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Design of a Methyl Methacrylate production plant

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Even the darkest night will end and the sun will rise.

Victor Hugo

En primer lugar, quiero agradecer a mi familia por el apoyo que me han dado durante todos estos años, así como a mi tutor Dr. José Gutierrez por su ayuda y dedicación en este trabajo.

1. SUMMARY

Methyl methacrylate is a monomer which is majority used to produce polymethyl methacrylate which has a wide range of applications due to his transparency, weather-resistance, and stability. Moreover, it is used to make methacrylate resins for coatings and inks.

Due to its importance, a great number of processes to obtain it has been developed, which are reliant on the different raw materials employed due to the expected location of the plant.

In this work it has been selected a process to produce methyl methacrylate from methacrolein as it has the advantage that is an intermediate that can be obtained from two of the three raw materials commonly used. Afterwards, it has been searched for improvements over it in patents to avoid inconveniences caused by the secondary by-products; and to increase the productivity. Finally, it is carried out the reactor selection and design, as well as the other equipment needed for its properly operation.

The plant design has been done without limitations when it comes to raw materials, services or energy needed and to achieve a production of 40.000 tones / year; the product would require a final purification so that it can be commercialised that is not included in the scope of this project.

Keywords: Methyl methacrylate, manufacturing process, equipment design, patents

2. RESUM

El metacrilato de metilo es un monómero que se utiliza mayoritariamente para producir polimetacrilato de metilo, el cual tiene una amplia variedad de aplicaciones debido a su transparencia, resistencia a la intemperie y estabilidad. Además, se utiliza para fabricar resinas de metacrilato para revestimientos y tintas.

Debido a su importancia, se ha desarrollado varios procesos para su obtención, que dependen de las diferentes materias primas empleadas debido a la ubicación prevista de la planta.

En este trabajo se ha seleccionado un proceso para producir metacrilato de metilo a partir de metacroleína, ya que tiene la ventaja de que es un intermediario que se puede obtener a partir de dos de las tres materias primas utilizadas. Posteriormente, se ha realizado un estudio de las diversas patentes para tener en cuenta las mejoras del proceso y así evitar inconvenientes en su operación, puesto que se forman productos secundarios; y también para aumentar la productividad. Finalmente se ha realizado la selección y diseño del reactor, así como del resto de equipos necesarios para alcanzar una producción de 40.000 toneladas/año. El producto obtenido requerirá de una purificación final para poder ser comercializado, la cual no está en el alcance de este proyecto.

Palabras clave: Metacrilato de metilo, proceso de producción, diseño de equipos, patentes.

1. INTRODUCTION

Methyl methacrylate is an organic compound which is used to produce polymer-based products such as acrylic glass, coatings and inks. In addition, it is considered as the most important methacrylic ester due to his usability as a raw material for the manufacture of methacrylate derivatives.

That is why it is interesting to be able to produce methyl methacrylate in an economic way and as simple as possible. Due to the high consumption of methyl methacrylate, it has been chosen to design a continuous methyl methacrylate production plant.

1.1. HYSTORY

In historical terms, in 1843 the acrylic acid was synthesized for first time. Nearly twenty years later, the methacrylic acid was formulated from it. This fact was an important step to its creation, since methacrylic acid, along with methanol, react producing ester methyl methacrylate, the single chemical compound from which other methacrylates are created.

In the early 1930s, British chemists Rowland Hill and John Crawford discovered polymethyl methacrylate at Imperial Chemical Industries (ICI) in the United Kingdom. The product was registered under the trademark Perspex.

At the same time, German chemist and industrialist Otto Röhm and Haas AG produced safety glass by polymerizing methyl methacrylate between two layers of glass. The polymer separated from the glass was trademarked as Plexiglass in 1933 (GmbH, 2020). So, both Perspex and Plexiglass were commercialized in the late 1930s.

In the United States, the DuPont Company introduced its own product named Lucite. The Lucite International was the first company in commercialising viable production of acrylic safety glass.

Moreover, during World War II, both sides used methyl methacrylate to create submarine periscopes, aircraft windshields and gun turrets. In fact, the airplane pilots whose eyes were injured by PMMA shreds healed much better than those damaged by standard glass.

Nowadays, methyl methacrylate is present in our lives. It is used to produce polymethyl methacrylate and so prove of this omnipresence, is the still popularity of trademarks like Plexiglas, Perspex o Lucite, being Plexiglas the least known in Spain.

1.2. GENERALITIES

1.2.1. Properties

Methyl methacrylate, also known as methyl 2-methylpropeonate according to IUPAC, has the chemical formula $C_5H_8O_2$ and the molecular weight of 100.121 g/mol. It is characterized of being a colourless, toxic and a flammable liquid.

Methyl methacrylate appears as a clear colourless volatile liquid. It is slightly soluble and floats on water and its vapours are heavier than air. Its odour is a characteristic quality is sulphur-like, sweet and sharp. Its hedonic tone results unpleasant for living beings; and it is also acrid and fruity.

Regarding its main properties, are as follows:

Table 1: Main properties of methyl methacrylate

Ionization Potential (eV)	9.70
Boiling Point (ºC)	101
Melting Point (ºC)	-48
Critic Temperature (ºC)	291
Autoignition Temperature (ºC)	435
Viscosity at 24ºC (mPa·s)	0.53
Vapor pressure at 25ªC	3.87
Specific gravity	0.939

1.2.2. Uses

Thanks to its acrid and fruity odour it is been used as a food additive and flavouring agent, and it also has organoleptic properties, as an aromatic, acrylic and fruity flavour.

As well, methyl methacrylate is a reactive resin, and the polymerized form is used as cement in dentistry, orthopaedic surgery and ophthalmology (Dunne, Clements, & Wang, 2014). The monomer form has relaxation effect on smooth muscle and it might be due to the nitric oxide-mediated response.

It is also used in the manufacture of methacrylate resins and plastics (example: Plexiglas, Lucite). The principal uses are cast sheet (advertising signs, building panels and sidings, lighting fixtures, skylights and glazing…), moulding/extrusion powder and coatings (lacquer, latex paints and enamel resins).

Nowadays, the largest application for methyl methacrylate (80%) is to produce polymethyl methacrylate, which resins are employed to make products that require good optical clarity, weather-resistance, and stability. Its major use is in surface coatings, generally emulsion polymers for architectural and maintenance paints.

In less proportion, it is also used to produce copolymers such as methyl methacrylate-butadiene-styrene, which its resins are used as a modifier for clear rigid PVC and in food and pharmaceutical packaging.

In Asia, they are new applications related to transparent acrylonitrile-butadiene-styrene resins that are used in computer casings and mobile phones.

1.2.3. Risks and toxicity

Methyl methacrylate is included in Special Health Hazard Substance List because of its flammable and reactive properties, so its risks and possible damages have to be taken into account.

1.2.3.1. Flammability

In terms of flammability, it is considered, according to the National Fire Protection Association (NFPA), a material belonging to Class IB Flammable Liquid: the flash point is below 22.8ºC (73ºF) and the boiling point at or above 37.8ºC (100ºF); and so is regarded as severe risk.

In case it provokes a fire, it produces toxic gases and containers can explode. Due to its properties, water is not efficient to this kind of explosions, so it must be used chemical substances like carbon dioxide, alcohol resistant foam or another foam agent so that it is in inert conditions.

1.2.3.2. Health issues

The methyl methacrylate exposure can cause short-term or long-term health effects.

In short-term effects, methyl methacrylate contact irritates the eyes, skin, nose and throat. Inhaling it can also irritate lungs and provoke coughing and trouble breathing. At higher levels, exposure can cause a liquid accumulation in lungs (pulmonary edema), a medical emergency that has to be attended immediately.

The long-term effects can take months or years. There is the possibility of cancer risk and sterility. It can also cause skin allergy, liver and kidney injuries and cause damage to the nervous system.

Good work practices can help to reduce dangerous exposures. It is recommended to the workers to change the clothing that has been contaminated by methyl methacrylate and to provide eye wash fountains in case of emergency use. Another recommended also stated is to wear protective gloves and clothing material, resistant googles and face shield when it is being manipulated.

Improper use of respirators is dangerous; such equipment should only be used if the workplace conditions require it (exposure over 50 ppm, considering that if it is higher than 1000 it is extremely hazardous).

1.2.3.3. Storage

It also has incompatibilities with nitrates, oxidizers, peroxides, strong alkalis, and moisture. Moreover, it may polymerize if it is subjected to heat, oxidizers or ultraviolet light.

Therefore, in terms of handling and storage, the methyl methacrylate has to be stored in tightly closed containers in a cool, well-ventilated area so that it is away from the conditions aforementioned before.

1.2.4. Environmental impact

Methyl methacrylate is not known to occur naturally, as it is industrially manufactured and used within closed systems. It can enter the environment during its storage, transport and use, potentially via wastewater and exhaust gases. Emissions to water, air and soil from production plants are about 0.46%; and most of it (98%) is emitted to air.

It is not used to persist in the environment due to its faster biodegradation in sewage treatment plants. It is also unlikely to bind to soil because of its low adsorption coefficient; and if it is released to atmosphere, it is degraded in a few days. Neither it is expected to accumulate in food.

It should be noted that upon short-term exposure on living beings, methyl methacrylate is dangerous to fish and invertebrates but not algae. On the contrary, it is not harmful to aquatic organisms upon long-term exposure.

2. OBJECTIVES

The main aim of this Final Degree Project is to design a plant in continuous to produce 40.000 tons of methyl methacrylate per year. With the purpose to achieve it, the followed tasks will be done:

- To carry out the selection of the process to produce methyl methacrylate in a short pathway and based on different first raw materials.
- To do a bibliographical research to find improvements that has been made over the process to increase the productivity.
- To do the basic engineering of the process according to the improvements founded over it.
- To select and design the reactor, as well as the other equipment required to accomplish the production demand.

3. METHYL METHACRYLATE PROCESS SELECTION

As stated in the bibliography, a wide variety of processes to manufacture methyl methacrylate have been developed on the basis of the different raw materials available in the respective locations, where it is desired to build the plant, and some of them were commercialised in industrial scale. In addition, some improvements have been carried out over time in some of the processes designed in order to reduce costs, improve the yield and conversion and to avoid producing some undesired products. These methods continue to be based on natural gas or crude oil, so that the manufacturing routes to produce it are categorized according to the hydrocarbon raw materials.

3.1. ETHYLENE PROCESSES

Methyl methacrylate can be manufactured on ethylene basis by different ways, whether the intermediate is propionaldehyde, propionic acid or methyl propionate. One of the process developed, called the Alpha process, allows to produce the methacrylic ester with methyl propionate as the intermediate. However, as with propionic acid, this process suffers from low conversion, despite the selectivity is high. It would be needed to implement large recycle streams or an improvement over the catalyst.

3.1.1. BASF’s process

BASF developed a C-2 process where methyl methacrylate is produced by ethylene and where the intermediate is propionaldehyde (Ullmann, 2011). On the first step, propionaldehyde is produced by a hydroformylation process where ethylene reacts with syngas using rhodium catalyst. Then, propionaldehyde reacts with formaldehyde in liquid phase to produce methacrolein. This last reaction is catalysed by a secondary amine and an acid to improve the conversion.

Once the methacrolein is provided, it is oxidized by air over a catalyst composed by molybdenum and tungsten, among others, to produce methacrylic acid. In the last step, the esterification of methacrylic acid with methanol is carried out to obtain methyl methacrylate. BASF operates a plant in Germany based on this process.

3.2. PROPYLENE PROCESSES

3.2.1. ACH process

The main worldwide pathway to produce methyl methacrylate continues being the acetone cyanohydrin process (Ullmann, 2011), which is the first process industrialized. By this process, acetone and hydrogen cyanide are first reacted to give acetone cyanohydrin. Afterwards, acetone cyanohydrin reacts with sulphuric acid, that has been added in excess, to produce α-sulphatoisobutyramide which, under heated conditions, gives methacrylamide sulphate. On a final stage, the hydrolysis-esterification of methacrylamide sulphate with methanol, using sulphuric acid as a catalyst, gives methyl methacrylate, methacrylic acid and ammonium bisulphate.

The main drawback of this process is the high costs of waste treatment since nearly 1,5 tons of ammonium bisulphate are produced for every ton of methyl methacrylate. Other disadvantages are the need of supply hydrogen cyanide and the cost and corrosivity of sulphuric acid.

3.2.2. Mitsubishi Gas Chemical Company process

This process was intended to improve the acetone cyanohydrin process with the aim of not using sulphuric acid and to cut down on the waste handling (Kirk & Othmer, 2005).

Firstly, the acetone cyanohydrin is produced as in the ACH process, which is hydrated to obtain α-hydroxy isobutylamide using manganese catalyst. Once produced, it is esterified by methylformate to produce methyl α-hydroxy isobutylate. Finally, it is dehydrated to provide methyl methacrylate. This process produces formaldehyde as a by-product instead of producing ammonium bisulphate. The formaldehyde is dehydrated with the aim of produce hydrogen cyanide, which is recycled.

Other routes based on 3 carbon hydrocarbons are mainly those that allow to obtain the methacrylic ester from propyne or isobutyric acid. It has been developed a single-step process but seems to be unavailable in an industrial scale due to the amount of propyne required. On the other hand, it is needed to improve the catalyst to be economically viable the industrialization of the isobutyric acid route (Kirk & Othmer, 2005).

3.3. C-4 FRACTION PROCESSES

In case of C-4 processes, some of them are directly discarded in this selection due to their disadvantages. These are the Escambia process due to the large amount of nitric acid required to be handled (Nagai, 2001); the methacrylonitrile route due to the ammonium bisulphate waste (Nagai & Ui, Trends and Future of Monomer-MMA Technologies, 2004) and the isobutane direct oxidation process due to the large number of reaction steps (Kirk & Othmer, 2005).

3.3.1. Direct oxidation process

Methyl methacrylate can also be manufactured using isobutylene or tert-butanol as raw materials (Nagai & Ui, Trends and Future of Monomer-MMA Technologies, 2004). In this case, isobutylene or tert-butanol first are oxidized with air to produce methacrolein, with allows to obtain methyl methacrylate by the same way that has explained in the BASF process. There are some variations of this route depending on whether the methacrolein is separated from the effluent of the first reactor or if it is directly introduced in the second reactor.

3.3.2. Direct oxidative esterification process

It has been carried out process intensification by Asahi Kasei in order to reduce the steps required to manufacture methyl methacrylate by two (Nagai & Ui, Trends and Future of Monomer-MMA Technologies, 2004). Through this process, first methacrolein is produced by isobutylene as a raw material in the same way as the direct oxidation process. In contrast, in the next step is carried out an oxidative esterification reaction where methacrolein and methanol reacts in liquid phase with oxygen in gas phase to produce the desired methacrylic ester.

3.4. PROCESS COMPARISON

One of the most important aspects to consider when it comes to select the process is the raw materials location and costs, as this will determine the overall cost of the plant that is going to be designed. Once taken into account all the processes mentioned, the Mitsubishi Gas Chemical company process it is discarded due to the long pathway that it presents. The direct oxidative esterification process not only allows to manufacture methyl methacrylate in a shorter pathway, but also is flexible in terms of raw materials due to the fact that methacrolein can be produced by ethylene, isobutylene or tert-butanol with both the BASF or the direct oxidation process. In addition, the direct oxidative esterification process does not produce ammonium bisulphate, avoiding issues regarding to its waste management. For these reasons commented, the direct oxidative esterification process has been chosen to design the methyl methacrylate plant from methacrolein.

4. PATENT RESEARCH

Once selected the process, it has been searched for the carried out by Asahi, as well as for patents that stated new developments over the direct oxidative esterification to carry out the process design. The ones selected are those indicated above.

4.1. ASAHI PROCESS

The direct oxidative esterification process developed by Asahi was commercialised in an industrial scale employing a stirred tank reactor. According to a recent publication (Liang et. al., 2019), the reactor operates at 50ºC of temperature and 1 bar, and the conversion and selectivity to obtain methyl methacrylate are respectively 98.8% and 85.9%. The liquid phase effluent of the reactor is separated from the gas phase in a gas-liquid separator and it is fed to a distillation column. Afterwards, the methanol and methacrolein recovered from the top of the distillation column are recycled to the reactor whilst the liquid phase of the bottom of the distillation column is sent to the purification stages to obtain methyl methacrylate with high purity.

However, a selectivity in a range of from 80% to 85% approximately is still unsatisfactorily for being commercialised (US patent 6,040,472) as the secondary reactions produce by-products such as methyl formate, carbon dioxide and water, which difficult the final separation and purification of the methyl methacrylate. Moreover, the polymerization reactions of methacrolein must be avoided because it causes obstruction and deactivation of the catalyst (US patent 0,280,620).

It has also been stated that when it is tried to reduce the amount of methanol in excess to increase the productivity, the yield decreases. Another disadvantage of the process is that recycling the excess of methanol and the separation of the by-products requires a lot of energy (Nagai & Ui, Trends and Future of Monomer-MMA Technologies, 2004). For these reasons, it has been searched in patents for improvements that have been made on the reactor before doing the process design.

During the research, it that has been found patents that informs about new catalyst developed that reduce the selectivity of some of the secondary reactions. These patents have not been preselected as the main criteria that has been decided is to consider those that provides experimental results of the reactor applying the new catalyst innovated. The final selection will be made considering the conversion and selectivity of the reactor, as well as the operation conditions and the reactor type.

4.2. PATENT US0280628

This patent claims that it has been achieved a conversion and selectivity to methyl methacrylate up to 69.8% and 97.2% respectively in a long period of time employing a tubular reactor in a laboratory scale. It is stated that, to reach these values, it is necessary that the concentration of methacrolein in the reactor is always equal or less than 15% and the ratio between the liquid volume in litres and the catalyst weight in the reactor in kilograms is equal or less than 4.

In the process proposed in this patent, firstly the liquid stream of methanol and methacrolein is mixed with a gas stream of oxygen and nitrogen previous feeding it into the catalytic reactor at 6 bars. The gas stream that enters the reactor has a concentration of 7% in volume of oxygen to avoid explosive atmospheres in the reactor, whereas the liquid steam that enters the reactor is stoichiometrically in excess of methanol.

The reactor operates with an external heat exchanger to maintain the temperature at 80ºC. The output stream of the reactor is then cooled with a heat exchanger and, afterwards, the gas phase is separated from the liquid phase in a gas-liquid separator. The liquid phase remained is then conveyed to a neutralization tank to adjust the pH at a value of 7. Finally, the methyl methacrylate is withdrawn to a further purification and the remaining liquid phase is recirculated to the reactor.

This patent does not specify neither how to detach the methyl methacrylate from the rest of the liquid products of the reactor, nor the temperature of the stream that enters the reactor and at which temperature is cooled the stream that leaves it. Moreover, and the conversion is lower than in the Asahi process. Despite of that facts, the main advantages are the high selectivity and the fact that the reactions take place in a tubular reactor. In industrial scale, it would be used a multi-tubular reactor, which has a large surface area to exchange the heat generated.

4.3. PATENT US0251301

This patent has similarities with the previous commented as far as the process is concerned and also the conversion and selectivity achieved are the same, whereas it is used another catalyst, the feed enters the reactor at 11 bars and the temperature of the tubular reactor is maintained at 70ºC.

The patent specifies the importance of maintaining the pH at least between 5 and 9. In case that it is higher, it would be harmful for the stability of the catalyst. On the other hand, if the pH is lower than indicated, secondary reactions would be favoured causing the formation of the by-product 1,1-dimethoxyisobutene, which would lead to a reduction of the yield and the stability of the catalyst and also would complicate the separation of the final product.

However, it is stated that the liquid phase stream that leaves the gas-liquid separator, after being adjusted its pH in the neutralisation tank, it is recirculated to the reactor at least the 50% of it, preferably the 90%. That recirculation is carried out with the aim that there is a great deal of liquid in the reactor, increasing the amount of oxygen that is dissolved in it and in contact with the catalyst. This might be beneficial to achieve the conversion indicated, but has the disadvantage that the methyl methacrylate produced is also recirculated in that high percentage to the entrance of the reactor, instead of being withdrawn and purified to obtain it as the final product, which significantly decreases the productivity of the overall process.

4.4. PATENT US0206897

This patent provides a pathway to produce methyl methacrylate from ethylene. Since the objective is to design a process where methacrolein can be produced by ethylene, this patent has also been taken into consideration for the process design. It would be needed three reactors to produce methyl methacrylate according to it, as previously it must be produced the propionaldehyde and methacrolein. However, it has been focused on the last reactor of the pathway as it is the one of interest in this project.

As it is stated, the methacrolein produced must be separated from the other products of the second reactor before being fed to the last reactor with oxygen and methanol in slight excess. The reactor employed to produce methyl methacrylate is a slurry stirred tank reactor as the oxygen is bubbled through it and the catalyst is suspended in the liquid. Once the reaction take place at 50ºC and at atmospheric pressure, the products leaves the reactor with the catalyst. To obtain methyl methacrylate in high concentration, the patent proposes that first it is separated from the catalyst by filtering, and then it is separated from the by-products by distillation.

The main drawback of the patent is that the conversion of methacrolein and selectivity to produce methyl methacrylate are 50% and 90%, values lower than in the Asahi process. Another disadvantage is that, as the catalyst is not fixed in the reactor like in a fixed bed, it must be also supplied with the reactants and separated from the products. In addition, the stirred reactor tank would also require an external heat exchanger, but the surface area would be limited.

4.5. PATENT COMPARISON

After taking into consideration all patents mentioned above, it has been inclined to the reactor of patent US0280628 as the best option because, despite the fact that the conversion is lower than in the original process considered, the selectivity is higher and the reactor type eases the withdraw of the reactions heat. In addition, the reactor operates at a higher temperature and at a lower pressure in comparison with ones in the patent US0251301, which means that it would be needed to withdraw less amount of the heat generated; and also that the power required to be provided by the pumps and fans previous the reactor will be lower.

The patent US0206897 is going to be considered when it comes to employ the methacrolein that is obtained from an ethylene process, but the reactor proposed is discarded due to the reactor type and low yield. The Asahi process reactor works at the same temperature and pressure as the reactor commented in this patent, but the yield is lower in the latter case. That is related to the fact that, when methanol is not at sufficient excess, both the conversion and the selectivity tend to lessen (US patent 5,969,178).

5. METHYL METHACRYLATE PROCESS DESIGN

5.1. DESIGN BASES

The main objective of this project is to design a methyl methacrylate plant from methacrolein operating in continuous mode that accomplishes the demands of producing 40.000 tons per year. The plant is going to be designed operating 8.000 hours / year. No limitations have been considered in terms of the amount of resources, energy and raw materials needed.

The process will be designed considering the secondary reactions that causes the formation of carbon dioxide and methyl formate, and its separation from the methyl methacrylate and other by-products. Contrary to the Asahi process, in the patent selected is commented that during the experiments there was no obstruction in the tubes because the polymeric by-products were not formed, so they have not been considered. Other by-products are formed such as methacrylic acid, but as the selectivity of the main reaction is very high and these do not influence the reactor and the process design, they have neither taken into account.

The final product would need a further purification to obtain it at a concentration of 99,9% for being commercialised. That final separation will not be in the scope of in this project, as it will be focused on the design of the methyl methacrylate reactor and the auxiliary equipment needed for the reactor operation.

5.2. RAW MATERIALS

Before carrying out the process design, firstly it is going to select the raw materials that are available in the market and the methacrolein employed whether it is produced from ethylene or isobutylene.

In the case where methacrolein is obtained from isobutylene by the Asahi process, it is separated with high purity in an absorption column employing methanol as absorbent (Liang et. al., 2019). That would be beneficial for our process design as it can be considered that only methanol is withdrawn by the stream of methanol; and because the absorbent is also a reactant, so that it has not to be treated as an impurity.

However, in a study carried out to determine the relationship between the amount of methacrolein obtained and the flow rate of methanol fed in the absorption column, it has been stated that the preferred methanol flow rate is 3000 kmol/h to obtain approximately 74.5 kmol/h of methacrolein (Liang et. al., 2019). If the flow rate of methanol is lower, it would be constantly wasted part of the methacrolein produced. Otherwise, when the methanol flow rate is higher, the extra amount of methacrolein that can be obtained gradually decreases and there is no point in increasing the absorbent flow rate up to this value as it does not compensate the costs associated.

Considering that the inlet stream of methanol to the absorption column has the flow rate mentioned, the output stream of interest will have a concentration of 5% in mass of methacrolein approximately, which means that the excess of methanol is way higher than the indicated in the patent. It would be needed to reduce the amount of methanol to achieve the operation conditions stated in the patent.

On the other hand, the methacrolein can be obtained from ethylene with propionaldehyde as the intermediate, which reacts with formaldehyde in presence of a secondary amine and an organic acid. By this way, an aqueous and an organic phase are formed after cooling the reaction mixture produced. The organic phase contains a 90% of methacrolein, which can be separated from the other products by distillation (US patent 0,206,897).

In this project, the methacrolein considered is that obtained from ethylene because it requires an addition of methanol in the process and it is assumed that have impurities. As no information about the methacrolein obtained by this way has been found, it has assumed that the propionaldehyde is the main impurity and that methacrolein has a purity of 99.9%, as it is available in the market in that concentration and that it is at 25ºC. The process that is going to be designed would also be valid for the other case if the excess of methanol is reduced.

Therefore, the following raw materials and supplies are needed in the process:

- Methacrolein, which will be supplied with a concentration of 99.9% with propionaldehyde.
- As commented in the patent, the oxygen will be fed to the reactor in a concentration of 7% with nitrogen.
- The reaction will take place with excess of methanol, which will be supplied with a purity of 99.9% with water.

- To adjust the pH, it will be employed sodium hydroxide at a concentration of 50% with water. It is stated in the patent that it is fed a solution of sodium hydroxide at 1% with methanol and, as no information has been found about the amount of it that is needed, it has maintained that proportion for the feeding to the mixing tank.
- It is not expected that the pH increases over the maximum value of 6.5 but in case that it happened, sulphuric acid at a concentration of 98% will be fed to adjust it.

5.3. BLOCK DIAGRAM

Once it is known the raw materials that are going to be employed, the production process is being designed considering the proposition of the patent, but some changes have been made over it.

At first, it was suggested that a neutralisation tank is placed to adjust only the pH of the recirculated stream, which then is combined with all the raw materials streams. Instead of that, it has been decided that the methacrolein, methanol and the sodium hydroxide streams are also fed to a mixing tank to ensure that the pH of the liquid phase of the stream that enters the reactor is between the optimum range. In it, the will be a homogenization of the streams, the pH will be adjusted, and the temperature will be increased up to a value of 51ºC, taking advantage of the fact that the recycling stream is at a temperature of 63ºC.

Due to the heat provided by the recirculation stream in the mixing tank, the propionaldehyde switches to gas phase. It is removed after the mixing tank in a gas - liquid separator as it is an impurity and to avoid issues when it comes to pump the liquid phase remaining.

The output liquid stream of the gas - liquid separator is then heated to reach a temperature of 60ºC. At the same time, the gas stream of oxygen and nitrogen is compressed and heated to the same temperature. Both streams are then combined and fed to the catalytic reactor.

The products that leaves the reactor are not going to be cooled previous separating both phases formed as indicated in the patent. This decision has been made because, as the reactor is cooled so that the maximum temperature on it is of 80ºC, the methacrolein and methanol that have not reacted leaves the reactor at gas phase, amongst others, whereas the methyl methacrylate and water were at liquid phase. If it is cooled so that these raw materials are condensed then, after separating the gas phase remaining, it would be needed to be distilled to separate them from the water and methyl methacrylate. That would imply more costs as it would be needed an extra equipment and to provide more industrial services not only to condense those raw materials, but also to vaporize them again.

Finally, after separating the liquid phase that leaves the reactor, it is cooled and stored as the final product of the process. The gas phase withdrawn is cooled at a temperature of 63ºC to assure the condensation of methanol and methacrolein. These compounds are then separated from the gas phase remaining and recirculated to the mixing tank. By this way, these raw materials are reused as they react in liquid phase and the by-products methyl formate and carbon dioxide, amongst others, are eliminated, avoiding the need of a purging stream that withdraw a fraction of the raw materials recirculated.

A block diagram is shown hereafter, where it is represented the stages of the process, as well as the raw materials to provide in it and the residual gases that are withdrawn.

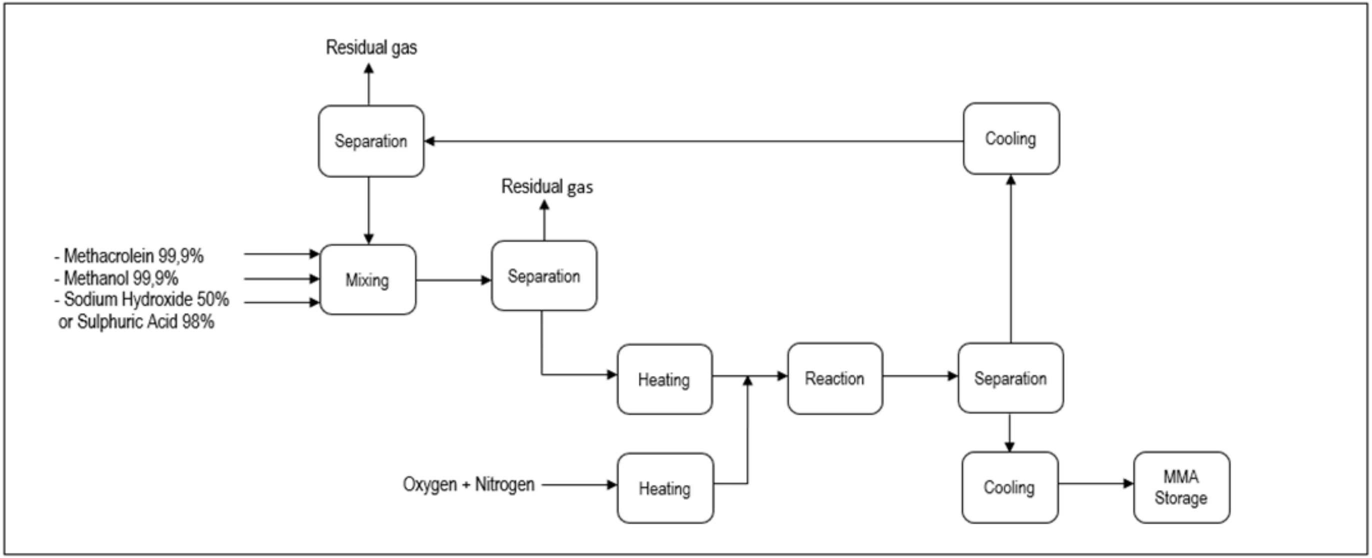


Figure 1: Process Blog Diagram

5.4. PINCH ANALYSIS

There are streams in the process designed that requires an exchange of heat, which entails costs due to the supply of hot and cold services. To reduce the energy consumption in services, a pinch analysis has been made over the process. In this analysis, the heat that need to be withdrawn from the reactor is not included as it will be cooled with cold services to ensure its properly operation. Therefore, the streams that requires an exchange of heat that are considered in the analysis, are as follows:

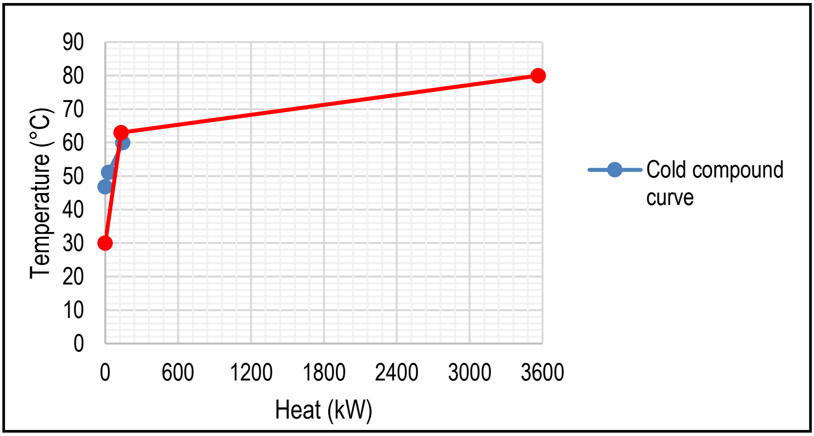
- Liquid phase stream inlet to reactor.
- Oxygen and nitrogen stream inlet to reactor.
- Recirculating stream.
- Methyl methacrylate stream to storage tank.

The first two are cold streams which must be heated whereas the other two are hot streams that must be cooled. The results obtained are shown below:

Table 2: Pinch Analysis results

Pinch point	-
Minimum cooling by services (kW)	3524
Minimum heating by services (kW)	0

According to the results obtained, no heating services are needed and there is no pinch point. That is because a great amount of heat needs to be cooled in the recirculating stream, mainly due to the condensation of methacrolein and methanol. These results are obtained from the following graphs.



The cold and hot compounds curves are first carried out:

Figure 2: Hot and cold compound curves

The compound curves are then displaced to ensure a minimum variation of temperature of 20ºC between the curves so that the heat exchangers to design are not of high dimensions, despite that it requires more services than if it were lower.

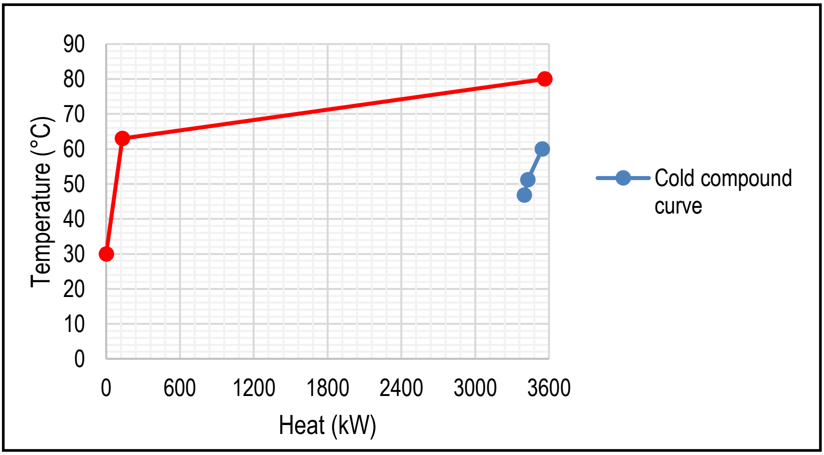


Figure 3: Compound curves displaced

In the previous graph can be determined the minimum cold services. In addition, it is observed that there are no minimum hot services. In the following graph it can also be found that information and the inexistence of the pinch point.

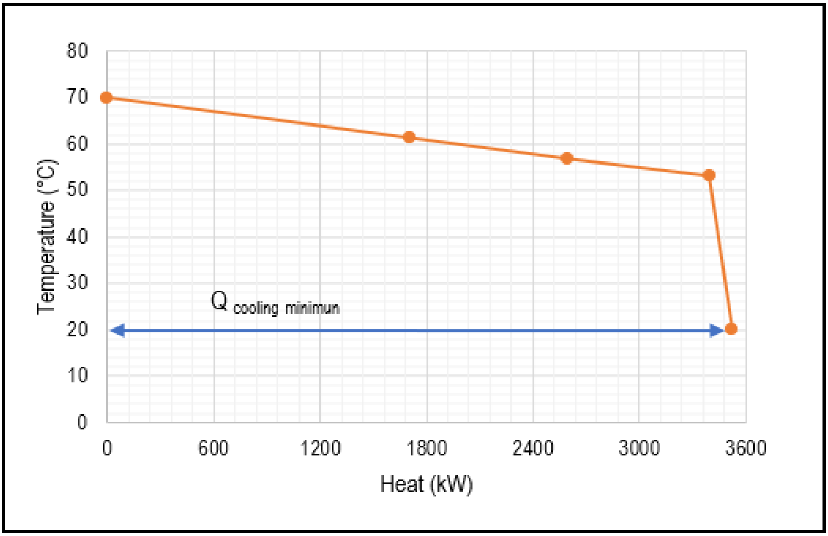


Figure 4: Grand compound curves

Due to the results obtained, the heat exchange network diagram has been done without the pinch point and verifying that the minimum variation of temperature of 20ºC is accomplish in all the heat exchangers between the streams that enter or leaves it in the same size. Is can be seen in it the heat exchangers proposed to exchange heat between the streams and the heat exchangers that provides cold services to achieve the final temperature desired.

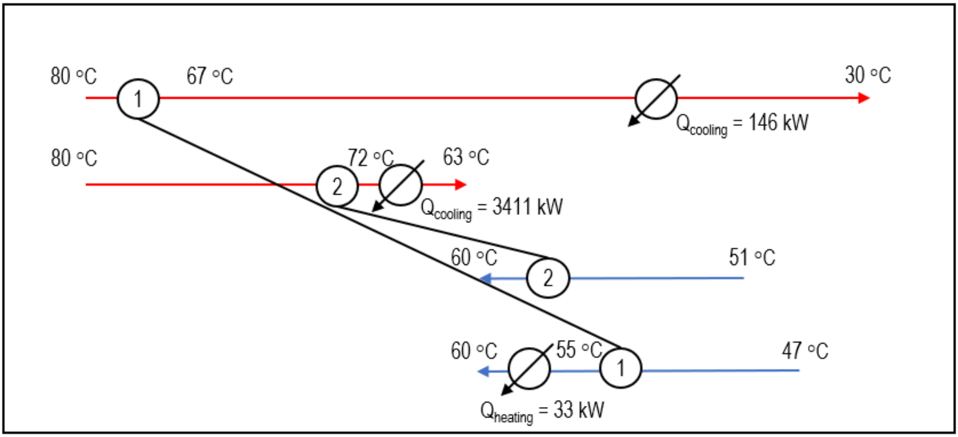


Figure 5: Heat exchange network diagram

It has only been reduced the energy to exchange by a 7%. As it can be observed it is needed a heat exchanger for cooling services and another for heating services.

Therefore, the heat exchangers that are needed in the process according to the Pinch Analysis are as follows:

- H.E.01, were the liquid phase inlet to reactor tubes side is heated to 60ºC employing the recycling stream.
- H.E.03, were the oxygen and nitrogen inlet to reactor is heated to 55ºC employing the methyl methacrylate final stream.
- H.E.04 were the oxygen and nitrogen inlet to reactor is heated to 60ºC employing hot services.
- H.E.05, were the methyl methacrylate stream is cooled to 30ºC employing cold services.
- H.E.06, were the recirculating stream is cooled to 63ºC employing cold services.

Once the Pinch Analysis is done, it can be detected that one more heat exchanger is needed to heat the gas stream that enters to the reactor (H.E.02) and that the heat exchanger previously commented to provides heat services (H.E.04) is going to be oversized. That is because, if it is not present, the reactants streams are not heated in the start-up of the plant as the recycling and the methyl methacrylate streams does not flow towards the heat exchangers yet. Also, these are useful to ensure that the raw materials stream achieves the temperature required for the reactor operation.

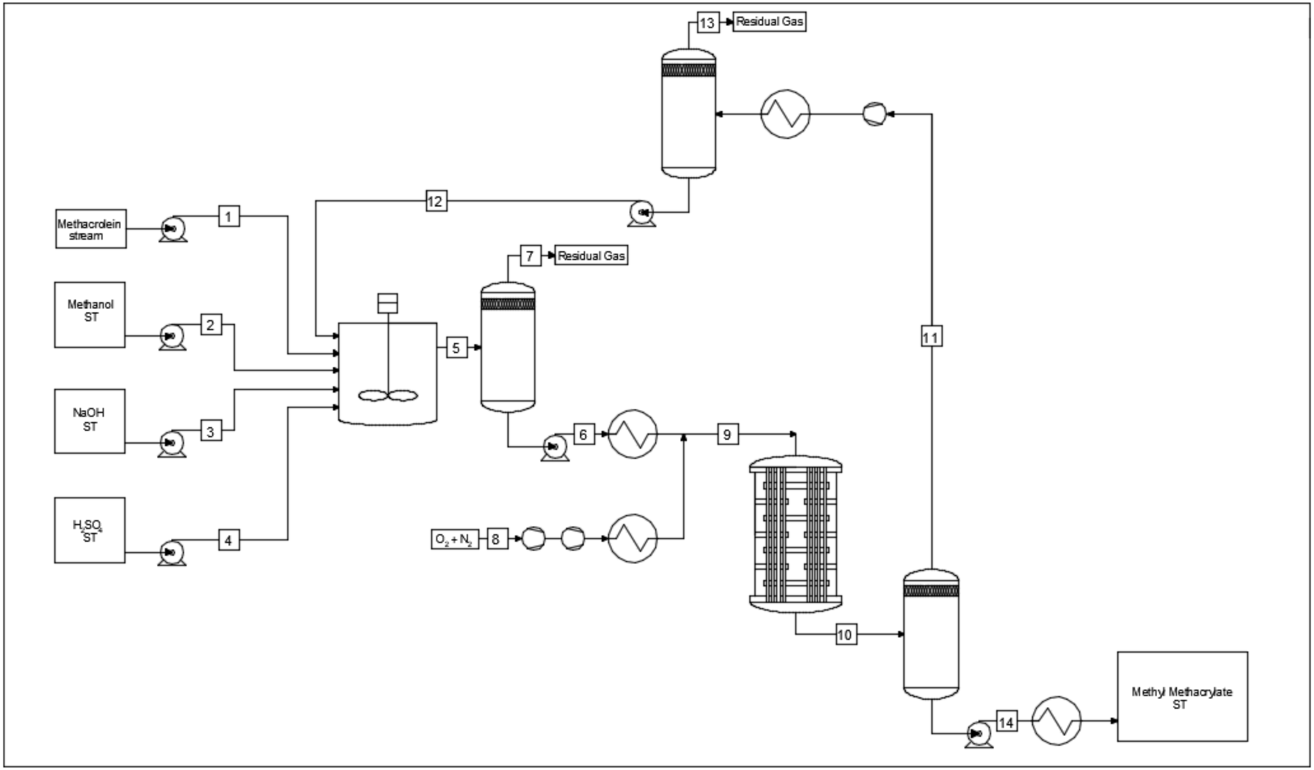
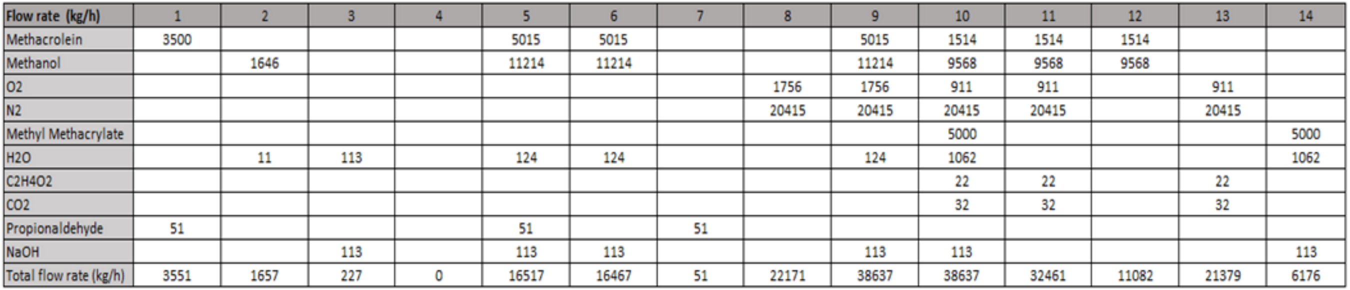


Figure 6: Process Flow Diagram previous applying the Pinch Analysis

Table 3: Mass Balance



Flow rate (kg/h)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Methacrolein	3500				5015	5015			5015	1514	1514	1514		
Methanol		1646			11214	11214			11214	9568	9568	9568		
O2								1756	1756	911	911		911	
N2								20415	20415	20415	20415		20415	
Methyl Methacrylate										5000				5000
H2O		11	113		124	124			124	1062				1062
C2H4O2										22	22		22	
CO2										32	32		32	
Propionaldehyde	51				51		51							
NaOH			113		113	113			113	113				113
Total flow rate (kg/h)	3551	1657	227	0	16517	16467	51	22171	38637	38637	32461	11082	21379	6176

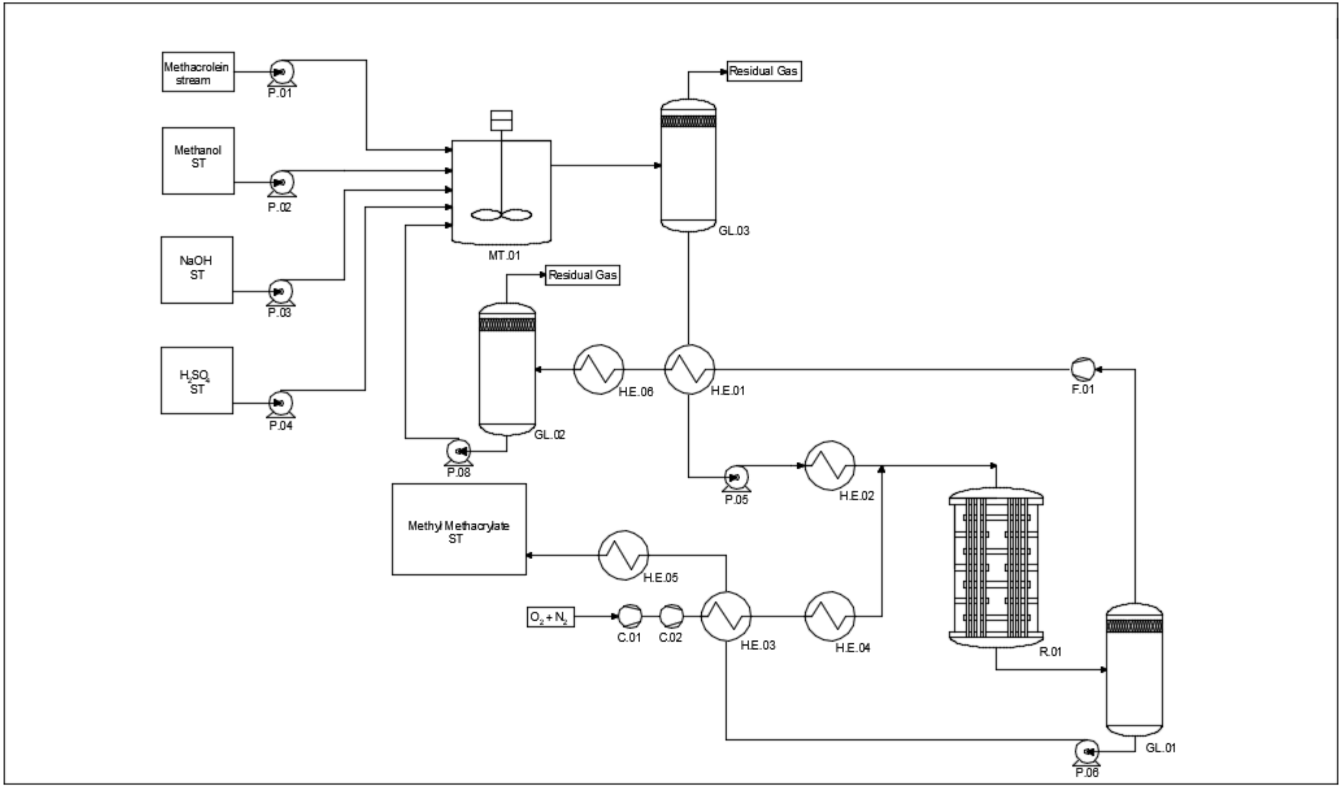


Figure 6: Process Flow Diagram after applying the Pinch Analysis

6. PROJECT SPECIFICATIONS

6.1. REACTOR

The multiphasic reactor is the most important equipment to design as the methyl methacrylate productivity depends directly on its performance. It has been studied the reactions that took place in the reactor, as well as the heat that must be removed and the operation conditions to select the reactor type and subsequently carry out its design.

6.1.1. Chemical reactions

6.1.1.1. Main reaction

The reaction to produce methyl methacrylate by direct oxidative esterification is at follows:

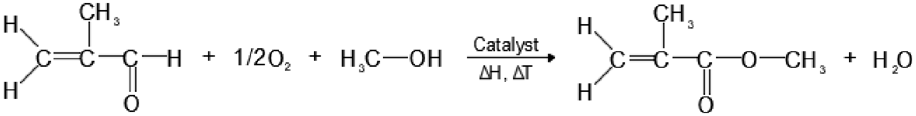


Figure 8: Oxidative esterification reaction of methacrolein

The methacrolein and methanol reacts in liquid phase with oxygen gas to generate methyl methacrylate and water, both in liquid phase. A solid catalyst is used for the reaction, which is carried out at 6 bar and at a temperature range between 60ºC and 80ºC.

6.1.1.2. Secondary reactions

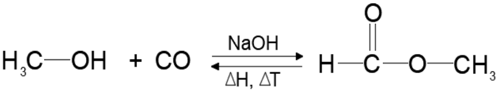
The secondary reactions are carried out at the same pressure and temperature indicated before, as they occur simultaneously with the main reaction. As stated before, the secondary reactions considered are those that form methyl formate and carbon dioxide.

Methyl formate in industrial scale is produced by the carbonylation of methanol in presence of a strong base (Ullmann, 2011). By this equilibrium reaction, methanol reacts in liquid phase with carbon monoxide in gas phase to obtain methyl formate, also in gas phase. The concentration that can be obtained of methyl formate decreases with temperature and increases with pressure. In this case, the basic chemical compound that is present in the reaction mixture is the sodium hydroxide used in the mixing tank to increase the pH.

According to the US Patent 6,168,072, when the direct oxidative esterification to produce methyl methacrylate is carried out, methanol also reacts with oxygen to generate two moles of water per mole of methyl formate. Therefore, the carbon monoxide is formed due to the incomplete combustion of methanol in gas phase.

$$H_3C—OH + O_2 \xrightarrow[\Delta H,\ \Delta T]{} CO + 2H_2O$$

Figure 9: Incomplete combustion of methanol



$$H_3C—OH + CO \underset{\Delta H,\ \Delta T}{\overset{NaOH}{\rightleftarrows}} H—\overset{\overset{\displaystyle O}{||}}{C}—O—CH_3$$

Figure 10: Carbonylation of methanol

Carbon dioxide is another by-product formed by the combustion of methanol with oxygen, both in gas phase, which also generates water. The water formed in the reactions will be in liquid phase due to the temperature of operation.

$$2H_3C—OH + 3O_2 \xrightarrow[\Delta H,\ \Delta T]{} 2CO_2 + 4H_2O$$

Figure 11: Complete combustion of methanol

It is not only the main reaction, but also the secondary ones considered that are exothermic so there will be a heat of reactions implied.

6.1.2. Reactions conversion, selectivity and space-time yield

6.1.2.1. Conversion and selectivity

According to the patent selected, after 73 hours operating the reactor carried out in laboratory scale, the conversion of methacrolein and its selectivity for the formation of methyl methacrylate were 70.8% and 97.4% respectively; and after 512 hours the values of these parameters were 69.8% and 97.2% respectively. It is observed a very slight decrease with time so that the latter values mentioned can be considered constant. Therefore, the conversion of methacrolein and selectivity for the formation of methyl methacrylate that are taken into account are 69.8% and 97.2% respectively, as the plant will operate in continuous in large periods of time.

In case of the secondary reactions, as no information is provided, it is considered that the selectivity for the formation of methyl formate is equal to the selectivity of the formation of carbon dioxide.

6.1.2.2. Space-time yield

The space-time yield is defined as 4.06 mole of methyl methacrylate formed per kilogram of catalyst in the reactor and hour, as stated in the patent when the conversion and selectivity are those indicated above.

6.1.3. Operation mode

The reactor can be differentiated whether it operates in adiabatic or nonadiabatic. The adiabatic operation is specifically used when the heat of the reactions is small as the temperature is an important factor that can influence the selectivity and the conversion of the reactions. The nonadiabatic operation is employed when there is a large heat of reactions and, as the reactions stated are very exothermic, it has been decided to operate the reactor by this way. Moreover, the range recommended of the reactor temperature operation is between 60ºC and 90ºC, so that it can be assumed that the main reaction is sensitive to the temperature and operating outside this range may cause a decrease in the yield.

When it comes to nonadiabatic operation, the reactor can be operated in isotherm or in non-isotherm conditions. In the patent selected is not specified at which temperature the reactants enter to the reactor, but it is indicated that experimentally it has been cooled to maintain a temperature in the reactor of 80ºC. It has been decided not to operate in isotherm conditions. Instead of it, the inlet temperature of the reactants will be 60ºC, the minimum recommended; and that the reactor will be cooled with an external heat exchanger so that the temperature does not exceed the 80ºC. By this way, the patent requirements are fulfilled, and it is not withdrawn as much heat as it would be if the inlet temperature were higher.

6.1.4. Patent requirements

The raw materials stream that enters the reactor accomplish the proportions of 30.9 kilograms of methacrolein per each 69.1 kilograms of methanol. This stream also conveys the sodium hydroxide fed in the mixing tank, water as an impurity and the gas phase. The proportion of 7 kilograms of oxygen per each 93 kilograms of nitrogen is also maintained; and the flow rate of the gas phase is adjusted so that it is in excess and to achieve the main requirements stated in the patent. To overcome the pressure drop, the pressure of the stream inlet to the reactor tubes if 6 bar.

Table 4: Reaction stream that enter / leaves the reactor

Flow rate (kg/h)	**R**	**P**
C_4H_6O	5015	1514
CH_4O	11214	9568
O_2	1756	911
N_2	20415	20415
$C_5H_8O_2$	-	5000
H_2O	124	1062
$C_2H_4O_2$	-	22
CO_2	-	32
NaOH	113	113
Total flow rate	38637	38637

Table 5: Verification of the patent requirements

Requirements	Patent	R	P
Stationary weight concentration of methacrolein in the reactor	≤15%	13%	4%
Factor F	≤4	1.6	0.5

In the tables above, R refers to the raw materials stream that enters the reactor, P refers to the stream that leaves the reactor containing the products of the reactions; and the factor F refers to the quotient between the liquid volume of the reaction mixture in litres and the catalyst mass in kilograms.

A first approximation of the mass of catalyst, it is calculated with the space-time yield stated before. The amount of catalyst introduced in the catalyst will be higher as the reactor will be oversized, but that will not affect to achieve the requirement because the more catalyst is introduced, the lower the factor F is for the same liquid volume. As the conditions are achieved both in the entrance and in the exit of the reactor, it can be assumed that are achieved on the whole reactor.

6.1.5. Heat of the reactions

The heat generated during the reactions has been calculated taking into account whether the chemical compounds react in liquid or gas phase and the initial and final temperature. The values of the constant pressure heat capacity were considered constant in the cases where no more information was found about its variation with temperature. As the reactions are very exothermic, it is considered that the temperature increases instantaneously to the temperature maximum desired of 80ºC in the reactor when the reactions take place. The calculations are attached in the appendix and the results obtained for each reaction are shown in the table below. In case of the methyl formate, the calculations have been done based on the global reaction.

Table 6: Enthalpy of reaction and heat generated for each global reaction

Reactions	**Methyl methacrylate**	**Methyl formate**	**Carbon dioxide**
Enthalpy of reaction (kJ/mol)	297.73	460.76	1453.54
Heat generated (kJ/h)	1.41E+07	1.33E+05	4.87E+05

In the table it can be observed that the main reaction generates most of the heat to remove, but that the secondary reactions also contributes significantly to generate heat despite its low selectivity. Therefore, the total heat to withdraw per hour is of 1.137.847 kJ/h, as part of the heat of the reactions is used to heat the chemical compounds to reach the temperature of 80ºC.

6.1.6. Reactor selection

To select the reactor type, it must be taken into consideration that in laboratory scale, the reactions were carried out in a tubular reactor, which contained the catalyst. Moreover, as said before, there is a huge amount of heat to withdraw. Therefore, the reactor that has been chosen is a multi-tubular fixed bed reactor, as it has more surface to exchange the heat generated by the reactions due to the fact that it is provided with a great number of tubes and also because it is more compacted.

The patent indicates the possibility to use slurry bubble column, or a slurry stirred tank instead when the reactor has a large volume, but a fixed bed reactor would be more suitable to withdraw the heat generated. In addition these slurry reactors have the drawback that the catalyst must be constantly fed to the reactor and removed from the effluent of it; and in the case of the slurry stirred tank, the flow regime would not be the same that in a tubular reactor, which is more closer to a plug flow.

6.1.7. Reactor design

The design of the reactor is done with the aim to maintain the operation conditions when it is working, specially prioritizing the control of the temperature over the whole reactor.

Firstly, since in laboratory scale the reactions were carried out inside the tubes, the reactor will operate in the same way, so that the catalyst is going to be placed inside of them. When it comes to the flow in the tubes, it is decided to be downward, as most of the reactors of this type operates by this way to avoid the movement of the catalyst. That implies a great amount of pressure to be provided by the previous pump and compressor to ensure that both the liquid and gas phase conveys in that direction and to overcome the pressure drop of the multiphasic reactor.

As far as the refrigerant is concerned, water is chosen as the cooling stream, which enters and leaves the reactor through the shell side. To control the temperature, the cooling stream generally conveys in parallel or in cross flow in fixed bed reactors. The possibility of conveying the water stream in opposite direction from the stream inside the tubes is discarded as this configuration does not provide a properly control of the temperature. That is because, when the stream that contains the reactants enter inside the tubes and the reactions start, the tubes would be in contact with the water stream warmed whereas, when the stream is nearly leaving the tubes, it would be in contact with the water stream at the lowest temperature; causing that the temperature inside the tubes is not as stable as in other configurations.

In case of parallel flow, this configuration has the advantage regard the cross flow that the whole reactor is equipped with tubes. On the other hand, in the inlet and outlet zone the flow is not uniform, so that only in the central region between the distributor plates can the reaction be carried out. However, the main disadvantage why it is discarded the parallel flow regarding the stream inside tubes is because the heat transfer is lower than in cross flow, so that it is not properly to use this configuration when a large amount of heat needs to be removed.

Therefore, it is decided that the fixed bed reactor is going to be provided with disk and doughnut baffle plates to ensure a transversal flow of the water stream across the tubes. In this configuration, it must be taken into consideration that the heat withdrawn by the water is lower at the extremes of the baffle plates zones, as it is there where water flow is not transversal as it changes the direction. To solve it, the central zone and the ones nearest the shell are generally not equipped with tubes (Eigenberger, 1992).

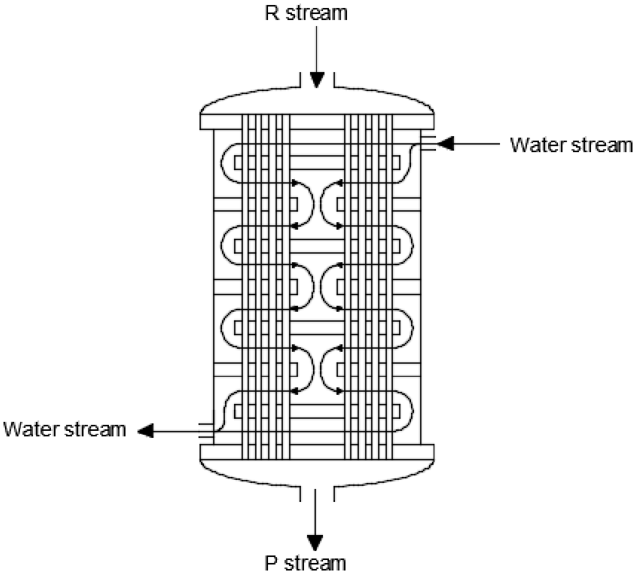


Figure 12: Multitubular fixed bed reactor selected (scheme made with Autocad)

6.1.8. Catalyst type, dimensions and voidage

It is stated in the patent selected the procedure followed to prepare the catalyst and that after being analysed, the composition determined was of 0.9% of golden and 1.1% of nickel oxide (II) in a support of magnesia and silicon monoxide. By this way, it can be estimated that the density of the catalyst is of 2843 kg/m^3.

In addition, it is commented that the average diameter of the catalyst in a fixed bed reactor should be over 200 micrometres, with a maximum particle size of 20 millimetres so that there is enough area of contact between the catalyst and the reactants.

The ratio between the tube and the particle diameter is an important factor to maintain the proportion of the void volume in the tubes. Experimentally the catalyst employed was in powder form with an average diameter of 5 nanometres, but the tube diameter is not specified. Therefore, this parameter cannot be maintained due to the lack of information. Moreover, the catalyst is these dimensions are not suitable for the circulation of the streams inside the tubes, so it is agglomerated in pellets.

There is a wide range of pellets shape to use, so the criteria taken into consideration is to select that one that has a high surface area per volume and that causes a low pressure drop. It has been graphed and determined a correlation between the voidage and the ratio between the tube diameter and the pellet equivalent to a sphere diameter (F. Benyahia et. al., 2005) for different pellet shapes within a range of pellet dimensions. The voidage is defined as the quotient between the void volume and the inside tube volume. From the different options purposed, the 4-hole cylindrical pellets have a great surface area compared to other shapes as spheres and solid cylinders. Moreover, it has the higher range of voidage, between 0.8 and 0.6, which means that it will cause the lowest pressure drop. For these reasons, this pellet shape is selected.

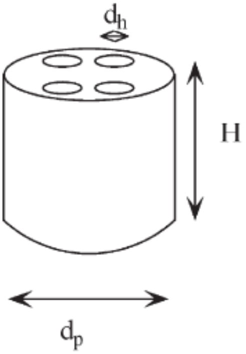


Figure 13: Pellet shape selected

In the graphs of the article it can be observed that, when the ratio between the diameters lessens, the voidage increases rapidly; and when the ratio increases, the voidage lessens until it is practically constant.

The increase of voidage when the ratio is low is known as wall effect. That happens because, when the catalyst is filled in the tubes, the catalyst is not uniformly distributed in the region closest to the walls of the tubes, which lead to a higher void space in that zone. If the catalyst equivalent diameter increases to much, the non-uniformity is extended along the tube diameter, which has de drawback that causes the formation of preferential channels, reducing considerably the contact between the reactants and the catalyst and, subsequently, the yield of the reactor.

On the other hand, under a certain value of catalyst equivalent diameter, it is distributed so that the voidage is minimum and nearly not affected by it, which is not interesting as the pressure drop is strongly influenced by the voidage.

The reactor was first designed employing the catalyst so that the voidage in the tubes were of 0.6 to avoid absolutely the wall effect, but not only the pressure drop was much higher than the operation pressure but also operating in that conditions would be unaffordable as it would require a great amount of pressure to be provided by the pump and compressor previous the reactor. The pressure drop is calculated with the Ergun equation. As the stream inside the tubes is a mixture of gas and liquid phase, the pressure drop is calculated considering the liquid flow and that the tube section is the volumetric fraction of the liquid multiplied by the tube section.

Instead of it, the voidage in the tubes has been selected an average value of 0.7 so that the pressure drop is lower and it is not much affected by the wall effect as it would be if it were the maximum value of 0.8.

The catalyst pellet dimensions are calculated taking into account that the dimensions and ratios of the pellet are between those used to determine the correlation, the tubes dimensions indicated afterwards, and that the pellet diameter is calculated by iteration with the pellet volume equivalent to sphere diameter. The results are shown as follows.

Table 7: Pellet dimensions

d_p (mm)	9.71
d_h (mm)	2
H (mm)	12.24

Table 8: Verification of the pellet characteristics

4-hole cylinder pellet	**Range covered**	**Value considered**
H / d_p	1.14 – 1.26	1.2
d_h	2 – 3.5	2
Tube diameter / d_p	1.9 – 8.4	2.25

It can be observed the height and the particle diameter are under the 20 millimetres indicated as the maximum catalyst size. Therefore, due to the fact that it is not specified the dimensions of the reactor tubes employed in the patent selected to maintain the ratio previously mentioned, it can be assumed that the wall effect does not affect the contact between the reactants and the catalyst negatively enough to lessen the yield of methyl methacrylate.

Another important aspect to bear in mind is the life of the catalyst. The catalyst can be deactivated after being employed during long periods of time due to chemical, mechanical, or thermal causes. In this project the process has being designed as if the life of the catalyst is sufficient long that it does not need to be stopped. However, it has taken into consideration that the heads are removable so that the catalyst can be replaced.

When it comes to introduce the catalyst into the reactor, it must be ensured that it is filled so that the pressure drop in each tube is approximately the same with a permissible error of 5%. Otherwise it may be broken pellets on it or a void space higher than expected (Foumeny et. al., 2001).

6.1.9. Reactor volume

To determine the reactor tubes volume, firstly is calculated the minimum mass of catalyst with molar flow of methyl methacrylate produced and the space-time yield. Once calculated, the total the volume is determined with the density of the catalyst and applying the quotient between void volume and inside volume equal to 0.7. The total volume of the tubes calculated is 17.3 m^3 after increasing it by a 20% due to security reasons.

It has also been determined the volume with the surface area needed to exchange the heat generated by the reactions to know if more tubes are needed. This surface area is calculated knowing that, for cooling the heat generated by the reactions, it is needed 9071 kg of water per hour that enters at 25ºC and leaves the reactor at 55ºC. The total volume was calculated employing tubes with the dimensions indicated afterwards, which was lower than the ones calculated using the space-time yield. Therefore, the volume employed is that calculated with the space-time yield and the surface area of the tubes is enough to exchange the heat.

6.1.10. Reactor tubes

The reactor cylindrical tubes dimensions are selected from the common employed in heat exchangers. The number of tubes needed are calculated so that the total internal tubes volume is achieved. As a high volume is required, a great number of tubes are needed, which is frequent in this type of reactors. As far as the disposition of the tubes is concerned, they will be in square configuration because, even though the tubes occupy more space in this configuration, it allows the mechanical cleaning.

Table 9: Reactor tubes

Number of tubes	4669
Outer diameter (mm)	28.65
Inner diameter (mm)	25.40
Tube length (m)	7.32
Pitch number (m)	0.036

6.1.11. Reactor shell

The reactor shell dimensions are calculated with the bundle diameter of the tubes as if it were a heat exchanger. However, in this case not all the inside shell reactor is equipped with tubes, so that the empty spaces must be considered.

It has not been found a way to estimate the distance of the empty spaces related to the reactor dimensions. Otherwise, in the patent US 9,713,800 it is provided an example of a multi-tubular fixed bed reactor shell and tube dimensions that has been simulated as well as the diameter of the central hole surrounded by the tubes. Therefore, as the dimensions of the reactor designed are similar to it by this way, it has decided to leave the same space in the central zone and, and the half of it in the zone closest to the shell as the water stream flow rate is the half that when it conveys across the central zone.

Table 10: Reactor shell

Bundle diameter of the tubes (m)	2.64
Hole space in the central zone (m)	0.75
Void space in the closest zone to the shell (m)	0.375
Inner shell diameter (m)	4.89

6.1.12. Reactor baffles

As far as baffles are concerned, when it is employed disk and doughnut baffles plates in heat exchangers, this equipment is commonly designed so that the space between this type of baffles is between 20% and 45% of the shell inside diameter.

However, in the heat exchangers there is no large spaces left without tubes as in the multi-tubular reactor designed, so that the shell diameter would be way lower for the same number of tubes. If the reactor baffles are designed as indicated in heat exchangers, it would be very few baffles and the cross flow of the water stream would not be achieved properly. For this reason, it has been decided that the spacing between the baffles is of the 20% of the bundle diameter of the tubes without considering the empty space of the central zone of the shell, increasing the number of baffles inside the shell.

Table 11: Reactor baffles

Baffle spacing (m)	0.53
Number of baffles	13
Disk baffle diameter (m)	3.4
Doughnut baffle inner diameter (m)	0.75
Doughnut baffle outer diameter (m)	4.89

6.1.13. Reactor materials

The reactor is expected to be constructed with stainless steel AISI 316. This material is slightly more expensive than the stainless steel AISI 304, which is the ones commonly used, but has the advantage that is more resistant to corrosion, so that it can last longer time in contact with the corrosive chemical compounds.

6.1.14. Reactor couplings

The reactor couplings not only needed to support the high pressure of the stream in the tube side but also, as said before, have to allow the removal of both the heads and the tubes so that the tubes can be replaced and, as said before, that the catalyst can be replaced.

The diameters of the tubes that enters and leaves the reactor from both shell and tube sides are shown below. The pipe diameter is calculated so that stream that flows in the tubes side is conveyed at a velocity of 10 m/s and that the water stream is conveyed at a velocity of 1 m/s. The diameters are standardized to nominal diameters by choosing the first consecutive diameter larger than the one determined so that it is available in the marked.

Table 12: Reactor couplings

	Nominal diameter
Inlet stream to tube side	300
Outlet stream from tube side	400
Inlet stream to shell side	65
Outlet stream from shell side	65

6.2. PUMPS, FAN AND COMPRESSOR

In the plant it is required equipment to impulse the streams along the plant. Pumps are employed for the flow of liquids, a fan to impulse the recycling stream towards the gas – liquid separator, and a compressor for the gas stream that enters the reactor.

It has been made a distinction between the fan and the compressors because the oxygen and nitrogen stream require both an increase of pressure and temperature to achieve the reactor operation conditions, and the compressors operating in isentropic would accomplish it while conveys the gas phase to the reactor. Moreover, the compressors are suitable when it is needed to highly increase the pressure of the flows, more the other two options indicated.

In this project it is considered that the gas stream is compressed at a pressure of 9 atm, employing two compressors in series to take advantage of the increase of the temperature to reduce the energy needed in heating the stream, despite the drawback that a lot energy is consumed as a great flow rate has to be compressed at this high pressure. It is employed two compressors because otherwise the compression ratio would be very high for only one compressor. The compressor ratio it is decided to be the same in both compressors with a value of 3. The pressure to be compressed considered is higher than the pressure in the entrance of the reactor as there will be a pressure drop in the pipes and in the heat exchangers.

6.3. GAS – LIQUID SEPARATORS

This equipment consists of a vertical vessel that allows the separation of the gas and liquid phases by the action of gravity and is favoured by the wire mesh pad deentrainer, which causes the agglomeration of the liquid droplets so that these precipitates more easily due to their own weight.

As it is of interest that the liquid is well separated from the gas, so that it is not recycled to the reactor or lost, depending on which one is referred; it is convenient that it is designed with a higher pressure and a lower temperature than the inlet stream.

As far as the residence time of the liquid is concerned, it has been considered in the design of these equipment a time of 20 minutes. Moreover, once the minimum diameter was calculated, it was adjusted so that the gas-liquid separator does not have a very high height.

Table 13: Gas – liquid dimensions

	GL.01	GL.02	GL.03
Gas height (m)	1.8	1.4	1.7
Liquid height (m)	2.2	2.2	2.6
Diameter (m)	1.1	2	1.5

6.4. MIXER AND PH ADJUSTMENT TANK

The mixer tank is designed with a blend time of 30 minutes. This decision has been made to ensured that there is enough time to adjust the pH with the acid or basic stream, whether it is the case. The impeller selected is a six pitched blade turbine, as it is stated that is effective for both turbulent and laminar regime and for solid suspensions such as the sodium hydroxide stream.

Table 14: Tank specifications

Liquid volume (m^3)	12.3
Liquid height (m)	8.3
Tank diameter (m)	1.4
Impeller diameter (m)	1
Baffle width (m)	0.1
Blade width (m)	0.2
Impeller height above the vessel floor (m)	0.5
Impeller power (kW)	15.7

6.5. STORAGE TANKS

The storage tank volume is calculated so that the raw materials are stored thirty days of the capacity demanded for the proper operation of the plant. On the other hand, the sulphuric acid volume considered is the same one as the sodium hydroxide storage tank.

The sulphuric acid and the sodium hydroxide are stored in a cylindric vertical storage tanks at atmospheric pressure. On the other side, the methyl methacrylate and the methanol have to be stored following the ASME regulations as are liquid volatile and flammables.

Table 15: Storage tanks volume

	Volume m³
Methanol ST	1519
Sodium hydroxide ST	120
Sulphuric acid ST	120
Methyl methacrylate ST	4597

6.6. HEAT EXCHANGERS

As said before, the heat exchangers 4 and 2 operates in the set-up of the plant or when it is needed to heat or cool the streams to control the process. Therefore, these heat exchangers have been designed taking into consideration that when the plant starts to operate the heat exchanges 1 and 3 are not working.

Table 16: Heat exchangers design

	Configuration	Shell side stream / Tube side stream	Number of tubes	Heat (kW)
H.E.01	2- 4	Liquid raw materials/ Recycling	70	88.4
H.E.02	2 - 4	Water steam/ Liquid raw materials	22	88.4
H.E.03	2 - 4	Gas raw materials/ Methyl methacrylate	44	51.8
H.E.04	2 - 4	Water steam/ Gas raw materials	40	84.8
H.E.05	2 - 4	Water steam/ Methyl methacrylate	71	198
H.E.06	1 - 2	Methyl methacrylate/ Cold water	430	3411

6.7. PIPING

The diameter of each pipe where the fluids flows between the equipment is calculated considering the velocities of 1 m/s in case of liquids or 10 m/s in case of gas or liquids and gas streams. The pipes are indicated according to the stream that flows in it in the same way as the process flow diagram and the results are shown below. As the reactor, all the pipes are made by stainless steel AISI 316.

Table 17: Stream pipe diameters

Stream number	Nominal diameter
1	40
2	32
3	8
4	8
5	90
6	90
7	6
8	300
9	300
10	400
11	400
12	80
13	350
14	250

6.8. INDUSTRIAL SERVICES

The industrial services needed are water at 130 ºC and 3 bars for heating, as well as water at 25ºC for cooling. In addition, it would be needed the gas stream of oxygen at 7% of concentration with nitrogen at the same temperature as a raw material for the reactor.

7. CONCLUSIONS

By all means, it can be concluded that the main objective of this project is accomplished, to meet the demands of 40.000 tonnes of methyl methacrylate per year by designing a process with a short pathway that has been enhanced to increase its productivity and feasibility in industrial scale, even if it requires a further purification for commercialise the product.

The process designed, takes advantage of the temperature of operation to avoid to distillate the outlet reactor stream to recycle the main raw materials, and also uses its high heat after the reaction for heating the raw materials, so that the cooling services lessens. Moreover, the reactor designed is more suitable to exchange the heat of the reactions, and its configuration eases the control of the temperature. The control of the temperature is an important factor as the process is temperature-sensitivity so that a poor control of this parameter could lead to a decrease of the yield amongst other drawbacks, such as an unexpected increase of volume due to the vaporization of fluid inside it.

However, this process is not very suitable to follow the first part of the direct oxidative esterification process designed as the methacrolein obtained by it is in a great excess of methanol, which implies that it would not achieve the requirement of operating under a proportion of liquid volume lower than the ones required.

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ACRONYMS

O_2 = Oxigen

N_2 = Nitrogen

H_2O = Water

CH4O = Methanol

$C_2H_4O_2$ = Methyl formate

NaOH = Sodium hydroxide

ST = Storage tank

P.0X = Pump

C.0X = Compressor

GL.0X = Gas-liquid separator

H.E.0X = Heat exchanger

R.0X = Reactor

T= temperature

Cp^o= heat capacity

Q = heat

w = mass flow

H^o= Standard enthalpy

Vr = reactor volume

ε= void volume / volume of the reactor

εm = mean voidage

U= Overall heat transfer coefficient

A = Area of exchange

ΔTml = Mean logarithmic temperature difference

Amin = minimum area

n_tubes = number of tubes

D_t = diameter of the tubes

L = length of the tubes

A_{tubes} = surface area of the tubes

N_{pitch} = number of pitch

de = external diameter of the tubes

Dbundle = bundle diameter

Di_{shell} = shell diameter

D_h = hole diameter

$D_{surroundings}$ = surroundings distance inside the reactor without tubes

e_{shell} = thickness of the shell

Do_{shell} = outer shell diameter

$B_{spacing}$ = baffle spacing

D_{Bdisk} = diameter of the disk baffle

d_{pe} = particle diameter equivalent to spherical shape

H = particle height

V_p = particle volume

S_p = surface of the pellet

Φ = sphericity

μ = viscosity

vs = velocity inside the tubes

ρ = density

V_{tank} = Tank volume

D_T = Tank diameter

B = Baffle width

D_a = Impeller diameter

W = Width of blade

H_L = Height of liquid

Z_a = Height of impeller above the vessel floor

N_{Re} = Reynolds number

N = rotational speed

P = Power

N_p = Power number

K = separation constant

ρl = liquid density

ρg = gas density

vgas = maximum gas velocity

dmin = minimum diameter

qg = volumetric flow rate of the gas

Fg = fraction of cross section available for the gas flow

Doutgas = diameter of the nozzle where flows the outlet gas stream

Doutliquid = diameter of the nozzle where flows the outlet liquid stream

Lliquid = height of liquid in the gas liquid separator

Lgas = height of gas in the gas liquid separator

APPENDICES

APPENDIX 1: MASS BALANCE

a) Mass Balance on the Reactor:

- Methacrolein (MAL) consumption for achieve the production demand of methyl methacrylate (MMA):

$$\frac{40.000.000 \text{ kg MMA}}{8000 \text{ h}} * \frac{1 \text{ kmol MMA}}{100.121 \text{ kg MMA}} * \frac{1 \text{ kmol MAL}}{1 \text{ kmol MMA}} * \frac{100 \text{ kmol MAL total}}{69.8 \text{ kmol MAL reacted}} * \frac{70.09 \text{ kg MAL}}{1\text{kmol MAL}}$$

$$= 5014.7 \frac{\text{kg MAL}}{\text{h}}$$

- Methanol consumption 69.1% in weight regard methacrolein:

$$5014.7 \frac{\text{kg MAL}}{\text{h}} * \frac{69.1 \text{ kg CH3OH}}{30.9 \text{ kg MAL}} = 11214.1 \frac{kg\ CH3OH}{h}$$

- Sodium hydroxide inlet and outlet of the reactor as it is 1% in weight regard methanol:

$$11214.1 \frac{\text{kg CH3OH}}{\text{h}} * \frac{1 \text{ kg NaOH}}{99 \text{ kg CH3OH}} = 113.3 \frac{\text{kg NaOH}}{\text{h}}$$

- Mass flow rate water inlet to reactor 0.1% regard methanol and 50% regard NaOH:

$$11214.1 \frac{\text{kg CH3OH}}{\text{h}} * \frac{0{,}1 \text{ kg H2O}}{99.9 \text{ kg CH3OH}} + 113.3 \frac{\text{kg NaOH}}{\text{h}} * \frac{\text{kg H2O}}{\text{kg NaOH}} = 124.5 \frac{\text{kg H2O}}{\text{h}}$$

- O_2 stream inlet to reactor esteemed: 1756.1 kg / h. This flow rate will later be checked if it accomplishes with the restrictions of the patent.

- N_2 inert 93% volume regard O_2 that enters and leaves the reactor as it is an inert:

$$1756.1\ \frac{\text{kg O2}}{\text{h}} * \frac{\text{1 kmol O2}}{\text{32 kg O2}} * \frac{\text{93 kmol N2}}{\text{7 kmol O2}} * \frac{\text{1 kmol N2}}{\text{28 kg N2}} = 20414.6\ \frac{\text{kg N2}}{\text{h}}$$

- Mass flow rate of methacrolein leaving the reactor as its conversion is 69.8%:

$$5014.7\ \frac{\text{kg MAL}}{\text{h}} * (1 - 0{,}698) = 1514.4\ \frac{\text{kg MAL}}{\text{h}}$$

- Mass flow rate of methanol leaving the reactor:

$$\frac{\text{40.000.000 kg MMA}}{\text{8000 h}} * \frac{\text{1 kmol MMA}}{\text{100,121 kg MMA}} * \frac{\text{1 kmol CH3OH}}{\text{1 kmol MMA}} * \frac{\text{100 kmol CH3OH}}{\text{97,2kmol CH3OH}} * \frac{\text{32,04 kg CH3OH}}{\text{1kmol CH3OH}}$$

$$= 1646.2\ \frac{\text{kg CH3OH consumed}}{\text{h}}$$

$$11214.1\ \frac{\text{kg CH3OH}}{\text{h}} - 1646.2\ \frac{\text{kg CH3OH consumed}}{\text{h}} = 9568.0\ \frac{\text{kg CH3OH}}{\text{h}}$$

- Mass flow rate O_2 leaving the reactor:

  - O_2 consumed for the formation of MMA:

$$1646.2\ \frac{\text{kg CH3OH consumed}}{\text{h}} * \frac{\text{1 kmol CH3OH}}{\text{32.04 kg CH3OH}} * \frac{\text{97.2 kmol CH3OH consumed in the reaction}}{\text{100 kmol CH3OH}}$$

$$* \frac{\text{0.5 kmol O2}}{\text{1 kmol CH3OH}} * \frac{\text{32 kg O2}}{\text{1 kmol O2}} = 799.0\ \frac{\text{kg O2}}{\text{h}}$$

  - O_2 consumed for the formation of methyl formate (MF):

$$1646.2\ \frac{\text{kg CH3OH consumed}}{\text{h}}*\frac{\text{1 kmol CH3OH}}{\text{32.04 kg CH3OH}}*\frac{\text{1.4 kmol CH3OH consumed in the reaction}}{\text{100 kmol CH3OH}}$$

$$*\ \frac{\text{1 kmol O2}}{\text{2 kmol CH3OH}}*\frac{\text{32 kg O2}}{\text{1 kmol O2}}=11.5\frac{\text{kg O2}}{\text{h}}$$

- O_2 consumed for the formation of CO_2:

$$1646.2\ \frac{\text{kg CH3OH consumed}}{\text{h}}*\frac{\text{1 kmol CH3OH}}{\text{32.04 kg CH3OH}}*\frac{\text{1.4 kmol CH3OH consumed in the reaction}}{\text{100 kmol CH3OH}}$$

$$*\ \frac{\text{3 kmol O2}}{\text{2 kmol CH3OH}}*\frac{\text{32 kg O2}}{\text{1 kmol O2}}=34.5\frac{\text{kg O2}}{\text{h}}$$

Therefore, the total O_2 consumed is:

$$799\frac{\text{kg O2}}{\text{h}}+34.5\frac{\text{kg O2}}{\text{h}}+11.5\frac{\text{kg O2}}{\text{h}}=845.0\ \frac{\text{kg O2}}{\text{h}}$$

And, subsequently, the mas flow of O_2 leaving the reactor is:

$$1756.1\frac{\text{kg O2}}{\text{h}}-845.1\frac{\text{kg O2}}{\text{h}}=911.0\ \frac{\text{kg O2}}{\text{h}}$$

- The mass flow rate of N_2 leaving the remains invariable as it is inert:

$$20414.6\frac{\text{kg N2}}{\text{h}}$$

- The mass flow rate of MMA leaving the reactor is:

$$5014.7\ \frac{\text{kg MAL}}{\text{h}}*\frac{\text{1 kmol MAL}}{\text{70.09 kg MAL}}*\frac{\text{69.8 kmol MAL reacted}}{\text{100 kmol MAL total}}*\frac{\text{1 kmol MMA}}{\text{1 kmol MAL}}*\frac{\text{100.121 kg MMA}}{\text{1 kmol MMA}}$$

$$= 5000.0 \frac{\text{kg MMA}}{\text{h}}$$

- The mass flow rate of MF leaving the reactor is:

$$11.5 \frac{\text{kg O2}}{\text{h}} * \frac{1 \text{ kmol O2}}{32 \text{ kg O2}} * \frac{1 \text{ kmol MF}}{1 \text{ kmol O2}} * \frac{60.05 \text{ kg MF}}{1 \text{ kmol MF}} = 21.6 \frac{\text{kg MF}}{\text{h}}$$

- The mass flow rate of CO_2 leaving the reactor is:

$$34.5 \frac{\text{kg O2}}{\text{h}} * \frac{1 \text{ kmol O2}}{32 \text{ kg O2}} * \frac{2 \text{ kmol CO2}}{3 \text{ kmol O2}} * \frac{44.01 \text{ kg CO2}}{1 \text{ kmol CO2}} = 31.6 \frac{\text{kg MF}}{\text{h}}$$

Once done the mass balance calculations in the reactor it is verified that with the gas flow rate established the concentration in weight in both the inlet and the outlet streams inside the tubes is below 15%.

Table 18: Verification of the concentration of methacrolein in weight in the reactor

	Inlet	Outlet
Methacrolein % weight	13%	4.09%

b) Mass Balance on the gas – liquid separators:

In these equips the different phases are separated: the gas phase leaves by the upper side whereas the liquid phase leaves by the lower side. The results are as follows:

Table 19: Gas – Liquid Separator 1 mass balance

	GL.01		
Mass flow rate (kg/h)	**10**	**11**	**14**
Methacrolein	1514	1514	0
Methanol	9568	9568	0
O_2	911	911	0
N_2	20415	20415	0

Methyl Methacrylate	5000	0	5000
H_2O	1062	0	1062
$C_2H_4O_2$	22	22	0
CO_2	32	32	0
Propionaldehyde	0	0	0
NaOH	113	0	113
Total flow rate	38637	32461	6176

Table 20: Gas – Liquid Separator 2 mass balance

	GL.02		
Mass flow rate (kg/h)	**5**	**7**	**6**
Methacrolein	5015	0	5015
Methanol	11214	0	11214
O_2	0	0	0
N_2	0	0	0
Methyl Methacrylate	0	0	0
H_2O	124	0	124
$C_2H_4O_2$	0	0	0
CO_2	0	0	0
Propionaldehyde	51	51	0
NaOH	113	0	113
Total flow rate	16517	51	16467

Table 21: Gas – Liquid Separator 3 mass balance

	GL.03		
Mass flow rate (kg/h)	**11**	**13**	**12**
Methacrolein	1514	0	1514
Methanol	9568	0	9568
O_2	911	911	0
N_2	20415	20415	0
Methyl Methacrylate	0	0	0
H_2O	0	0	0
$C_2H_4O_2$	22	22	0

CO_2	32	32	0
Propionaldehyde	0	0	0
NaOH	0	0	0
Total flow rate	32461	21379	11082

c) Mass Balance on the mixing and pH adjustment tank:

In the tank, the stream 5 leaves it with the combination of all the other streams:

$$w_1 + w_2 + w_3 + w_4 + w_{12} = w_5$$

Table 23: Mixing and pH adjustment tank mass balance

	Mixing and adjustment pH tank					
Mass flow rate (kg/h)	**1**	**2**	**3**	**4**	**12**	**5**
Methacrolein	3500	0	0	0	1514	5015
Methanol	0	1646	0	0	9568	11214
O_2	0	0	0	0	0	0
N_2	0	0	0	0	0	0
Methyl Methacrylate	0	0	0	0	0	0
H_2O	0	11	113	0	0	124
$C_2H_4O_2$	0	0	0	0	0	0
CO_2	0	0	0	0	0	0
Propionaldehyde	51	0	0	0	0	51
NaOH	0	0	113	0	0	113
Total flow rate	3551	1657	227	0	11082	16517

APPENDIX 2: ENERGY BALANCE

a) Energy Balance on the Reactor:

To do the energy balances, it has been found in some cases the correlation of the enthalpy and the heat capacity with the temperature according to the National Institute of Standards and Technology (NIST):

$$H^o_T - H^o_{298,15} = A*T + B*T^2/2 + C*T^3/3 + D*T^4/4 - E/T + F - H$$

$$Cp^o = A + B*T + C*T^2 + D*T^3 + E/T^2$$

Where:

- T= temperature (K) / 1000
- Cp^o= heat capacity (J/mol*K)
- H^o= Standard enthalpy (kJ/mol)

Table 24: Coefficients to estimate standard enthalpy and heat capacity according to NIST

	O_2 (g)	H_2O (l)	CO_2 (g)	N_2 (g)	NaOH (s)
A	31.32234	-203.606	24.99735	28.98641	419.4837
B	-20.23531	1523.29	55.18696	1.853978	-1717.754
C	57.86644	-3196.413	-33.69137	-9.647459	2953.573
D	-36.50624	2474.455	7.948387	16.63537	-1597.221
E	-0.007374	3.855326	-0.136638	0.000117	-6.046884
F	-8.903471	-256.5478	-403.6075	-8.671914	-517.8662
G	246.7945	-488.7163	228.2431	226.4168	933.0738
H	0	-285.8304	-393.5224	0	-425.9312

It has been calculated the heat to increase the temperature of each compound as well as the heat of reactions. The enthalpy of formations are at 25ºC:

$\Delta Hf\ C_4H_6O$ = -138.5 kJ/mol

$\Delta Hf\ CH_3OH$ = -238.4 kJ/mol

$\Delta Hf\ C_5H_8O_2$ = -388.8 kJ/mol

$\Delta Hf\ H_2O$ = -285.83 kJ/mol

$\Delta Hf\ C_2H_4O_2$ = -365.9 kJ/mol

- Reaction of formation of MMA:

ΔHr^o = -297.73 kJ/mol

$Qr = \Delta Hr^o \cdot w_{9r1,\ MAL}$

$$= -297.73\ \frac{\mathrm{kJ}}{\mathrm{mol}} * 5014.7\ \frac{\mathrm{kg\ MAL}}{\mathrm{h}} * \frac{1000\ \mathrm{mol\ MAL}}{70.09\ \mathrm{kg\ MAL}} * \frac{69.8\ \mathrm{mol\ MAL\ reacted}}{100\ \mathrm{mol\ MAL}}$$

= -14868509.1 kJ/h

$Q_{MAL} = w_{9r1,MAL} \cdot cp_{MAL} \cdot \Delta T$

$$= 99.74 \cdot 10^{-3}\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}} * 5014.7\ \frac{\mathrm{kg\ MAL}}{\mathrm{h}} * \frac{1000\ \mathrm{mol\ MAL}}{70.09\ \mathrm{kg\ MAL}} * \frac{69.8\ \mathrm{mol\ MAL\ reacted}}{100\ \mathrm{mol\ MAL}} * (342 - 333)K$$

= 44828.8 kJ / h

$Q_{O2} = w_{9r1,O2} \cdot (H^o_{353} - H^o_{298.15})_{O2} - (H^o_{333} - H^o_{298.15})_{O2}$=14809.8 kJ / h

$Q_{CH3OH} = w_{9r1,CH3OH} \cdot cp_{CH3OH} \cdot \Delta T$

$$= 79.9 \cdot 10^{-3}\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}} * 49940\ \frac{\mathrm{mol\ CH3OH}}{\mathrm{h}} * (337 - 333)K$$

= 18753.8 kJ / h

$Q_{MMA} = w_{9r1,MMA} \cdot cp_{MMA} \cdot \Delta T$

$$= 191.2 \cdot 10^{-3}\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}} * 49940\ \frac{\mathrm{mol\ MMA}}{\mathrm{h}} * (353 - 298)K$$

= 525164.6 kJ / h

$Q_{H2O} = w_{9r1,H2O} \cdot (H^o_{353} - H^o_{298.15})_{H2O} - (H^o_{333} - H^o_{298.15})_{H2O}$ = 207042.3 kJ/h

Qt = Qr + Σ Q =-14057909 kJ/h

- Reaction of formation of MF:

ΔHr^o = -460.76 kJ/mol

$Qr = \Delta Hr^o \cdot w_{9r2,\ CH3OH}/2$

$$= \text{-460.8}\ \frac{\text{kJ}}{\text{mol}} * 1646.2\ \frac{\text{kg CH3OH}}{\text{h}} * \frac{\text{1 kmol CH3OH}}{\text{32.04 kg CH3OH}} * \frac{\text{1.4 kmol CH3OH consumed in reaction}}{\text{2*100 kmol CH3OH}}$$

= -165711.0 kJ/h

$Q_{CH3OH} = (1/2)^* \ w_{9r2,CH3OH} \cdot (cp_{CH3OH\ (l)} \cdot \Delta T + \Delta Hvap + cp_{CH3OH\ (g)} \cdot \Delta T) + (1/2)^* \ w_{9r2,CH3OH} \cdot (cp_{CH3OH(l)} \cdot \Delta T)$

$$= (1/2)^*\ 1646.2\ \frac{\text{kg CH3OH}}{\text{h}} * \frac{\text{1 kmol CH3OH}}{\text{32.04 kg CH3OH}} * \frac{\text{1.4 kmol CH3OH consumed in reaction}}{\text{2*100 kmol CH3OH}} * \left[79.9 \cdot 10^{-3}\ \frac{\text{kJ}}{\text{mol K}} * (338 - 333)K + * \ 37.6\ \frac{\text{kJ}}{\text{mol}} + 46.8 \cdot 10^{-3}\ \frac{\text{kJ}}{\text{mol K}} * (353 - 338)K\right]$$
$$+ (1/2)^*\ 1646.2\ \frac{\text{kg CH3OH}}{\text{h}} * \frac{\text{1 kmol CH3OH}}{\text{32.04 kg CH3OH}} * \frac{\text{1.4 kmol CH3OH consumed in reaction}}{\text{2*100 kmol CH3OH}} * \left[79.9 \cdot 10^{-3}\ \frac{\text{kJ}}{\text{mol K}} * (338 - 333)K\right]$$

= 27830.6 kJ / h

$Q_{O2} = w_{9r2,O2} \cdot (H^o_{353} - H^o_{298.15}) - (H^o_{333} - H^o_{298.15})$=213.3 kJ / h

$Q_{C2H4O2} = w_{9,C2H4O2} \cdot (cp_{C2H4O2(l)} \cdot \Delta T + \Delta Hvap + cp_{C2H4O2\ (g)})$=

$$= 49939.6\ \frac{\text{mol C2H4O2}}{\text{h}} * \left[64.38 \cdot 10^{-3}\ \frac{\text{kJ}}{\text{mol K}} * (353 - 325)K + \ 29\ \frac{\text{kJ}}{\text{mol}} + 44.06 \cdot 10^{-3}\ \frac{\text{kJ}}{\text{mol K}}\right]$$

= 7642.1 kJ / h

$Q_{H2O} = w_{9r2,H2O} \cdot (H^o_{353} - H^o_{298.15})_{H2O} - (H^o_{333} - H^o_{298.15})_{H2O}$ = 2982.0 kJ/h

Qt = Qr + Σ Q =-1334411 kJ/h

- Reaction of formation of CO_2:

$\Delta Hr^o = -1453.42$ kJ/mol

$Qr = \Delta Hr^o \cdot w_{9r3,\ CH3OH}$

$$= -1453.42\ \frac{\text{kJ}}{\text{mol}} * 1646.2\ \frac{\text{kg CH3OH}}{\text{h}} * \frac{1\ \text{kmol CH3OH}}{32.04\ \text{kg CH3OH}} * \frac{1.4\ \text{kmol CH3OH consumed in the reaction}}{100\ \text{kmol CH3OH}}$$

= -522761.5 kJ/h

$Q_{CH3OH} = w_{9r3,CH3OH} \cdot (cp_{CH3OH\ (l)} \cdot \Delta T + \Delta Hvap + cp_{CH3OH\ (g)})$

$$= 1646.2\ \frac{\text{kg CH3OH}}{\text{h}} * \frac{1\ \text{kmol CH3OH}}{32.04\ \text{kg CH3OH}} * \frac{1.4\ \text{kmol CH3OH consumed in reaction}}{2{*}100\ \text{kmol CH3OH}} * \left[79.9 \cdot 10^{-3}\ \frac{\text{kJ}}{\text{mol K}} * (338 - 333)K + * \ 37.6\ \frac{\text{kJ}}{\text{mol}} + 46.8 \cdot 10^{-3}\ \frac{\text{kJ}}{\text{mol K}} * (342 - 338)K\right]$$

= 27830.6 kJ / h

$Q_{O2} = w_{9r3,O2} \cdot (H^o_{353} - H^o_{298.15})_{O2} - (H^o_{333} - H^o_{298.15})_{O2} = 639.9$ kJ / h

$Q_{CO2} = w_{9r3,CO2} \cdot (H^o_{353} - H^o_{298.15})_{CO2} - (H^o_{333} - H^o_{298.15})_{CO2} = 1515.7$ kJ / h

$Q_{H2O} = w_{9r3,H2O} \cdot (H^o_{353} - H^o_{298.15})_{H2O} - (H^o_{333} - H^o_{298.15})_{H2O} = 5964.2$ kJ/h

$Qt = Qr + \Sigma\ Q = -486811.0$ kJ/h

Table 25: Heat of chemical compounds not reacted:

	ni (mol/h)	**ΔHi(kJ/mol)**	**Q [kJ/h]**
Methanol	298625	38.69	11554287
Methacrolein	21607	34.19	738850
O_2	28470	1.62	46253
N_2	729092	1.60	1168710
H_2O	6917	4.15	28675
NaOH	2832	1.23	9528

Therefore, the total heat is Q = 1131479.1 kJ/h

b) Energy balance on the mixer tank:

In the mixer tank it is calculated the temperature of the outlet stream as the recycling stream enters at a higher level than the other streams. It is accomplished that:

$Q_{2,MAL} + Q_{11,MAL} + Q_{1,CH3OH} + Q_{11,CH3OH} + Q_{1,CH3OH} + Q_{1,H2O} + Q_{4,H2O} + Q_{2,PROPIONALDEHYDE} + Q_{4,NAOH} = 0$

- Heat of methacrolein:

$Q_{2,MAL} = w_{2,MAL} \cdot cp_{MAL} \cdot \Delta T =$

$$49939.6\ \frac{\mathrm{mol\ C2H4O2}}{\mathrm{h}} * 99.7 \frac{\mathrm{J}}{\mathrm{mol\ K}} * (Toutlet - 298)K$$

$Q_{11,MAL} = w_{11,MAL} \cdot cp_{MAL} \cdot \Delta T =$

$$21607.1\ \frac{\mathrm{mol\ C2H4O2}}{\mathrm{h}} * 99.7 \frac{\mathrm{J}}{\mathrm{mol\ K}} * (Toutlet - 336)K$$

- Heat of methanol:

$Q_{1,CH3OH} = w_{1,CH3OH} \cdot cp_{CH3OH} \cdot \Delta T =$

$$51378.2\ \frac{\mathrm{mol\ CH3OH}}{\mathrm{h}} * 79.9 \frac{\mathrm{J}}{\mathrm{mol\ K}} * (Toutlet - 298)K$$

$Q_{11,CH3OH} = w_{1,CH3OH} \cdot cp_{CH3OH} \cdot \Delta T =$

$$9568\ \frac{\mathrm{mol\ CH3OH}}{\mathrm{h}} * 79.9 \frac{\mathrm{J}}{\mathrm{mol\ K}} * (Toutlet - 298)K$$

- Heat of water:

$Q_{1,H2O} = w_{1,H2O} \cdot cp_{H2O} \cdot \Delta T =$

$$51378.2\ \frac{\mathrm{mol\ CH3OH}}{\mathrm{h}} * 79.9 \frac{\mathrm{J}}{\mathrm{mol\ K}} * (Toutlet - 298)K$$

$Q_{4,H2O} = w_{1,H2O} \cdot cp_{H2O} \cdot \Delta T =$

$$9568\ \frac{\mathrm{mol\ CH3OH}}{\mathrm{h}} * 79.9 \frac{\mathrm{J}}{\mathrm{mol\ K}} * (Toutlet - 298)K$$

- Heat of propionaldehyde:

$Q_{1,PROPIONALDEHYDE} = w_{1,\ PROPIONALDEHYDE} \cdot (cp_{PROPIONALDEHYDE} \cdot \Delta T + \Delta Hvap + cp_{PROPIONALDEHYDE} \cdot \Delta T)$

=

$$872.1\ \frac{\text{mol CH3OH}}{\text{h}} * \left[134.7\frac{\text{J}}{\text{mol K}} * (322-298) + 134.7\frac{\text{J}}{\text{mol K}} * (Toutlet - 322)\right]$$

- Heat of sodium hydroxide:

$Q_{4,NAOH}= w_{4,NAOH} \cdot cp_{NAOH} \cdot \Delta T=$

$$113.3\ \frac{\text{mol CH3OH}}{\text{h}} * 59.5\frac{\text{J}}{\text{mol K}} * (Toutlet - 298)$$

Resolving the aforementioned equation it is obtained that the temperature of the outlet stream of the mixing tank is of 324K which is higher than the propionaldehyde boiling point, so that it switches to gas phase, just as considered in its heat calculation.

c) Energy to exchange in heat and cold zones:

The heat is calculated in the same way than the previous one, apart from the hot stream 2, where has taken into account that methanol and methacrolein switch to liquid phase:

Table 26: Energy balance of the cold stream 1 (C1):

Stream 5	**Flow rate (kg/h)**	**Flow rate (mol/h)**	**Cp (J/mol K) inlet**	**T intlet (K)**	**Cp (J/mol K) outlet**	**T outlet (K)**	**Q (J)**
Methacrolein	5015	71547	100	324	100	333	6.31E+07
Methanol	11214	350004	80	324	80	333	2.47E+08
H_2O	124	6917	75	324	75	333	4.75E+06
Propionaldehyde	51	872	135	324	135	333	1.04E+06
NaOH	113	2832	61	324	61	333	1.92E+06
						Q (kW)	**88.39**

- Cold stream 2 (C2):

The stream is compressed at a pressure at 9 atm in three isoentropic compressor. The final temperature after being compressed is calculated by:

$$\text{Tinlet} = 25ºC * \left(\frac{P2}{P1}\right)^{\frac{k-1}{k}} = 46.8ºC$$

Where:

- k is equal to 1,4 for diatomic gases.
- P2 = 9 atm
- P1 = 1 atm

As it is decided to employ two compressors: the ratio of compression is calculated as:

$$\text{Ratio} = \left(\frac{P2}{P1}\right)^{\frac{1}{n}} = 3$$

Where

- n= number of compressors = 2

In case that n = 1, the ratio would be 9 which is very high for a compressor

Table 27: Energy balance of the cold stream 2 (C2):

Stream 8	Flow rate (kg/h)	Flow rate (mol/h)	Cp (J/mol K) inlet	T intlet (K)	Cp (J/mol K) outlet	T outlet (K)	Q (J)
N_2	20415	729092	29.14	320	29.15	333	2.82E+08
O_2	1756	54878	29.50	320	29.59	333	2.28E+07
Total	22171	783970	-	-	-	-	3.05E+08
						Q (kW)	**84.80**

Table 28: Energy balance of the hot stream 1 (H1):

Stream 14	**Flow rate (kg/h)**	**Flow rate (mol/h)**	**Cp (J/mol K) inlet**	**T intlet (K)**	**Cp (J/mol K) outlet**	**T outlet (K)**	**Q (J)**
MMA	5000	49940	191.20	353	191.20	303	-4.77E+08
H_2O	1062	59014	75.60	353	75.32	303	-2.28E+08
NaOH	113	2832	59.53	353	61.10	303	-7.11E+06
Total	6062	108954	-	-	-	-	-7.13E+08
						Q (kW)	**-197.96**

Table 29: Energy balance of the hot stream 2 (H2):

Stream 11	**Flow rate (kg/h)**	**Flow rate (mol/h)**	**Cp (J/mol K) inlet**	**T intlet (K)**	**Cp (J/mol K) outlet**	**T outlet (K)**	**Q (J)**
Methacrolein	1514	21607	99.7	353	99.7	336	-7.32E+08
Methanol	9568	298625	79.9	353	37.6	336	-1.15E+10
O_2	911	28470	29.7	353	29.6	336	-1.55E+07
N_2	20415	729092	29.2	353	29.2	336	-3.66E+08
$C_2H_4O_2$	22	360	64.4	353	64.4	336	-3.94E+05
CO_2	32	719	39.5	353	38.8	336	-6.54E+05
Total	32461	1078873	-	-	-	-	-1.26E+10
						Q (kW)	**-3499.43**

APPENDIX 3: PINCH ANALYSIS

The following are the streams selected for the analysis, which heat needed or to exchange has been calculated before. In case of the condenser (H2) it has been determined the average of the product of the heat capacity and the mass flow.

Table 30: Heat and temperatures displaced

Stream	w·cp (kW/°C)	Inlet T (°C)	Outlet T (°C)	Inlet T corrected (°C)	Outlet T corrected (°C)	Q (kW)
C1	10.0	51	60	61	70	88.39
C2	6.4	47	60	57	70	84.80
H1	4.0	80	30	70	20	-197.96
H2	205.8	80	63	70	53	-3499.43

In the following table, the heat in each interval is calculated considering the total of the w·cp products of each current passing through the indicated temperature range. There is no pinch point as it is defined as there is no interval which value of the heat corrected indicated in Q hoard is 0.

Table 31: Heat cascade

				Q hoard (kW)
T intervals		Streams	Q (kW)	0
70	61	C1, C2, H1, H2	1701.7	1702
61	57	C2, H1, H2	894.8	2596
57	53	H1, H2	797.3	3394
53	20	H1	130.7	3524

APPENDIX 4: REACTOR DESIGN

To carry out the reactor design, firstly it has been calculated the density of the catalyst taking into consideration that the catalyst was prepared with 108 gr of SiO_2 and with 51.2 gr of magnesium nitrate hexahydrate. Considering that there were no loses of material during the preparation:

$$51.2\ \mathrm{g\ Mg(NO_3)_2 \cdot 6\ H2O} * \frac{1\ \mathrm{mol\ Mg(NO_3)_2 \cdot 6H2O}}{256.41\mathrm{g\ Mg(NO_3)_2 \cdot 6H2O}} * \frac{1\ \mathrm{mol\ MgO}}{1\ \mathrm{mol\ Mg(NO_3)_2 \cdot 6H2O}} * \frac{40.304\mathrm{g}}{1\mathrm{mol\ MgO}}$$

$$= 8.05\mathrm{g\ MgO}$$

As it is stated that an 1.1% is made by nickel oxide (II), 0.9% is made by gold and the 98% remaining is made by the support of which the proportions can be estimated and 108 gr of SiO_2 per each 8.05 gr of MgO. Therefore, the density of the catalyst (ρcat.) is calculated multiplying the mass fraction per the density of each of its components:

0.912 * 2634 kg/m^3 SiO_2 + 0.068 * 3580 kg/m^3 MgO+ 0.009*19300 kg/m^3 Au+ 0.011*6.67 kg/m^3 NiO = 2843 kg / m^3 =ρcat.

The mass of catalyst (m. cat) required is calculated with the space time residence:

$$\frac{49940\ \mathrm{mol\ MMA}}{\mathrm{h}} * \frac{\mathrm{kg\ catalyst}}{4.08\ \mathrm{mol\ MMA}} = 12300\ \mathrm{kg\ of\ catalyst\ minimum} = m.cat$$

To verify the second condition of the reactor related to the liquid reactor volume and the mass of catalyst, it has been determined the volumetric flow rate with the densities of the liquids or solid and, in case of the gases, applying the ideal gas equation:

Table 32: Volumetric flow rate in the reactor

	Volumetric flow rate (m^3/h)	
	Reactants	**Products**
Methacrolein	6	81
Methanol	14	1124
O2	174	107
N2	2317	2744
Methyl Methacrylate	0	5
H2O	0.1	1
C2H4O2	0	1
CO2	0	3
NaOH	0.1	0.1
Total flow rate	2511	4067

The volume of the reactor is obtained by the following equation, taking into account that it is increased a 20% for security reasons:

$$\mathrm{Vr.} = \frac{\mathrm{m.cat}}{\rho\mathrm{cat.}*(1\text{-}\varepsilon)}*1{,}2=17{,}3\ \mathrm{m}^3$$

Where:

- Vr.= reactor volume
- ε= void volume / volume of the reactor = 0.7

The area of exchange needed is calculated by:

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

Where:

- U= Overall heat transfer coefficient ($W/m^2 \cdot {}^{o}C$)
- A= Area of exchange (m^3)

- ΔTml = Mean logarithmic temperature difference (ºC)

From bibliography is found an U for gases between 20 and 40 BTU/(ft2 h ºF) and a U for organic solvents between 100 and 300 BTU /(ft^2 h ºF). Calculating the mean of these values it is determined a U of 1306 W/m^2 K. Therefore, the area needed minimum employing a water stream with temperatures of 25ºC and 55ºC is:

$$A_{min} = 8.1\ m^3$$

The reactor tubes selected are from an internal diameter of 1'' and a length of 24 ft. The number of tubes is calculated by:

$$n_{tubes}=\frac{4\ \mathrm{Vr.}}{\frac{\Pi * \mathrm{dt}^2 * \mathrm{L}}{\mathrm{L}}}=4669$$

Where:

-d_t is the inner diameter of the tubes

- L is the length of the tubes

Once calculated the number of tubes, it is verified that the exchange area is equal or higher than the needed:

$$A_{tubes}= \pi \cdot d_t \cdot L \cdot n_{tubes} = 2271\ m^3 > A_{min}$$

The number of pitch (N_{pitch}) is calculated 1.25 the distance of the external diameter:

$$N_{pitch} = 1.25 \cdot de = 0.036\ m$$

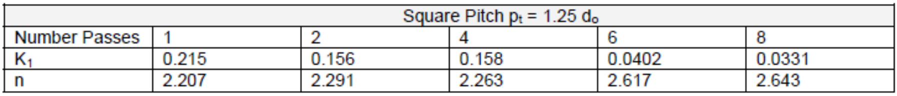
Where:

-d_e is the external diameter of the tubes with a value of 28.65 mm

The bundle diameter (Dbundle) without considering the central zone without tubes is calculated by:

$$\text{Dbundle}=\text{de}^{*}\left(\frac{\text{ntubes}}{\text{Kt}}\right)^{\wedge}\left(\frac{1}{\text{N1}}\right)=2.64\ \text{m}$$

Where Kt and N1 are parameters depending on the number of passes and if it is in square or triangular configuration. In this case the values of Kt and N1 are 0.215 and 2.207 respectively.



Square Pitch $p_t = 1.25\ d_o$					
Number Passes	1	2	4	6	8
K_1	0.215	0.156	0.158	0.0402	0.0331
n	2.207	2.291	2.263	2.617	2.643

Figure 14: Data to determine the bundle diameter

The shell diameter is calculated considering the baffle spacing of 0.750 m in the central zone without tubes, and 0,375m in the surroundings closest to the shell wall. Therefore, the shell diameter is calculated by:

$$Di_{shell} = D_{bundle} + D_{hole} + 2\cdot D_{surroundings} = 4.89\ \text{m}$$

Taking a thickness shell of 14 mm (e_{shell}), the outer shell diameter is:

$$Do_{shell} + 2\cdot e_{shell} = 4.92\ \text{m}$$

The baffle spacing ($B_{spacing}$) is calculated as the 20% of the bundle diameter:

$$B_{spacing} = 0.2 \cdot D_{bundle} = 2.64\ \text{m}$$

The diameter of the disk baffle (D_{Bdisk}) is equal to:

$$D_{Bdisk} = Db_{undle} + D_{hole} = 3.39 \text{ m}$$

On the other hand, the inner diameter of the doughnut baffle it equal to the diameter of the central hole: 0.750m; and the outer diameter of the doughnut baffle is equal to the inner shell diameter: 4.92 m.

When it comes to calculate the dimensions of the catalyst pellet type 4-hole cilinder it has been taken into account the following data:

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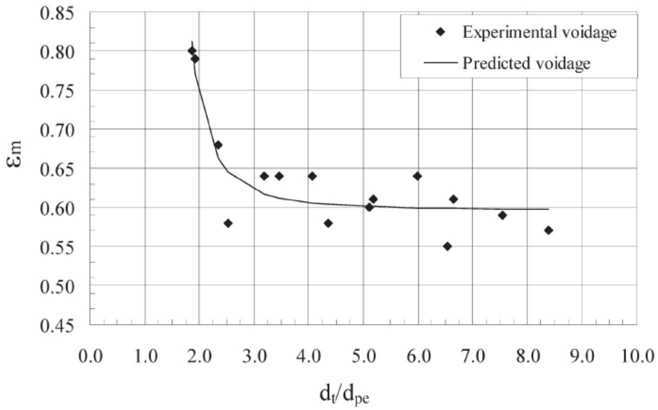

Figure 5. Mean voidage in packed beds of 4-hole cylindrical particles.

Figure 15: Mean voidage – diameter ratio in 4-hole pellets

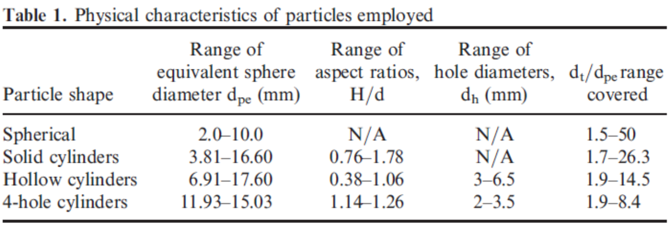

Table 1. Physical characteristics of particles employed

Particle shape	Range of equivalent sphere diameter d_{pe} (mm)	Range of aspect ratios, H/d	Range of hole diameters, d_h (mm)	d_t/d_{pe} range covered
Spherical	2.0–10.0	N/A	N/A	1.5–50
Solid cylinders	3.81–16.60	0.76–1.78	N/A	1.7–26.3
Hollow cylinders	6.91–17.60	0.38–1.06	3–6.5	1.9–14.5
4-hole cylinders	11.93–15.03	1.14–1.26	2–3.5	1.9–8.4

Figure 16: Characteristics of the particles in the experiments

Table 33: Pellets parameters considered

Mean voidage (εm)	0.7
d_t / d_{pe}	2.25
H / d_p	1.2
d	2

Where:

- d_{pe} = particle diameter equivalent to spherical shape (mm)
- H = particle height (mm)
- d_h = hole diameter (mm)

To calculate its dimensions, firstly is calculated the particle diameter equivalent to spherical shape with the inner diameter of the tubes and the previous ratio d_t / $d_{pe.}$ obtaining a value of:

$$d_{pe} = 11.29 \text{ mm}$$

Afterwards, by iteration it is supposed a value of the particle diameter, it is calculated its height and volume (V_p), and it is verified if the particle diameter equivalent to the spherical shape is equal to the previous value calculated:

$$d_p = 9.71 \text{ mm}$$

$$H = d_p \cdot H / dp = 12.24 \text{ mm}$$

$$V_p = \frac{\Pi * H * d_p{}^2}{4} - 4 * \frac{\Pi * H * d_h{}^2}{4} = 753.27 \text{ mm}$$

$$d_{pe} = \left(\frac{6 * V_p}{\Pi}\right)^{1/3} = 11.29 \text{ mm}$$

To calculate the pressure drop, it is needed the sphericity of the particle:

$$\mathrm{S_p}=2*\left(\frac{\Pi * \mathrm{d_p}^{\,2}}{4}-4*\frac{\Pi * \mathrm{d_h}^{2}}{4}\right)+\Pi * \mathrm{d_p}*\mathrm{H}+4*\Pi * \mathrm{d_h}*\mathrm{H}=804.22\ \mathrm{mm}^2$$

$$\phi=\frac{\Pi * \mathrm{d_{pe}}^{\,2}}{\mathrm{Sp}}=0.5$$

Where:

- S_p = surface of the pellet (mm^2)
- Φ = sphericity

As in the reactor tubes conveys liquid and gas phase, the pressure drop is calculated c considering the liquid flow and the volumetric fraction of the liquid multiplicated by section of the tube as the section of the tube. The Ergum equation is:

$$\Delta P = -L * \left[\frac{150 * \mu * vs * (1-\varepsilon)^2}{\Phi^2 * d_p{}^2 * \varepsilon^3}+\frac{1.75 * \rho * vs^2 * (1-\varepsilon)}{\Phi * d_p * \varepsilon^3}\right]$$

Where:

- μ = viscosity = 4.11E-4 Pa·s
- vs = velocity inside the tubes = 0.325 m/s
- ρ = density = 853.5 kg/m^3

Therefore ΔP = 1.78 atm

Finally, the inlet pressure is: Pinlet = Poperation + ΔP = 7.7 atm

APPENDIX 5: EQUIPMENT DESIGN

a) Mixer tank design:

The mixer tank is designed establishing a blend time of 30 min. Therefore, the effective volume inside the mixing tank considering that it is increased a 20% for security reasons is:

$$Vtank = q * tb * 1.2 = 12.3\ m^3$$

Where:

- q= volumetric flow rate entering the mixer tank = 20.5 m^3/h
- tb= blend time
- 1.2= security factor

The dimensions of the impeller and the tank has been calculated maintaining these ratios.

$$\frac{D_T}{B} = 12$$
$$\frac{D_a}{W} = 5{,}66$$
$$\frac{H_L}{D_T} = 6$$
$$\frac{Z_A}{D_T} = 1/3$$
$$\frac{D_T}{D_a} = 3$$

Where:

- D_T = Tank diameter = 1.4 m
- B = Baffle width = 0.11 m
- D_a = Impeller diameter = 1 m
- W = Width of blade = 0.18 m
- H_L = Height of liquid = 8.26 m
- Z_a = Height of impeller above the vessel floor = 0.46

This mixing tank is equipped with 4 baffles and the impeller is a pitched-blade turbine which has 6 blades. To calculate power consumed in agitation first is determined the Reynolds number:

$$N_{Re} = \frac{{D_a}^2 * N * \rho}{\mu} = 2.17 \cdot 10^6$$

Where N is the rotational speed, it is selected a value of 140 rpm so that it is well mixed. Therefore:

- N = rotational speed = 140 rpm
- ρ = 804.9 kg / m3
- μ = 5.62E-04 Pa·s

From the following graph it can be determined a power number (Np) of 1.5 for this type of impeller and Reynolds number:

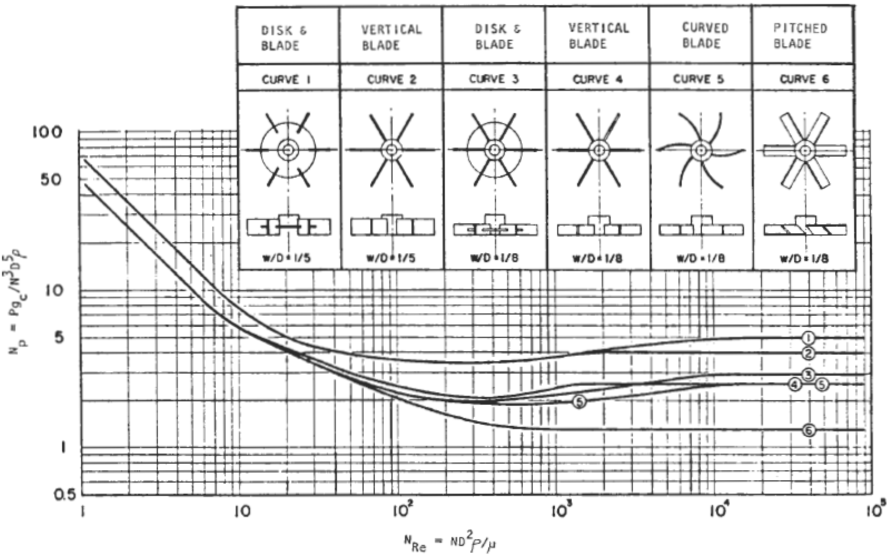

Figure 16: Graph number of power – number of Reynolds for different impellers

The power consumed in agitation is:

$$P = N_P * \rho * N^3 * {D_a}^5 = 15337\ W$$

b) Gas – liquid separators design:

It is done as example the design of the GL.01.

The gas velocity maximum in the gas liquid separator is calculated as:

$$vgas = k * \left[\frac{\rho l}{\rho g} - 1\right]^{\frac{1}{2}} = 1.5\ m/s$$

Where:

- k= separation constant, which has a value of 0.35 because it is employed a mesh deentrainer.
- ρl = liquid density, in this case 942 kg/m^3
- ρg= gas density, in this case 8 kg/m^3

The minimum diameter is calculated as:

$$dmin = \left[\frac{4 * qg}{Fg * \Pi * vgas}\right]^{\frac{1}{2}} =$$

Where:

- qg= volumetric flow rate of the gas, in this case 4060 m3/h
- Fg = fraction of cross section available for the gas flow. As it is a vertical vessel, Fg=1

The following heights are considered to design this equipment, therefore:

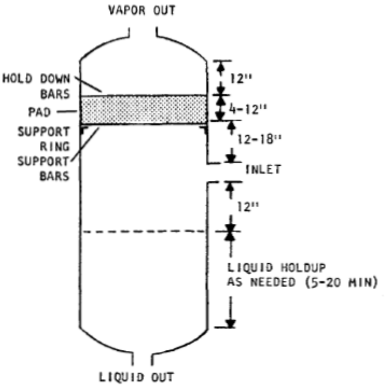

Figure 17: Gas – liquid separator dimensions considered

The diameter of the nozzle where flows the outlet gas stream is:

$$Doutgas = \left[\frac{4 * qg}{\Pi^* voutletg}\right]^{\frac{1}{2}} = 0.38\ m$$

Where voutlet is the velocity at which the gas stream leaves the equipment established as 10 m/s.

The diameter of the nozzle where flows the outlet liquid stream is:

$$Doutliquid = \left[\frac{4 * ql}{\Pi^* voutletl}\right]^{\frac{1}{2}} = 0.048\ m$$

Where voutletl is the velocity at which the liquid stream leaves the equipment established as 1 m/s and ql is the liquid flow rate, in this case 6.4 m^3/h.

The height of liquid is calculated as:

$$Lliquid = \frac{4 * ql * tr}{\Pi^* dmin^2} = 0.048\ m$$

Where tr is the residence time of the liquid established as 20 min.

The height of gas is calculated as:

$$Lgas = (12\ inch + 12\ inch + 18\ inch + 12\ inch) * \frac{0.0254\ metres}{1\ inch} + Doutgas = 1.75\ m$$

c) Heat exchangers design:

. It is done the H.E.01 as an example:

The heat is determined after calculating the energy balances and after applying the Pinch analysis: Q = 88.4 kW

The heat exchanger area is calculated as:

$$Q = F * U * A * \ \Delta Tml$$

In the heat exchangers it is applied a correction factor. In the case were a condensation is carried out it has a value of 1 and it is selected a configuration of 1 - 2. In other cases, it is calculated for both configurations 1 - 2 and 2 - 4 regard to the number of passes as and it is selected the one with higher value:

$$F_{12} = \frac{\left[\ln\left(\frac{1-P}{1-P\cdot R}\right)\right]\cdot\sqrt{R^2+1}}{\ln\left[\left(\frac{2-P\left(R+1-\sqrt{R^2+1}\right)}{2-P\left(R+1+\sqrt{R^2+1}\right)}\right)\right]\cdot(R-1)}$$

$$F_{24} = \frac{\frac{\sqrt{R^2+1}}{2\cdot(R-1)}\cdot\ln\left(\frac{1-P}{1-P\cdot R}\right)}{\ln\left[\left(\frac{2/P-1-R+(2/P)\cdot\sqrt{(1-P)\cdot(1-R\cdot P)}+\sqrt{R^2+1}}{2/P-1-R+(2/P)\cdot\sqrt{(1-P)\cdot(1-R\cdot P)}-\sqrt{R^2+1}}\right)\right]}$$

$$P = \frac{t2-t1}{T1-t1}$$

$$R = \frac{T1 - T2}{t2 - t1}$$

Where:

- t1= temperature of the stream that enters in the tube side.
- t2= temperature of the stream that leaves by the tube side.
- T1= temperature of the stream that enters in the shell side.
- T2= temperature of the stream that leaves by the shell side.

$$F_{1-2} = 0{,}97 \qquad ; \qquad F_{2-4} = 0{,}94$$

In this case is selected the configuration 2 – 4 according to the previous results. The overall heat transfer coefficient is estimated from bibliography between 20 and 60 BTU/(ft2 h ºF). Therefore, it is selected an overall heat transfer coefficient of a value of 227 W/m2·ºC.

The total area calculated by this way is:

$$At = 19.12\ m^2$$

The tubes dimensions selected according to the commonly used are:

Table 34: Tube dimensions

External diameter (mm)	28.65
Internal diameter (mm)	25.4
Length (ft)	10

The exchange area of the tubes is calculated as:

$$Atube = \pi * de * L = 0.27\ m^2$$

The bundle diameter is calculated as in the reactor:

$$\text{Dbundle}=\text{de}^{*}\left(\frac{\text{ntubes}}{\text{Kt}}\right)\wedge\left(\frac{1}{\text{N1}}\right)=423\ mm$$

The shell diameter is calculated with the following graph:

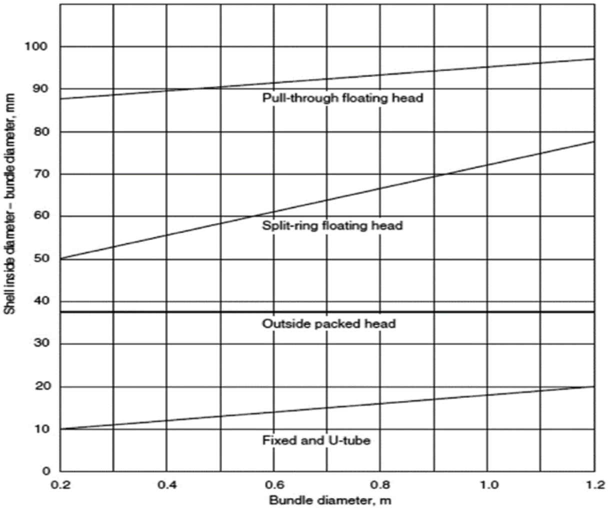

Figure 18: Bundle diameter and shell diameter relationship

Therefore, in this case:

$$Di_{shell} = D_{bundle} + 11mm = 0{,}434\ m$$

The outer shell diameter is calculated taking into account a thickness of 3.2 mm:

$$Do_{shell} + 2\cdot e_{shell} = 3.63\ m$$

The baffle spacing is assumed the average between 20% and 45% of the shell diameter.

Baffle spacing = 0.5 m

Number of baffles = 21

Tables 35: Heat exchangers specifications

HEAT EXCHANGER H.E.01					
Configuration	2 – 4	Shell side		Tube side	
Mass flow (kg/h)		16517		32461	
Temperature (inlet/outlet)(K)		353	345	324	333
Q (kW)	88.4	U J/(s*m2*K)	227	ΔTml (K)	20.5
Shell					
Shell inner diameter (m)		0.434	Shell outer diameter (m)		0.437
Tubes					
External diameter (mm)		28.65	Internal diameter (mm)		25.40
Thickness (mm)		1.63	Length (m)		3.048
Baffles					
Number baffles	21	Spacing (m)	0.14	Thickness (mm)	4.8

HEAT EXCHANGER H.E.02					
Configuration	2 – 4	Shell side		Tube side	
Mass flow (kg/h)		7644		32461	
Temperature (inlet/outlet)(K)		324	333	403	383
Q (kW)	88.4	U J/(s*m2*K)	300	ΔTml (K)	64.3
Shell					
Shell inner diameter (m)		0.258	Shell outer diameter (m)		0.262
Tubes					
External diameter (mm)		28.65	Internal diameter (mm)		25.40
Thickness (mm)		1.63	Length (m)		2.4384
Baffles					
Number baffles	28	Spacing (m)	0.08	Thickness (mm)	4.8

HEAT EXCHANGER H.E.03					
Configuration	2 – 4	Shell side		Tube side	
Mass flow (kg/h)		22171		6062	
Temperature (inlet/outlet)(K)		353	340	320	328
Q (kW)	51.8	U J/(s*m2*K)	200	ΔTml (K)	22.5
Shell					
Shell inner diameter (m)		0.357	Shell outer diameter (m)		0.360
Tubes					
External diameter (mm)		28.65	Internal diameter (mm)		25.40
Thickness (mm)		1.63	Length (m)		3.048
Baffles					
Number baffles	25	Spacing (m)	0.12	Thickness (mm)	4.8

HEAT EXCHANGER H.E.04					
Configuration	2 – 4	Shell side		Tube side	
Mass flow (kg/h)		7333		22171	
Temperature (inlet/outlet)(K)		320	333	403	383
Q (kW)	84.8	U J/(s*m2*K)	150	ΔTml (K)	66.4
Shell					
Shell inner diameter (m)		0.339	Shell outer diameter (m)		0.342
Tubes					
External diameter (mm)		28.65	Internal diameter (mm)		25.40
Thickness (mm)		1.63	Length (m)		2.438
Baffles					
Number baffles	21	Spacing (m)	0.11	Thickness (mm)	6.4

HEAT EXCHANGER H.E.05					
Configuration	2 – 4	Shell side		Tube side	
Mass flow (kg/h)		16411		6062	
Temperature (inlet/outlet)(K)		353	303	298	308
Q (kW)	198.0	U J/(s*m2*K)	568	ΔTml (K)	18.2
Shell					
Shell inner diameter (m)		0.438	Shell outer diameter (m)		0.441
Tubes					
External diameter (mm)		28.65	Internal diameter (mm)		25,40
Thickness (mm)		1.63	Length (m)		3.048
Baffles					
Number baffles	20	Spacing (m)	0.14	Thickness (mm)	4.8

HEAT EXCHANGER H.E.06					
Configuration	2 – 4	Shell side		Tube side	
Mass flow (kg/h)		282789		32461	
Temperature (inlet/outlet)(K)		345	336	298	308
Q (kW)	3411.0	U J/(s*m2*K)	483	ΔTml (K)	37,5
Shell					
Shell inner diameter (m)		0.956	Shell outer diameter (m)		0.959
Tubes					
External diameter (mm)		28.65	Internal diameter (mm)		25.40
Thickness (mm)		1.63	Length (m)		4.877
Baffles					
Number baffles	15	Spacing (m)	0.31	Thickness (mm)	4.8

d) Storage tanks:

The volume is calculated so that it is storage 30 days. The results are shown below:

- Methanol storage tank

Table 36: Methanol ST volume

	Mass flow rate (kg/h)	Volumetric flow rate (m3/h)
Methanol	1646	2
Water	166	1.67E-01
Total flow rate	1812	2
	Volume (m^3)	**1519**

- Sodium hydroxide storage tank:

Table 37: Sodium hydroxide ST volume

	Mass flow rate (kg/h)	Volumetric flow rate (m3/h)
NaOH	113	5.32E-02
Water	113	1.14E-01
Total flow rate	227	1.67E-01
	Volume (m^3)	**120**

- Sulphuric acid storage tank is estimated to have the same volume that the previous one.

- Methyl methacrylate storage tank:

Table 38: Sodium hydroxide ST volume

	Mass flow rate (kg/h)	**Volumetric flow rate (m3/h)**
MMA	5000	5.32
Water	1062	1.07
Total flow rate	6062	6.38
	Volume (m^3)	**4597**