysis was used to know a parameter (parameter b and yellow index) which could be compared with the *b value*, ($V_B$) measured in factory. This parameter b allows knowing the one yellow index. To measure this index was used a Minolta Chroma Meter CT-310 (Figure 24).


**Figure 24:** Minolta Chroma Meter CT-310, used to measure the *parameter b*.

This equipment offers four different systems for measuring colour difference ( Δ(Yxy), Δ(L*a*b*), Δ(L*C*H*) and Hunter Δ(Lab)). The system that was used was the Δ(L*a*b*).

#### *2.3.2.1 Δ(L*a*b*) System*

This system represents more closely the human sensitivity to colour. Equal distances in this system approximately equal perceived colour differences. L* is the lightness variable; a* and b* are the chromaticity coordinates. Their defining equations are

$$L^* = 116\left(\frac{Y}{Y_n}\right)^{1/3} - 16 \qquad \textbf{Eq. 1}$$

$$a^* = 500\left[\left(\frac{Y}{X_n}\right)^{1/3} - \left(\frac{Y}{Y_n}\right)^{1/3}\right] \qquad \textbf{Eq. 2}$$

$$b^* = 200\left[\left(\frac{Y}{Y_n}\right)^{1/3} - \left(\frac{Z}{Z_n}\right)^{1/3}\right] \quad \textbf{Eq. 3}$$

Where X, Y and Z are measured tristimulus values of specimen and $X_n$, $Y_n$, $Z_n$ the tristimulus values of the light source used (Table 7)

**Table 7:** Tristimulus values of the light source.

| **"Light Source" index** | **$Y_n$** | **$X_n$** | **$Z_n$** |
|---|---|---|---|
| "C" | 98,072 | 100,00 | 118,225 |
| "$D_{65}$" | 95,045 | 100,00 | 108,892 |

Colour difference values ΔL*, Δa*, and Δb* are calculated according to the following formulas.

$$\Delta L^* = L^* - L_t^* \quad \textbf{Eq. 4}$$

$$\Delta a^* = a^* - a_t^* \quad \textbf{Eq. 5}$$

$$\Delta b^* = b^* - b_t^* \quad \textbf{Eq. 6}$$

Where L*, a* and b* measured values of specimen and$L_t^*$, $a_t^*$ and $b_t^*$ values of target colour (Figure 25).

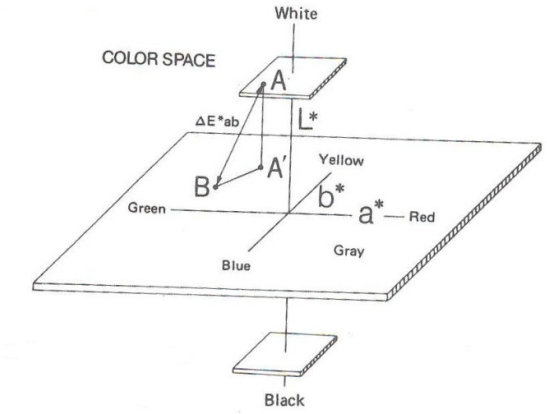



**Figure 25:** Scheme of measure units of colorimetry (A – target colour; B – specimen's colour; A' – target colour at the same lightness level as specimen's colour).

To apply this technique a distilled water calibration was required, according to the following procedure.

*2.3.2.1.1 Calibrating to Distilled Water*

1. Turn ON the equipment;
2. Put distilled water into the sample cell (Sample cell used for calibration should have the same optical path length as the one which will be used for measurements);
3. Insert sample cell into cell holder;
4. Press *CALIBRATE*, and then change the calibration value to the ones represented in Table 8.

**Table 8:** Calibration values for Minolta Chroma Meter CT-310.

| **"Light Source" index** | **Y** | **x** | **y** |
|---|---|---|---|
| "C" | 100,00 | 0,3101 | 0,3162 |
| "D65" | 100,00 | 0,3127 | 0,3290 |

For this analysis, it was also needed a calibration with a selected liquid. The procedure is described in 2.3.2.1.2.

*2.3.2.1.2 Calibrating to User-Selected Liquids*

1. After calibrate with distilled water (2.3.2.1.1) put selected liquid into sample cell.
2. Insert sample cell into cell holder.
3. Press *CALIBRATE*. The display at right will appear for about five seconds, and then change to lower display, showing previously set calibration values. But, once these values for NaOH solution of 6M, and DMSO are unknown these values are assumedly the same as the distilled water (Table 8);
4. Press *COLOR SPACE SELECT* to desired colour space (Yxy or L*a*b*);
5. Set calibration data for selected liquid by using number keys.
6. Press *MEASURE* after *READY* lamp on measuring units' lights. Display at right will appear and three measurements will automatically be taken for better accuracy;
7. After about five seconds. "*End*" will replace "*CA*L" in the display and the calibration of selected channel is completed [11].

To get the measurement of the required parameters the following procedure was used.

#### *2.3.2.2 Absolute Measurements*

1. Put liquid to be measured into sample cell. Sample cell used for measurements should have the same optical path length as the one which was used for calibration;
2. Insert sample cell into cell holder;
3. Insert cell holder into sample chamber of measuring unit;
4. Press MEASURE after READY lamp on measuring unit lights. Display will show colour space in use for a few seconds and then measured value will be displayed. Data will be automatically stored in memory [11].

The value obtained from this equipment allows the yellow index (YI) measure from Eq. 7 and the parameter b.

$$YI = 100 \times \left(1 - \frac{0{,}8467 \times Z}{Y}\right) \quad \textbf{Eq. 7}$$

### 2.3.3 High Performance Liquid Chromatography

The identification of products and impurities was made applying HPLC technique, to that was used a chromatograph Agilent (series 1100) with a detector of Diode Array (Figure 26).

As in any chromatographic technique, separation occurs due to thermodynamic partitioning between the sample components in the mobile and stationary phases. In this process the separation takes place in solution inside a chromatographic column with 15cm which can resist to high pressures (63bar), created by a moving liquid mechanically pumped through the column [12].

When separated macromolecules leave the column, they are detected by one electrical device with signals proportional to the concentration of the analyte.

**Figure 26:** Equipment of High Performance Liquid Chromatography.

The procedure for solid samples is:

1. Weight ±200mg in a volumetric flask of 50mL of the solid sample;
2. Add the solvent (DMSO) till complete the volume of the volumetric flask;
3. Put the volumetric flask in a ultrasound, to dissolve all the solid, for five minutes;
4. Take 1,5mL of the volumetric flask to a vial, to further analysis.

For liquid samples, the procedure is almost the same, but instead of weigh ± 200mg insert 5 or 10 mL of the sample and complete the volume of the volumetric flask with the dissolvent.

The vials introduced in the HPLC it is only analysed 20µL, with the wavelength of 340nm, because it is at this wavelength that the coloured compounds are detected.

### *2.3.4 b Value*

The apparatus to measure this colour parameter was not available in the CEPSA Centre, so the samples were send to CEPSA QUIMICA, where this parameter was measured.

## *2.4 Planning*

During these five months was intended to achieve what is described in the Table 9

**Table 9:** Study Plane Schedule.

| |
|---|
| **HPLC Product Analysis** |
| - Product purity level assessment |
| - Validation of the method for impurities quantitification in the product |
| **Impurities Identification** |
| - Identification of impurities responsible for *b value* |
| **Colorimetry** |
| - Assessment between colour's parameters and *b value* |
| **Product Hydrogenation** |
| - Influence of temperature, pressure and hydrogenation time on *b value* and on impurities |

# 3 Experimental Results and Discussion

In this chapter it will be shown the results obtained of the hydrogenations and their analysis. It will also explain some options that were taken during purification study of isophthalic acid.

## *3.1 Comparison of different PIPAs from CEPSA QUIMICA*

CEPSA has some PIPAs with a good range of *b values*. These PIPAs with *b value* higher than 4 were obtained when the catalyst was already used or when it was needed to raise the quantity of PIPA produced (Table 10).

**Table 10:** *b value* of samples from CEPSA QUIMICA S.A..

| Sample | *b value* |
|---|---|
| IPA M | 8,27 |
| PIPA 1 | 1,90 |
| PIPA 2 | 2,60 |
| PIPA 3 | 5,20 |
| PIPA 4 | 5,30 |
| PIPA 5 | 1,80 |
| PIPA 6 | 4,10 |
| PIPA 7 | 2,00 |
| PIPA 8 | 3,30 |
| PIPA 9 | 4,60 |
| PIPA 10 | 1,10 |
| PIPA 11 | 1,30 |
| PIPA 12 | 1,10 |

At CEPSA Centre was decided to say that PIPAs with less than 4 of *b value* to call PIPA with low *b value*, and those with more than 4 to call PIPA with high *b value*. From this last table is possible to observe that the purification reduce the *b value*.

## *3.2 Purification Studies*

### 3.2.1 Reactions of hydrogenation at atmospheric pressure

First attempts to scale-down hydrogenation step were based on hydrogenations at atmospheric pressure. It is a simplified way to check the process, but it provided an easier and safer handling when compared to high pressure tests (avoiding high pressure reactors).

These tests were made to check *i)* an alternative way to test catalysts at laboratory scale, *ii)* to evaluate experimental reproducibility and (if possible) *iii)* to evaluate regenerated catalyst´s behaviour.

First problem found when trying to test catalysts at room temperature comes from the fact that isophthalic acid is solid at ambient temperature. But at the same time, an IPA´s liquid environment is required to carry on the catalytic process. Since IPA has a very low solubility in water, an aqueous NaOH solution was employed to guarantee total solubility. But this way brings one problem, because it promotes the change from isophthalic acid form to its salt form (base form). To analyse the results of these hydrogenations, it was needed to make the reverse process, is that, after hydrogenation it was necessary to add an aqueous HCl solution to get isophthalic acid in its acid form.

The obtained samples were analysed by HPLC. The chromatogram has main compound, IPA (retention time of 7,2 minutes). The peaks that appear before IPA's peak are associated to "polar impurities", and those that appear after 7,2 minutes to "non polar impurities". This notation is defined in terms of their relative polarity when compared to IPA; it means that impurities that appear before IPA are more polar than IPA. The polar peaks appear first on the chromatogram because of the characteristics of the column. The column is a non polar one, so the polar molecules have a short retention time, and the non polar molecules, due to its affinity to the column, have a long retention time.

The next equations are used to relate the polar and non polar impurities with IPA.

$$\%A_p = \frac{\sum Polar\ areas}{Area\ of\ IPA} \times 100 \qquad \textbf{Eq. 8}$$

$$\%A_{ap} = \frac{\sum Non\ polar\ areas}{Area\ of\ IPA} \times 100$$ **Eq. 9**

The most important by-products are located in the non polar one because the non polar compounds are those which are supposedly responsible for the yellow colour of the final product.

**Table 11:** Results obtained from the hydrogenations at atmospheric pressure.

| Name[1] | Catalyst | Weight of catalyst, g | Temperature °C | Pressure, bar | Time, h | Volume of Solvent, mL | Observations | % Polar Area | % Non Polar Area |
|---|---|---|---|---|---|---|---|---|---|
| IPA-NOV-H2-1h-Patm-Pd/C-Iman.Peq. | A | 1,3 | Room temperature | atm | 1 | 30 | Small magnetic agitator | 0,98 | 1,66 |
| IPA-NOV-H2-1h-Patm-Pd/C-Iman.Grand. | A | 1,3 | Room temperature | atm | 1 | 30 | Big magnetic agitator | 0,99 | 1,59 |
| Erep1 | A | 1,3 | Room temperature | atm | 1 | 30 | —— | 1,06 | 1,04 |
| Erep2 | A | 1,3 | Room temperature | atm | 1 | 30 | —— | 2,37 | 1,40 |
| Erep3 | A | 1,3 | Room temperature | atm | 1 | 30 | —— | 1,22 | 1,96 |
| SSH1 | A | 1,3 | Room temperature | atm | 1 | 30 | Catalyst protect with a metal basket | 1,09 | 2,57 |
| SSH2 | A | 1,3 | Room temperature | atm | 1 | 30 | Catalyst protect with a metal basket | 1,08 | 2,75 |
| SSH3 | A | 1,3 | Room temperature | atm | 1 | 30 | Catalyst protect with a metal basket | 1,02 | 2,95 |
| HN-1 | A | 1,3 | Room temperature | atm | 1 | 30 | Used nitrogen instead of hydrogen | 1,35 | 3,09 |

[1] All tests used NaOH (48g/L) as dissolvent.

From Table 11 it is possible to observe that the size of magnetic stir bar does not have any influence to the results of $\%A_p$ and $\%A_{ap}$, because in the tests IPA-NOV-H2-1h-Patm-Pd/C-Iman.Peq and in IPA-NOV-H2-1h-Patm-Pd/C-Iman.Grand the percentage of polar areas and non polar areas are almost the same. With these two tests was possible to confirm that the agitation only help the total dissolution of IPA in NaOH, and the size of magnetic stir bar does not has influence to the hydrogenation process.

The next tests (Erep1, Erep2 and Erep3) were made to observe the drop of yield of A, because the catalyst used in Erep2 was the same used to do Erep1, and the catalyst used in Erep3 was used after Erep2. These successive tests had the expected results, because the drop of yield in polar areas was reflected in the increase of the $\%A_{ap}$. This happen because the catalyst is deactivated with the sequence of the reactions

The tests SSH1, SSH2 and SSH3 had a higher $\%A_{ap}$, because the catalyst was in a small basket, with very small mesh, so the contact between the catalyst and IPA in solution was reduced. Once the Palladium is in the external area of the catalyst, the action of the catalyst is very dependent on the contact so the $\%A_{ap}$ is higher than usual.

HN-1 was a test to observe the capacity of adsorption of the carbon from the catalyst, to colourful compounds, because the initial %Aap of IPA M (%Aap (IPA M) = 4,40) is reduced to 2,54, so it can be said that this catalyst is the most appropriate to make this purifications because the carbon from the catalyst has adsorption properties and the palladium helps the hydrogenation.

In attempt to see the effects of a used catalyst in hydrogenations were made the HJ's tests. These tests (see Table 12) used B catalyst. This catalyst was used in hydrogenations in factory, and was washed with different solvents to see if it was possible to reuse it. This washing[1] had the intention to remove impurities (products adsorbed in the pores) that were absorbed by the carbon from the catalyst. Unfortunately the results were not very satisfactory because the percentage of non polar area did not reduce. All test had a $\%A_{ap}$ surrounding the value of 2,5, but this is still a high value, so the possibility of regeneration of the catalyst by this way was abandoned by now for the responsible from CEPSA.

[1] These catalysts were washed in Research Laboratory of CEPSA.

**Table 12:** Results of hydrogenations at atmospheric pressure with washed catalyst.

| Name | Catalyst | Weight of catalyst, g | Temperature, ºC | Pressure, bar | Time of hydrogenation, h | Solvent | Volume of Solvent, mL | % Polar Area | % Non Polar Area |
|---|---|---|---|---|---|---|---|---|---|
| HJ-1 | B washed with acetone | 1,348 | Room Temperature | atm | 1 | NaOH 48g/L | 30 | 2,25 | 2,54 |
| HJ-2 | B washed with water | 1,314 | Room Temperature | atm | 1 | NaOH 48g/L | 30 | 1,23 | 2,56 |
| HJ-3 | B washed with DMSO | 1,335 | Room Temperature | atm | 1 | NaOH 48g/L | 30 | 1,42 | 2,48 |
| HJ-4 | B washed with water and NaOH | 1,307 | Room Temperature | atm | 1 | NaOH 48g/L | 30 | 2,36 | 2,12 |
| HJ-5 | B washed with acetic acid | 1,164 | Room Temperature | atm | 1 | NaOH 48g/L | 30 | 0,57 | 2,21 |

### 3.2.2 Hydrogenation at semi-continuous device

As the results of hydrogenations at atmospheric pressure were not as good as expected (bad reproducibility), it was decided to change the system into the one described in 2.2.2. With this system it was possible to control the flow of nitrogen and hydrogen. In the next table are presented the results.

**Table 13:** Results of hydrogenations at semi-continuous.

| Name | Catalyst | Weight of Catalyst, g | Temperature, ºC | Pressure | Time of hydrogenation | Solvent | Volume of Solvent, mL | Gas | % Polar Area | % Non Polar Area |
|---|---|---|---|---|---|---|---|---|---|---|
| E-1 | sin | — | Room temperature | atm | 1 hour | NaOH 48g/l | 30 | $N_2$ | 1,23 | 3,60 |
| E-2 | A | 1,318 | Room temperature | atm | 1 hour | NaOH 48g/l | 30 | $N_2$ | 2,32 | 2,57 |
| E-3 | A | 1,312 | Room temperature | atm | 1 hour | NaOH 48g/l | 30 | $N_2$ | 2,79 | 2,36 |
| E5 t1 | A | 2,625 | Room temperature | atm | 5 min | NaOH 48g/l | 60 | $H_2$ | 2,32 | 3,43 |
| E5 t2 | A | 2,625 | Room temperature | atm | 10 min | NaOH 48g/l | 55 | $H_2$ | 2,35 | 3,28 |
| E5 t3 | A | 2,625 | Room temperature | atm | 15 min | NaOH 48g/l | 50 | $H_2$ | 2,35 | 3,28 |
| E5 t4 | A | 2,625 | Room temperature | atm | 30 min | NaOH 48g/l | 45 | $H_2$ | 2,39 | 3,01 |
| E5 t5 | A | 2,625 | Room temperature | atm | 1 hour | NaOH 48g/l | 40 | $H_2$ | 2,72 | 2,28 |
| E6 t1 | A | 2,611 | Room temperature | atm | 5 min | NaOH 48g/l | 60 | $H_2$ | 2,35 | 3,35 |
| E6 t2 | A | 2,611 | Room temperature | atm | 10 min | NaOH 48g/l | 55 | $H_2$ | 2,82 | 3,40 |
| E6 t3 | A | 2,611 | Room temperature | atm | 15 min | NaOH 48g/l | 50 | $H_2$ | 1,65 | 3,05 |
| E6 t4 | A | 2,611 | Room temperature | atm | 30 min | NaOH 48g/l | 45 | $H_2$ | 1,45 | 8,04 |
| E6 t5 | A | 2,611 | Room temperature | atm | 1 hour | NaOH 48g/l | 40 | $H_2$ | 1,66 | 2,39 |
| E7 t1 | A | 2,613 | Room temperature | atm | 5 min | NaOH 48g/l | 60 | $H_2$ | 2,39 | 3,01 |
| E7 t2 | A | 2,613 | Room temperature | atm | 10 min | NaOH 48g/l | 55 | $H_2$ | 2,72 | 2,28 |
| E7 t3 | A | 2,613 | Room temperature | atm | 15 min | NaOH 48g/l | 50 | $H_2$ | 2,35 | 3,35 |
| E7 t4 | A | 2,613 | Room temperature | atm | 30 min | NaOH 48g/l | 45 | $H_2$ | 2,82 | 3,40 |
| E7 t5 | A | 2,613 | Room temperature | atm | 1 hour | NaOH 48g/l | 40 | $H_2$ | 1,65 | 3,05 |

The E-1 was a bank sample because was not used any catalyst and without hydrogen and it was made just to have a start point. E-2 and E-3 were made to see the power of catalyst without hydrogen, and it had a reduction off 44% (in average) in $\%A_{ap}$ in respect with IPA M. These two test confirm the power of adsorption of the catalyst, because the percentage of impurities, more non polar than isophthalic acid, has reduced, just for the power of adsorption of carbon from the catalyst.

The E-5, E-6 and E-7 were made to see the evolution of the hydrogenation in time, at 5, 10, 15, 30 and 60 minutes. From Figure 27 it is possible to observe that exists a slight decrease in percentage of non polar areas with time, to an average value of 2,39. The E6 at 30 minutes had a $\%A_{ap}$ very high, but if this point is not considered is possible to get a higher correlation factor.

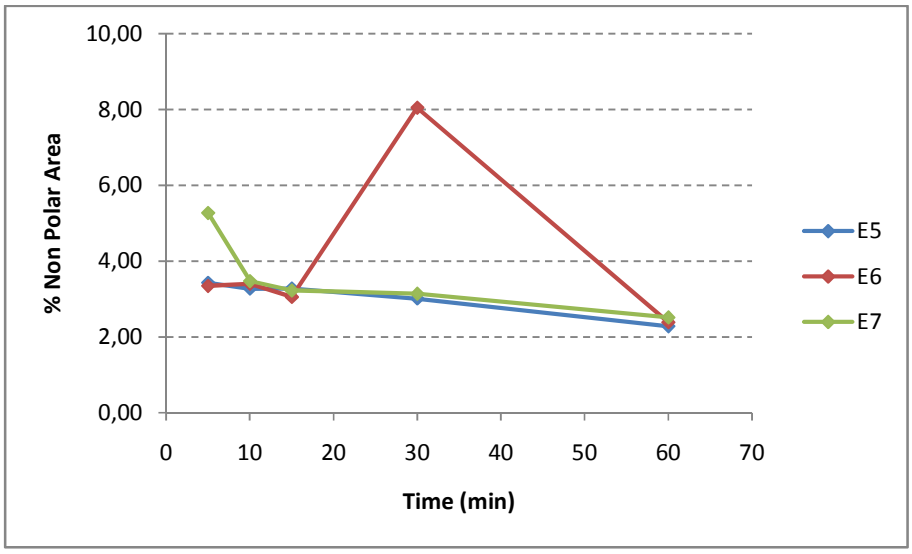



**Figure 27:** Evolution of hydrogenations E-5, E-6 and E-7 with time.

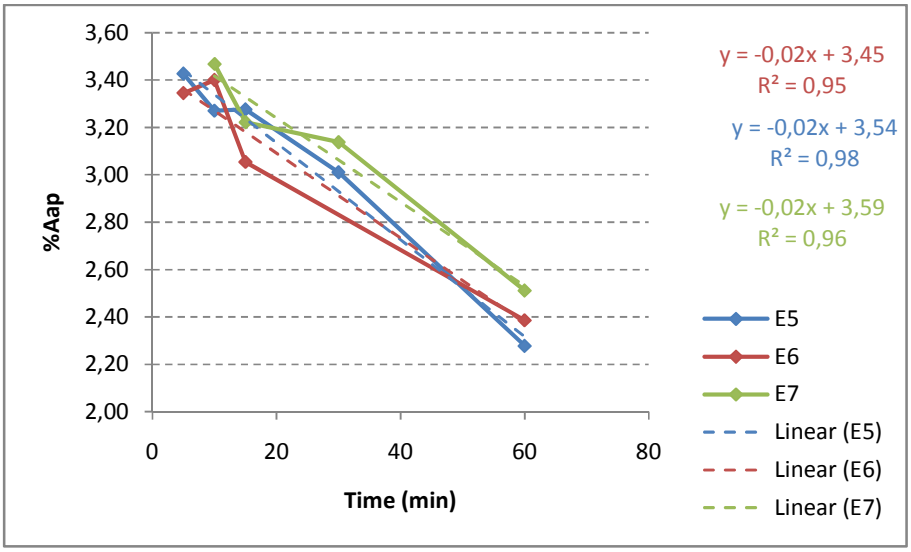



**Figure 28:** Evolution of hydrogenations with semi-continuous system, with their trend lines.

This method was abandoned because it had not reproducibility, and the dissolution in NaOH was deflecting the reality from the factory, because the solvent is water at high temperature and pressure instead of a solution of NaOH. This solvent had other problem; the solution of NaOH, due to its properties was damaging the catalyst, and corrupting the results.

As result of this conclusion this method was abandoned and the study turned to other face of the problem. Once the impurities responsible for the yellow colour were unknown, the work developed in CEPSA, started to know which were the compounds responsible for the high *b value*, so it could possible to develop a method to reduce this value.

## *3.3 Impurities Identification*

The identification of the impurities from PIPA was made in collaboration with the Analysis Department from CEPSA. This department analysed different samples with very distinct *b values,* in order to identify the most probable compound to which peak. This analysis was made by HPLC – MS. The characteristics of the HPLC – MS chromatograph are in Table 14.

**Table 14:** Characteristics of the HPLC – MS [13].

| | |
|---|---|
| **Liquid Chromatograph** | Agilent – series 1200 |
| **Column** | Agilent Zorbax Eclipse XDB – C18<br>4,6 × 100 mm × 3,5 µm |
| **Elluent** | ACN / H2O (pH = 2,3 with formic acid)<br>Elution in gradient |
| **Temperature** | 40 ºC |
| **Detector** | DAD/MSD |

The impurities identified which suffered more changes after the purification processes of IPA were fluorenones, benzophenones, biphenyls and anthraquinone (all mono and poly carboxylics).

After a bibliographic research to find the colour of this impurities, with the goal to define which were the responsible for the yellow colour, the fluorenones dicarboxylics, poly-carboxylics anthraquinones, tricarboxylics benzophenones and the bicarboxylics and tricarboxylics phenyls were found to have a yellow colour [14]. All these impurities are in the non polar zone of the chromatogram, except the bicarboxylics phenyls.

## *3.4 Colorimetry Analysis*

To evaluate the efficiency of the purifications procedures of IPA made in CEPSA, the *b value* (measured in CEPSA QUIMICA), parameter b and yellow index and the optical density were correlated. In the Table 15 is shown these parameters for some samples.

**Table 15:** Results of the Colorimetry analysis.

| Origin | Sample | *b value* | Par. b (NaOH) | Par. b (DMSO) | YI (NaOH) | YI (DMSO) | D.O. (340nm) |
|---|---|---|---|---|---|---|---|
| **IPA from CEPSA QUIMICA** | **IPA M** | 8,27 | 12,120 | 3,850 | 17,245 | 5,140 | —— |
| **PIPA with low *b value*** | **PIPA 1** | 1,90 | 4,773 | —— | 6,944 | 0,730 | 1,279 |
| | **PIPA 2** | 2,60 | 7,430 | —— | 10,748 | 0,660 | 1,607 |
| | **PIPA 5** | 1,80 | 3,003 | 0,350 | 4,394 | 0,430 | 0,840 |
| | **PIPA 7** | 2,00 | 6,990 | 0,520 | 10,174 | 0,770 | 1,550 |
| | **PIPA 8** | 3,30 | 5,603 | 0,740 | 8,273 | 0,930 | 1,490 |
| | **PIPA 10** | 1,10 | 1,150 | 0,270 | 1,586 | 0,200 | 0,4797 |
| | **PIPA 11** | 1,30 | 1,617 | —— | 2,300 | -0,010 | 0,516 |
| | **PIPA 12** | 1,10 | 0,973 | —— | 1,339 | 0,190 | 0,503 |
| **PIPA with high *b value*** | **PIPA 3** | 5,20 | 5,373 | 1,960 | 7,800 | 2,100 | 1,570 |
| | **PIPA 4** | 5,30 | 10,097 | —— | 14,458 | 1,890 | 2,200 |
| | **PIPA 6** | 4,10 | 4,787 | 1,247 | 6,929 | 1,750 | 1,324 |
| | **PIPA 9** | 4,60 | 7,037 | 1,630 | 10,264 | 1,470 | —— |
| **PIPA's from CEPSA Centre**[1] | **C-1** | 8,17 | 8,787 | 2,600 | 12,668 | —— | —— |
| | **C-3** | 7,60 | 10,307 | 4,860 | 14,769 | 7,120 | —— |
| | **C-4** | 1,96 | 5,273 | 5,213 | 8,430 | 8,450 | —— |
| | **C-5** | 1,28 | 4,407 | —— | 7,152 | —— | —— |
| | **C-6** | 0,69 | 1,760 | 1,890 | 4,014 | 2,880 | —— |
| | **C-8** | 2,64 | 10,170 | —— | 16,763 | —— | —— |
| | **C-10** | 2,53 | 5,403 | 7,480 | 8,034 | —— | —— |

[1] These PIPAs were previously purified.

With these results it was possible to have the followings graphics.

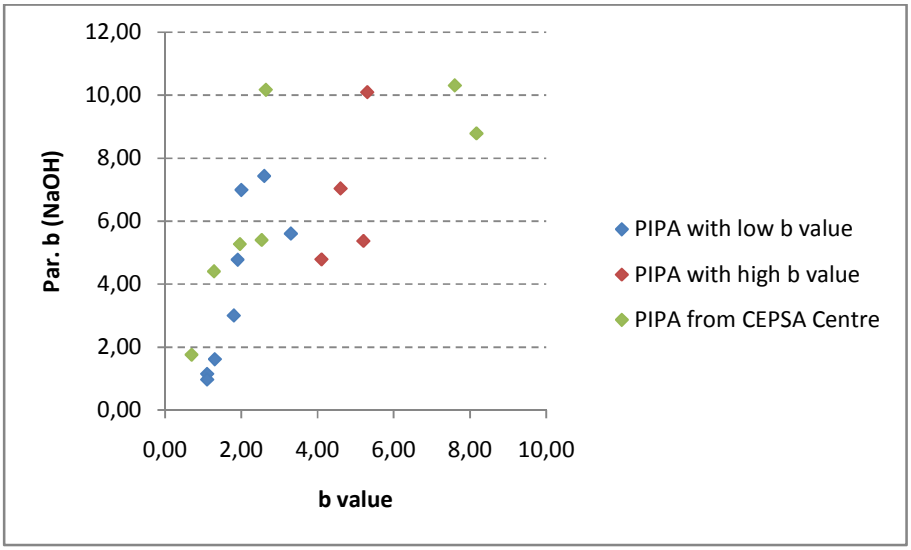



**Figure 29:** Relation between Parameter b (with NaOH) and *b value*.

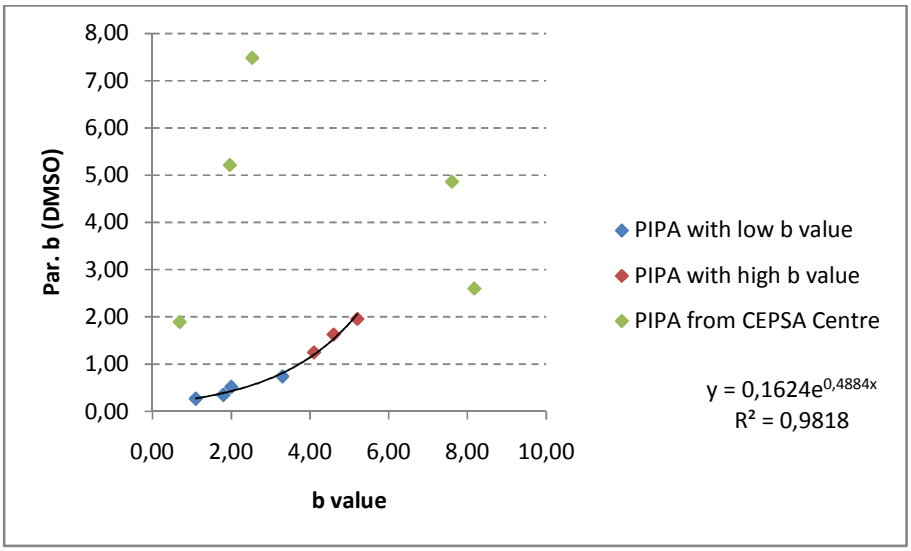



**Figure 30:** Relation between Parameter b (with DMSO) and *B value*.

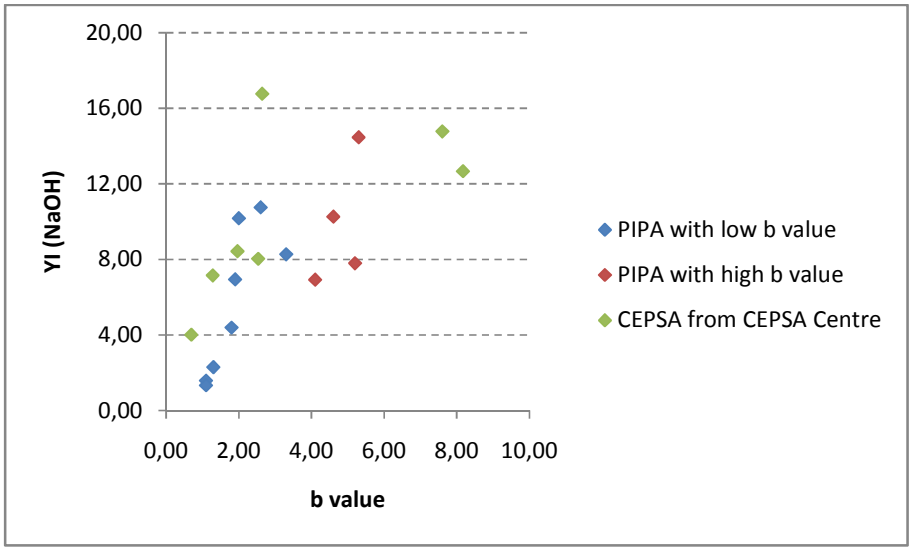



**Figure 31:** Relation between yellow index (with NaOH) and the *b value*.

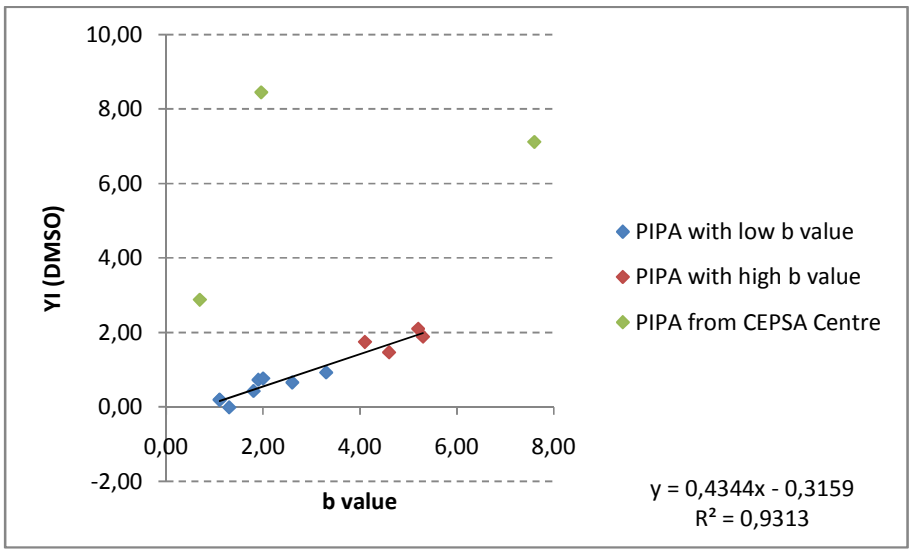



**Figure 32:** Relation between yellow index (with DMSO) and the *b value*.

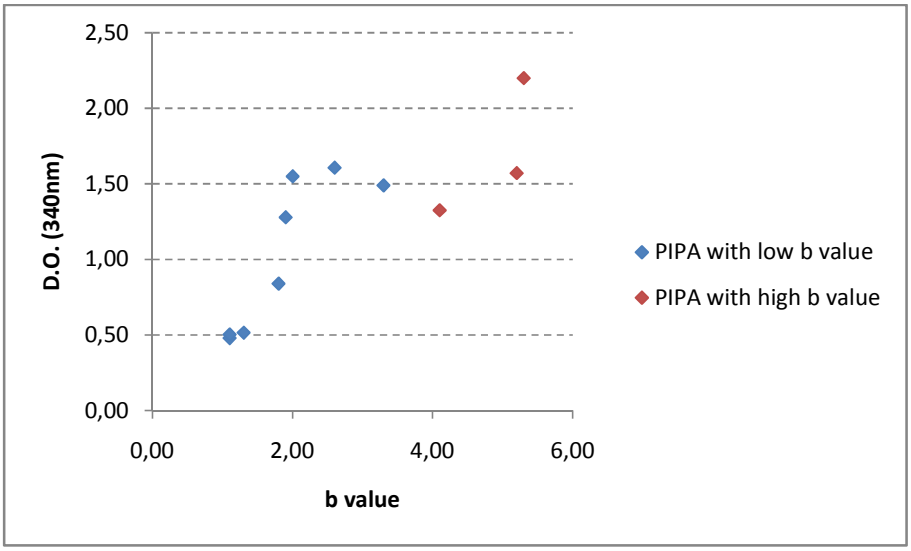



**Figure 33:** Relation between optical density and the *b value*.

From the Figure 29 it is possible to observe that for all PIPAs it is impossible to obtain a trendline to associate the parameter b, with NaOH as solvent, with *b value*.

The Figure 30, that relates the *b value* with parameter b with DMSO as solvent, shows that only for PIPAs produced in CEPSA QUIMICA exist a exponential correlation, but with a low correlation factor (0,9818). For PIPAs purified in CEPSA Centre this correlation is not applied, because the points are dispersed.

Once again it is impossible to obtain any relation using NaOH solution as solvent, because in Figure 31 all points are dispersed and no trendline is adjustable.

The relation between *b value* and the yellow index, with DMSO as solvent, represented in Figure 32 shows that only for PIPAs produced in CEPSA QUIMICA is possible to obtain a linear relation, but with a low correlation factor (0,9313). The yellow index with DMSO, as dissolvent, was obtained just for three PIPA's produced in CEPSA's Centre, and with these three points was not viable to get any correlation.

The optical density, was only determined for PIPAs produced in CEPSA QUIMICA because was not obtained any good relation for the others parameters, so was used the products that the CEPSA' Centre had in more quantities. The relation between the *b value* and the optical density at 340nm, represented in Figure 33, once again was not possible to get any good linear relation.

Aqueous NaOH solution was initially used, but after the suspicion that this solvent has been alternating the properties of the isophthalic acid, because of the changes from the acid form to the basic form and again to the acid form, was used dimethyl sulfoxide for being an

aprotic solvent. The results obtained were the same, it means that neither with DMSO a good relation for all PIPAs was obtained.

The next figure shows the changes provoked by the alteration of the dissolvent. The blue points represent the some samples dissolved in NaOH, the red ones represent the same samples but with DMSO, and the yellow points represent few samples dissolved with DMSO and filtrated with a 0,22μm filter. It was possible to observe a good alteration in the correlation factor in result to the change of dissolvent, although was only possible to get a 0,9842 correlation factor. It observed that almost every sample have adjusted the logarithmic curve, but the sample PIPA SOL C-1, C-4, C-6, C-10 had a different behaviour. The C-1 and C-4 were produced with nitrogen, so it is reasonable that these two samples had a different behaviour because, did not suffered a hydrogenation. The C-6 and C-10 produced with hydrogen, but the C-6 with fresh catalyst and C-10 with used catalyst, so from Figure 34 it is observed that with used catalyst the parameter b increase and with fresh catalyst the parameter b reduce.

With all these data, was conclude that exist any phenomenon in the treatments made in CEPSA's Centre affect the measured parameters, so it is not possible to get any reliable relation. The solution to get a real *b value* was to send the samples to CEPSA QUIMICA, so in their laboratories this colour parameter was measured.

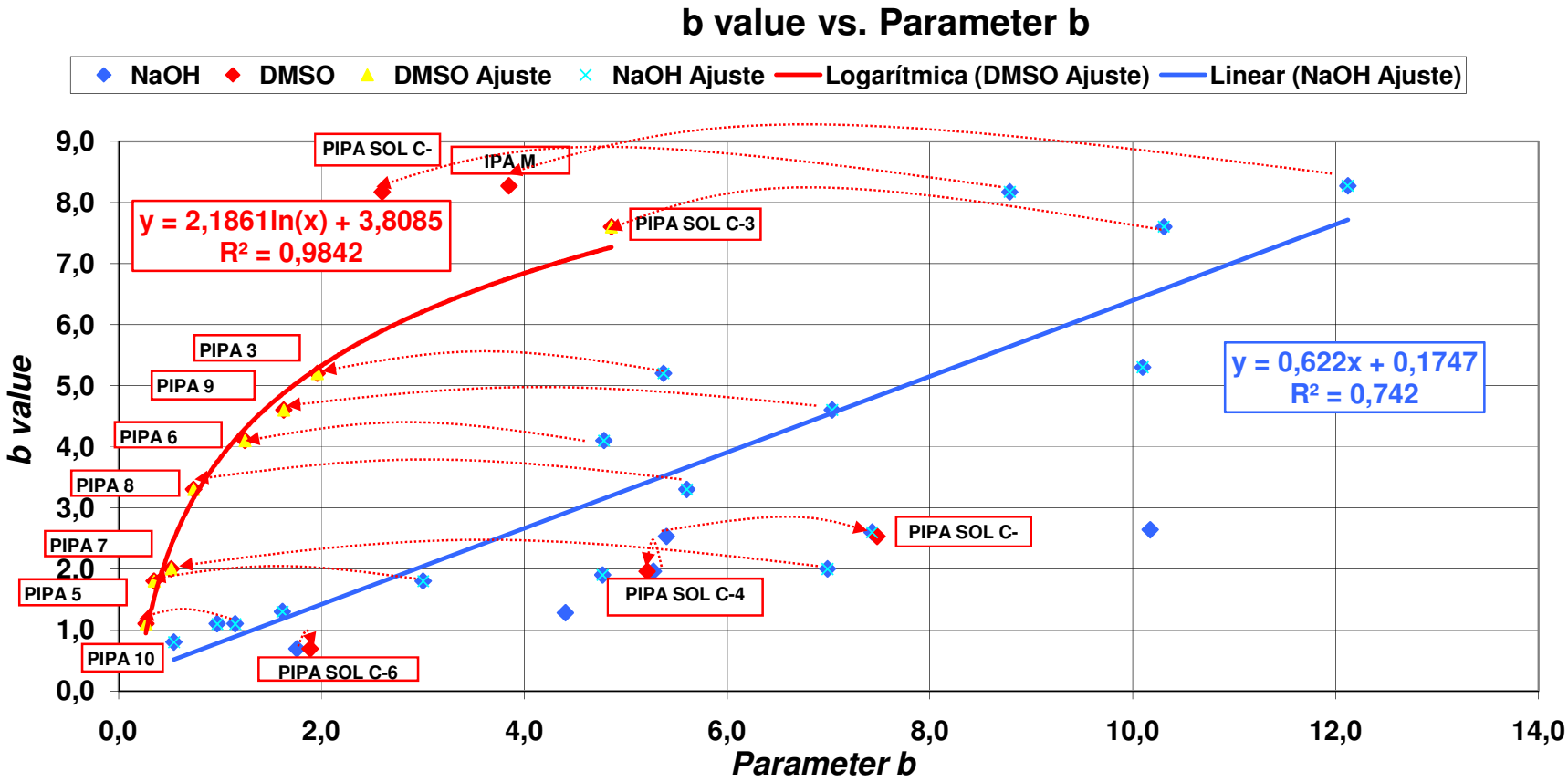



**Figure 34:** Graphic representation from the parameter b and the *b value*, with both solvents, NaOH and DMSO.

## *3.5 Hydrogenations in Autoclave Reactor*

It was decided to send all samples produced in CEPSA's Centre to CEPSA QUIMICA to measure the *b value of experimental samples* with their own technique in order to homogenize the analytical procedure, so no solvent would be applied. The *b value* measured by CEPSA QUIMICA use a wafer, so no exist any interference produced by the dissolvent.

After knowing the compounds that could be responsible for the yellow colour, it was planed a whole of tests to know the influence of some variables on these impurities. The variables that were tested were the temperature, pressure and time of hydrogenation. These variables were chosen because, at a fixed LHSV (conditioned by market demands, although it could be adjusted into a short operative range), the only parameters that could be adjusted to improve the colour of the final product were T and P.

**Table 16:** Operational condition in the process of purification of IPA.

| Condition | Value |
|---|---|
| Temperature, °C | 224 |
| Pressure, bar | 34 |
| IPA/ catalyst/time, kg IPA/kg catalyst.h | 5,7 |

These reactions were made in semi-batch conditions. The conditions applied to this system were batch for IPA and catalyst, and continuous for hydrogen. In the laboratory it was not possible to reproduce the purification in a fixed bed due to its operational problems. As it was described before, IPA was very low solubility with water, so all system had to be at high temperatures. One of the problems is the cold points that mean that if IPA passed by some equipment that did not had the defined conditions, IPA would crystallize and the system would have a problem to flow the product.

Initially was made a study to know the quantities to use in these tests. In the system (autoclave reactor) there was a conditional factor, because the catalyst basket only has a capacity to have a determined weight. So after knowing the weight of catalyst, the weight of IPA and the volume of water could be determined. In the factory the percentage of IPA in solution after the oxidation reactor is 35%, but the tests were made with 20%, to have more wet area of the catalyst basket.

The weight of catalyst that can be in the catalyst basket is 10,5g, in average, so the quantity of IPA would be 59,85g/h. If the percentage of IPA in solution was 35%, the volume of water would be 111mL, but if the percentage of IPA in solution was 20%, the volume of water would be 239mL.

To wet all catalyst's basket would be necessary a volume of slurry of 391mL, so if the percentage of IPA in solution would be 35%, the total volume of slurry would be 171mL, because the slurry density is approximately 1g/cm$^3$, and if the percentage of IPA in solution would be 20%, the total volume would be 299mL. So, for these two percentages the basket would not be totally wet so the solution was to double the weight of IPA, without changing the relation with the catalyst. To maintain the relation between IPA and the catalyst the time of hydrogenation passed for two hours, instead of one hour. With the double quantity of IPA in solution only the percentage of 20% could wet the all basket, because was possible to get a total volume of 598mL, more than 391mL, and instead of the 342mL produced by the 35% of IPA in solution.

As it was explained before, the hydrogenation reactions were made in batch, so it was need to find a velocity of rotation similar to the linear velocity observed in the hydrogenation reactor from the factory. It was known that the linear velocity of the purification reactor was 65,82cm/min, so if the angular velocity of this system was approached to the linear velocity verify in the factory, it could be possible to apply the next equation.

$$v = w \times R \qquad \textbf{Eq. 10}$$

$v - linear\ velocity$
$w - angular\ velocity$
$R - radius$

The whole catalyst basket contains four small baskets, represented in Figure 35. The radius is approximately 1cm, so the angular velocity should be 66rpm. Unfortunately, at this velocity, the external diffusional limitations are not totally eliminated due to a complex scale-down step related to different operating procedures (fixed bed vs. rotating basket). That is because not all the transversal liquid flow passes through the catalyst area, as there exist an empty space between basket and reactor wall, so a fraction of the liquid do not cross catalyst basket (see figure from Table 6) . In order to minimize external restrictions, a 10x safety factor was employed to assure a minimal external mass transfer resistance. So the angular velocity applied was 600rpm.

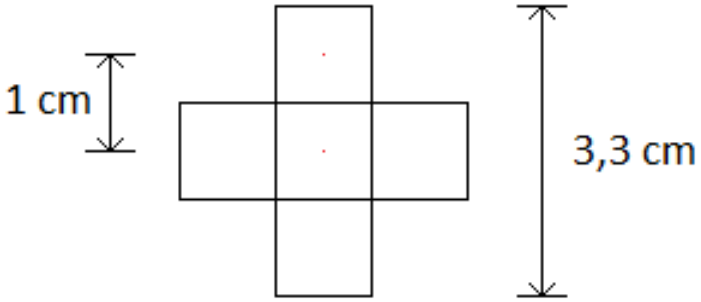



**Figure 35:** Scheme of the catalyst basket.

**Table 17:** Hydrogenation's reactions in the autoclave reactor.

| Test | Temperature, °C | Pressure, bar | % IPA | Weight of catalyst weighed, g | IPA | Weight of IPA, g | Weight of IPA weighed, g | Weight of water, g | Volume of water (mL) | Weight of Slurry, g | Catalyst | Time, h | *b value* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 224 | 34 | 20% | 10,585 | IPA M | 119,63 | 119,63 | 479 | 480 | 599,63 | A | 2 | 1,45 |
| 2 | 237 | 38 | 20% | 10,582 | IPA M | 119,60 | 119,62 | 478 | 480 | 599,62 | A | 2 | 0,86 |
| 3 | 237 | 30 | 20% | 10,502 | IPA M | 118,69 | 118,73 | 475 | 475 | 593,73 | A | 2 | 1,52 |
| 4 | 212 | 38 | 20% | 11,082 | IPA M | 125,16 | 125,16 | 500 | 500 | 625,16 | A | 2 | 1,50 |
| 5 | 212 | 30 | 20% | 10,952 | IPA M | 123,78 | 123,84 | 495 | 495 | 618,84 | A | 2 | 2,13 |
| 6 | 224 | 34 | 20% | 10,693 | IPA M | 120,85 | 120,51 | 482 | 485 | 605,51 | A | 1 | [1] |
| 7 | 237 | 38 | 20% | 10,475 | IPA M | 118,39 | 118,48 | 474 | 475 | 593,48 | A | 1 | [1] |
| 8 | 237 | 30 | 20% | 10,731 | IPA M | 121,28 | 121,38 | 485 | 485 | 606,38 | A | 1 | [1] |
| 9 | 212 | 38 | 20% | 10,603 | IPA M | 119,84 | 119,73 | 479 | 480 | 599,73 | A | 1 | [1] |
| 10 | 212 | 30 | 20% | 11,119 | IPA M | 125,67 | 125,68 | 503 | 505 | 630,68 | A | 1 | [1] |

[1] This value was not available, at time, for this work

These samples were also analysed by HPLC. The following analysis was made considering the areas of peaks from the impurities indentified before present in the chromatograms obtained by HPLC (Appendix 6.1). This evaluation has an error of 0,1%.

From chromatograms was detected that at 237°C:

- Biphenyl tricarboxylics do not suffer changes with the increase of the pressure;
- Benzophenones dicarboxylics, also, do not suffer changes with the raise of the pressure;
- Biphenyl dicarboxylics decrease with the raise of the pressure;
- Fluorenones dicarboxylics maintain without alterations to the increase of the pressure.

From chromatograms at 212°C

- Methyl benzene dicarboxylic rises with the increase of pressure;
- Biphenyl tricarboxylics, also, rise with the increase of pressure;
- Benzophenones dicarboxylics do not suffer alterations with the increase of pressure;
- Biphenyl dicarboxylics also keep without changes with the increase of pressure;
- Fluorenones dicarboxylics maintain without alterations to increases of pressure.

At 30 bar, the chromatograms obtained show that:

- Methyl benzene dicarboxylic decrease with the raise of temperature;
- Biphenyl tricarboxylics have a increase facing the increase of temperature;
- Benzophenones dicarboxylics keep without alterations to the increase of temperature;
- Biphenyl dicarboxylics also keep without changes facing the increase of temperature;
- Fluorenones dicarboxylics decrease with the raise of temperature.

At 38 bar, it is observed that:

- Methyl benzene dicarboxylics decrease with the raise of temperature;
- Biphenyl tricarboxylics decrease with the increase of temperature;
- Benzophenones dicarboxylics also decrease with the increase of temperature;
- Fluorenones dicarboxylics decrease with the raise of temperature;

The temperature is from these two variables, the one which has more influence on the changes of the impurities. This observation is based on the kinetic law, because temperature

affects exponentially the reaction's velocity (affect directly the $K_0$ – reaction velocity constant) and the pressure is normally affected by a power coefficient.

The variable time of hydrogenation has more influence on the fluorenones dicarboxylics, because is the area of these peaks that suffer more changes. With only one hour of hydrogenation the area of fluorenones dicarboxylics is higher than with two hours, it means that exist more of this compound with one hour of hydrogenation. These fluorenones dicarboxylics can be the result of condensation of benzoic acid and formyl benzoic acid.

With the results from the laboratory from CEPSA QUIMICA, it was possible to associate the conditions of hydrogenation with the *b value*. The results with two hours of hydrogenation are in Table 18 and are represented in Figure 36.

**Table 18:** *b value* of PIPAs with two hours of hydrogenation.

| | | **Temperature, ºC** | | |
|---|---|---|---|---|
| | | **212** | **224** | **237** |
| **Pressure, bar** | **30** | 2,13 | ——— | 1,52 |
| | **34** | ——— | 1,45 | ——— |
| | **38** | 1,50 | ——— | 0,86 |

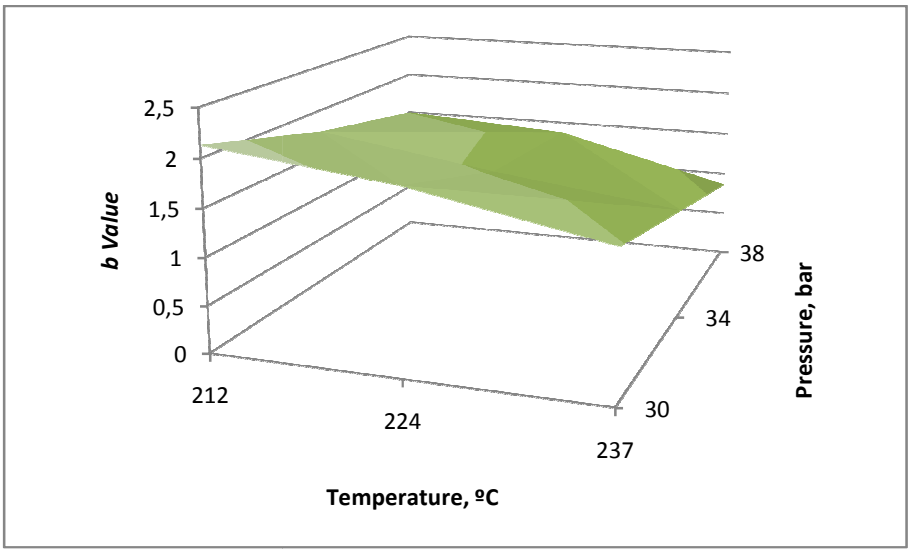



**Figure 36:** Representation of the *b value*, with temperature and pressure.

From the last figure is possible to see that the *b value* decrease with the high temperatures and high pressures. As it was shown before, temperature is the most important variable, but high pressure also improves this reaction. This pressure is the sum of vapour pressure, because IPA is dissolved in water, and hydrogen pressure. With the increase of temperature, the vapour pressure also increase, so to keep the total pressure constant the hydrogen pressure decrease.

# 4 Conclusion

In this work, different kinds of systems to hydrogenate the IPA were proved, and after that the main objective was to identify the impurities responsible for the yellow colour of IPA and to see the influence of variables as temperature, pressure and hydrogenation time.

The tested systems to hydrogenate at laboratory scale showed that they are not reproducible. The other problem of these systems was the use of NaOH as solvent, so they do not represent the reality of a hydrogenation at an unit device, because the solvent used is water at high temperature and pressure.

The reuse of used and washed catalyst did not have good results, because the percentage of non polar area did not reduce, it means that the different solvents used to wash the used catalyst were not the most efficient.

With these results was need to know which were the impurities responsible by the yellow colour of PIPA, so using one work developed in Analysis Department of CEPSA and chromatograms obtained by HPLC was concluded that the yellow compounds could be fluorenones, tricarboxylics phenyls. This impurity may appear in the final product due to a condensation between benzoic acid and 3-formyl benzoic acid, which are by-product of isophthalic acid.

Besides that, was intent to obtain a method to relate the *b value* with a colour parameter, so the samples could be analysed in the laboratory of CEPSA instead of being send to CEPSA QUIMICA to measure the *b value*. The numerous tests that were made shown that no exists one parameter that could be linked with the *b value*. With this colorimetry analysis was possible to comprove that the NaOH as dissolvent pulled apart the results, and the best solvent was the dimethyl sulfoxide.

The hydrogenations planned to be made in the autoclave had the goal to see the influence of temperature, pressure and time of hydrogenation on *b value*. The temperature had a range between 212°C and 237°C, the pressure between 30bar and 38bar and time of hydrogenation was one and two hours.

Between temperature and pressure, is the temperature the variable that has more influence, because in a kinetic law, the velocity of reaction is affected exponentially by the temperature and pressure affect the reaction velocity by a power coefficient. Time of hydrogenation shows more influence in the fluorenone dicarboxylics area, because the possible condensation between benzoic acid and formylbenzoic acid has more quantity in its peak with only one hour than with two hours.

*B value*, only for two hours of hydrogenation, decreases with the increase of temperature and pressure, because with most extreme conditions the hydrogenations are favoured. And it is possible to observe in Table 17 the lower *b value* (0,86) is obtained for 237°C and 38bar. The PIPA obtained with these conditions is a very good PIPA because the *b value* is very low and it is the lowest b value obtained in CEPSA Centre and in CEPSA QUIMICA.

For the future, it suggested to do more experimental points and to apply HPLC-MS to quantify the impurities and to create a relation between the operational conditions, *b value* and the quantity of the identified impurities. Other suggestion is to get a kinetic model, to understand the alterations provoked by temperature and hydrogen pressure.

# 5 References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# 6 Appendix

## *6.1 Appendix 1 - Chromatograms from HPLC*

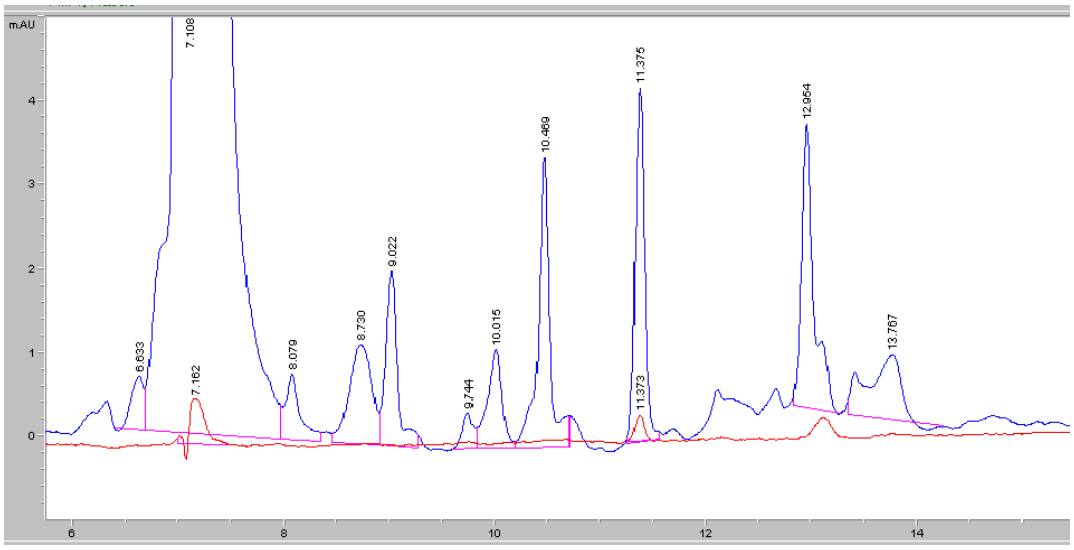


**Figure 37:** Chromatogram of hydrogenations in autoclave at 224°C, 34bar and 2 hours of hydrogenation.

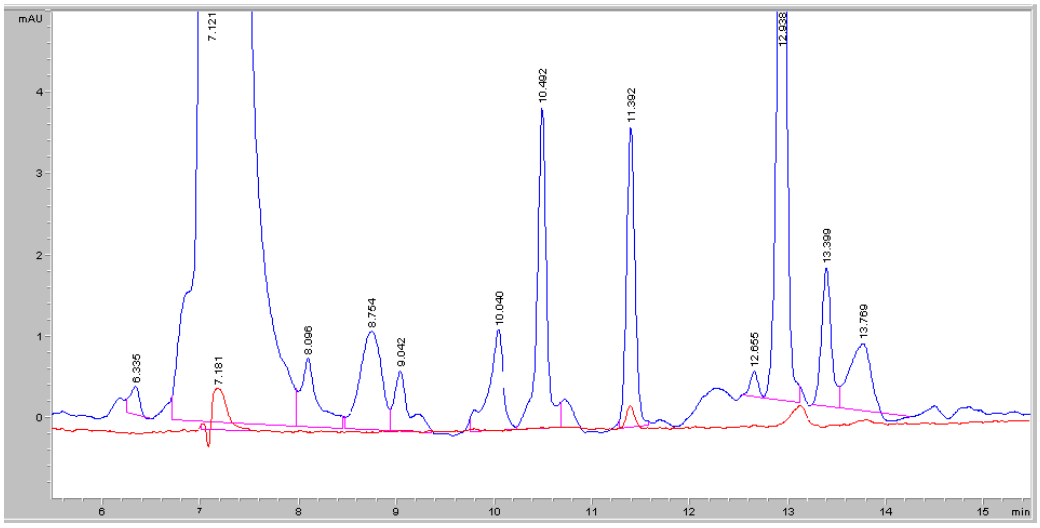


**Figure 38:** Chromatogram of hydrogenations in autoclave at 237°C, 38bar and 2 hours of hydrogenation.

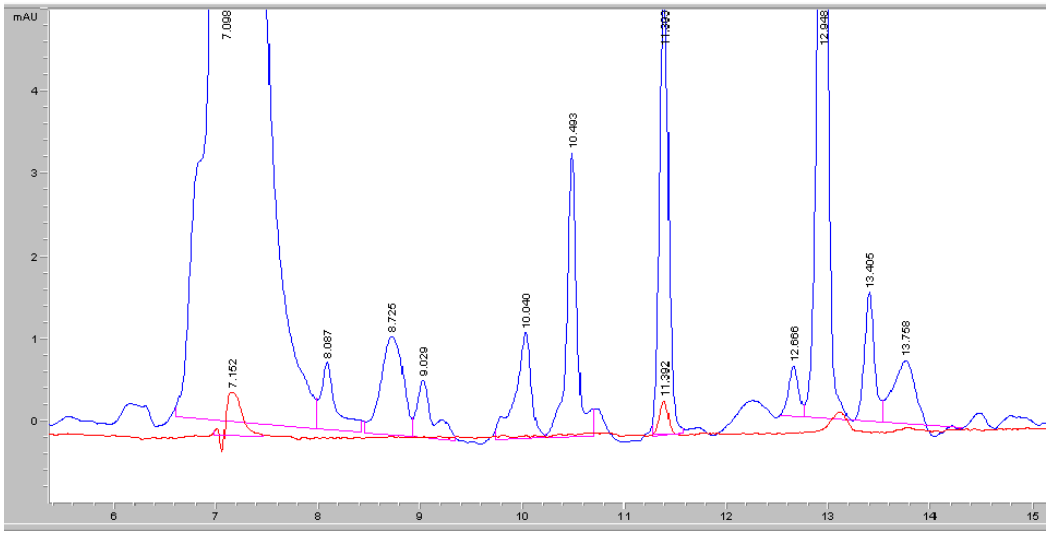


**Figure 39:** Chromatogram of hydrogenations in autoclave at 237°C, 30bar and 2 hours of hydrogenation.

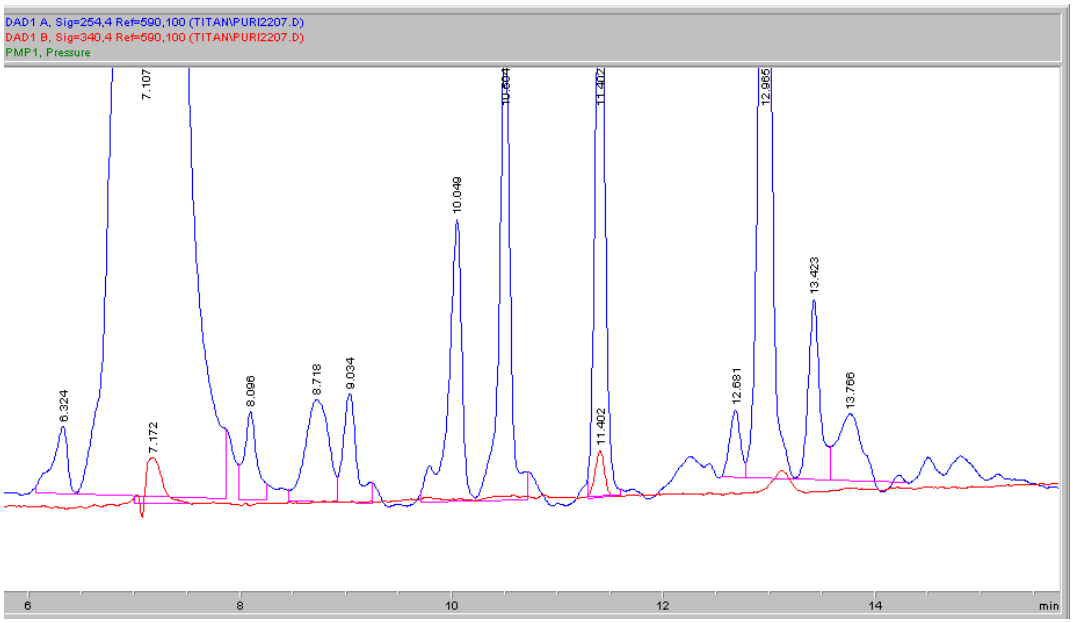


**Figure 40:** Chromatogram of hydrogenations in autoclave at 212°C, 38bar and 2 hours of hydrogenation.

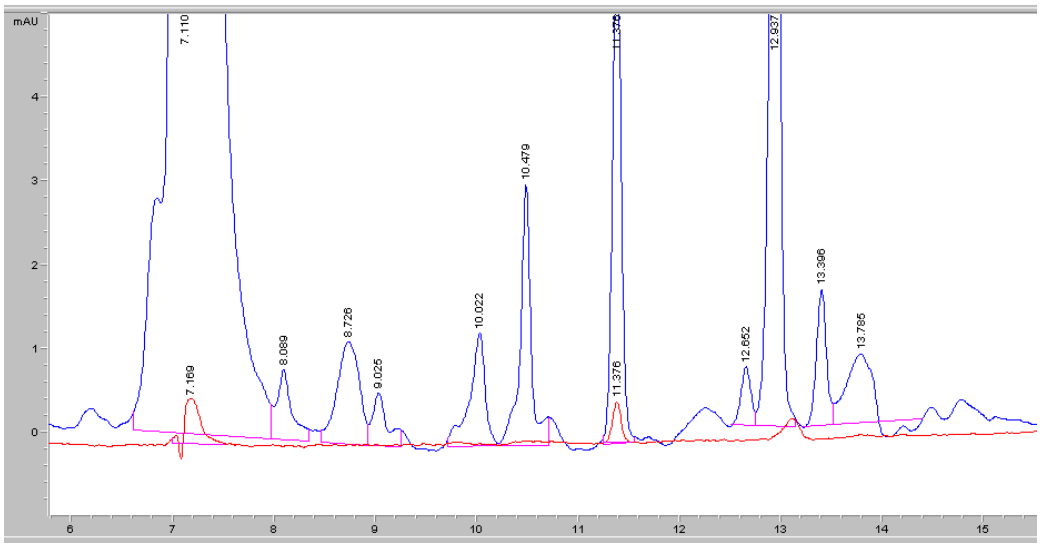


**Figure 41:** Chromatogram of hydrogenations in autoclave at 212°C, 30bar and 2 hours of hydrogenation.

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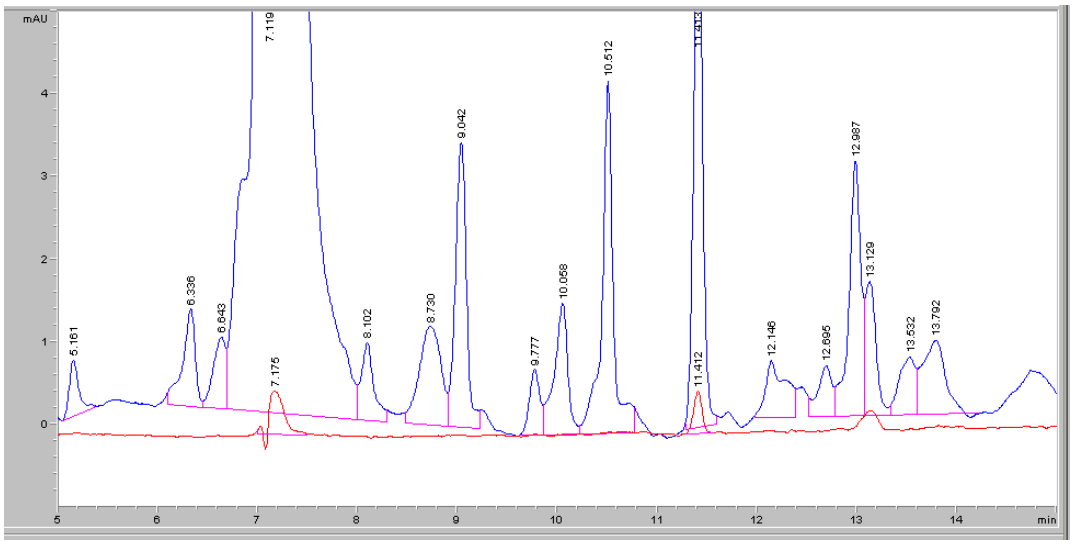


**Figure 42:** Chromatogram of hydrogenations in autoclave at 224°C, 34bar and 1 hours of hydrogenation.

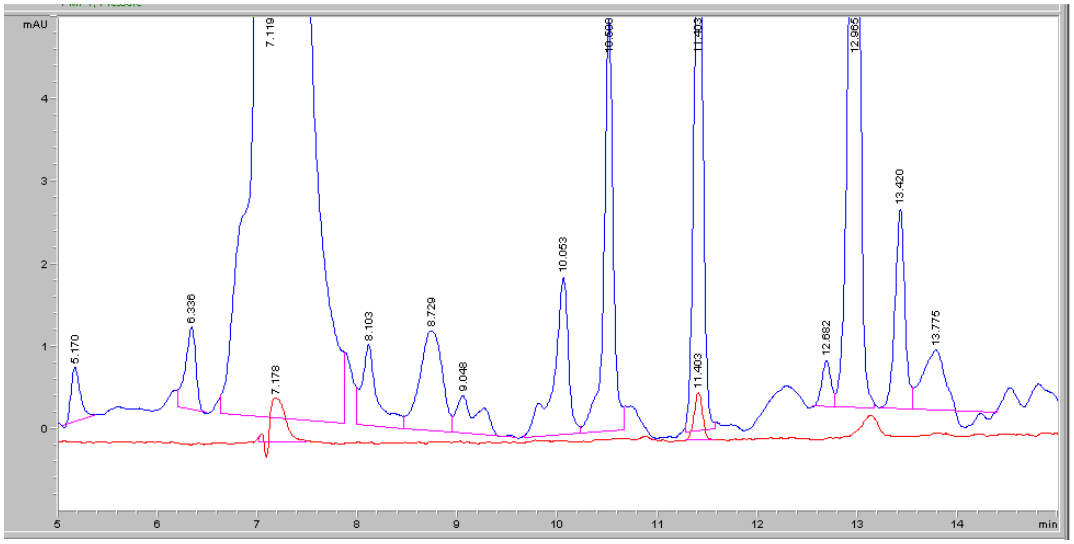


**Figure 43:** Chromatogram of hydrogenations in autoclave at 237°C, 38bar and 1 hours of hydrogenation.

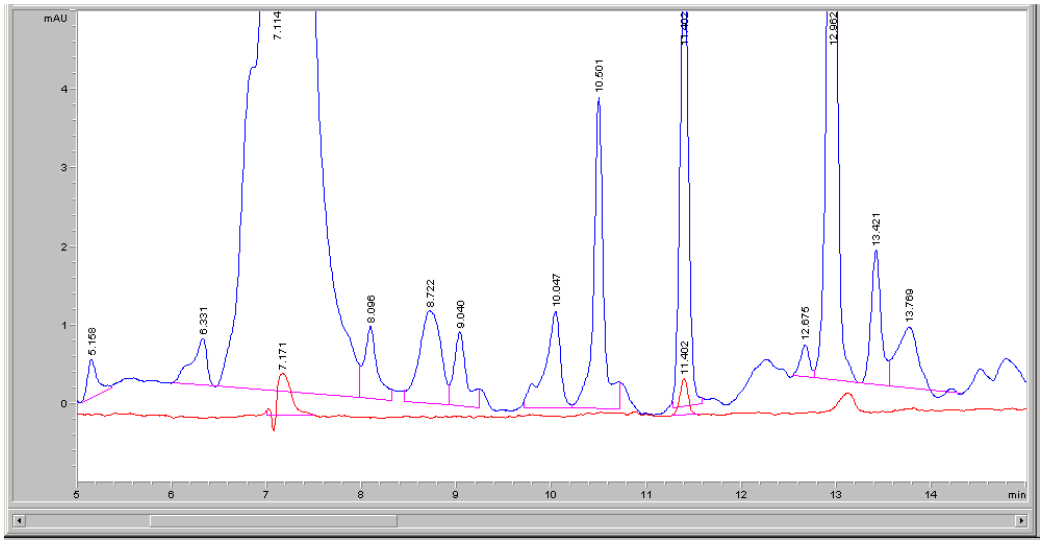


**Figure 44:** Chromatogram of hydrogenations in autoclave at 237°C, 30bar and 1 hours of hydrogenation.

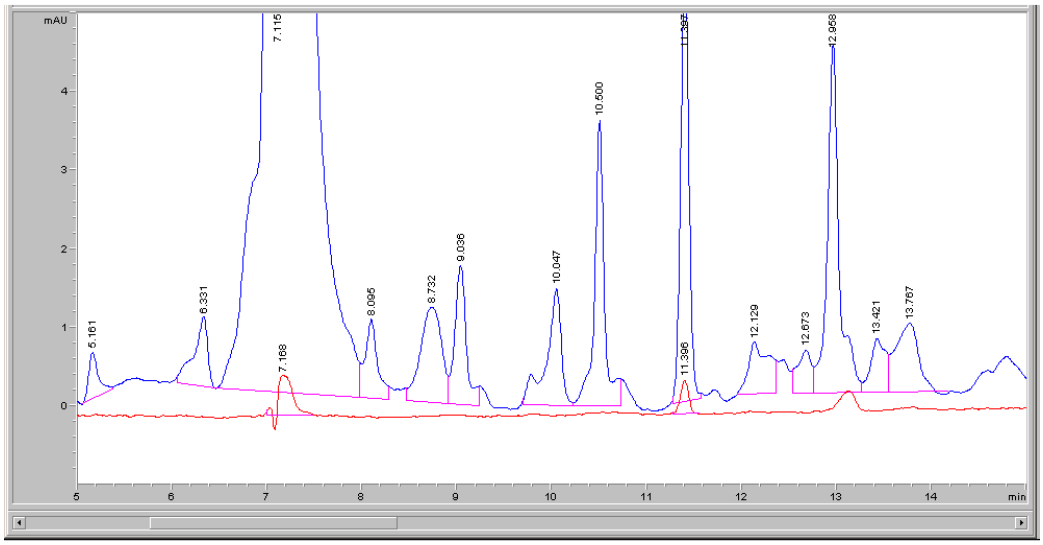


**Figure 45:** Chromatogram of hydrogenations in autoclave at 212°C, 38bar and 1 hours of hydrogenation.