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Cumene oxidation to cumene hydroperoxide

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Dissertação para obtenção do grau de Mestre em

Engenharia Química

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Resumo

O presente trabalho teve como objectivo o estudo da oxidação de cumeno a hidroperóxido de cumeno (CHP), a reacção chave de um processo industrial de produção de fenol.

Pretendeu-se estudar a oxidação de cumeno a CHP a fim de poder-se optimizá-la, determinando as condições óptimas de operação, bem como escolhendo o catalisador mais adequado para melhorar o processo, aumentando a selectividade a CHP e a velocidade de oxidação. Foi necessário estabelecer um equilíbrio entre a velocidade de oxidação de cumeno e a selectividade a CHP.

Concluiu-se que para obter as condições a que se trabalha actualmente na CEPSA QUÍMICA: 93ºC, uma velocidade de oxidação de cumeno de $15 g.l^{-1}.h^{-1}$ e uma selectividade a CHP de 91%, o melhor catalisador é um óxido misto de manganês e outro metal, suportado. Com este catalisador, consegue-se também alcançar as condições com que se pretende trabalhar de futuro, 80ºC com uma velocidade de oxidação na ordem das $12\text{-}15 g.l^{-1}.h^{-1}$ e uma selectividade a CHP em torno dos 93-95%.

Palavras – Chave

Cumeno
CHP
Catalisador
Selectividade
Velocidade de oxidação

Abstract

This work is based on the study of cumene oxidation to CHP, the key reaction of a phenol production industrial process.

It is intended to study the cumene oxidation to CHP in order to be able to optimize it, determining the optimal operation conditions as well as choosing the most suitable catalyst that improves the process, increasing the selectivity to CHP and the oxidation rate. It is needed to establish an optimized balance between oxidation rate of cumene and selectivity to CHP.

It was concluded that to work under the actual conditions of CEPSA QUÍMICA, 93ºC with an oxidation rate of IPB of 15g.l^{-1}.h^{-1} and a selectivity to CHP of 91%, the best catalyst is a supported mixed oxide composed by manganese and other metal. With this catalyst, it is also possible to achieve the desired conditions to operate in the future, 80ºC with an oxidation rate in the range of 12-15g.l^{-1}.h^{-1} and a selectivity to CHP around 93-95%.

Key-words

Cumene
CHP
catalyst
selectivity
oxidation rate

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Abbreviations list

IPB – isopropylbenzene
CHP – cumene hydroperoxide
DIPB – diisopropylbenzene
DMPC – dimethylphenylcarbinol
ACP – acetophenone
AMS – α-methylstyrene
CAC – crude acetone column
Cu – copper
CuO – cupric oxide
Mn – manganese
L/d – length/diameter
XRF – X-ray fluorescence
HPLC – high performance liquid chromatography
GC-MS – Gas chromatography – Mass spectrometry
S_{BET} – BET surface area

1. Introduction

This work is based on the study of cumene (or isopropylbenzene – IPB) oxidation to cumene hydroperoxide (CHP), the key reaction of the phenol production industrial process currently in use worldwide [1].

All experimental work was performed in the CEPSA Research Center (*Compañía Española de Petróleo S. A.*) in Alcalá de Henares.

1.1. History of commercial phenol production

Until the advent of commercial phenol synthesis in the early part of the twentieth century, the only available source of phenol was a natural physical by-product recovery of coal and petroleum refinery operations. Since that time, synthetic phenol production has grown in importance to the extent that it now accounts for all nearly all global output required to keep pace with the growth in global demand [2].

More than 99% of phenol produced worldwide is from synthetic processes. The first synthetic phenol was produced by sulfonation of benzene and hydrolysis of the sulfonate [3]. In 1924, Dow Chemical started to commercialize synthetic phenol based on the direct chlorination of benzene to chlorobenzene, but later a different variation of this process was developed based on the oxychlorination of benzene with hydrochloric acid (HCl) to form chlorobenzene. In the early 1960s Scientific Design developed a non-chlorination route to phenol based on the production of cyclohexane intermediate and Schenectady Chemical Company attempt to commercialize a direct air oxidation route for benzene-to-phenol, based on the vapor phase oxidation of benzene.

In 1940 Hercules and BP Chemicals began the development of the CHP based route to phenol, which since that time has become the dominant technology in the world for the production of phenol [2]. The drawback of this process is the substantial extent of acetone co-production – 0.46 kg of acetone and 0.75 kg of phenol per kg of cumene feedstock [3]. The CHP based route is about 95% of world synthetic phenol production and its principal licensors are KBR (Kellogg-Brown&Root), Sunoco/UOP and GE/Lummus [4].

Since the market for acetone is much lower than the market for phenol, it justifies the investment and technology development for more profitable processes [5].

During the 1960s, DSM developed the toluene oxidation route to phenol production, but this route results in significant levels of by-products, such as benzaldehyde, benzyl alcohol and benzoic acid. Other commercial synthetic route to phenol known to be in current operation is a variation of the CHP route to phenol which incorporates acetone recycling, which is a technology developed by Mitsui. This approach eliminates the co-production of acetone that is converted to propylene which in turn reacts with benzene to form cumene [2].

One of the most promising challenges in the catalytic oxidation field is to obtain phenol from the direct oxidation of benzene, and there were several developments in the last 15 years regarding the type of oxidants, catalysts and operation conditions. From the different approaches investigated, the ones that stand out are those involving oxidation with nitrous oxide or hydrogen peroxide [6].

1.1.1. Phenol demand

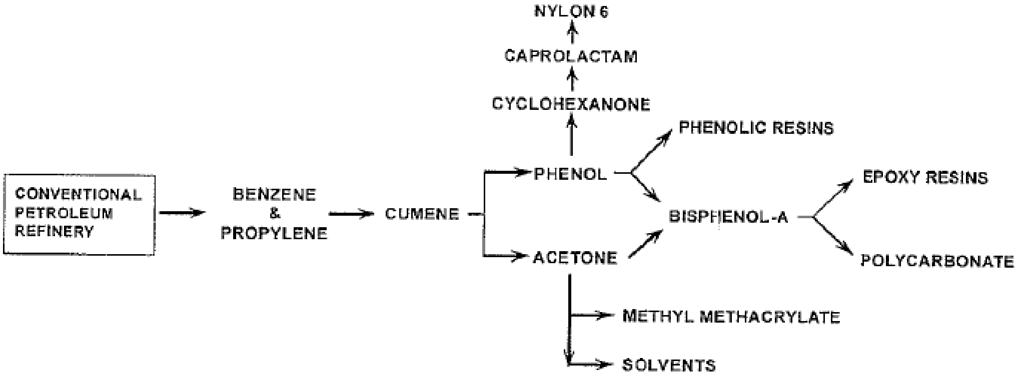

Figure 1 - Petrochemical market value chain for CHP based phenol production.

The dominant derivative growth market for phenol is bisphenol A [2], which is obtained from phenol and acetone, and has become increasingly important as the starting material for polycarbonates and epoxy resins. Phenol is also used to produce phenol-formaldehyde resins. Aniline can be obtained from phenol, where the hydroxyl group of phenol is substituted by means of ammonolysis. Adipic acid is obtained from phenol by oxidative cleavage of the aromatic ring. Salicylic acid is synthesized by addition of CO_2 to phenol.

All these products have considerable economic importance because they are used for the production of a wide range of consumer goods and process materials: adhesives, laminates, impregnating resins, raw materials for varnishes, emulsifiers and detergents, plasticizers, herbicides, insecticides and rubber chemicals [7].

Global phenol demand has been growing at an average annual growth rate of 4.2%/year since 1999 and it was projected to grow at an average annual growth rate of 4.8%/year until 2008 [2]. However, in 2008 the global production and consumption of phenol were almost 8.9 million metric tons despite the decrease of global capacity utilization from 94% in 2007 to 88%. Phenol consumption is estimated to have increased by 1.4% in 2008, and is expected an average growth of 4.3% per year from 2008 to 2013, declining to 2.8% per year from 2013 to 2018. Utilization rates are expected to increase gradually, ranging from the high 80s to the low 90s [6].

1.2. Phenol production in CEPSA

In the industrial center located in Nuevo Puerto, in Palos de la Frontera, Huelva, CEPSA has a company that is responsible for all the commercial phenol production in Spain: CEPSA QUÍMICA, before known as ERTISA. This company receives part of the feedstock from the refinery La Rábida, located next to it.

CEPSA QUÍMICA has two different production lines: methylamines and derivatives, and cumene, phenol and acetone [8].

1.2.1. Cumene production in CEPSA QUÍMICA

Cumene is produced by reacting benzene and propylene in the liquid phase over an acidic catalyst.

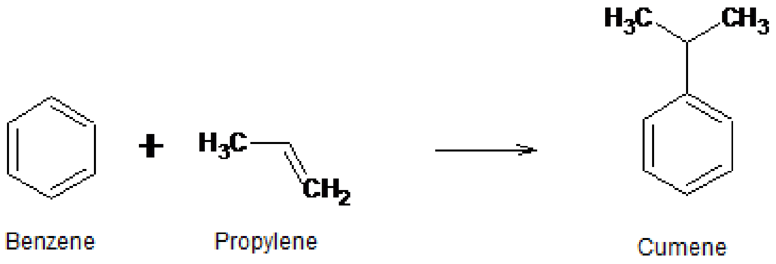

Figure 2 – Cumene production in CEPSA QUÍMICA.

The forward reaction, commonly called alkylation, is highly favored thermodynamically. This reaction is very selective, and *n*-Propylbenzene is the isomer more thermodynamically favorable than IPB, but is produced only as a minor by-product because the primary carbon in the propylene molecule is less reactive than the secondary carbon. The secondary carbon is chemisorbed on the acidic site of the catalyst to form a carbonium ion that then reacts with benzene to form IPB [3].

In CEPSA QUÍMICA the process used for producing cumene is the Q-Max process, patented by UOP, which uses an acid zeolite for alkylation of benzene with propylene, both supplied by the refinery. This zeolite is non-corrosive and regenerable, avoiding the significant maintenance and catalyst disposal problems associated with solid phosphoric acid and aluminum chloride systems [9].

A Q-Max unit consists of an alkylation reactor, a distillation section and a transalkylation reactor. Both of them are fixed-bed reactors [9].

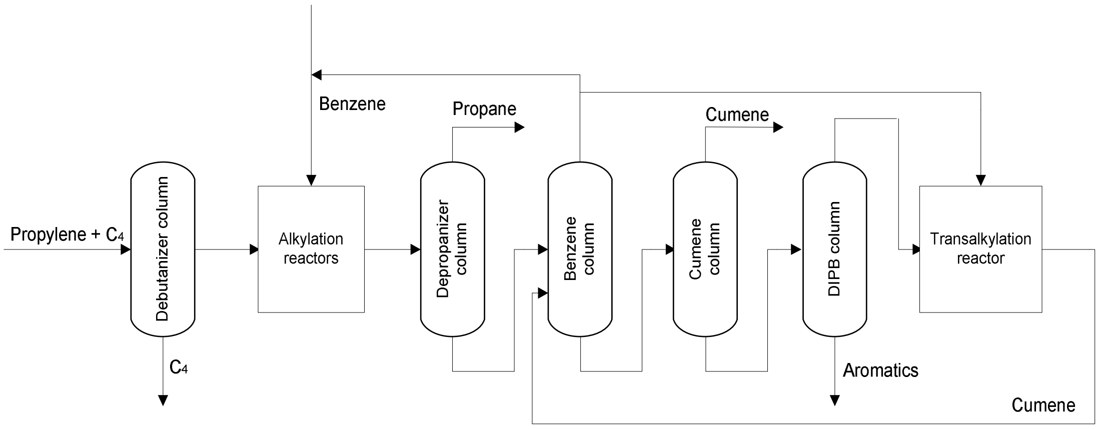

Figure 3 – Simplified flowsheet of cumene production in CEPSA QUÍMICA.

First of all, as propylene supplied has also butane and butene, it needs to be separated before following to the alkylation section. That process is carried out in a debutanizer column and pure propylene is obtained in a lateral flow [2].

Alkylation of benzene with propylene is the main reaction of the cumene production. This is an exothermic reaction. Benzene must be recycled to maintain the profile of temperature and the benzene-propylene ratio must be high [11]**Erro! A origem da referência não foi encontrada.**. Effluent from the alkylation reactor is sent to the depropanizer column and its bottom is sent to the benzene column where benzene is collected overhead and recycled. The benzene column bottom is sent to the cumene column where cumene product is recovered overhead. The bottom from this column, containing mostly diisopropylbenzene (DIPB), is sent to the DIPB column where DIPB is recovered and recycled to the transalkylation reactor. The bottom from the DIPB column consists of a small stream of heavy aromatic by-products which are normally blended into fuel oil. Steam or hot oil provides the heat for the product fractionation section.

A portion of the recycle benzene from the top of the benzene column is combined with the recycle DIPB from the overhead of the DIPB column and sent to the transalkylation reactor. In this reactor DIPB and benzene are converted to additional IPB. The effluent from the transalkylation reactor is sent to the benzene column.

The Q-Max process provides excellent cumene product quality, 99.97 wt% purity, and a near-stoichiometric cumene yield, higher than 99.7 wt% [9].

1.2.2. Phenol production in CEPSA QUÍMICA

CHP based route to phenol takes place in two reaction steps. In the first one IPB undergoes liquid phase oxidation by air to CHP and in the second one CHP is cleaved in the presence of an acid catalyst to form phenol and acetone as a co-product [2]. Both reactions are exothermic [11].

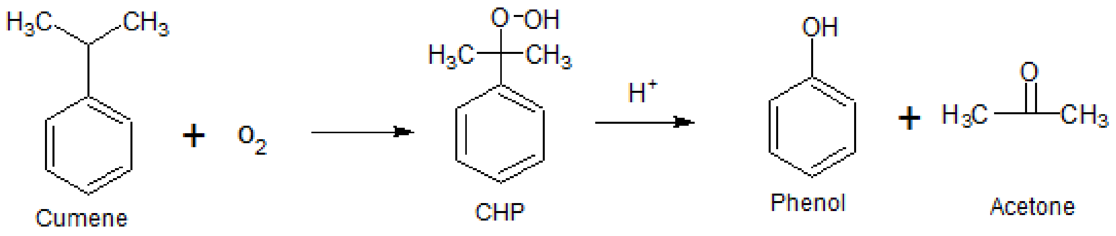

Figure 4 – Phenol production in CEPSA QUÍMICA.

Cumene oxidation to CHP proceeds through a free radical mechanism that is essentially auto-catalyzed by CHP [8]. CHP, as all the organic peroxides, has the peroxy function group, -O-O-, which is unstable and active, once that it is sensitive to heat and incompatible with many materials such as acids, bases, metals and ions [10]. So, it is stable at normal temperatures and conditions but it can decompose easily. The reaction is carried out in the presence of sodium carbonate or hydroxide, which performs as a buffer and neutralizes by-product organic acids formed during the course of reaction.

Major by-products formed in the oxidation reactor include dimethylphenylcarbinol (DMPC) and acetophenone (ACP). Increases in CHP concentration and temperature result in increased by-products, some of which inhibit the reaction rate (phenol as an example). Consequently, the reaction is preferably carried out in a bubblecap type column, or in a series of reactors, in which lower temperatures are maintained as the CHP concentration increases. The concentration of CHP in the oxidation reactor is kept between 20 and 30 wt% to prevent excessive by-product formation.

The second step of the phenol production starts with the excision reaction of CHP, which is highly exothermic and very quick. One approach to heat removal is refluxing acetone in the reactor.

Minor reactions occurring in the cleavage reactor include the dehydration of the DMPC formed in the cumene oxidation reactor to form α-methylstyrene (AMS), the reaction of DMPC with phenol to form cumyl phenol, and the dehydration of acetone to form mesityl oxide. The AMS may be recovered and sold for a by-product credit. Alternatively, the AMS may be dehydrogenated to form IPB, which can then be recycled to the oxidation reactor. A tarry residue composed of high boilers such as dimers of AMS and polymers is also formed in the cleavage reaction [2].

CEPSA QUÍMICA has three plants in operation to produce phenol. The plant 1 is stopped, nowadays, but it can work with recycles from plant 2 and plant 3. The plant 2 is the only one that never works with recycles, is the cleanest one. The plant 3 is working nowadays with recycles from plant 2 and plant 3, but used to work without any recycle when plant 1 is working.

1.2.2.1. Phenol plants

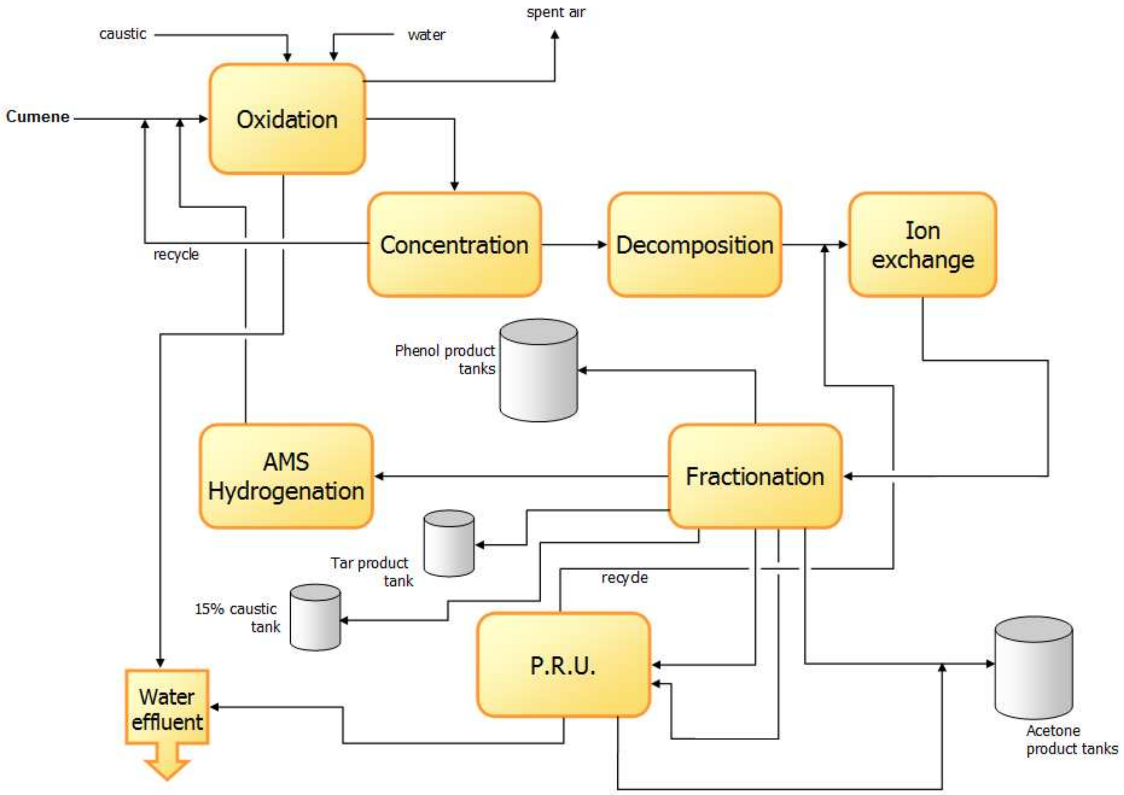

Figure 5 – Block diagram of phenol process.

The oxidation process of IPB to CHP takes place in four oxidation reactors in series. The oxygen required is directly obtained from the air and the reaction is carried out in an alkaline environment [12]. Soda is used to control the pH of the reaction and it is added continuously in aqueous solution at 5 wt%. The problem with the addition of soda is the possible formation of sodium salts by the reaction between CHP and soda.

The velocity of this chemical reaction increases with temperature and CHP concentration in the initiation step. However these conditions lead to the formation of by-products, so it must reach a compromise solution where the reaction rate is acceptable and the formation of by-products is minimum.

The output stream of the fourth oxidation reactor has a CHP concentration near 30% and it's concentrated by passing it through a preflash and three film vacuum evaporators. After this, the stream has a CHP concentration of about 80%.

The CHP excision reaction is highly exothermic and it occurs in two reactors. To eliminate the excess of acidity of the products, phenol and acetone, they pass through resins cameras. There are two resins cameras operating in series while a third one is in regeneration.

In the fractionation section, phenol and acetone are separated and purified. IPB and AMS are also separated and recycled to the oxidation section. Phenol is purified, by reaction of carbonyls, forming compounds with different boiling points that can be separated from phenol by distillation.

The fractionation section has six distillation columns in series. In the first fractionation section the crude phenol is separated from acetone, in two distillation columns. In the first one, crude acetone column (CAC), acetone is obtained in the head stream and all the other compounds are obtained in the bottom stream of the column, and in the second one, finished acetone column (FAC), acetone is separated from cumene, water and heavy hydrocarbons. Acetone is obtained in a lateral stream near the column head. In the second fractionation sector the crude phenol is separated from water and other compounds. There is a tar column to remove the heavy compounds obtained in the bottom stream of the CAC. The head stream of this column is sent to the AMS column, where AMS is separated from cumene and from phenol. In the phenol column, 2-metylbenzofuran (2MBF), traces of water, acetone and cumene are removed from phenol. Phenol is obtained in the bottom stream of this column, and its purity is about of 99,9%. It is sent to the phenol rectifying column where phenol is obtained in the head stream. The bottom stream is sent to the tar column.

The AMS obtained is washed with soda to remove traces of phenol. The portion not intended for sale is hydrogenated to recover cumene.

In phenol plant 1, when it is working, or nowadays in phenol plant 3, there is also a phenol recovery unit (PRU) where phenol is recovered from sodium phenolate (formed by reaction between phenol and soda), wastewater, cumene and AMS [11].

1.3. Cumene oxidation to CHP

Henceforth will be explained in more detail how occurs the cumene oxidation, taking into account the mechanism of the reaction, the compounds involved and the type of catalyst used.

1.3.1. Mechanism of cumene oxidation to CHP

The objective in oxidation is to maximize the selectivity of the IPB to CHP reaction while minimizing by-product formation, all the while maintaining the safest possible operating conditions. The major competing reactions result in the formation of DMPC and ACP [12].

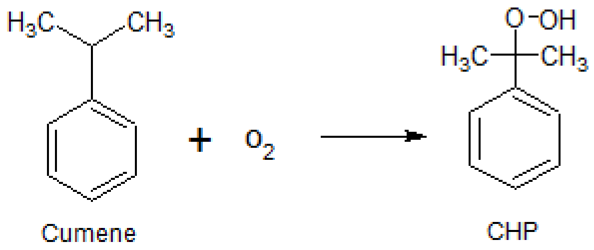

Figure 6 – Cumene oxidation to CHP.

This reaction releases 27,7kcal/mol, in liquid phase at 25ºC. The oxidation is a free radical chain reaction and the reaction mechanism involves three sequential steps: initiation, propagation and termination/combination. The free radical chain reaction proceeds autocatalytically following initiation.

Initiation can be described as the step that involves the generation of the cumyl free radicals. These radicals are generated by the thermal decomposition of CHP and the subsequent reaction of the intermediate radicals formed with IPB [12].

The initiator is the product of the reaction, CHP, and its presence favors the formation of radicals and thus improves the velocity of this phase. That is the reason why in all the reactions the feed presents 4% of CHP in the cumene.

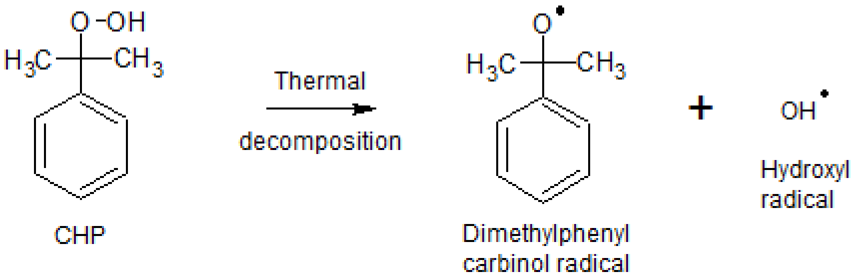

Figure 7 – CHP thermal decomposition.

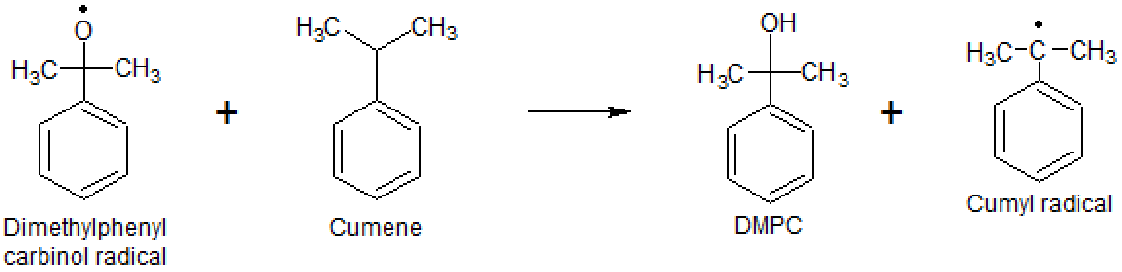

Figure 8 – DMPC and cumyl radical production.

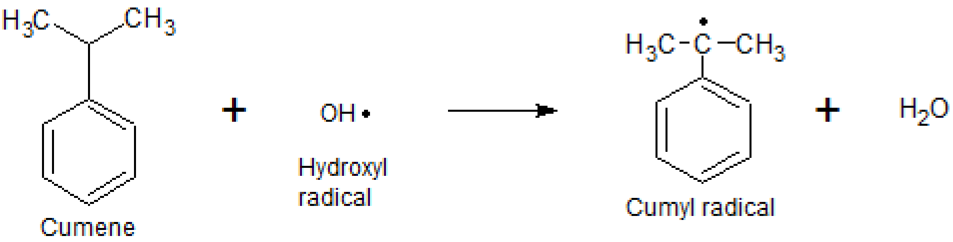

Figure 9 – Cumyl radical formation, from cumene and hydroxyl radical.

The cumyl radicals propagate the free radical chain reaction by reacting with oxygen to form CHP while the cumyl radical itself is regenerated. The second step, propagation, is the rate controlling reaction for cumene oxidation, as it involves both the formation of CHP and the cumyl radical [12].

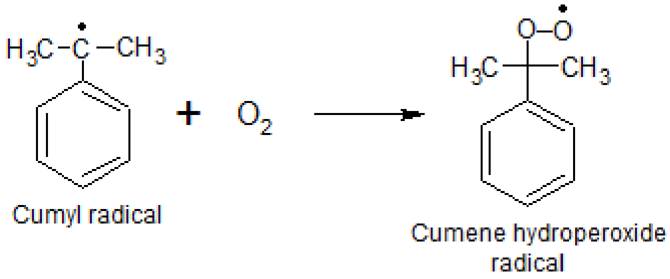

Figure 10 – Cumene hydroperoxide radical formation.

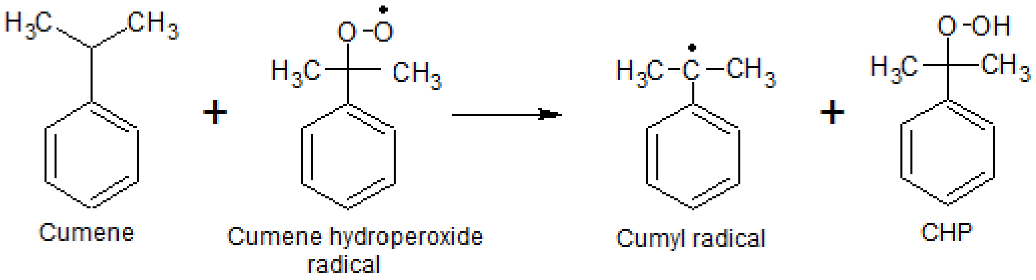

Figure 11 – CHP production.

Termination reactions cause disappearance of the radicals and thus stop the chain reaction [12]. In this step occurs the decomposition of the CHP and DMPC is formed, and subsequently is also formed AMS.

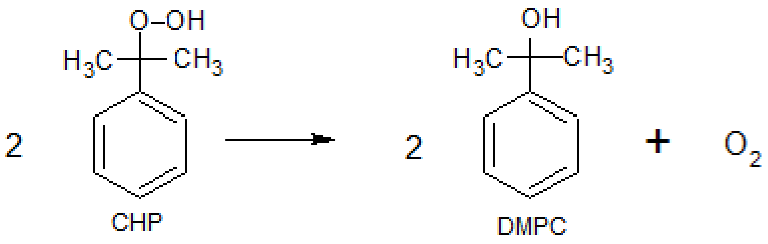

Figure 12 – DMPC production from CHP.

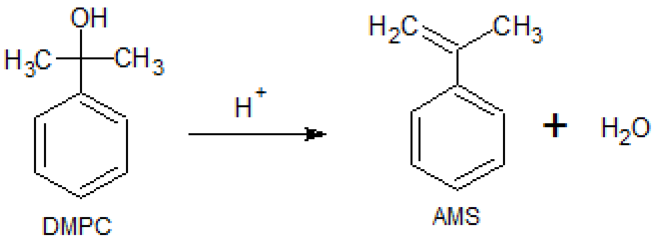

Figure 13 – AMS formation from DMPC.

ACP is formed from the dimethylphenyl carbinol radical or/and from IPB with oxigen.

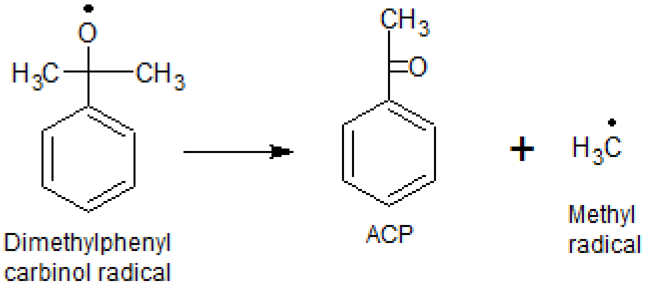

Figure 14 – ACP production.

Besides the by-products mentioned above, trace quantities of other by-products have been found, as dicumylperoxide and dicumylphenol.

Any phenol present in the oxidation system will inhibit the oxidation reaction. The cumene peroxide radical reacts with a phenol molecule to form CHP and a phenyl radical, but this radical does not have the power to attack IPB to continue the chain (and is ultimately removed from the system by reaction with another radical).

1.3.2. Catalysts used in the cumene oxidation to CHP

The development of efficient catalysts for the selective oxidation of hydrocarbons by molecular oxygen has remained a difficult challenge to the catalytic science.

Since 1970’s, many catalysts have been used, especially transition metal compounds. For all these catalyst systems, copper (Cu) compounds were excellent catalysts not only with regard to the reaction activity but also with regard to the CHP selectivity [1].

In 1996, it was discovered that some polymer supported catalysts can catalyze the reaction between IPB and oxygen to form CHP via a free radical mechanism. An effective catalyst is prepared by supporting copper acetate [$Cu(OAc)_2$] onto Chelex, which is a divinylbenzene cross-linked polystyrene with paired iminodiacetate, with a Cu(II) content of 0.6mmol/g of dry support. Using this catalyst at 80ºC, the CHP formation rate is higher than that initiated by CHP itself which is a standard industrial process. Furthermore, the selectivity to CHP of the catalyzed reaction is also better than that initiated by CHP. The results obtained with this catalyst are superior to those catalyzed by free radical initiator, by heterogeneous catalysts (Cu, silver, platinum on support) or by homogeneous catalysts of metal salts (naphthenates of zinc and cadmium). However, this catalyst cannot be used at temperature above 90ºC [13].

Nanostructure materials have attracted a great interest in recent years because of their particular physical and chemical properties. The cupric oxide (CuO) nanoparticle could effectively catalyze the oxidation of IPB to CHP under mild conditions with molecular oxygen as oxidant. The high reaction activity for aromatic selective oxidation and the recyclability of the catalyst make this system attractive for potential industrial applications. CuO nanoparticle showed higher conversion and yield as compared to CuO prepared by the conventional method or CuO/ɣ-Al_2O_3 under the same reaction conditions and it can act as an initiator as well as a catalyst [1].

In the study of cumene oxidation rate catalyzed as a function of the metal salt, it was found the effectiveness of the metal ion follows the order: Mn(II) > Cu(II) > Cobalt(II) > Nickel(II) > Iron(II). The CHP selectivity of the Mn(II) is less than that of Cu(II). Furthermore, it was also found that among the various Cu(II) salts, including acetate, sulfate, nitrate, chloride and bromide, the acetate is superior to the other anions in terms of reaction rate. It was also found that the selectivity to CHP decreases when the catalyzed reaction is carried out at high temperature, in the presence of catalyst with high metal loading, or in the presence of a large amount of catalyst [13].

In this work, it was tried to prepare and test several catalysts to determine the best one to improve the cumene oxidation to CHP, increasing the selectivity to CHP and the oxidation rate of cumene. So it is studied the behavior of two heterogeneous catalysts of manganese with different valence: the catalyst 1 is monometallic and the catalyst 2 is bimetallic, both supported.

2. Description and experimental part

2.1. Facilities description

The facilities used to carry out the experiments of cumene oxidation to CHP in different conditions are explained below.

2.1.1. Glass reactor of 250ml

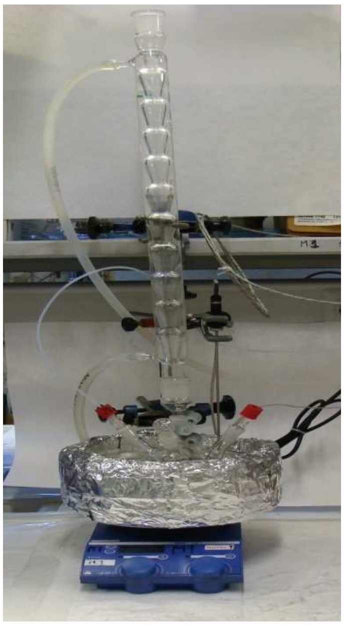

Figure 15 – Glass reactor of 250ml with the magnetic heating plate.

This reactor, a 250ml flask, operates in batch and it is located in a silicone bath to operate at the desired temperature. The bath is on a magnetic heating plate, which controls the agitation speed inside the reactor. It has three openings, one central and one in each side. The central one is connected to a condenser, which operates with water as the cooling fluid, to avoid the removal of volatile organic compounds. In one side are introduced the gases and a thermocouple and the other side is used to take samples, with a glass pipette. The analysis of these samples allows the evolution of the reaction through the time, in different conditions.

The flow of synthetic air or nitrogen is controlled by a mass flow controller connected to the computer. There is a three-way valve that allows the choice of the gas enters the reactor (nitrogen or air).

The catalysts tests are carried out in the flask. Several catalyst families are tested under different reaction conditions and different amounts of catalysts, to analyze the activity and the selectivity of the reaction.

2.1.2. Glass reactor of 1l


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Figure 16 – Glass reactor of 1l with the motor that promotes the agitation.

Subsequently, to perform a greater number of experiments in a larger volume, in batch and at atmospheric pressure, a glass reactor, similar to the one described above, was set up. This reactor has a heating jacket connected to a hot bath to maintain a uniform temperature inside the reactor and at the desired conditions for the reaction. It is also fitted with a motor, which is responsible for the agitation inside the reactor (1000 r.p.m.).

If the results obtained, after testing catalyst and its conditions, are consistent, the catalyst is tested in the pilot plant.

2.1.3. Pilot plant

Figure 17 and 18 – Autoclave reactor of 1l with the motor that causes the agitation and pilot plant (1 – feed tank, 2 – product collection tank and 3 – gas-liquid separator).

The core of the pilot plant used in the experiments is the autoclave reactor. There are two very similar systems on the pilot plant, differing only in the material of the reactor, one is built in glass and the other one in stainless steel. The glass reactor was constructed and used before the steel reactor, to provide the idea of how should be the system inside the reactor. Then, when it appeared that everything was working as it should, the steel reactor was constructed in order to operate in safety conditions. Then, it is a more detailed description of the pilot plant with the stainless steel reactor.

So the equipment used to produce the experiment in pilot plant is an autoclave reactor with all of the process streams. On pilot plant there are also feed and product collection tanks, valves, pumps, cooling, a gas-liquid separator and control devices. The autoclave is fitted with gas and liquid entries, exit, agitator with baffles and several openings to introduce the thermocouple, the filtration system, the cage with catalyst and to get samples with a pipette. In the exterior of the reactor there is a motor to promote the agitation. It is connected to input and output lines of gas and liquid that make up plant architecture.

The gas supply comes from gas bullets. A mass flow controller sets the flow and the correct position of the valves along the pipeline to the right passage of gas through the lines.

There are two parallel lines of gases, one of nitrogen and the other one of synthetic air. The entry of one or the other is controlled by automatic actuation of a valve from the computer. Nitrogen should be feed when the reactor is being loaded (after stopping the reaction and during the cleaning of the reactor), until it reaches the desired temperature and when some parameter of the reaction is uncontrolled. Nitrogen is an inert gas that prevents cumene oxidation begins. The oxidation should start when the temperature is stable and at that moment synthetic air is added, and is taken as time zero in the kinetic studies.

The feed stream from the storage tank of raw material, which is fitted with a scale Mettler-Toledo GmbH IND425-A15, passes through a pump and enters the reactor. The pump flow (1.2ml/min to 2.8ml/min) will determine the residence time inside the reactor (6h^{-1} to 13.7h^{-1}), according to the operation flow. After the reaction, the product stream passes through a gas-liquid separator Nivecal Jacoher. The gas stream that leaves the separator passes through a condenser that uses cold water to condense organic compounds from the gas phase. Then it passes through a kammer valve Ventile DN/PN that controls the pressure inside the reactor and goes to the general conduct collection of gases. The liquid stream that leaves the gas-liquid separator passes through a kammer valve Ventile DN/PN that controls the liquid level in the separator and follows into a product collection tank, fitted with a scale Mettler-Toledo GmbH IND425-A15 to control the amount of product formed, and a manual on/off valve for emptying it.

In the pilot plant there are two baths. The hot bath (at 82-83ºC) is connected to heating jacket of the reactor to maintain the temperature at 80ºC inside the reactor, and the cold one (at 10-15ºC) is to avoid IPB evaporation.

All the pipes and tanks in the pilot plant were constructed with stainless steel 316.

The computer has the Intellution FIX View software, which allows the viewing and control of several parameters in the plant from the control room.

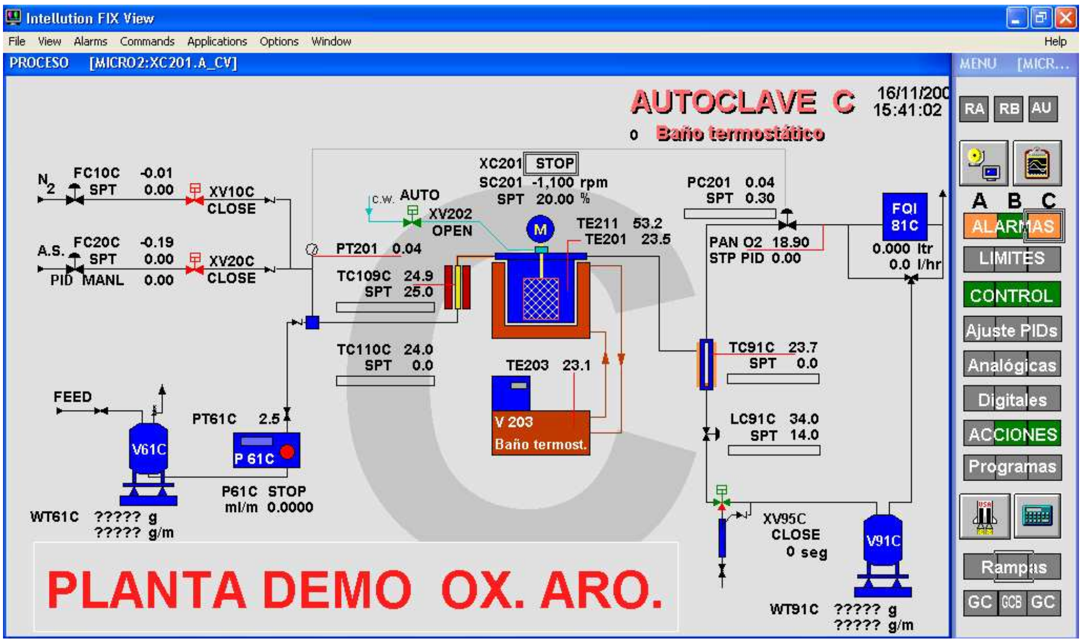


Figure 19 – Control panel of the pilot plant with Intellution FIX View software.

Figure 19 shows the control panel of the plant that was stopped at the time. As can be seen, it is quite simple. At the center is located the autoclave, with the heating jacket, the agitation motor, the pre-heater and the thermal bath. The pre-heater is not currently in use and the rotation measurer is deactivated. Thus, in the reactor, only the internal temperature is measured, which is related to the hot bath temperature.

On the left, above, are the entries of the gases that can be fed to the reactor and the feed tank is located below, which is supported on a scale in order to everyone be able to know when it should be loaded. This tank is connected to a pump that lets everyone chooses the operation flow.

On the right is, at the top, the control valve pressure of the reactor, combined with a pressure gauge, and below, the gas-liquid separator, which is connected to the product collection tank. This tank is also supported on a scale to know when it needs to be empty. Before the product collection tank there is an output that allows the collection of product samples.

In this control panel, besides all the values of gas flow, pressure and liquid level, the values of the respective set points are also presented.

The control of the cumene oxidation plant is crucial since it works near the limits of flammability and CHP is a potentially unstable compound which can decompose violently.

2.1.3.1. Autoclave reactor of 1l

Figure 20 – Autoclave reactor of 1l.

The gas stream enters the reactor, connected from the top with a pipe, circulates through its inside and is distributed through a diffuser, a perforated crown ring, near the bottom of the reactor. The holes in the crown allow the diffusion of very small bubbles of air to promote a good mixing and slowing the rise of such bubbles.

The edge of the reactor is a hollow steel tube. It is joined with baffles, at the lower end, which agitates the reactor mixture.

When the system is working in continuous, there is an exit for the reaction products, which volume of output is constant and equal to the feed entry (when working on stationary). It consists of a tube with a filter placed at a length such that the filter bottom surface is supported (not submerged) on the liquid surface. The liquid that passes through the filter, with some air, passes through a gas-liquid separator and follows into the product collection tank. The gas flow is diverted to the gas line.

On the top of the reactor, the edge is joined with a magnetic action motor, which causes the rotation. The maximum number of revolutions per minute that can be achieved with this engine is 1500 r.p.m.

The safety valve opens to reduce pressure inside the reactor when it reaches a certain limit, previously defined as 3bar, to avoid situations of risk. The operation pressure is fixed at 0.3bar.

The reactor is previously cleaned with a solution of sodium pyrophosphate and soda to create a thin alkaline layer on the walls inside the autoclave in order to prevent the material interacts with the reaction and encouraging the formation of phenol, because of the acidic environmental. After this passivation a cleaning test is made to eliminate the soda of the lines and the autoclave interior.

2.1.3.2. Autoclave reactor of 8l

Figure 21 – Autoclave reactor of 8l.

Recently, a new stainless steel reactor was built, with 15l of capacity that usually operates with 8l. The operation system is exactly the same as the autoclave reactor of 1l, however this reactor has also a filter in the gas entry. This reactor was built following the same assumptions as the autoclave of 1l, keeping the same ratio L/d and the agitator was oversized.

2.2. Catalysts preparation

The study of the improvements in the cumene oxidation focuses on the introduction of a catalyst in the reaction, so far autocatalytic. The two types of heterogeneous catalysts, monometallic and bimetallic, were prepared by two different methods: incipient wetness impregnation and wet impregnation, followed by water elimination in a rotary evaporator vacuum.

2.2.1. Incipient wetness impregnation

This method, also referred to as dry impregnation or capillary impregnation, involves contacting a dry support with only enough solution of the impregnant to fill the pores of the support. The volume of liquid needed is usually determined by slowly addition of small quantities of the solvent to a well stirred weighed amount of support until the mixture turns slightly liquid (also comparable to volume pore obtained with the BET method). This weight/volume ratio is then used to prepare a solution of the precursor salt having the appropriate concentration to obtain the desired metal loading. Since all the impregnant solution is adsorbed into the pores of the support, this procedure can be used to prepare specific, predetermined metal loadings on the catalyst [14]. It is essential that the desired loading of the active component is present in an amount of solution not exceeding the pore-volume of the support. An obvious advantage of an impregnation and drying procedure is that no waste water is produced, and material dissolved in the solution cannot get lost. Another attractive feature is that the procedure can be used with shaped support particles [15]. Currently, most of the catalysts prepared following this method present high dispersion.

2.2.2. Wet impregnation

This method differs from the one above in the excess of water used. So, after the impregnation another step is needed: water elimination. In this case, rotary evaporation has been used for this purpose.

2.2.2.1. Rotary evaporator vacuum

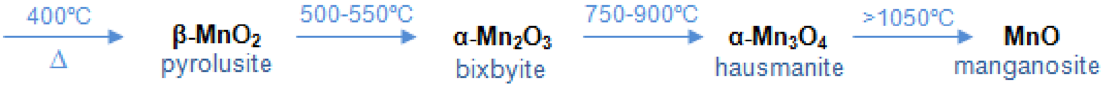
Figure 22 – Rotary evaporator used to eliminate the water.

The rotary evaporator is a device used in organic laboratories for the efficient and gentle removal of solvents from mixtures by evaporation under control. A typical rotary evaporator has a heatable water bath to keep the solvent at a constant temperature during the evaporation process. The solvent is removed under controlled vacuum, trapped by a condenser and collected for easy reuse or disposal [16].

The main components of a rotary evaporator are: a motor unit which rotates the evaporation flask containing the mixture; a vapour duct which acts both as the axis for sample rotation and as vacuum-tight conduit for the vapour being drawn off the mixture; a vacuum system to substantially reduce the pressure within the evaporator system; a heated fluid bath, to heat the mixture being evaporated; a condenser; a condensate-collecting flask at the bottom of the condenser, to catch the distilling solvent; and a mechanical or motorized mechanism to quickly lift the evaporation flask from the heating bath.

The rotary evaporator used is a BUCHI *Rotavapor* R-210/R-215 Model.

In this work, the manganese catalysts studied have different valence and the both are supported. The several stages of manganese oxidation are presented below.



$$\xrightarrow[\Delta]{400^\circ C} \beta\text{-}MnO_2 \xrightarrow{500\text{-}550^\circ C} \alpha\text{-}Mn_2O_3 \xrightarrow{750\text{-}900^\circ C} \alpha\text{-}Mn_3O_4 \xrightarrow{>1050^\circ C} MnO$$

Figure 23 – Different stages of manganese oxidation.

The manganese, when oxidized, passes through different stages. Depending on the support used, at about 400ºC the salt is decomposed and with oxygen it is formed the first manganese oxide, pyrolusite. When the environment is around 500ºC appears the bixbyite that becomes hausmanite when the temperature reaches 750 - 900ºC. The manganosite is finally formed above 1050ºC.

The supported catalysts have a support on which an active substance is dispersed. That support provides to the catalyst higher specific surface, greater strength and higher porosity [17]. The active phase of the catalyst gives it great activity.

2.3. Catalysts characterization

After the catalyst preparation, it was sent to the Analysis Department of the Research Center and then they sent us the catalyst characterization data.

2.3.1. Nitrogen adsorption/desorption isotherms

Nitrogen adsorption at boiling temperature, 77 K, represents the most widely used technique to determine catalyst surface area and to characterize its porous texture. The adsorption isotherm represents the nitrogen adsorbed volume against its relative pressure. Isotherm shape depends on the solid porous texture. According to IUPAC classification six types can be distinguished, but only four are usually found in catalyst characterization [18].

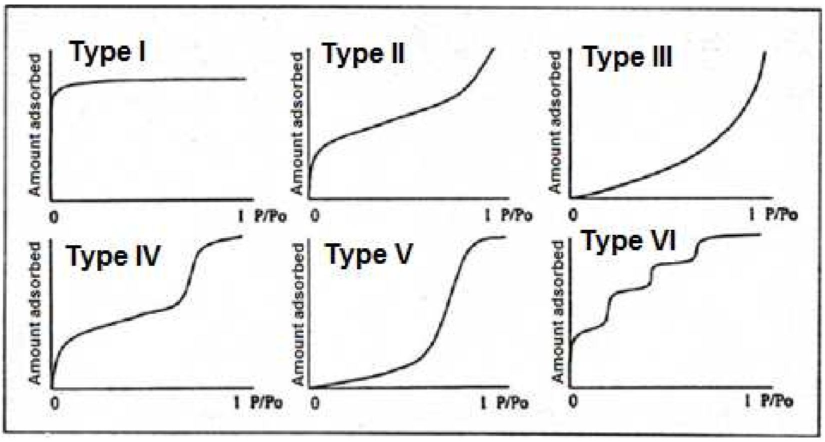


Figure 24 – Adsorption types.

The type I isotherm is characteristic of microporous solids. The adsorption takes place also at very low relative pressures because of strong interaction between pore walls and adsorbate. Typical examples of microporous solids are active carbons, zeolites and zeolite-like crystalline solids.

The type II is characteristic of non-porous or macroporous solids. At low relative pressure formation of a monolayer of adsorbed molecules is the prevailing process, while at high relative pressure a multilayer adsorption takes place: the adsorbate thickness progressively increases until condensation pressure has been reached. The pressure of first monolayer formation is lower if the interaction between adsorbate and adsorbent is stronger, but monolayer and multilayer formation processes are always overlapped.

The type III isotherm occurs when adsorbate-adsorbent interaction is low and the type IV is characteristic of mesoporous solids. At low relative pressures the process does not differ from what happens in macroporous solids. At high relative pressures the adsorption in mesopores leads to multilayer formation until, at a pressure dependent on Kelvin-type rules (larger mesopore higher pressure), condensation takes place, giving a sharp adsorption volume increase. As mesopores are filled adsorption continues on the low external surface.

The type V isotherm, like the type III is characteristic of weak interactions adsorbate-adsorbent, but differs from the previous one in the end that is not asymptotic. Type VI isotherm is rare but this type of adsorption occurs only for solid with a uniform ultramicroporous solids, almost non-porous surface. The pressure at which adsorption takes place depends on surface-adsorbate interaction, so, if the solid is energetically uniform, the whole process happens at a well-defined pressure. If the surface contains few groups of energetically uniform sites, a stepped isotherm must be expected, each step corresponding to the adsorption on one group of sites. Since all the catalyst surfaces are widely heterogeneous this behavior has never been observed. Stepped-like isotherms have been obtained only in the case of well crystallized zeolites or silicalite [18].

The model, developed by Brunauer, Emmet and Teller in 1940's, still remains the most diffuse tool to determine the monolayer volume (V_m) of the adsorbate, and then the surface area (A_s) of solids by the equation

$$A_s = \frac{V_m}{22414} \times N_a \times \sigma \qquad (1)$$

where N_a is Avogadro number and σ the area covered by one nitrogen molecule. The σ value generally accepted is 0.162 nm^2.

V_m can be estimated by the three parameters BET equation, assuming that: the heat of adsorption of first monolayer is constant (the surface is uniform as concerns the adsorption); the lateral interaction of adsorbed molecules is negligible; the adsorbed molecules can act as new adsorption surface and the process can repeat itself; the heat of adsorption of all monolayers but the first is equal to the heat of condensation. The equation (three parameters BET equation) has the form

$$V_{\mathrm{ads}} = V_{\mathrm{m}} \frac{cp/p_s}{1 - p/p_s} \frac{1 - (n+1)(p/p_s)^n + n(p/p_s)^{n+1}}{1 + (c-1)(p/p_s) - c(p/p_s)^{n+1}} \qquad (2)$$

where V_{ads} is the adsorbed volume, *c* is a parameter related to heat of adsorption and liquefaction, p/p_s is the relative pressure and *n* is parameter related to the mean number of layer that can be formed on the solid. If $n \to \infty$ the equation assumes the following form, known as two parameters BET equation:

$$V_{\mathrm{ads}} = V_{\mathrm{m}} \frac{cp/p_s}{(1-p/p_s)(1+(c-1)p/p_s)} \tag{3}$$

BET model has been submitted to many criticisms, because real surfaces do not follow the assumption of the model. Nevertheless in the range of relative pressure 0.05-0.35 it is capable to interpolate the experimental data for most solids, giving surface area values near to the mark. Nowadays BET method is the most widely used to determine surface area of solids and it can be regarded as a reference method. The main lack of applicability is the case of microporous solids: in this case the monolayer volume computed by BET equation corresponds to the micropore volume plus the monolayer volume on the surface external to micropores [18].

2.3.2. X-Ray fluorescence

Figure 25 – X-Ray fluorescence equipment.

XRF (X-ray fluorescence) spectrometry is a non-destructive analytical technique used to identify and determine the concentrations of elements present in solid, powdered and liquid samples in the more accessible atoms of the surface. The XRF spectrometer measures the individual component wavelengths of the fluorescent emission produced by a sample when irradiated with X-rays [19].

The XRF equipment used is an Axios PANalytical.

2.3.3. X-Ray diffraction

Figure 26 – X-Ray diffraction equipment.

X-ray diffraction is a physical phenomenon that occurs when a monochromatic beam of X rays interacts with a crystalline substance. The dispersion that the X-ray beam produces by the material (keeping the wavelength of radiation) and the constructive interference of waves produce the X-ray diffraction, documented in a diffractogram. A diffractogram of a polycrystalline sample is used to identify the crystalline phases, both qualitative and quantitative aspects, once that each crystalline solid has its characteristic diffractogram [20].

The X-Ray diffraction equipment used is an X'Pert PRO PANalytical.

2.4. Samples analysis

2.4.1. High performance liquid chromatography (HPLC)

Figure 27 – HPLC used in laboratory.

To analyze the concentration of CHP, IPB and other by-products, HPLC technique is used. The samples, taken from the reactors at different times, are introduced into glass vials for analysis. With the HPLC, the evolution of the reaction can be followed, by the quantity of each species formed.

The high performance liquid chromatography can separate, identify and quantify components of similar characteristics in complex mixtures, which often are impossible by other means [21]. Molecules can be separated according to their charges, sizes and molecular weight, as well as by their polarity and redox potential.

In the HPLC technique, the sample is forced through a column that is packed with irregularly or spherically shaped particles or a porous monolithic layer (stationary phase – SiO_2-C_{18}) by a liquid (mobile phase – acetonitrile/water) at high pressure [22]. After the separation, the compounds pass through the detector and are identified by retention time. Elution time varies depending on the interactions between the stationary phase, the molecules being analyzed and the solvent gradient (usually the temperature is fixed) [21]. The qualitative analysis is based on elution times while the quantitative analysis is based on heights or areas of chromatographic peaks which are related to the concentration.

The amount of CHP is difficult to determine by gas chromatography because hydroperoxides are thermally unstable and tend to decompose in the injector of a gas chromatograph (it is almost impossible to know the amount that is lost in the injector) and this is the reason why HPLC is used to analyze the samples of the reaction.

The equipment used is an Agilent HPLC 1100 with two eluents for the analysis: water and acetonitrile, both polar and miscible. The column is an ACE C18, apolar, with 150mm of length, 4.6mm of diameter, 3µm of particle size, 100Å of pore size and 300m^2/g of BET surface area. The peak detector is composed of an ultraviolet-visible lamp which can work in a wide wavelengths range (DAD – diode array detector). This analysis uses a wavelength of 254nm, which is the maximum absorbance of aromatic compounds.

The problems presented during HPLC use are associated to the pressure increase in the column, which can cause its deterioration. It is due to the appearance of air bubbles in the pipes from the filter eluents, because they are dirty or there is air into their bottles. There was also the need to place prefilters in column to improve its performance.

2.4.1.1. Calibration curve

The HPLC calibration is made by analyzing samples of the products taking place in the reaction with known concentrations. The elution time obtained for each component will identify the peak of the same component in samples of unknown composition. With the calibration curve it is possible to know the concentration of each component.

2.4.2. Gas chromatography – Mass spectrometry

Figure 28 – Gas chromatograph - mass spectrometer used in laboratory.

The GC-MS was used to identify some compounds present in the reaction environment.

The analysis of samples from the reactor, before and after oxidation, allows knowing the impurities and the species formed. This analysis helped to identify the reactions representing the system.

The main molecules identified are IPB, phenol, AMS, acetophenone, DMPC, CHP and some phenolic derivatives.

The GC-MS is an equipment of Agilent Technologies, 6890N. The column is an HP5-MS that has 50m of length, 0.25mm of diameter, 0.5µm of particle size and the maximum temperature that can be reached is 350ºC.

In this equipment, the liquid sample enters and is evaporated in the injector, separating each component along the column. The gas molecules arrive at the detector at different retention times and, under vacuum and with an electric shock, the molecule breaks where is less stable. The fragments are characteristic of each molecule and they are compared with a broad list of compounds spectra in order to be able to identify the molecule.

3. Results and discussion

4. Conclusion

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