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Grau en Enginyeria Química

Treball Final de Grau

Basic engineering of polyol polyester production process.
Ingeniería básica del proceso de producción del Poliéster Poliol.

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“La ciencia se compone de errores, que a su vez son los pasos hacia la verdad”

Julio Verne

En primer lugar, agradecer a mi familia el apoyo incondicional durante todos estos años, que ha sido fundamental para seguir adelante.

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SUMMARY

Polyester polyol is a polymeric organic compound characterized by the presence of ester groups and terminal hydroxyl groups. Nowadays, polyol polyesters are the second most important group of oligo-polyols for the production of polyurethanes, representing around 18% of the polyols used.

In recent years, the production of polyurethanes has increased significantly to produce foams, adhesives, paints, textile fibbers and automotive components. Consequently, the polyester polyol production necessary to satisfy the demand has also increased.

For this, the basic engineering of the polyester polyol production process has been carried out with the aim of manufacturing the required polyester polyol amount by designing a discontinuous plant, whose time and batch sizing must be determined in order to satisfy the annual demand for the product.

The design does not present limitations of resources, but of time. The design must meet the demand for the desired annual production of polyester polyol. In this project, there's a stirred tank reactor working in batch mode, a rectification column, a condenser and a collection tank, each with its auxiliary equipment, its control and automation.

Through all the concepts listed above, the equipment will be dimensioned to meet an annual demand of 9000 tons considering its operating conditions, mode and the time of each stage of the production process.

Keywords: Polyester polyol, batch plants, polycondensation, polymers

RESUMEN

El Poliéster poliol es un compuesto orgánico polimérico caracterizado por la presencia de grupos éster y grupos terminales de grupos hidroxilo. A día de hoy, los poliésteres polioles son el segundo grupo más importante de oligo-polioles para la producción de poliuretanos, representando alrededor de un 18% de los polioles usados.

En los últimos años, la producción de poliuretanos ha aumentado notablemente para la producción de espumas, adhesivos, pinturas, fibras textiles y componentes de automóviles. En consecuencia, también ha aumentado la producción de poliéster poliol necesario para producir los productos anteriormente citados.

Para ello, se ha realizado la ingeniería básica del proceso de producción del poliéster poliol con el objetivo de fabricar la demanda requerida mediante el diseño de una planta en discontinuo, cuyo tiempo y dimensionado deberán ser determinados para tal de satisfacer la demanda anual del producto.

El diseño no presenta limitaciones de recursos, pero si de tiempo. Se debe realizar un diseño que permita satisfacer la demanda necesaria para la producción anual de poliéster poliol. En este proyecto se cuenta con: un reactor tanque agitado en discontinuo, una columna de rectificación, un condensador y un tanque de recogida, cada uno con su equipo auxiliar, su control y automatización.

Mediante todos los conceptos enumerados anteriormente, se realizará el dimensionado de los equipos para tal de satisfacer una demanda anual de 9000 toneladas, sus condiciones de operación, modo y el tiempo de cada etapa del proceso de producción.

Palabras clave: Poliéster Poliol, plantes batch, policondensación, polímeros

INTRODUCTION

Polyester polyols are produced for the post-production of polyurethanes, characterised by the presence of ester groups and terminal hydroxyl groups.

Polyester polyol is the second most important group of polyols for production of polyurethanes after polyether polyols. They represent around 18% of the polyols used globally in polyurethanes, corresponding to a total worldwide production of around 600000 tons / year. About 60% of polyester polyols being produced un Europe. [1]

At the beginning, polyester polyols were the only available polyols to the polyurethanes industry. Nowadays, first position takes place for the polyether, in the total polyol usage in the polyurethane industry (around 80%).

The characteristics of polyester polyol based polyurethanes are explained by a better crystalline structure in the urethane segment. The most important segments of polyester polyols applications are those of polyurethane elastomers (43% of global polyester polyols consumption), flexible foams (15-18%), coatings, adhesives, rigid foams, synthetic leather and sealants. [2]

Polyester polyols have an intrinsic defect; they are liable to hydrolyse under high humidity/ temperature conditions. To prevent the hydrolysis of polyester-based polyurethanes a worldwide research effort, led to the synthesis of polyester polyols with improved hydrolysis resistance.

Due to the increase of its demand, down below has been studied a basic engineering process to produce polyester polyol working in batch mode. One of the advantages of working in cycles is the flexibility to produce a variety of different product variations, or different products. For polyester polyols production, this condition is essential. We can use some different types of acids and glycols, and working in batches allows being the consecutive production of different compounds using the same installation.

1.1 PRODUCTION OF POLYESTER POLYOL

The polyester polyols are obtained by the polycondensation reaction between dicarboxylic acids and diols (or polyols). The polycondensation reaction is an equilibrium reaction, the equilibrium being shifted to the formation of polyester polyol by continuous removal of water from the reaction system.

The main reaction shown in the figure 1 is the one that takes place in the reactor, using a specific catalyst depending the process.

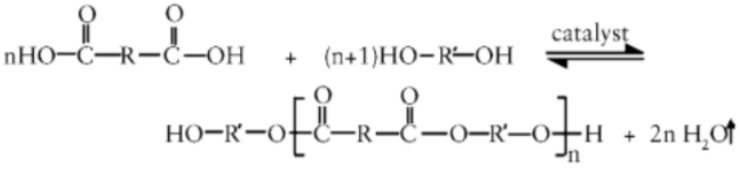


Figure 1. Polyester Polyol formation reaction

In order to generate terminal hydroxyl groups an excess of glycol is currently used. The reaction takes place in a catalysed reaction conditions to obtain a low reaction time and low final acidity.

First, we need to choose our reactants depending the final properties we want to achieve. In the table 1 can be seen the most used polyols and Dicarboxylic acids to produce polyester polyols:

Table 1. Type of Polyols

No.	Polyol	Formula	Hydroxyl number mg KOH/g
1	Ethyleneglycol (EG)	$HOCH_2CH_2OH$	1807.6
2	Diethyleneglycol (DEG)	$(HOCH_2CH_2)_2O$	1057.2
3	1,2 Propyleneglycol (PG)	$HOCH_2CH(CH_3)OH$	1474.3
4	1,4 Butanediol (BD)	$HO\text{-}(CH_2)_4\text{-}OH$	1245.0
5	Neopentyl glycol (NPG)	$(CH_3)_2C(CH_2OH)_2$	1078.8
6	1,6 Hexanediol (HD)	$HO\text{-}(CH_2)_6\text{-}OH$	949.3
7	Glycerol	$(HOCH_2)_2CHOH$	1827.3
8	Timethylolpropaane (TMP)	$(HOCH_2)_3CCH_2CH_3$	1379.5

Table 2. Type of Dicarboxylic acids

No.	Dicarboxylic acid	Formula	Acid number mg KOH/g
1	Adipic acid (AA)	$HOOC(CH_2)_4COOH$	767.78
2	Glutaric acid	$HOOC(CH_2)_3COOH$	849.2
3	Succinic acid	$HOOC(CH_2)_3COOH$	950.1
4	Sebacid acid	$HOOC(CH_2)_8COOH$	555.4
5	Azelaic acid	$HOOC(CH_2)_7COOH$	603.2

Dysfunctional monomers are used to obtain a linear polymer and monomers with functionality larger than two create ramified chains. The property we would like to have is flexibility and the best option we have is adipic acid and Diethylene glycol used as a flexible foam in pigment carriers, soft elastomers, shoe Sholes, coatings and adhesives.

1.1.1. REACTION PROCESS

As said before, the most important phase of the process is the formation of polyester polyol by a direct polyesterification between adipic acid and diethylene glycol under an inert atmosphere in a conventional stirred stainless steel batch reactor. The formation of polyester polyol is produced in one phase, so it will be the first product formed inside, at the same time as water.

The introduction of the reagents in the reactor have a specific order that must be followed. The first thing to bring in the system is the diethylene glycol (DEG). At the same time of the insertion, the heating system is turned on to reach a temperature of 60-90 ºC. Then the dicarboxylic acid (AA) is added and the temperature reaches the 200-240ºC. By the time the AA enters, the formation of the final product has started. The polyester polyol is being produced at the same time as water, that needs to be removed to push the equilibrium to the polyester formation.

While the reaction is taking place, a removal of water is being done to favour the production of polyester polyol. Around 90 % of the total water is distilled under the system conditions. During this step, the carboxyl and hydroxyl groups decreases substantially and the polyesterification reaction rate decreases rapidly, especially because the reaction becomes low in catalytic acid (AA).

The distillation is done with a rectification column pulling apart the water and the diethylene glycol that has been dragged by the evaporation. After the separation of the compounds, the DEG returns inside the system to react with the AA. The water is directed to a vessel passing by a condenser to be stored as a liquid with 3% of diethylene glycol. First, the column works at 1 atmosphere and after, to keep the extraction of the water, the pressure is decreased at 30 mbar to evaporate the water at a lower temperature.

After all the water, has been removed, the reaction is stopped and the polyester polyol can be taken out to be storage.

1.1.2. BATCH PLANTS

Nowadays, working in discontinuous mode is very common in some types of productions. In this type of production, the work on any product is divided into few operations and each operation is completed for the whole lot before proceeding to the next operation. Each batch contains identical items but every batch is different from the others. A fixed quantity or batch rather than continuous supply is required. An operation on a batch is performed by one group and then it is passed on to other groups for subsequent operations.

The main characteristics of batch production are:

- Large variety of products are manufactured in lots or batches.
- Machines and equipment are arranged according to the sequence of operations.
- Both general and special purpose machines are used.

There are many advantages to batch production, including reduced initial costs and operating costs, a wide range of associated products, and a flexible production process and scale. Additional advantages include many of those typically associated with mass industrial and commercial production.

One of the major advantages is the reduction of time required to produce a single product, because multiple products are pushed through the same process at the same time.

As known, plants that carry out the polyester polyol process are multipurpose, they produce more than one type of product. In this project, the design will be made to produce just one product, to simplify the design.

2. OBJECTIVES

The main objective of this project has been to design a production process of polyester polyol to satisfy the annual demand of 9000 tons per year. To achieve this production, it is required to indulge the following tasks:

- To do the basic engineering of the production process of the polyester polyol.
- Select the necessary equipment and its dimensions for the annual demand of the product.
- Define the control and automation of the process by the design of the P&D.
- To study how the variables involved, evolve along the process.

3. PRODUCTION PROCESS

The production of the polyester polyol contains several stages, but the most important part is the formation of polyester polyol.

The reactants of the process are the adipic acid and the diethylene glycol, reacting between them producing polyester polyol and water. The reaction is favoured in catalysed medium. After pushing the equilibrium to polyester polyol formation by continuous removal of water, the reaction is stopped and the product unloaded.

This whole process represented in the figure 2 is an overall diagram, which contains all the equipment required to achieve the process.

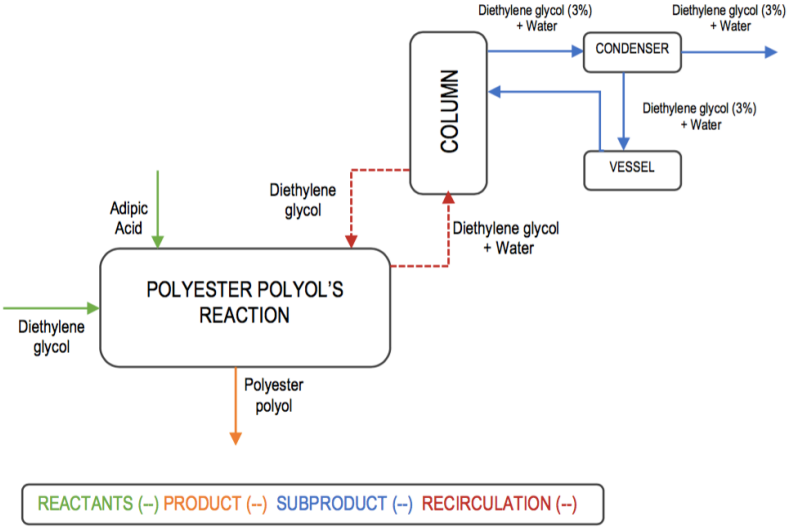


Figure 2. Overall diagram of in & outs

3.1 RECIPE

First, the nitrogen is fed into the reactor to inert the system and it's also needed an inert atmosphere to operate between diacids and glycols. After, a small portion of diethylene glycol (3%) is introduced into the system, to check the inert atmosphere has been done properly. If everything is alright, the vacuum is done until the system reaches 30 mbar. When the safety atmosphere is achieved, the atmospheric pressure is recovered.

Once the preparation of the reactor is done, which is assumed around forty-five minutes later, the diethylene glycol is fed into the reactor, automatically, taking on thirty minutes. At the same time, the heating system is turned on to reach a temperature around 90 ºC simultaneously with the agitation system.

When the temperature reaches the 90 ºC, the adipic acid is feed into the reactor through a suction pipe, otherwise, the plant will get covered from dust and the system will experience a loss of mass, it is needed 1 hour and 20minutes. At the same time of the addition, the reaction starts between the reactants, and the formation of the polyester polyol and water starts. The temperature increases until 220 ºC to ensure the vaporization of the water.

As said before, the main reaction is an equilibrium that needs to be pushed to the formation of polyester polyol. To favour the reaction, it is need a continuous removal of water that is done when the system reaches a temperature of 100 ºC, when the water starts boiling. As the water starts evaporating a 1 atmosphere, the distillation column is switched on, fed by water and diethylene glycol, that has been dragged by the evaporation. The distillation takes place at 100 ºC and after 4 hours, a 90% of the water has been removed. The vacuum is done to low down the evaporation temperature and remove the rest of the water inside the reactor, to assure this phenomenon happens, the temperature lows down to 50ºC and the pressure to 30 mbar. [1]

When all the water has been removed from the reactor and all the diethylene glycol has reacted with the adipic acid to produce polyester polyol, the reaction needs to be stopped. After, the cooling system activates to decrease at least 15 ºC the temperature from the maximum reached inside the reactor to start the extraction of the final product.

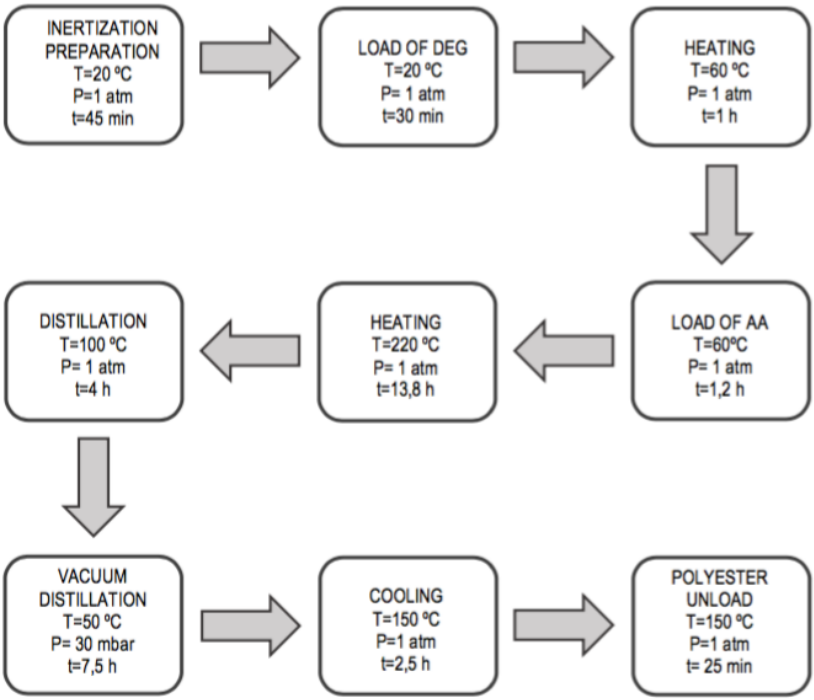


Figure 3. Block diagram

3.2 DESIGN BASES

The main objective of this project is to produce the amount of polyester polyol sufficient to satisfy all its demands of 9000 tons/year, being the calculation base for the design of the basic engineering of this project.

In this project, there are no resources limitations. The kind of limitations this design faces is to meet the annual demand with the annual production of polyester polyol.

To start with, the sizing of the batch needs to be fixed. As the annual production is set up in 9000 tons/year, it has been studied that the reactors working in this process have a volume around 30-50 m^3, which would imply sizes of batch of polyester polyol of 26660 kg/day.

On the other hand, the timing of the batch time is determined with 18 hours of process, since the feeding of the N_2 in the reactor until the extraction of the final product.

3.3 EQUIPMENT SELECTION

The equipment selected needs to satisfy the demand of polyester polyol fixed before, taking in account the fact of using the less number of equipment possible. Therefore, it will be needed:

- 1 Stirred tank reactor (R-01)
- 1 Distillation column (RC-01)
- 1 Condenser (C-01)
- 1 Vessel (V-01)

In the stirred batch tank reactor (R-01) is carried out the main reaction with the diethylene glycol and adipic acid solution and where the formation of polyester polyol and water takes place. Through the external and internal heating system, the reactor reaches temperatures of 220-240ºC using heating oil as a heater fluid. All the evaporated water must be directed to a rectification column (RC-01) due to push the equilibrium to the formation of polyester polyol. The water leaving the column goes to a condenser (C-01) to increase the temperature to be stored in the vessel (V-01) as a liquid.

On the other hand, the diethylene glycol dragged into column must be returned inside the reactor (R-01) to keep the reaction going on. Next step of the polyesterification reaction is to decrease the pressure to 400-200 Pa to decrease the temperature in the head of the column (RC-01). The evolution of the reaction is monitored by measuring the quantity of water distilled and by the determination of acid number, hydroxyl number and viscosity.

Finally, the resulting polyester polyol is stored.

3.4 DIAGRAM PROCESS

The main objective of this section is to provide the reader a general vision of the process with all its equipment and services. Since now, it has been seen the black box in the figure 2, which represents de whole process but in a generic way.

In the figure 4 can be seen the flowsheet of the production process of the polyester polyol which contains the equipment said before (stirred tank reactor, distillation column, condenser and final vessel) and how all of them are connected between each other. Also, it is shown how the service of cooling/heating organic oil system works.

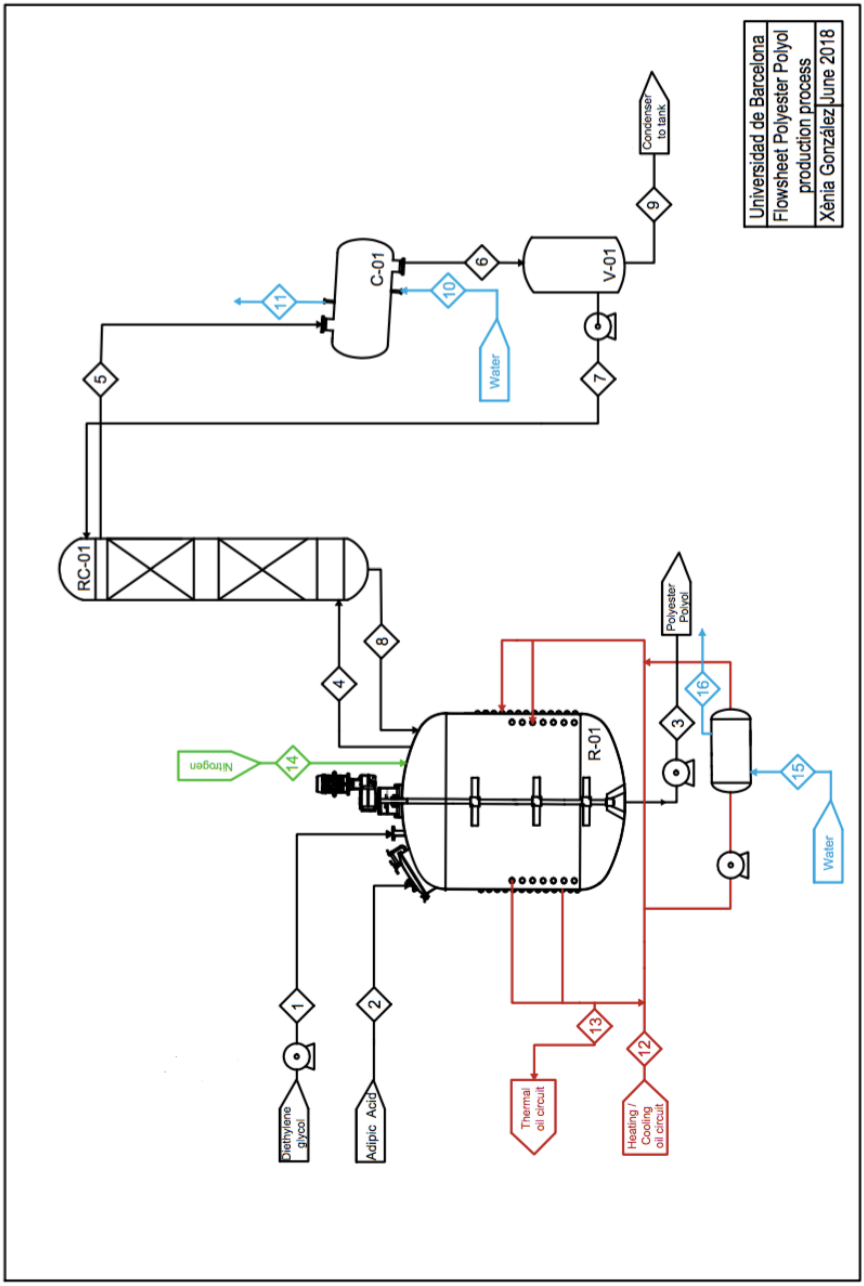


Figure 4. Flowsheet

3.5 CALCULATION BASES

One of the most important things need to be considered is the batch size and it has been done with the material and energy balances of the system considering always the main objective of the process.

Design bases

First of all, it should be reminded the main objective: the production of 9000 tons/year of polyester polyol, this will be the calculation base of the production process. In every batch are produced 26660 kg of polyester polyol, which means that in one year 337 batches are produced. In the table 3 are shown the base calculations of every batch:

Table 3. Base calculation

	kg/batch
Diethylene glycol	12711
Adipic acid	17000
Water	3051
Polyester Polyol	26660

It has been very complicated to design the size batch because the amount of every reactant in the system can vary in function of how the process is working on. This means, every batch can be different than the next one, in terms of amount of reactants, to achieve the main objective.

Mass balance

Once the amount per batch is known, it should be determined the inputs and outputs in each equipment. Down below there are the quantities entering and leaving every part of the equipment: the reactor, the column and the condenser.

Table 4. Global mass balance

	Reactor		**Rectification column**		**Condenser and Veseel**	
	Inputs (kg/day)	Outputs (kg/day)	Inputs (kg/day)	Outputs (kg/day)	Inputs (kg/day)	Outputs (kg/day)
Diethylene glycol	12711	72	72	72	72	72
Adipic acid	17000	0	0	0	0	0
Water	0	3.051	3051	3051	3051	3151
Polyester polyol	0	26660	0	0	0	0

4. DESIGN SPECIFICATIONS

The specifications of a project are a fundamental part of it, where it is shown all the equipment and auxiliary equipment and includes all the information required. Also, it will be the shown the pipes, valves and its distributions inside the plant.

4.1 REACTOR R-01

The most important and complex part is the batch reactor, where the polyester polyol is formed. In this project, there's going to be one reactor with its heating, cooling system and auxiliary equipment.

The reactor R-01 has been designed with one restriction, the volume needed of polyester polyol per year. The reactor can't be enormous or very small, it should have a dimension between 30-50 m^3.

Following down below, the reactor has been designed to satisfy the annual demand of the product chosen and all its equipment so now, it will be choosing the reactor that fulfil all our demands.

4.1.1. STIRRED TANK REACTOR

The reactor R-01 is used to produce polyester polyol through diethylene glycol and adipic acid. The design has been made considering the properties of all the products inside the reactor, the temperature, the pressure, the density and the material. As said before, all the reactors that carry out this type of reactions don't have dimensions superior than 50 m^3.

Thereunder, there are the general specifications of the reactor shown in the Table 5:

Table 5. Reactor characteristics

	DIMENSIONS OF R-01
Effective volume [m^3]	30.4
Total volume [m^3]	35
Diameter [m]	2.68
Total high [m]	4.4
Effective high [m]	3.7

The conditions and properties of the reactor are shown in the Table 6:

Table 6. Reactor general specifications

	R-01
Position	Vertical
Material	AISI 316
Working temperature [ºC]	+20/+220
Working pressure [mbar]	30/1000

As seen, it is going to be used a stirred tank reactor with agitation working in batch mode. The reactor has a total volume of 35 m^3, which accomplishes our requirement. Apart from general considerations, the reactor has a heating/cooling system which needs to be design. Below, there are all the general specifications of the reactor's equipment: agitation, heating and cooling system.

First of all, for an effective design of the heating and cooling system it has to be clear the temperatures wanted to be reached, the transmission area and the heating and cooling fluid going to be used.

In this project, the heating system it will be fundamental. The reaction that takes place is a polycondensation, this means there is going to water as a product which must be removed of the system to push the equilibrium to the other side to keep on the reaction. The heating system has to be design to achieve a temperature of 220ºC inside the reactor to assure the evaporation of the all the water produced. To reach a high temperature, it is needed a powerful heat exchanger because the effective area is slight. In this case, the heating system consist in a half-

pipe jacket and an internal helical coil exchanger. With both heaters, it will be guaranteed a good transfer area and a high final temperature.

Before the design of both exchangers, it must be established the total heat the reaction needs to reach the objective temperature. Taking in account the amount of water that wants to be removed and its vaporization constant the total heat needed to be contributed is 68,37 kW.

Half-Pipe Jacket

To reach the temperature that the process requires, a half-pipe jacked must cover all the effective area of the reactor to guarantee a good exchange area between the fluids. When the first reactant is introduced into the reactor, the temperature starts to rise until it reaches 90ºC and then, the second reactant is added and the final temperature attains the 220 ºC. To provide heat to the system, it is used heating organic oil at 260ºC which leaves the reactor at 230 ºC.

In the Table 7 are the properties of the half-pipe jacket:

Table 7. Split half-pipe characteristics

	REACTOR R-01
Jacket type	Split half-pipe
Operation	Heating
Fluid	Heating oil
Exchange area [m^2]	34
Heating power [kW]	31
Fluid flow [m^3/h]	1.8
U [kJ/ (h*m2*ºC)]	1800
ΔT_{ml}	43.28

As seen in the reactors' properties, the effective area is 34 m^2 and all must be used to provide heat into the system. Although, with this area it is not enough to contribute enough heat to reach the target temperature, so it will be needed another heating system to reach the heating power required. In this occasion, it has been chosen an internal helical coil exchanger that will provide the 38 kW missing.

Table 8. General heat properties

Total heat [kW]	69
Half-pipe jacket [kW]	31
Internal helical coil [kW]	38

Internal helical coil exchanger

The internal exchanger consists of a helical coil fabricated out of a metal pipe that is fitted in the annular portion of two concentric cylinders. The fluid circulated through the coil wall and the annulus, with heat transfer taking place across the coil wall. The dimension of both cylinders are determined by the velocity of the fluid in the annulus needed to meet the heat transfer requirements. This type of exchangers are pretty effective when there's lack of space.

Table 9. Helical coil exchanger characteristics

	REACTOR R-01
Type	Internal helical coil exchanger
Operation	Heating
Fluid	Heating oil
Exchange area [m^2]	75
Heating power [kW]	38
Fluid flow [kg/h]	2.3
U [kJ/ (h*m^2*ºC)]	1000
ΔT_{ml}	43.28
Length [m]	238
Number of coils	30
High [m]	2.8
Diameter [m]	0.1

Agitation system

The agitation system is a fundamental part of the equipment which maintains the mixture homogenized. The agitator consists of three paddle impellers with four pitched blades located in different highs to homogenize all the reactor.

The properties which define the agitation system are the type, size, material and the rotational speed. When all those properties are well defined, it can be chosen the agitation system that best fits from the supplier's offers.

One of the most important things which define an agitation system is the viscosity of the fluid. Depending on this value, the properties will be ones or others to provide the best homogenization possible.

In the Table 10 are the qualities of the agitation system:

Table 10. Agitation general specifications

Type of force	Mechanical
Type of agitator	Paddle
Impeller shape	6 pitched blades
Number of impellers	3
Material	AISI 316 L

Here, in the table 11 can be seen the dimensions of the agitator:

Table 11. Agitation characteristics

Diameter [m]	0.89
Height [m]	0.53
	1.83
	3.13
Rotational speed [rpm]	120
Power supplied [W]	12380

It has been chosen 3 impellers to make sure the homogenization is reached in every high of the reactor. The highs have been decided to be equidistant between them and one of them must be on the top of the reactor to make sure the adipic acid, which is solid, gets well mixed with the diethylene glycol.

4.2 DISTILLATION COLUMN RC-01

In the process, one of the unit operations taking place is the distillation in one rectifying column. This step is about splitting apart de water and the diethylene glycol dragged from the reactor vapours.

The rectifying column starts working three and a half hours after the process has started. At the beginning, there's no evaporation because the process hasn't reached the boiling temperature and no vapours arrive at the column. When the reactants inside the reactor achieve a temperature of 100 ºC, the rectifying column starts working, separating the water away from the diethylene glycol. The water is directed to a condenser so it can be stored as a liquid. It should be known that this water contains 3% of diethylene glycol that can't be split apart. The diethylene glycol obtained from the distillation must be returned inside the reactor to maintain the reaction.

After 4 hours distilling it is impossible to keep separating the water from the diethylene glycol at 150ºC and at 1 bar. It is necessary to decrease the pressure and the temperature to keep on the distillation. The vacuum is done inside the reactor and the pressure lows downs to 30 mbar and the rectifying process goes on at 50ºC.

When seven and a half hours have passed, the vacuum is recovered and the distillation keeps going on at 100 ºC during 2 more hours.

The amount of water distilled is different when it starts than when it ends. When the reaction begins, the amount of water formed and distilled is much more sizable than when the reaction is about to stop because the concentration of carboxylic and hydroxyl groups decrease substantially and the polyesterification reaction rate decreases rapidly, especially because it becomes low in catalytic acid.

The column has two inputs and two outputs. The first input (stream 4) comes from the reactor and it is composed of vapour water and some glycols which had been dragged with the

vapours. This stream is very important because is the one removing the water from the reaction and it necessary to ensure the diameter of this pipe is wide enough to make sure all the water evaporated at the beginning of the reaction is distilled properly. The second input (stream 7) comes from the vessel. The function of the stream is to direct some of the water with 3% of glycol from the final vessel to the column to repeat the distillation and ensure the water contains the less quantity of glycols as possible. The first output (stream 5) of the column is located on the top of the column which contains water from the distillation and 3% of glycols that couldn't be distilled. This stream is directed to the condenser and vessel where the water will be stored. The second output (stream 8) is fundamental for the polycondensation reaction. As said before, the vapour water distilled from the process contains diethylene glycol that has been dragged with the vapours, but this glycol must go back to the reactor so the reaction can keep going on. This stream, returns the glycols distilled from the process to the reactor.

During the distillation stage, it hasn't been possible to study the evolve of the compositions along the process.

The table 12 shows the specifications of the rectifying column:

Table 12. Column general characteristics

	RC-01
High [m]	5
Number theoretical plates	10
Tray spacing [m]	0.5
Working temperature [ºC]	+50/+150
Working pressure [mbar]	30/1000
Material	AISI 316

4.3 CONDENSER C-01

During the distillation process, all the water leaving the column must be condensed and stored in one vessel. To develop this process its needed a shell-and-tube exchanger between the column and the final vessel to decrease the temperature of the water leaving the distillation column.

The condenser will be working at the same time as the column so as long as the distillation goes on, the water will be refrigerated. The water will be fed in the condenser at 50-55ºC and will leave to the vessel at 45ºC. It will be used water as cooling fluid at a temperature of 20ºC.

To design the condenser, it has been considered the worst conditions the installation could face. In this case, the mass flow that enters the condenser has been doubled just in case the steam rate variates. Also, and the cooling fluid refrigerates at 20ºC because depending the season we cannot have lower temperatures.

The table 13 shows the main characteristics of the condenser:

Table 13. Condenser characteristics

	Condenser
Type	Shell-and-tube exchanger
Function	Cooling
Cooling fluid	Water
Exchange area [m^2]	16
Fluid flow [kg/h]	508
Number of pipes	50
Diameter of the pipes [cm]	2
Surface of the pipe [cm^2]	0.09
Working pressure [mbar]	30/1000
Working temperature [ºC]	+20/+55
Material	AISI 316

4.4 VESSEL V-01

The last part of the process consists in one stirred vessel which is the one storing all the condenser water with 3% of diethylene glycol. This water will be headed to biological treatment [1] and will be unloaded after every batch. It has been design to storage two batch, just in case it can't be unloaded so it could keep all the water removed from the system during two days.

Table 14. Vessel characteristics

Volume [m^3]	6
Material	AISI 316
Working temperature [ºC]	+45/+55
Working pressure [mbar]	1000

4.5 PIPING

All the reactants and products must flow inside the pipes installed which connect all the equipment between them and allows the properly operation. To calculate the diameter, it has been considered that the velocity of the fluid inside the pipes is 1 m/s. As said during the design of the distillation, the flow rate if the pipes entering and leaving the column cannot be defined because there's no information of how the concentration inside the column evolves through the time. So, the diameters of the pipes 4,5,6,7,8 have been decided by vendor.

In the table 17 will be seen all the specifications of the pipelines, its diameter, function and the fluid which circulates.

Once all the pipes are well defined it must establish a nomenclature for all the pipes which will show all the properties in a very simple way. This nomenclature has 4 abbreviations which are: Diameter - Material -Fluid inside the pipes - Location.

As seen before all the diameters are defined and the material of the pipes, which is steel AISI 316 represented with a P. The next one is the fluid inside every pipe that will be classified as: reactant (R), final product (FP), intermediate mix (IM), Cooling fluid (C), heating fluid (H), Inert fluid (N). Finally, the zone where the pipes are located: Reactor zone (100), Distillation zone (101), Condenser zone (102) or Vessel (103).

Table 15. Pipes specifications

Pipe	Function	DN[inches]	Product
1	Reactant's loading	2	Diethylene glycol
3	Product unloading	3	Polyester Polyol
4	Product transfer	12	Diethylene glycol, water
5	Product transfer	12	Diethylene glycol (3%), water
6	Product transfer	4	Diethylene glycol (3%), water
7	Product recirculation	2	Diethylene glycol (3%), water
8	Product recirculation	2	Diethylene glycol, water
9	Product unloading	1/2	Diethylene glycol (3%), water
10	Cooling fluid	3	Cooling water
11	Cooling fluid	3	Cooling water
12	Heating fluid	3	Heating organic oil
13	Heating fluid	3	Heating organic oil
14	Inert fluid	3/4	Nitrogen
15	Cooling fluid	3	Cooling water
16	Cooling fluid	3	Cooling water

Table 16. Pipe nomenclature

Pipe	DN [inches]	Material	Fluid	Location	Nomenclature
1	2	P	R	100	2"-P-R-100
3	3	P	FP	100	3"-P-FP-100
4	12	P	MI	101	12"-P-IM-101
5	12	P	MI	102	12"-P-IM-102
6	4	P	MI	103	4"-P-IM-103
7	2	P	MI	101	2"-P-IM-101
8	2	P	MI	100	2"-P-IM-100
9	1/2	P	FP	103	½"-P-FP-103
10	3	P	C	102	3"-P-C-102
11	3	P	C	102	3"-P-C-102
12	3	P	H/C	100	3"-P-H/C-100
13	3	P	H/C	100	3"-P-H/C-100
14	3/4	P	N	100	¾"-P-N-100
15	3	P	C	100	3"-P-C-100
16	3	P	C	100	3"-P-C-100

5. P&D

The piping and instrumentation diagram is where is being shown all the piping and equipment's in the process flow, together with the instrumentation and control devices. The main functions of the P&ID are to show the interconnection of the process equipment and the control instrumentation.

In this section, what is going to be seen are the process piping and mechanical equipment and process control instrumentation (name, numbers, unique tag identifiers).

5.1 CONTROL AND AUTOMATION OF THE PROCESS

The most important part to design an effective control is to locate the parameters which ones the system depends on. If those parameters are well controlled, the process will go on as planned. On the other hand, what is also needed to know is the parameters which ones can create a perturbation in the system. There are two types of perturbations, the ones coming from the process and can be controlled or the ones coming from outside the process that cannot be controlled and some adaptations and modifications will be needed.

In this case, for the polyester polyol production the most important variable is the temperature. The whole process depends on the temperature that will be measured in every device (reactor, column, condenser and heating/cooling system) and directly connected with the heating/cooling system which will react in order to get to the target temperature.

On the other side, the automation is a traditional engineering sense providing automated solution to physical activities. It consists on the integration of an automatic control of various parameters to reduce human efforts and time to increase accuracy. The automation of this process will be done to:

- **Flow rate**: The flow rate must be controlled in order to assure the amount of reactants loaded in the reactor. It must be loaded inside the unit a specified quantity of each reactant, otherwise the reaction will go wrong and it won't be possible to achieve the production wanted. Also, it will be controlled the flow entering in the condenser, which is cooling water and determinates the temperature reached.

- **Pressure**: As explained before, there are a few modifications of the pressure during the process so it must be checked that the pressure inside the reactor is the correct. To make a properly automation on the top of the reactor there's a venting valve which will rectify the pressure inside if needed. It is very important because the system is working at high temperatures and the pressure can increase suddenly occasioning important problems. If this happens, the safety valve opens to evacuate the vapours.

- **Level:** On the top of the reactor there is a high controller to make sure the level of the tank is not higher than it should, this would mean something went wrong with the loading of the reactants.

- **Temperature:** The reaction that takes place inside the reactor is a polycondensation type, producing water and the product needed. The water needs to be removed from the system and this process will be controlled with the temperature in every device of the process. The rector's temperature will be controlled with three transmitters measuring the variable inside the reactor, in the half-pipe jacket exchanger and in the internal coil exchanger. Depending of the target temperature inside the reactor, the action of both exchangers will be to decrease or increase the thermal oil flow rate. The column's temperature will be measured with two transmitters located at the top and at the bottom of the temperature. Both of them will make sure the temperature reached inside the column is enough to keep the distillation going on. The last device needed to control is the temperature of the condenser, but it will be done with the flow rate of the cooling water.

When all the variables mentioned before are well controlled, the process should take place with no unforeseen situations.

Down below will be seen all the instrumentation needed in every stream to make a sure every stream is well controlled:

Table 17. Instrumentation nomenclature

Pipe / Location	Instrumentation	Nomenclature
1	Flow transmitter	FT-01
4	Temperature transmitter	TT-04
10	Flow transmitter	FT-02
Reactor	Temperature transmitter	TT-01
Reactor	Pressure transmitter	PT-01
Reactor	Level transmitter	LT-01
Half-pipe jacket	Temperature transmitter	TT-02
Internal coil	Temperature transmitter	TT-03
Column	Temperature transmitter	TT-05
Column	Temperature transmitter	TT-06
Condenser	Temperature transmitter	TT-07

As long as the most important variable to control is the temperature inside the reactor, in the next subsection it has been studied how to do a proper and exhaustive control of this parameter to make sure the temperature reached inside the device is the target one.

Down below can be seen the control and automation of the polyester polyol:

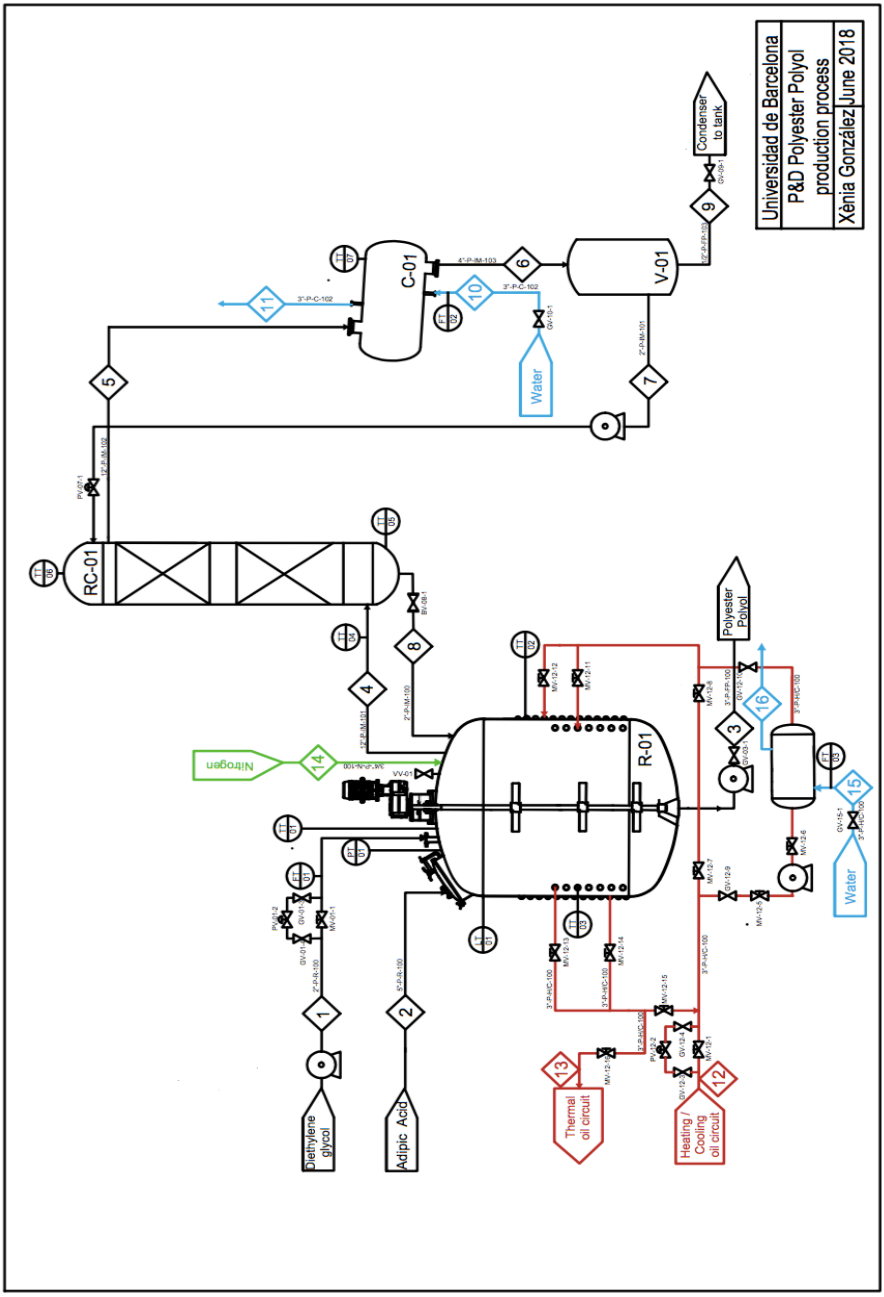

Universidad de Barcelona
P&D Polyester Polyol production process
Xènia González June 2018
RC-01
R-01
C-01
V-01
Diethylene glycol
Adipic Acid
Nitrogen
Water
Water
Polyester Polyol
Condenser to tank
Thermal oil circuit
Heating / Cooling oil circuit

Figure 5. P&D

5.1.2 Temperature automation

As sais before, the temperature is the most important parameter needed to be controlled because it controls the reaction of polyester polyol. It should be remained that the process faces a polycondensation reaction where water is produced and removed to push the equilibrium. If the temperature is not high enough, it won't be possible to get the water outside the system and the final product will contain impurities.

The temperature inside the reactor will be controlled during all the process and modified as required by the heating/cooling system. It has been design how the temperature will be controlled by using two circuits in one through several valves connected between each other creating different paths depending on the action wanted to achieve (cooling or heating).

Heating circuit

The heating circuit will be the first one to be explained as being the first taking place. To start with, the heating process will be done with thermal oil entering the system at 260ºC from an external oil circuit. The oil flows through the pipe 3"-P-H/C-100 and follows the path where the valves are open which are: MV-12-1, MV-12-7, MV-12-8, MV-12-11, MV-12-12, MV-12-13, MV-12-14 AND MV-12-16. Those are the valves that create the first path becoming the heating circuit. The heating oil, after doing all the route, leaves the system at 230ºC and is directed to the thermal circuit where the temperature will be increased and redirected to the heating circuit.

This circuit will control de temperature inside the reactor during 14,8 hours, as long as the heating process is going on. The reactor temperature transmitter will measure the temperature inside the reactor and will check if the it is at the target point. If the temperature inside the reactor is lower than 220ºC, the valve MV-12-1 will open to the maximum to let pass the higher thermal oil flow. If the temperature of the system is higher than 220ºC, the valve MV-12-1 will be closed partially to decrease the thermal oil's flow rate.

The figure 6 shows the path of the thermal oil, being the one that has all the green valves.

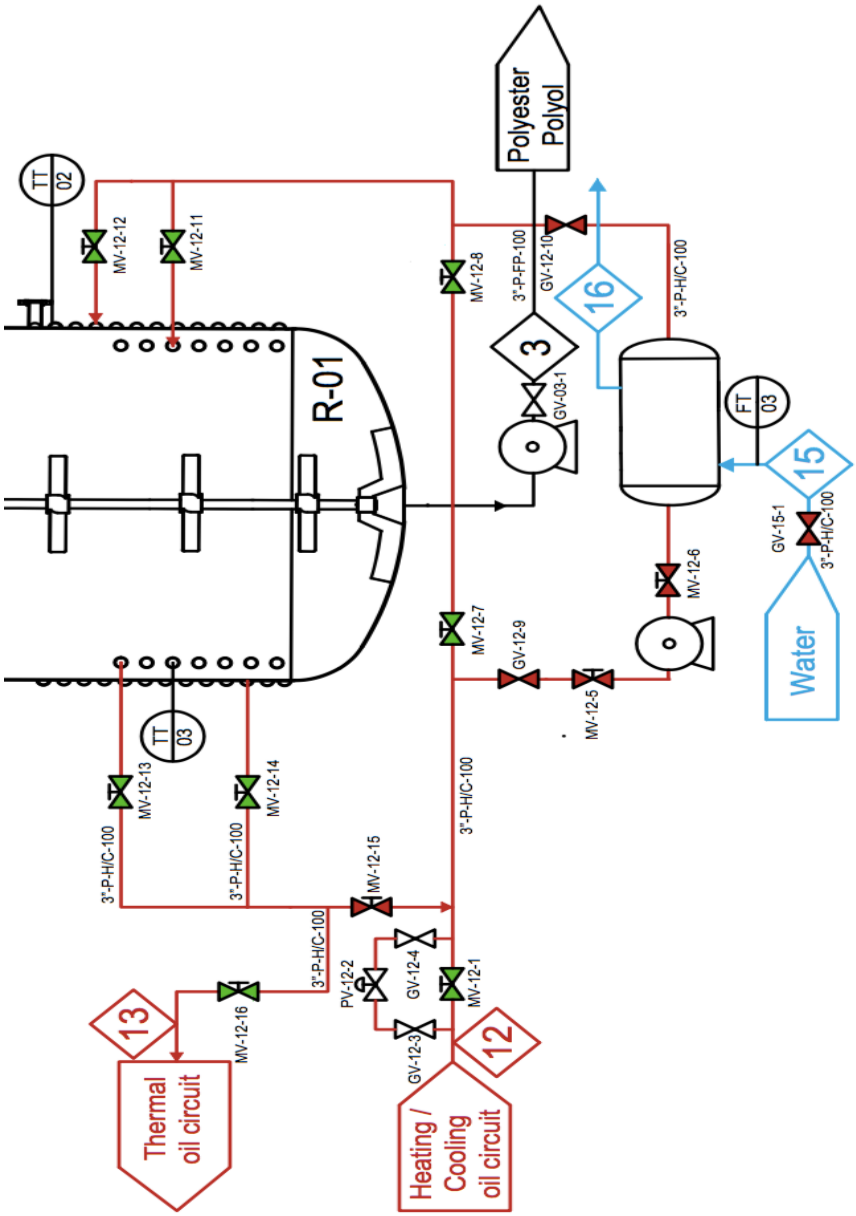


Figure 6. Heating circuit

Cooling circuit

The cooling circuit will be used in the final step of the process to decrease the temperature of the final product. As said before, for heating and cooling it will be used the same circuit, but using different paths, and the same fluid, thermal oil.

The refrigeration will be possible by closing the valves MV-12-1, MV-12-7, MV-12-8 and MV-12-16, creating a closed circuit with no entries and exits, becoming a recirculation of the thermal oil. To decrease the temperature of the thermal oil it has been design an external refrigeration with cooling water which lows down the oil temperature and in consequence the temperature inside the reactor. To use this path, the valves GV-12-9, MV-12-5, MV-12-6, GV-12-10 and MV-12-15 need to be open and let the thermal oil flow thought the refrigeration circuit.

The cooling circuit will be used during the cooling stage two and a half hours until the unloading of the product has finalized. The figure 7 shows the cooling circuit:

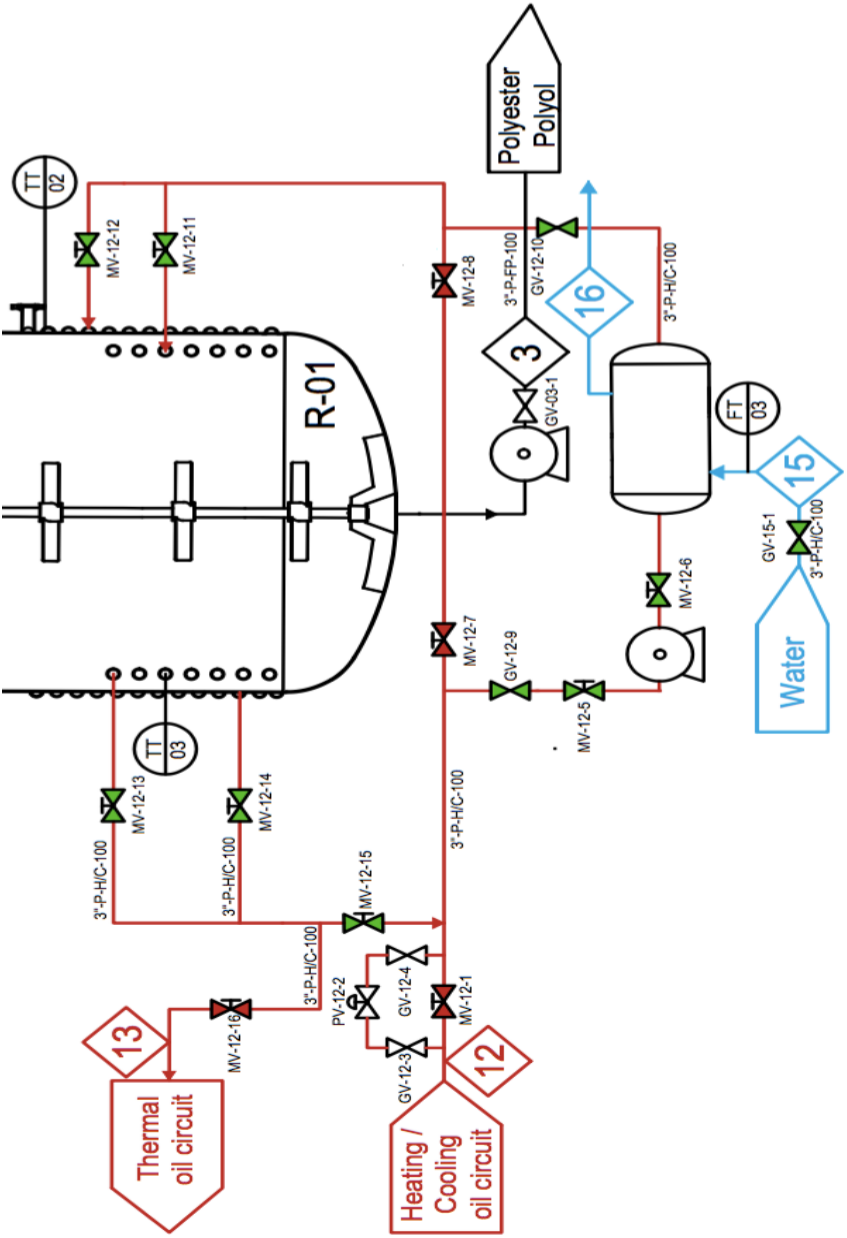


Figure 7. Cooling circuit

5.2. VALVES SPECIFICATIONS

Once the P&D is done it must be specified all the devices working to obtain a well-controlled process. Basically, the valves located in every pipe will be explained down below how they work and where are situated. In the P&D it can be seen three types of valves: Gate, Pneumatic and manual valves.

Table 18. Valves nomenclature

Pipe	Function	Nomenclature
1	Manual valve	MV-01-1
	Pneumatic valve	PN-01-2
	Gate valve	GV-01-4
	Gate valve	GV-01-4
3	Gate valve	GV-03-1
7	Pneumatic valve	PV-07-1
8	Flanged valve	BV-08-1
9	Gate valve	GV-09-1
10	Gate valve	GV-10-1
R	Venting valve	VV-01
12	Manual valve	MV-12-1
	Pneumatic valve	PV-12-2
	Gate valve	GV-12-3
	Gate valve	GV-12-4
	Manual valve	MV-12-5
	Manual valve	MV-12-6
	Manual valve	MV-12-7
	Manual valve	MV-12-8
	Gate valve	MV-12-9
	Gate valve	MV-12-10
	Manual valve	MV-12-11
	Manual valve	MV-12-12
	Manual valve	MV-12-13
	Manual valve	MV-12-14
	Manual valve	MV-12-15
	Manual valve	MV-12-16
15	Gate valve	GV-15-1

6. OPERATION

6.1 GENERAL CONSIDERATIONS

In this section, it will be seen the scheduling of the process and all the considerations that have been decided. First of all, it should be remembered that the main objective in this project is to produce 9000 tons per year of polyester polyol so this is the most important restriction this project has, to satisfy its annual demand.

On the other hand, it is known that the duration of one batch takes 18 hours and in one batch it is obtained 26600 kg of polyester polyol. To achieve the main objective of 9000 tons per year it will be needed 337 batches to reach the annual demand of the product.

6.2 BATCH TIME

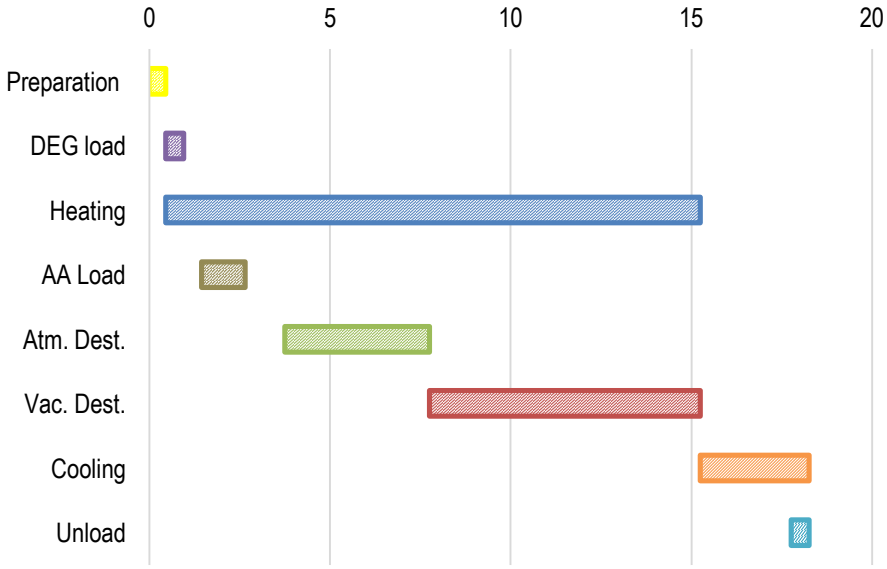
The polyester polyol process has many stages all of them making the process last 18hours. In total 8 activities are taking places during the process, all different between them and it is required the whole installation to keep on the process.

Working in batch mode allows more flexibility during the process and when developing more than one product. Also, it is very common to work on campaigns, overlapping one batch with another one to save time when producing. In this case, it has been impossible to work in campaigns because there is just one equipment and it can't be used to produce more than one batch at the same time because they are already occupied.

Down below, in the table 19 it is shown how long every stage takes and how they overlap between each other:

Table 19. Duration of the stages

Activity	Start time [h]	Duration [h]	End time [h]
Preparation	0	0.45	0.45
DEG load	0.45	0.5	0.95
Heating	0.45	14	15.25
AA Load	1.45	1.2	2.65
Atm. Dest.	3.75	4	7.75
Vac. Dest.	7.75	7.5	15.25
Cooling	15.25	3	18.25
Unload	17.75	0.5	18.25



Graphic 1. Gantt diagram

6.3 VARIABLES EVOLUTION

Once the batch time is well-defined with all the stages, batch time and size it will be done a study of how the most important variables of the system evolve during the process.

Those parameters studied will be the working temperature of the reactor and the column which is fundamental to achieve the project's goal. The pressure will be another variable studied in this section because during the production process we have many changes of the working pressure inside the reactor and column. The last variable will be the mass evolution during all the process.

Temperature of the reactor (----)

The temperature of the system is very important, and it suffers some changes during the process and it will be represented by the blue line in the first graphic. The initial temperature of the reactor is 25ºC, atmosphere temperature. Once the reactor starts working, the temperature is increased until 220ºC trough the half-pipe jacket and the internal helical coil exchangers. When it is reached the working temperature (220ºC) it must be maintained constant to keep the reaction and the evaporation on. After 14,8 hours of heating, the cooling stage starts to decrease the final product's temperature until 150ºC and it takes 3 hours. The line representing the temperature evolution shows the three stages of the temperature variation. The first stage, represented by a positive slope line showing how the temperature increases during the heating process. The second stage indicates that the temperature remains constant with a straight line. Finally, the cooling process is seen as a negative slope line.

Temperature of the column (----)

The temperature of the column works differently as the reactor's and is represented by a green line in the first graphic. At the beginning of the process, the column is not working because there aren't any vapours yet. As the reaction goes on and the temperature starts to increase and reaches 100ºC, the distillation starts and remains constant for 4 hours. After, the

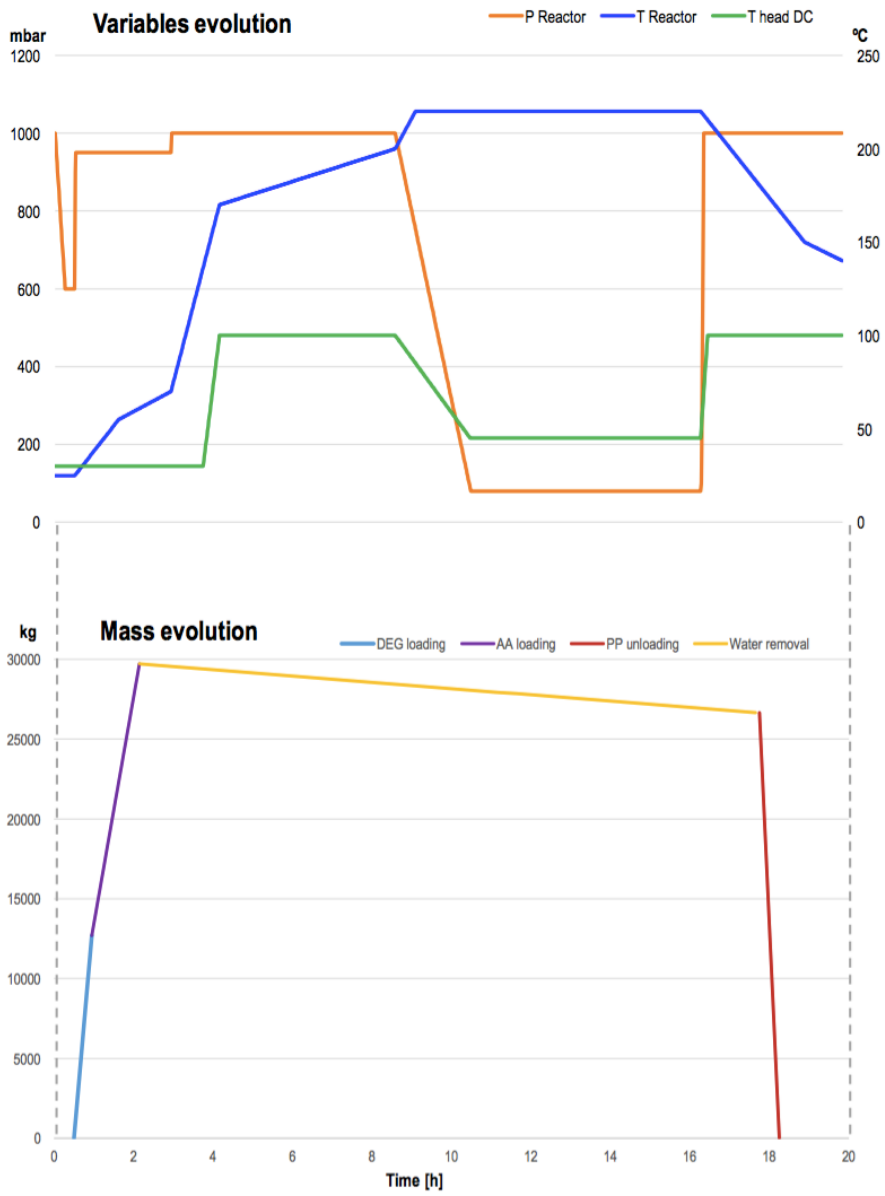
vacuum is done to decrease the temperature until 50ºC during 7,5 hours, so it is possible to maintain the removal of water. Once all the water is distilled, the temperature goes back to 100ºC. As shown in the graphic, at first the line remains constant at 25ºC, and when the temperature of the reactors starts to increase, so does the temperature of the column represented by a positive slope line. When it reaches 100ºC, it is maintained constant until the vacuum is done and the temperature decreases to 50ºC indicated by a negative slope line. After the temperature reaches again 100ºC to finalize the process.

Pressure (----)

The pressure of the process is represented by an orange line. It starts at atmospheric pressure and minutes after the vacuum is done inside the reactor to inert the reactor. After, the pressure increases until 950 mbar because it is being introduced the adipic acid in the system and a little depression it is needed to ensure the solid enters to the system. When the loading of the reactants has been done, the pressure is increased until 1000 mbar and it remains contstant until the vacuum is done to the column and the pressure decreases until 30mbar, represented by a negative slope orange line. When all the water has been removed, the vacuum is recovered, indicated by a positive slope line until 1000 mbar.

Mass evolution

During the process, the mass inside the reactor varies a lot so it will be studied as well. When the process starts, there is nothing inside the reactor until 45 minutes later, then the diethylene glycol and adipic acid are introduced inside the reactor, reaching the 29711 kg. When both reactants are in the reactor, the polycondensation reaction starts producing polyester polyol and water. As it can be seen in the following graphic, the removal of water remains constant but this doesn't happen in the real process. The mass of water removed at the begging is more sizable than at the end of the reaction, but as there's no information of the kinetic, it has been considered constants. At the end of the process, there's 26660 kg of polyester polyol which will be unloaded in 30 minutes to be stored.



Graphic 2. Process evolution

7. CONCLUSIONS

By all counts, and with the proven designs and results, it has been reached the main objective of the project, to satisfy the annual demand of polyester polyol which is 9000 tons per year by doing the basic engineering of the production process.

It has been design the whole process, starting with the batch dimension (timing and sizing) to obtain the amount of polyester polyol needed. To follow with, is has been design and dimensioned all the equipment needed to achieve our goal which consists in one stirred tank reactor, one distillation column, one condenser and one vessel.

Once all the process has been constructed, it has been design the flowsheet, the control and automation of the whole process (P&D), with an in-depth study of how the temperature is controlled inside the reactor to ensure a safety process.

Finally, it has been studied how the temperature of the reactor and column, the pressure and the mass evolve over the time to have a complete knowledge of the entire process.

Given all this points, it can be concluded that it has been done an effective design of the production process of the polyester polyol because it has been reached the main goal of the process, to meet the annual demand of polyester polyol.

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ACRONYMS

A: Area [m^2]

AA: Adipic Acid

C-01: Condenser

Cp: Calorific capacity [kJ/(kg·ºC)]

D_i: Impeller diamater [m]

DEG: Diethylene glycol

D_{eq}: Equivalent diamater [m]

D_{ext}: External diameter [m]

D_{int}: Internal diameter [m]

DN: Nominal diameter [inches]

D_t: Tank diameter [m]

L: Lenght [m]

M: Molecular mas [g/mol]

N: Rotational speed [rpm]

Np: Power number

Nt: Number of tubes

PP: Polyester polyol

Q: Exchanged heat [kJ]

q: Volumetric flow rate [m^3/s]

R-01: Reactor

RC-01: Distillation column

r_i: Internal radium

r_e: External radium

S_T: Section of the tube [m^2]

T: Temperature [ºC]

t: time [h]

V-01: Vessel

v: velocity [m/s]

V: Volume [m^3]

W_c: Cooling flow rate [kg/h]

W_h: Heating flow rate [kg/h]

ΔT: difference of temperature [ºC]

λ: latent heat [kJ/kg]

μ: Viscosity [Pa·s]

ρ: Density [m^3/kg]

APPENDICES

APPENDIX 1: SAFETY DATA SHEETS

Fichas Internacionales de Seguridad Química

ACIDO ADIPICO **ICSC: 0369**

MINISTERIO DE TRABAJO Y ASUNTOS SOCIALES ESPAÑA

INSTITUTO NACIONAL DE SEGURIDAD E HIGIENE EN EL TRABAJO

ACIDO ADIPICO
Acido hexanodioico
$C_6H_{10}O_4$/$HOOC(CH_2)_4COOH$
Masa molecular: 146.14

Nº CAS 124-04-9
Nº RTECS AU8400000
Nº ICSC 0369
Nº CE 607-144-00-9

TIPOS DE PELIGRO/ EXPOSICION	PELIGROS/ SINTOMAS AGUDOS	PREVENCION	PRIMEROS AUXILIOS/ LUCHA CONTRA INCENDIOS
INCENDIO	Combustible.	Evitar llama abierta.	Espuma, dióxido de carbono, pulverización con agua, polvo.
EXPLOSION	Las partículas finamente dispersas forman mezclas explosivas en el aire.	Evitar el depósito de polvo. Sistema cerrado, equipo eléctrico y de alumbrado a prueba de explosión de polvo. Evitar la generación de cargas electrostáticas (p. ej. con conexión a tierra)	En caso de incendio: mantener fríos los bidones y demás instalaciones por pulverización con agua.
EXPOSICION		¡EVITAR LA DISPERSION DEL POLVO! ¡HIGIENE ESTRICTA!	
• **INHALACION**	Tos, dolor de garganta.	Extracción localizada o protección respiratoria.	Aire limpio, reposo y someter a atención médica.
• **PIEL**		Guantes protectores, traje de protección.	Quitar las ropas contaminadas, aclarar la piel con agua abundante o ducharse.
• **OJOS**	Enrojecimiento, dolor.	Gafas ajustadas de seguridad o protección ocular combinada con la protección respiratoria.	Enjuagar con agua abundante durante varios minutos (quitar las lentes de contacto si puede hacerse con facilidad), después consultar a un médico.
• **INGESTION**		No comer, beber ni fumar durante el trabajo.	Enjuagar la boca, reposo y someter a atención médica.

DERRAMAS Y FUGAS	ALMACENAMIENTO	ENVASADO Y ETIQUETADO
Barrer la sustancia derramada e introducirla en un recipiente de plástico; si fuera necesario, humedecer el polvo para evitar su dispersión. Eliminar el residuo con agua abundante.		símbolo Xi R: 36 S: 2 CE:

VEASE AL DORSO INFORMACION IMPORTANTE

ICSC: 0369 Preparada en el Contexto de Cooperación entre el IPCS y la Comisión de las Comunidades Europeas © CCE, IPCS, 2005

Fichas Internacionales de Seguridad Química

ACIDO ADIPICO

ICSC: 0369

DATOS IMPORTANTES

ESTADO FISICO; ASPECTO
Polvo cristalino, incoloro e inodoro.

PELIGROS FISICOS
Es posible la explosión de polvo si se encuentra mezclada con el aire en forma pulverulenta o granular. Si está seca, puede cargarse electrostáticamente por turbulencia, transporte neumático, vertido, etc.

PELIGROS QUIMICOS
La sustancia se descompone al calentarla intensamente, produciendo humos tóxicos y corrosivos de ácido valérico y otras sustancias. La sustancia es un ácido débil. Reacciona con materiales oxidantes.

LIMITES DE EXPOSICION
TLV: 5 mg/m³ (como TWA) (ACGIH 1997)

VIAS DE EXPOSICION
La sustancia se puede absorber por inhalación del aerosol.

RIESGO DE INHALACION
La evaporación a 20°C es despreciable. Sin embargo, se puede alcanzar rápidamente una concentración nociva de partículas en el aire por dispersión.

EFECTOS DE EXPOSICION DE CORTA DURACION
La sustancia irrita los ojos y el tracto respiratorio. La inhalación del aerosol de la sustancia puede originar reacciones asmáticas (véanse Notas).

EFECTOS DE EXPOSICION PROLONGADA O REPETIDA
El contacto prolongado o repetido puede producir sensibilización de la piel. La exposición por inhalación prolongada o repetida puede originar asma.

PROPIEDADES FISICAS

Punto de ebullición: 338°C
Punto de fusión: 152°C
Densidad relativa (g/ml): 1.36
Solubilidad en agua: moderada (1.4 g/100 ml a 15°C)
Presión de vapor, Pa a 18.5°C: 10

Densidad relativa de vapor (aire = 1): 5.04
Punto de inflamación: 196°C
Temperatura de autoignición: 422°C
Coeficiente de reparto octanol/agua como log Pow: 0.08

DATOS AMBIENTALES

NOTAS

Los síntomas del asma no se ponen de manifiesto a menudo hasta pasadas unas pocas horas y se agravan por el esfuerzo físico. Reposo y observación médica son por ello imprescindibles. Cualquiera que haya presentado síntomas de asma debidos a la sustancia en cuestión, debe evitar el contacto con ella.

Código NFPA: H 1; F 1; R 0;

INFORMACION ADICIONAL

FISQ: 2-009
ACIDO ADIPICO

Los valores LEP pueden consultarse en línea en la siguiente dirección:
http://www.insht.es/

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Fichas Internacionales de Seguridad Química

DIETILENGLICOL			**ICSC: 0619** **Noviembre 2007**
	Etilendiglicol 3-Oxipentano-1,5-diol 2,2'-Oxibisetanol		2,2'-Dihidroxietil éter 2,2'-Oxidietanol
CAS: **RTECS:** **CE Índice Anexo I:** **CE / EINECS:**	**111-46-6** **ID5950000** **603-140-00-6** **203-872-2**	**$C_4H_{10}O_3$ / $(CH_2CH_2OH)_2O$** **Masa molecular: 106,1**	

TIPO DE PELIGRO / EXPOSICIÓN	**PELIGROS AGUDOS / SÍNTOMAS**	**PREVENCIÓN**	**PRIMEROS AUXILIOS / LUCHA CONTRA INCENDIOS**
INCENDIO	Combustible.	Evitar las llamas.	Polvo, espuma resistente al alcohol, pulverización con agua, dióxido de carbono.
EXPLOSIÓN			

EXPOSICIÓN		**¡EVITAR LA FORMACIÓN DE NIEBLAS DEL PRODUCTO!**	
Inhalación		Ventilación.	Aire limpio, reposo.
Piel		Guantes de protección.	Aclarar la piel con agua abundante o ducharse.
Ojos		Gafas de protección de seguridad.	Enjuagar con agua abundante durante varios minutos (quitar las lentes de contacto si puede hacerse con facilidad).
Ingestión	Dolor abdominal. Náuseas. Vómitos. Diarrea. Vértigo. Somnolencia. Confusión. Pérdida del conocimiento.	No comer, ni beber, ni fumar durante el trabajo.	Dar a beber uno o dos vasos de agua. Proporcionar asistencia médica inmediatamente. Ver Notas.

DERRAMES Y FUGAS	**ENVASADO Y ETIQUETADO**
Protección personal complementaria: filtro para gases y vapores orgánicos adaptado a la concentración de la sustancia en el aire. Recoger el líquido procedente de la fuga en recipientes precintables. Eliminar el líquido derramado con agua abundante.	**Clasificación UE** Símbolo: Xn R: 22 S: (2-)46 **Clasificación GHS** Peligro Nocivo en caso de ingestión. Provoca daños en el hígado por ingestión. Puede provocar somnolencia o vértigo.
RESPUESTA DE EMERGENCIA	**ALMACENAMIENTO**
Código NFPA: H1; F1; R0;	Mantener en lugar seco. Bien cerrado. Separado de oxidantes fuertes,

IPCS
International Programme on Chemical Safety

Preparada en el Contexto de Cooperación entre el IPCS y la Comisión Europea © IPCS, CE 2008

VÉASE INFORMACIÓN IMPORTANTE AL DORSO

Fichas Internacionales de Seguridad Química

DIETILENGLICOL	ICSC: 0619

DATOS IMPORTANTES

ESTADO FÍSICO; ASPECTO:
Líquido higroscópico, viscoso, incoloro e inodoro.

PELIGROS QUÍMICOS:
Reacciona violentamente con oxidantes fuertes originando peligro de incendio y explosión. Ataca algunas formas de plástico.

LÍMITES DE EXPOSICIÓN:
TLV no establecido.
MAK: 10 ppm; 44 mg/m^3; Categoría de limitación de pico: II(4); Riesgo para el embarazo: grupo C (DFG 2007).

VÍAS DE EXPOSICIÓN:
La sustancia se puede absorber por ingestión.

RIESGO DE INHALACIÓN:
Por evaporación de esta sustancia a 20 °C no se alcanza, o se alcanza sólo muy lentamente, una concentración nociva en el aire sin embargo, más rápidamente por pulverización o cuando se dispersa.

EFECTOS DE EXPOSICIÓN DE CORTA DURACIÓN:
La sustancia puede afectar al riñón, dando lugar a alteraciones renales. La sustancia puede afectar al sistema nervioso central y al hígado por ingestión. La exposición por ingestión puede producir la muerte.

PROPIEDADES FÍSICAS

Punto de ebullición: 245 °C
Punto de fusión: -6,5 °C
Densidad relativa (agua = 1): 1,12
Solubilidad en agua: miscible
Presión de vapor, Pa a 20 °C: 2,7
Densidad relativa de vapor (aire = 1): 3,7

Punto de inflamación: 124 °C c.c.
Temperatura de autoignición: 229 °C
Límites de explosividad, % en volumen en el aire: 1,6-10,8
Coeficiente de reparto octanol/agua como log Pow: -1,47

DATOS AMBIENTALES

NOTAS

En caso de envenenamiento con esta sustancia es necesario realizar un tratamiento específico; así como disponer de los medios adecuados junto a las instrucciones correspondientes.

INFORMACIÓN ADICIONAL

FICHA TÉCNICA POLÍMERO BASE

FT-7-0

POLIÉSTERES

CARACTERÍSTICAS TÉCNICAS

Formulación: Poliésteres $(-R-CO-O-R'-O-CO-R-)_n$ $(-O-R'-O-CO-R-CO-)_n$

R= rad ácido R'= rad alcohol

Clase: Polímeros de condensación: Termoplásticos o termorrígidos.

Aspecto de la granza: Gránulos. Resinas en disolución.

Homopolímeros: Poli (tereftalato de alquilo).
Polilactona.
Poliéster no saturado UP.
Policarbonato PC.

Copolímeros: Poliéster/poliéter.
Poliéster/carbonato.
Policarbonato/siloxano.

ADITIVOS

Estabilizantes : Benzofenonas.
Benzotriazoles

Endurecedores: Sales de cobalto.
Peróxido benzoilo.
Aminas.

Modificadores: Estireno, Vinil-tolueno, Silicona, Benzoguanamina, Melamina.

Lubrificantes: Acido esteárico.
Estearato metilo

Cargas y refuerzos: Asbestos, Sílice, Vidrio, Sulfato cálcico, Silicato cálcico, Dióxido de titanio. Fibra y mecha de vidrio.

Pigmentos: Dióxido de titanio, Óxido de cromo, Óxido de hierro, Litopón, Sulfuro de cadmio, Bencidinas.

Ignifugantes: Reactivos bromados.
Óxido antimonio.
Óxido aluminio trihidratado.

PROCESOS DE TRANSFORMACIÓN Y SUS TEMPERATURAS

Proceso	Temperatura (°C)
Moldeo por compresión (además, curado)	120-160
Moldeo por inyección	150, e, incluso, 280
Extrusión	150, e, incluso, 270

DATOS DE DEGRADACIÓN TÉRMICA

Temperatura degradación: Superior a 200°C pero, en general, inferior a 270-290°C. Estabilidad térmica moderada, la presencia de humedad favorece la degradación.

Características humos y vapores emitidos: Nieblas neutras o algo ácidas.

Productos degradación emitidos:

Principales:	**Secundarios**:
Acetaldehído	Benzoato de vinilo
Ácido tereftálico (producto de partida)	Cetonas
Dióxido de carbono	Agua (vapor)
Monóxido de carbono	Metano
Anhídridos orgánicos	Etileno
Ácido benzoico	Acetileno
Ácido p-acetilbenzoico	Ésteres metílicos de ácidos aromáticos
Acetofenona	

Características residuos degradación: Porcentaje ponderal: Mayor que 50
Aspecto y composición: Resina oscura alquitranosa

DATOS COMBUSTIÓN A CORTO TÉRMINO

Parámetro LOI: 20-24, y, hasta 30 para poliésteres con ignifugantes.

Temperatura ignición: 450°C

Productos de combustión: Dióxido de carbono, agua (vapor), monóxido de carbono, y, en menor cantidad, acetaldehído y etileno.

TOXICIDAD PRODUCTOS EMITIDOS

Producto	Acción sobre el organismo
Acetaldehído	Irritante
Dióxido de carbono	Asfixiante
Monóxido de carbono	Tóxico de la sangre
Anhídridos orgánicos	Irritantes y corrosivos
Cetonas	Narcóticos
Metano, etano, acetileno	Asfixiantes simples
Ésteres metílicos	Narcóticos y nocivos

APPENDIX 2: MANUAL OF CALCULUS

MASS BALANCE

To start with, the first thing needed to calculate global mass balance to have a full knowledge of every stream, the product/reactants which flows inside and the amount of each one. It should be remembered that this process works in batch mode, so we can just calculate the amount of each product that enters in the system or leaves:

Table 20. Mass balance

kg/batch	1	2	3	9
DEG	12711	0	0	72
AA	0	17000	0	0
PP	0	0	26600	0
H_2O	0	0	0	3051
N_2	0	0	0	0

SIZING OF THE QUIPMENT

In this section, will be seen all the calculation realized during the project to size all the equipment needed, which are: the batch reactor, the distillation column, the condenser and the vessel.

REACTOR (R-01)

The design of the stirred tank reactor has been done taking in account the daily production of polyester polyol which represents the main objective of the project:

Table 21. Volumes of the products/ reactants

	kg / batch	Volume [m3]
AA	17000	12.5
DEG	12711	11.3
PP	26660	22.4
H_2O	3051	3.1

Once all the amounts of every reactant/product are well known, supposing all the volumes are additives, the total volume of the reactor is 30,4 m^3. It should be considered that inside the tank will be an expansion chamber, because the process works with volatile vapours, which represents a 20% of the volume of the reactor. On the other hand, to dimensions the reactor it has been considered the heuristics:

$$H = 1.5 \cdot D_T$$

$$V = \pi \cdot (\frac{D_T}{2})^2 \cdot H + \frac{4}{3}\pi \cdot (\frac{D_T}{2})^3$$

Table 22. Characteristics of the R-01

Effective volume [m^3]	30.4
Total volume [m^3]	35
Diameter [m]	2.68
Total high [m]	4.43
Effective high [m]	3.69

Agitation system

For the design of an effective agitation system it is fundamental to know the viscosity of all the reactants/products inside of the system because this is the property that defines the agitation system. In this project, the viscosities of all of them are very similar as the water, but it must be remembered that the adipic acid is a solid at 25ºC, so the agitations system has to be very powerful to maintain the system homogenized.

The dimensions of the impellers are directly proportional to the size of the reactor, and it has been calculated with the heuristics:

$$h = \frac{1}{2} - \frac{1}{3}H$$

$$D_{impeller} = \frac{1}{3} \cdot D_{reactor}$$

Once known the high from the bottom of the reactor, which is 0.53m it has been considered the need of 3 impellers equidistant between each other's to ensure the homogenization inside the reactor.

The power of the agitation system has been calculated with the Reynolds number, which depends of the fluid using in every process. The number of power is directly proportional to the number of Reynolds, and the parameters b and x are related to the type of regime of circulation.

$$Re = \frac{D^2 \rho \, Np}{\mu}$$

$$Np = b \, Re^x$$

$$P = Np \, \rho \, N^3 D^5$$

Table 23. Agitation variables

Peached paddle impeller		
Regime	b	x
Laminar	35	-1
Turbulent	2	0

Table 24. Agitation characteristics

Height [m]	0.53
	1.83
	3.13
Rotational speed [rpm]	120
Power supplied [W]	12380
$D_{impeller}$	0.89
D_i/Dt	0.33
Re	217068

Half-pipe jacket exchanger

First of all, to design an effective heat exchanger it is need to know the amount of heat needed and the surface available.

To start, it is going to be calculated the total heat to evaporate all the water inside the reactor with it's latent heat:

$$Q = wc \cdot \lambda c = 3051 \frac{kg}{day} \cdot 1800 \frac{kJ}{kg} = 5.9 \cdot 10^6 \frac{kJ}{day}$$

$$Q = 5.9 \cdot 10^6 \frac{kJ}{day} \cdot \frac{1\ day}{24\ hours} \cdot \frac{1\ hour}{3600} = 69\ kW$$

Once the total heat is known, the following step is to calculate the total exchange area to provide to the system the power required:

$$\Delta Tml = \frac{\Delta T_2 - \Delta T_1}{\ln(\frac{\Delta T_2}{\Delta T_1})} = 43.28$$

- t1: Entry temperature of thermal oil= 260ºC
- t2: Exit temperature of thermal oil = 230ºC
- T1: Entry temperature of the product inside the reactor = 220ºC
- T2: Exit temperature of the product inside the reactor = 220ºC

The temperature of the reactor will remain constant at 220ºC and the heating fluid, which is organic thermal oil will enter the system at 260ºC and will leave at 230ºC.

$$Q = A \cdot U \cdot \Delta Tml$$

$$A = \frac{Q}{U \cdot \Delta Tml} = \frac{5.9 \cdot 10^6 \frac{kJ}{day}}{1800 \frac{kJ}{h \cdot m^2 \cdot ºC} \cdot 43.28} = 76\ m^2$$

It should be remained that the effective area of the reactor is 34 m^2 so we don't have enough surface to provide the power required. The solution will be solved by the installation of another exchanger inside the reactor.

Now, it will be calculated how much heat can be provided with a surface of 34m^2 and the rest of the heat will be reached with and helical coil exchanger.

$$Q = A \cdot U \cdot \Delta Tml = 34m^2 \cdot 43{,}28 \cdot 1800 \frac{kJ}{h \cdot m^2 \cdot ºC} = 2.6 \cdot 10^6 \frac{kJ}{day}$$

$$Q = 2.6 \cdot 10^6 \frac{kJ}{day} \cdot \frac{1\ day}{24\ hours} \cdot \frac{1\ hour}{3600} = 31\ kW$$

The flow rate of the organic thermal oil can be calculated with:

$$Q = wc \cdot cp \cdot (Te - Ts)$$

$$wc = \frac{Q}{cp \cdot (Te - Ts)} = \frac{2.6 \cdot 10^6 \frac{kJ}{day}}{2000 \frac{kJ}{kgºC} \cdot (260 - 230)ºC} = 44 \frac{kg}{day}$$

Table 25. Half-pipe jacket characteristics

Jacket type	Split half-pipe
Operation	Heating
Fluid	Heating oil
Exchange area [m²]	34
Heating power [kW]	31
Fluid flow [kg/h]	1.8
U [kJ/ (h*m2*ºC)]	1800
ΔT_{ml}	43.28

Internal helical coil exchanger

The helical coil will be located inside the reactor, covering almost all the effective area from the inside of the reactor. The total heat needed to provide with this exchanger is:

$$Total\ heat = 69\ kW = Heat\ from\ external\ jacket + heat\ from\ the\ helical\ coil$$

$$Heat\ from\ the\ helical\ coil = 69kW - 31kW = 38\ kW$$

With the total heat needed to provide with the internal helical coil it can be calculated the surface of the exchanged are. It will remain constant the $\cdot \Delta Tml$ but the U coefficient will vary as the exchanger has changed.

$$A = \frac{Q}{U \cdot \Delta Tml} = \frac{3.2 \cdot 10^6 \frac{kJ}{day}}{1000\ \frac{kJ}{h \cdot m^2 \cdot ºC} \cdot 43.28} = 75\ m^2$$

Once the area is defined, the next step is to calculate the length of the pipe and the number of coils needed to reach the area.

$$L = \frac{A}{\pi \cdot d} = \frac{75\ m^2}{\pi \cdot 0.1\ m} = 237m$$

$$one\ turn = \sqrt{(2 \cdot \pi \cdot re)^2 + 0.15^2} = \sqrt{(2 \cdot \pi \cdot \frac{2.68}{2} m)^2 + 0.15^2} = 7.8\ m$$

$$Number\ of\ turns = \frac{L}{one\ turn} = \frac{237m}{7.8} = 30\ turns$$

The flow rate of the organic thermal oil can be calculated with:

$$Q = wc \cdot cp \cdot (Te - Ts)$$

$$wc = \frac{Q}{cp \cdot (Te - Ts)} = \frac{3.2 \cdot 10^6 \frac{kJ}{day}\frac{kJ}{day}}{2000 \frac{kJ}{kg ºC}(260 - 230) ºC} = 54 \frac{kg}{day}$$

Table 26. Helical coil characteristics

	REACTOR R-01
Type	Internal helical coil exchanger
Operation	Heating
Fluid	Heating oil
Exchange area [m²]	75
Heating power [kW]	38
Fluid flow [kg/h]	2.3
U [kJ/ (h*m2*ºC)]	1000
ΔT_{ml}	43.28
Length [m]	238
Number of coils	30
High [m]	2.8
Diameter [m]	0.1

CONDENSER (C-01)

To dimension the condenser, it has been fixed the amount of water needed to be condensed, 3051 kg/day. The distillation process lasts 11.5 hours so the amount of water has been fractioned into 11.5, simulating that the flow rate remains constant.

$$Q = wc \cdot \lambda l = \frac{3051\ \frac{kg}{day}}{12\ h} \cdot 334.4\ \frac{kJ}{kg} = 8.5 \cdot 10^4\ \frac{kJ}{day}$$

$$Q = 8.5 \cdot 10^4 \frac{kJ}{day} \cdot \frac{1\ day}{24\ hours} \cdot \frac{1\ hour}{3600} = 1\ kW$$

$$\Delta Tml = \frac{\Delta T_2 - \Delta T_1}{\ln\left(\frac{\Delta T_2}{\Delta T_1}\right)} = 10.12$$

The temperature used to calculate the logarithmic temperature have been:

- t1: Entrance temperature if the cooling water = 20ºC
- t2: Exit temperature of cooling water = 30ºC
- T1: Entrance temperature of the distilled water = 55ºC
- T2: Exit temperature of the condensed water = 45ºC

$$Q = A \cdot U \cdot \Delta Tml$$

$$A = \frac{Q}{U \cdot \Delta Tml} = \frac{8.5 \cdot 10^4\ \frac{kJ}{day}}{1000 \cdot 10.12} = 9\ m^2$$

The condenser should have an exchange are of 9.33 m2 but, it must be design in the worst conditions, so it has been design to refrigerate the double flow rate of distilled water.

$$A = 16\ m^2$$

$$wc = \frac{3051\ kg\ of\ water}{12\ hours} = 254\ \frac{kg}{h}\ \rightarrow wc = 254\ \frac{kg}{h} \cdot 2 = 508\ \frac{kg}{h}$$

To calculate the surface of the tubes and the volumetric flow it has been supposed the length of the tubes, the velocity of the fluid and the external diameter of the tubes.

$$A = \pi \cdot De \cdot L \cdot Nt$$

$$Nt = \frac{A}{\pi \cdot De \cdot lenght} = \frac{16m^2}{\pi \cdot 0.02m \cdot 5m} = 50\ tubes$$

$$q = \frac{wc}{\rho} = \frac{508.5\frac{kg}{h}}{1000\frac{kg}{m^3}} = 0.508\frac{m^3}{h}$$

$$q\ per\ tube = \frac{q}{Nt} = \frac{0.508\,\frac{m^3}{h}}{50\ tubes} = 0.01\,\frac{m^3}{h}$$

$$ST = L \cdot r^2 \cdot \pi \cdot Nt = 5m \cdot (0.01m)^2 \cdot \pi \cdot 50\ tubes = 0.09\ m^2$$

Table 27. Condenser characteristics

	Condenser
Exchange area [m²]	16.80
Fluid flow [kg/h]	508.5
Volumetric flow [m³/h]	0.508
Volumetric flow per tube [m³/h]	0.01
Velocity of the cooling fluid [m/s]	2
Number of pipes	50
Diameter of the pipes [cm]	2
Surface of the pipe [m²]	0.09

VESSEL (V-01)

The design of the final vessel where the distilled water goes has been design to storage two batches, in case it can't be unloaded during one batch.

$$Total\ mass\ of\ water = 3051\ \frac{kg}{day}$$

$$Volume = \frac{Total\ mass\ of\ water}{\rho} = \frac{3051\ \frac{kg}{day}}{1000\ \frac{kg}{m^3}} = 3m^3$$

$$Final\ volume = V\ one\ batch \cdot 2 = 3.051\ m^3 \cdot 2 = 6\ m^3$$

PIPING

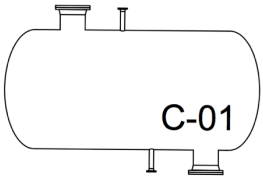
Along the process, it has been seen that there is no information of how the composition evolves during the time inside the distillation column. Down below will be calculated the diameter of the pipes 1, 3 and 9.

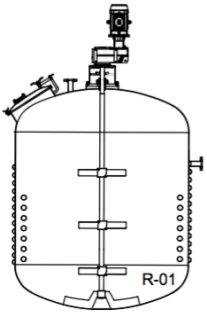
It must be remembered that the line 2, is not a pipe. As the adipic acid is a solid, it is used a suction pipe to load the product, but the diameter cannot be calculated but it has been chosen by vendor that will be 5" of nominal Diameter.

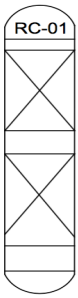
Table 28. Diameter of the pipes

Fluid	Pipe	Velocity [m/s]	Q [m^3/h]	DN[m]	DN[inches]
Diethylene glycol	1	2	22.7	0.05	2
Polyester polyol	3	2	44.8	0.07	3
Water + 3% Diethylene glycol	9	1	6.1	0.5	2

APPENDIX 3: SPECIFICATION SHEETS

SPECIFICATION SHEET		Equipment	Condenser
		N equipment	C-01
PROJECT	Basic engineering of polyester polyol		
	production process		
DESIGN			
Area [m2]	16	Position	Horitzontal
Temperature [ºC]	+20/+50	Material	
Pressure [mbar]	1000	Contact	AISI 316
HEAT TRANSMISION			
Exchanger	Shell-and-tube exchanger		
Operation	Cooling	Fluid	Water
Fluid flow [kg/h]	508	Power [kW]	2
PIPING			
Number of tubes	50		
Diameter [cm]	2		
Surface of pipe [cm2]	9		
Disposition pipes	Triangular		

<table>
<tr><td colspan="2" rowspan="2">SPECIFICATION SHEET</td><td>Equipment</td><td>Reactor</td></tr>
<tr><td>N equipment</td><td>R-01</td></tr>
<tr><td>PROJECT</td><td colspan="3">Basic engineering of polyester polyol production process</td></tr>
<tr><td colspan="4">DESIGN</td></tr>
<tr><td>Volume [m3]</td><td>35</td><td>Position</td><td>Vertical</td></tr>
<tr><td>Temperature [ºC]</td><td>+25/+220</td><td colspan="2">Material</td></tr>
<tr><td>Pressure [mbar]</td><td>30/1000</td><td>Contact</td><td>AISI 316</td></tr>
<tr><td>H/D</td><td>1.5</td><td>No-Contact</td><td>AISI 316</td></tr>
<tr><td colspan="4">HEAT TRANSMISION</td></tr>
<tr><td>Exchanger</td><td colspan="3">Half-pipe Jacket</td></tr>
<tr><td rowspan="2">Operation</td><td>Heating</td><td rowspan="2">Fluid</td><td rowspan="2">Organic oil</td></tr>
<tr><td>Cooling</td></tr>
<tr><td>Exchange area [m2]</td><td>34</td><td>Power [kW]</td><td>31</td></tr>
<tr><td>Exchanger</td><td colspan="3">Internal helical coil</td></tr>
<tr><td rowspan="2">Operation</td><td>Heating</td><td rowspan="2">Fluid</td><td rowspan="2">Organic oil</td></tr>
<tr><td>Cooling</td></tr>
<tr><td>Exchange area [m2]</td><td>75</td><td>Power [kW]</td><td>38</td></tr>
<tr><td colspan="2">AGITATION</td><td colspan="2" rowspan="5"> 
</td></tr>
<tr><td>Type</td><td>Paddle</td></tr>
<tr><td>Number of axes</td><td>1</td></tr>
<tr><td>Number of impellers</td><td>3</td></tr>
<tr><td>Impeller shape</td><td>6 pitched blade</td></tr>
<tr><td>Rotational speed [rpm]</td><td>120</td></tr>
</table>

SPECIFICATION SHEET		Equipment	Distillation column
		N equipment	RC-01
PROJECT	Basic engineering of polyester polyol production process		
DESIGN			
High [m]	5		
Temperature [ºC]	+50/+150		
Pressure [mbar]	30/1000		
Position	Vertical		
Material	AISI 316		

SPECIFICATION SHEET		Equipment	Vessel
		N equipment	V-01
PROJECT	Basic engineering of polyester polyol production process		
DESIGN			
Volume [m^3]	6		
Temperature [ºC]	+50/+150		
Pressure [mbar]	1		
Position	Vertical		
Material	AISI 316		