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Study and design of a Polyurethane foam recycling plant

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SUMMARY

As a result of scientific progress, different polymers with very different properties and uses have been developed. The use of these materials is very common, therefore, an unsustainable amount of waste is generated. One of these polymers is polyurethane (PU). The most common type of PU manufactured and the one that generates the most waste are foams, both rigid and flexible. In Spain, there is no defined route for this polymer, causing most of them to end up in landfills. Currently, we are avoiding storing them indefinitely in a landfill, trying to revalue them by reusing or recycling them, and if this is not possible, trying to convert them into energy and heat. Among all recycling methods, the most promising is chemical recycling through glycolysis, which is based on the depolymerization of PU to split it into its monomers using low molecular weight glycols. The industrial development of glycolysis in the split phase is limited by the fact that an excess of glycolysis agent is needed in order to obtain a recycled polyol with better properties that can be used to synthesize new PU foams. This excess of agent makes the process not economically viable. For this reason, an agent has been sought to provide a polyol with good properties from a cheaper agent than diethylene glycol (DEG). Crude glycerol, which is a by-product of biodiesel production, has been considered as an agent capable of depolymerizing PU and at a lower price than DEG. In order to treat a part of the polyurethane flexible (PUF) foam waste generated in Catalonia, a preliminary design of a glycolysis recycling plant has been carried out in the starting phase, to treat 440 t/year of PUF foam waste from mattresses using crude glycerol, as glycolysis agent, and stannous octoate as catalyst.

Keywords: Recycling,PUF flexible, Glycolysis, Crude glycerol,

RESUM

Como consecuencia del avance científico se han desarollado distintos polímeros con propiedades y utilidades muy diferentes. El uso de estos materiales es muy cuotidiano generandose un numero insostenible de residuos. Unos de estos polímeros es el poliuretano (PU). El tipo de PU mas fabricado y el que mas residuos genera son las espumas, tanto rigidas como flexibles. En España, no hay una ruta definida para este polímero, provocando que la mayoria acaben en el vertedero. Actualmente, se esta evitando almacenarlos de manera indefinida en un vertedero, intentando revalorizarlos mediante su reutilización o reciclaje, y si no es posible, intentar convertirlos en energia y calor. De entre todos los métodos de reciclaje, el mas prometedor es el reciclaje químico mediante la glicolisis, que se basa en la despolimerización del PU para dividirlo en sus monómeros utilizando glicoles de bajo peso molecular. Encontramos pocas plantas que operen con este proceso y la gran parte obtiene un producto monofasico .El desarollo industrial de la glicolisis en fase partida se encuentra limitado por el hecho de que se necesita un exceso de agente de glicolisis y poder obtener un poliol reciclado con unas mejores propiedades capaz de ser utilizado para sintetizar nuevas espumas de PU. Este exceso provoca que el proceso no sea viable económicamente . Por esta razón, se ha buscado un agente que proporcione un poliol con buenas propiedades a partir de un agente mas barato que el dietilenglicol (DEG). La glicerina cruda, que es un subproducto de la producción de biodiesel, se ha considerado como un agente capaz de despolimerizar el PU y a un precio mas inferior que el DEG. Con el fin de tratar una parte de los residuos de espumas flexibles de poliuretano (PUF) generados en Catalunya, se ha realizado un diseño preliminar de una planta de reciclaje de glicólisis en fase de partida, para tratar 440 t/año de residuos de espumas PUF procedentes de colchones utilizando la glicerina cruda, como agente de glicólisis, y el octoato estannoso como catalizador.

Palabras clave: Reciclaje, PUF flexible, Glicolisis, Glicerol crudo,

1. INTRODUCTION

In the world there is a global emergency regarding waste management. It is a fact that overpopulation coupled with a great technological advance has led to a large production of all kinds of materials to meet the needs of people. This large production has led to an excessive production of waste.

In recent years, many laws have been detected to regulate this waste management. A few years ago, a lot of waste was dumped into the environment which has caused a global climate change. As this emergency did not exist before, when developing a product, it was not considered what happened to it once it reached its useful life. In the absence of laws regulating this management, much of the waste ended up being disposed of through landfill storage. Little by little this methodology (mainly due to the large amount of waste and the fact that there were fewer and fewer methods left to dispose of the waste without compromising the environment) has been changing towards a more sustainable management mainly focusing on reuse and recycling. Currently, when a product is developed, a recycling or reuse pathway has already been defined once, this product becomes waste. If, due to the nature of the product, this pathway is not feasible, then the most sustainable possible way to dispose of the product would be defined.

1.1. PU

One of the most problematic waste products in the world (about 360 million tons), are those of a plastic nature [1]. The low biodegradability of these materials, together with the difficulty of efficient management when they reach the End-of-Life (EoL), have caused a great emergency worldwide [2]. These materials are high molecular weight polymeric products, solid in their final state, but at some stages of manufacture are sufficiently fluid so that they can be deformed into the desired shape by the action of heat and pressure [3]. From the point of view of general physical properties, three types of solid polymers are recognized: elastomers, thermoplastic polymers, and thermosetting polymers [1]. Elastomers are elastic materials like rubber.

Thermoplastic polymers are hard at room temperature, but when heated they become soft and fluid and can be molded. Thermoset polymers can be molded at room temperature or above, but when heated too much they become hard.

One of these solid polymers is PU, first manufactured in 1937 by Otto Bayer and his collaborators in Farben, Germany [3]. It eventually developed to such a scale that it is one of the most widely manufactured polymers in the world [3]. The main raw materials, apart from auxiliary reagents to modify polymer properties, used to prepare PU are isocyanates and polyols:

- Isocyanates, which are used in the preparation of PU, need to have two or more isocyanate groups in each molecule [3]. The most used are aromatic diisocyanates, such as toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) as they are cheaper and more reactive than other isocyanates [4].

- Polyols can be either polyethers or polyesters. Polyester polyols are made by reacting epoxides with compounds that have an active hydrogen atom [4]. In contrast, polyester polyols are manufactured by the polycondensation reaction of multifunctional carboxylic acids and polyhydroxyl compounds [3]. They can be classified according to their end use. Higher molecular weight polyols, with molecular weights from 2000 to 10000, are used to make more PUF, while lower molecular weight polyols are used to make stiffer products [1].

PU is manufactured by reacting polyhydric alcohols (the polyol) with molecular weights in the order of 200-20000 and functionalities ranging from 2 to 8 with isocyanates, which contain an -NCO- functional group in the presence of suitable catalysts to form urethane bonds [4]. Foaming agents help to expand the cells by increasing their volume to form the lightweight PU foam. Surfactants initiate and stabilize the PU cells and help to maintain the shape in which it has been processed. PU foam exhibits different properties depending on the type of polyol and isocyanate used. The different categories of foams are:

- PUF foams: Most of these foams are synthesized with a long chain of polyether polyols based on ethylene and propylene oxides. These foams can be classified into three types: conventional, viscoelastic, and high resilience (HR). Conventional foams are used to manufacture them in blocks and then molded into the final product, viscoelastic foams are used for mattresses and pillows, and HR foams are used mainly for seating

in the automotive industry. Most of these foams are synthesized with a long chain of polyether polyols based on ethylene and propylene oxides. Conventional ones are produced with a flexible polyether polyol or a blend of this polyol with a polymeric graft, with TDI. The polyether polyols for these foams have a molecular mass of between 2,800 to 4,000 g/mol. For de HR ones, they are produced from a long-chain polyether polyol with a molecular weight of 400-600 g/mol. And finally for viscoelastic, they are synthesized from a mixture of 2 polyols, one with a high molecular weight of polyether polyol and the other with a low molecular weight. This serves to break the symmetry of the PU matrix to obtain a lower resilience. The advantage of this foam is the distribution of pressure on the foam *[4].* PUF foam is a thermoset polymer. It is used in a very wide range of durable applications, notably in mattresses, upholstered furniture and in vehicles. As an example, nearly 90% of mattresses produced in the EU contain PUF foam (between 2 and 15 kg per unit) and over 90% of furniture upholstery is made of PUF foam. In Europe in 2012, it was estimated that 40% of the combined EoL mattresses and upholstered furniture tonnage (760 kTn) was incinerated (including energy recovery) and 60% (1140 thousand tonnes) was landfilled. Considering the volume of EoL mattresses only, this represents around 1920 olympic swimming pools of waste being landfilled *[5].*

- Rigid foams (PUR): They are produced with densities ranging from 20 to 800 kg/m^3. The preferred isocyanate is MDI *[5].* Its main end users are refrigeration and thermal products industries. The purpose of these foams is be used as an insulating material, thermal and acoustic.

- Microcellular foams for footwear: This type of material is composed of thermosetting and microcellular PU foam, which may or may not have an adhesive backing. These products exhibit good damping, sealing and vibration control because they have very low compression set properties *[3].* However, the open cell structure allows gases and vapors to pass through the material. These foams are specially designed for high performance gasketing and sealing applications, but they are also used in automotive, aerospace, electronics and medical industries for sound dampening and vibration control.

- - Coatings, adhesives, sealants, and elastomeric applications (CASE): In the synthesis of CASEs are used chain extenders such as 1,4-butanediol (BDO) with isocyanate such as MDI to form macro diols with a molecular weight of 1,000-2,000 g/mol *[5]*. The main end users are coatings, adhesives, and sealants industries.

1.2. RECYCLING OF PU FOAMS

It is a fact that the increasing amount of PU foam waste produced each year has led to develop recycling methods *[3]*, resulting in a more environmentally sustainable development. PU foams are the most problematic waste, due to their big volume and low density. The most important difficulties encountered are proper storage (no landfill) and relatively fast processing of the waste *[1]*.

For this purpose, various recycling methods have been developed depending on the material involved and the quality of the product obtained from recycled material. Once PU has been used, it loses certain properties, either due to the degradation it has undergone during use or due to the presence of substances found in the environment. This attenuation of properties makes it difficult to recycle the material. The most common methods of PU recycling are divided into 3 types: mechanical or physical recycling, chemical recycling, and thermochemical recycling. The two most common waste disposal methods are: energy conversion and landfill. A brief description will also be given on a process of PU waste disposal by biological degradation using bacteria and enzymes.

1.2.1. Mechanical recycling

Mechanical recycling methods are commonly used for all thermoplastic polymers. These methods relate to change the physical form of the waste (e.g., by mechanical operations such as grinding) to the shape suitable for further processing (by injection molding or extrusion). Mechanical operations, such as grinding and shredding, are the first step in producing components in the desired shape for subsequent chemical recycling *[1]*. The different types of physical recycling are:

-Regrinding:

This is a mechanical recycling process that generally involves two steps: grinding the PU foams to a fine powder and mixing it with the virgin polyol. Different size reduction technologies are used in the case of PU foam waste recycling, milling, cutting, and shredding. Cutting is used for PUR and PUF foams, and various cutters with many static and rotating blades are used *[7]*. These machines are usually equipped with sieves, which are responsible for the separation of PU particles characterized by their different size. Size reduction of PUF foams is difficult due to their elastic nature, so the grinding process of these materials is performed using liquid nitrogen when the materials are rigid *[6]*. The size of PUR foams can also be reduced by grinding pellets, balls, and impact discs. Pellet mills consist of two metal rollers that press the PU foam, and the resulting materials are powders or pellets. Ball mills consist of a hollow cylindrical shell that rotates around its axis and is partially filled with metal balls, which reduce the size of the PUR foam debris *[7]*. Impact disc mills are used for PU foams produced by reaction injection molding (RIM) or reaction reinforced injection molding (RRIM) *[9]*. PUF and PUR foams in the form of powder, fragments, granules, and pellets are raw materials for other mechanical recycling methods but are also valuable components for chemical recycling processes. The application of powdered foam waste as fillers is limited by the decrease of the mechanical properties of the final product *[10]*.

-Rebonding:

Is the most widely used method of mechanical recycling of PU foams since it reduces the waste from the manufacture of PU foams. The final product of this process is obtained by adhesion and bonding of small foam particles or remnants *[6]*. Typically, in the rebonding process, the shredded PU waste is placed in a mixer where the foam is sprayed with binder (adhesive). The amount of binder added to the PU foam waste affects the properties of the final material. The mixture is then compressed and molded at the same time to make products that are usually of cushioning type. During the compression stage, the mixture is subjected to a steam's flow which reacts with the binder leading to the formation of a functional polymer *[8]*. From an environmental point of view, the process is interesting because it allows us to reduce the volume of PU waste, but it has the disadvantage that the processed material has a lower mechanical strength than the original product and can therefore only be used for car cladding, carpet backing and furniture elements.

-Injection and compression molding:

    Compression molding of waste PU foam is related to the formation of products from fine waste particles (without any binder) under appropriate pressure and heat. This method is generally applied to PU materials obtained using RIM and RRIM materials. It is possible to obtain products with 100 wt.% of waste PU foams [6]. Compression molding of PUF foams and elastomer residues includes softening, self-adhesion under high heat and pressure. It is a fact that PUs has a segmented structure, which includes hard segments (isocyanate-based components) and soft segments (polyol-based components). The soft segments can possess a thermoplastic nature in the temperature range of 150°C to 220°C, and this is related to the type of polyol used and its functionality. On the other hand, injection molding is also a type of molding process that allows the recycling of PU polymer products. This method is also preferable for processing/blending PU with other thermoplastics for application in automotive parts, granulated PU (processed at 180°C and in a high shear compression of 350 bar to produce thermo-shaped products) can be used in the automotive industry [9].

Mechanical recycling methods of PU foam waste are effective recycling methods, which allows to obtain materials suitable for further processing e.g., by compression molding. The most important advantage of mechanical recycling is the low cost and simplicity of its realization. In addition, PU foam waste, regardless of whether it is rigid and/or flexible, is a raw material for various chemical recycling methods, such as glycolysis [1]. The most determining factor related to the mechanical recycling of PU foams is their selective collection [5]. The selection of the type of mechanical recycling method and processing conditions is mainly affected by the fact that flexible, semi-rigid and PUR foams can be produced using several different types of components.

1.2.2.   Chemical recycling

The non-biodegradability of synthetic polymers poses serious problems. To solve this problem, different types of recycling have been proposed. Chemical degradation is one of the best recycling methods. This degradation is defined as total depolymerization of the polymer to monomers, or partial depolymerization to oligomers and other chemicals substances [6]. Polymers are composed of many organic and inorganic substances, so they can be cleaved

using reagents such as water, alcohols, acids, glycols, and amines *[3]*. Depending on the reagents used, chemical degradation is classified into:

-Glycolysis:

Currently, glycolysis is the most widely used chemical recycling method for PUR and PUF foams *[6]*. It is based on a transesterification reaction in which a hydroxyl group of the glycol replaces the ester group containing a carbonyl carbon of the urethane bond *[11]*. The reaction lasts between 3-10 hours. This reaction produces polyols whose properties can be controlled to some extent and can be like those of the original material. There are two main directions of glycolysis ; The first leads to the recovery of polyols to produce PUR foam; the second, the so-called split-phase glycolysis leads to polyols to produce both PUF foam and PUR foam *[12]*. This split-phase process is based on the separate processing of the upper and lower layers of the glycolysis using an excess agent. The upper layer is mainly composed of polyols and the lower layer can be treated with propylene oxide, resulting in the formation of rigid polyols *[3]*. The main limitation of glycolysis is the difference in process parameters for PUF and PUR foams, which makes it necessary to separate very well the waste to be treated. This method is also more efficient when is applied to post-production waste due to the high sensitivity of the reaction to the presence of impurities that may appear in consumer waste *[5]*.

-Hydrolysis:

This is the second most important method of chemical recycling of PU. Much research has been done on PU degradation using liquid water (150-200°C) or steam. The end products are polyols, diamines, and carbon dioxide (CO_2) *[6]*. The polyols obtained can be blended with virgin polyol at a ratio of 20 wt.% to produce high quality PUF foams. An advantage of the process is that it can treat production waste as post-consumer waste. The resulting polyols can be used as additives to virgin polyol. The hydrolysis can work with two types of waste; PU once it has reached the end of its useful life and post-production waste. The disadvantage of the process is that the reactor requires a very large energy input, either for heating or pressure boosting, due to the critical conditions of the reaction, which provides unfavorable economics to the process and therefore has not been reproduced on a commercial scale *[13]*.

-Aminolysis:

It's the reaction of PU residues with amines such as dibutyl amine or monoethanol amine (MEA) under pressure and elevated temperatures. In this process, potassium and sodium hydroxide are the main catalysts [6]. There are few studies in the field of amine treatment for PU recycling. The main reaction products are polyols, aromatic amines, and carbamates. Finally, polyols that can be used in the new PUF formulation are separated as virgin polyol. The results show a significant change in the properties of the new foam when contaminants are not separated from the recycled polyol. PUFs are recycled by alkanolamines without catalyst at 150ºC to recover the polyol monomers and amine compounds [1]. The decomposition product is completely separated into two layers. The upper liquid layer is contaminated polyether polyol, and the lower liquid layer is methylene di phenyl amine and alkanolamine derivatives. Aminolysis has only been described for the recycling of PU foams and has not been developed for so-called CASE [23].

PU recycling is encouraged to reduce environmental pollution, minimize solid waste, and reduce the dependence on petrochemical resources. The chemical recycling method by glycolysis is more attractive in terms of quality of the resulting polyols and is useful for all types of PU waste [11].

1.2.3.   Thermo-chemical recycling

In thermochemical recycling of PU products, an attempt is made to use the waste stream as a source of energy, fuel, or some valuable monomers. The main types are:

-Pyrolysis:

The process of thermal decomposition of long polymer chains into less complex molecules under anaerobic conditions at elevated pressure. The main products -oil, gas, and ash- can be valuable to many industries [5]. During the process, mass loss starts at about 250°C and stabilizes at 80 wt.% loss at 300°C, while the remaining 20 % does not decompose until the temperature reaches 500°C. As demonstrated by Jomaa et al., [16] in 2015, the pyrolysis of PU progresses in two stages, corresponding to the decomposition processes, on the one hand of the polyol, and on the other hand, of the isocyanate. The ash remaining after pyrolysis is less than 3 wt.% of the initial PU. In the first stage, a yellow smoke and a viscous liquid are produced, followed by a slow decomposition of the liquid into gaseous products. The gases

released are mainly CO, CH_4, HCN, NH_3 and NO *[15].* An undoubted advantage of pyrolysis is the small number of residues left after the process and the possibility of using the resulting products in other petrochemical processes since the resulting gas is highly calorific and can therefore be used to obtain heat and energy. A disadvantage of this process is that the gas formed also contains toxic compounds such as hydrogen cyanide or benzene *[18].*

-Gasification:

It's a highly exothermic reaction of partial oxidation of PU where it is preheated to combine it with air and oxygen. Its main products are syngas (a mixture of mainly carbon monoxide and hydrogen) and ash. One of the most significant advantages of gasification is the absence of the need for waste separation. In addition, PUs mixed with other wastes can be used in the process. However, the economy of this process depends considerably on the potential use of syngas as a source of energy and feedstock for the synthesis of other products. Besides that, the use of atmospheric air as a reaction medium simplifies the process, but molecular nitrogen tends to reduce the energy obtained during gasification. According to research, gasification processes produce significant amounts of toxic hydrogen cyanide and nitrogen dioxide. The addition of a suitable catalyst can reduce this emission to some extent. The H_2 and CO produced can also be used in polyether's and isocyanates production *[17].*

-Hydrogenation:

This process is defined as a compromise between pyrolysis and gasification methods. The effect of heat and H_2 at high pressure results in gaseous and liquid products *[6].* Hydrogenation contains one more step than pyrolysis to produce even purer gases and oils by a combination of heat, pressure, and hydrogen. For this method to be useful, two important issues need to be addressed: the purity of the gases and oils derived from hydrogenation, and the associated costs to produce functional finished products. The products of hydrogenation can be used as fuel and chemical feedstock *[18].*

1.2.4.   Landfill

Landfilling is still the most common way of processing PU waste. The fraction of PU disposed of in this way reaches almost 50 wt.% of the waste, (combined post-consumer and post-production) *[5].* As PU foams are the most produced, they are also the biggest problem.

Due to their low density, they tend to accumulate and form large volumes. In addition, the large amount of air contained in the foam cells can provide, in case of fire, oxygen and impede efforts to extinguish the flames *[4]*. Another hazard related to landfill fires is the toxic fumes produced during the combustion of PU.

Recycling is a great alternative to landfilling, but despite a great effort by manufacturers and governmental bodies, it is still not a predominant method of PU waste disposal. Due to the poor biodegradability of PU together with the danger of accumulating these wastes, since 2004, countries such as Australia, Germany or Sweden have enacted regulations banning the use of landfill for disposal of plastic waste *[18]*. The EU banned high-carbon materials from ending up in landfills. Therefore, landfill treatment is not prudent.

This type of process involves a low investment because it requires a simple technology, although against it is the difficulty of finding a location that fits the legislature of the site, and the fact that its life is limited, since, once it reaches its maximum capacity, it is closed, and another location is sought. The concepts of improved waste management and improved landfill operation are intended to reclassify landfill as a balanced procedure. The landfill should be considered as a temporary storage site for waste awaiting recovery and further treatment, and not as a final storage solution. Depending on their condition and available technologies, the stored materials can be used as a stockpile for new products or as a source of energy *[5]*.

1.2.5.   Energy recovery

Energy recovery applies only to PUs that cannot be processed by any recycling method. Incineration to dispose of PU waste occupies an important position, since the burning of 1 kg of PU can produce a calorific value of about 7000 kcal/kg, i.e., it can provide heat comparable to the same weight in coal and only slightly less than the energy obtained from fuel oil *[18]*. Through incineration, the volume of waste can be reduced by 99%. PU foam waste can be crushed into granules and used as an alternative fuel to coal and oil and can be applied to cement *[10]*. The most important advantage of this process is the possibility of application for contaminated PUs or foams that are permanently bonded to wood, leather, or fabric *[6]*. Another advantage is that there is no possibility of recovering the materials from the combustion and incineration processes, therefore they get eliminated. This method is not flawless, especially since more and more PU foams contain flame retardants, added to increase the safety of users.

These additives make energy recovery difficult or even impossible. In addition, when high temperatures are applied, PU foams can release toxic and carcinogenic compounds, such as carbon monoxide, hydrogen cyanide and nitrogen oxides. PUs show much higher toxicity during thermal degradation under aerobic conditions since the amount of nitrogen oxide emitted under these conditions is well above acceptable levels [4]. The gases generated by combustion may also include isocyanates, which are highly toxic compounds. For all these reasons, this method is being phased out [18]. Even so, the compelling argument for increasing the percentage of PU waste supplied to thermal degradation rather than landfill is the amount of energy produced. Energy recovery today is the preferred technology for the treatment of EoL PU foam and is the one that is immediately able to divert great volumes of organic waste from landfills [5].

1.2.6. Biological degradation

One option to try to eliminate waste is through the action of biological agents. Biodegradation is the decomposition of organic substances by alive organisms or their enzymes resulting in a shortening of the polymer chains and the elimination of some of their parts [2]. This leads to the reduction of their molecular weight and, under favorable conditions, may even result in complete mineralization of the degraded material. However, complete degradation of larger polymers usually requires the cooperation of several different organisms. This process consists of the following stages: decomposition of the polymer into monomers, its reduction to simpler compounds and final degradation to dioxide of carbon, water, and methane (under anaerobic conditions). The decomposition of polymers under aerobic conditions takes place in any natural environment, however, decomposition under anaerobic conditions only occurs in landfills. Degradation in landfills can be carried out by natural microorganisms or with the addition of a set of microorganisms or an enzymatic mixture [18].

Biodegradation is more environmentally friendly than chemical degradation [1], as it does not require high temperatures and complex reagents. Moreover, it can be applied to the degradation of post-consumer waste. There are numerous research on biological degradation, but unfortunately most of them describe a limited part of this topic, as they usually apply only to one type of microorganism or PU. In contrast, others cover a broad spectrum of plastics, which does not allow a detailed analysis of each one of them. Although the modifications of PUs

applied to improve their degradability are very important, they do not solve the already existing environmental contamination problems *[18]*.

Biodegradation is divided into three categories: fungal biodegradation, bacterial biodegradation, and enzymatic degradation. Polyester PUs are much more susceptible to biological degradation than polyether PUs. Most of the enzymes identified as responsible for PU cleavage belong to the class of hydrolases. Unfortunately, despite promising results, PU biodegradation studies are still at the basic level stage. The main reason for this situation could be the long time needed to obtain results *[2]*.

1.3. GLYCOLYSIS OF PU FOAMS

The increasing applications of PU materials result in more waste, which in turn have a devastating effect on the earth; therefore, EoL waste management is one of the most important issues in today's world. Although incineration and landfilling are the most common procedures adopted for waste disposal, both cause environmental problems such as air and soil pollution *[18]*. In addition, the former causes global warming and the latter causes water pollution. Consequently, finding economical and environmentally friendly methods is a high priority issue for researchers to overcome this problem. Fortunately, recycling is an attractive solution from an environmental point of view, and there is a growing interest from researchers in recycling PU waste.

Chemical recycling by glycolysis reaction is one of the most important recycling methods, especially for PUR and PUF foams because it requires mild reaction conditions *[12]*. The formation of glycolysis products follows the PU degradation mechanism under the reaction of glycol hydroxyl groups. The following is a brief description of glycolysis for each type of PU.

1.3.1. PUF foam

To demonstrate that glycolysis was a suitable process to recover polyol for use in the synthesis of new PUFs, a group of researchers from Hungary reported an environmentally friendly chemical method to recover polyol from flexible PUFs based on polyether polyol and TDI *[19]*. The fastest degradation and lowest kinematic viscosity of the products were achieved with a mixture of diethanolamine (DEA) and ethylene glycol (EG) in a 1:1 ratio. This recovered

polyol, due to its low purity, could only be used to synthesize industrial adhesive. Later, this same group would confirm the formation of CO_2 during the glycolysis reaction.

Initially, they encountered the problem that the recovered polyol had such poor properties that it could only be used to synthesize PUR or semi-rigid foams [18]. Through various investigations, it has been determined that the best glycolysis agent is DEG to obtain a biphasic product. It has been developed for all types of PU and in all cases gives very similar values [12]. On the other hand, Santos et al., [20] demonstrated the effectiveness of metal catalysts, in particular zinc acetate, compared to amine catalysts, which were the ones used until then.

To discover possible commercial scale applications of polyols obtained by one-step glycolysis, Benes et al., [21] selected two types of flexible PU residues, both based on polymeric methylene di phenyl isocyanate (PMDI) and polyether polyol. They used various types of reagents such as DEG, di propylene glycol (DPG), propylene glycol (PG) and EG, as well as DEA, as catalyst. Their studies revealed that DPG was the most efficient glycol because it gave a single homogeneous liquid phase without the need to separate the glycolysis products. This polyol was successfully used in combination with polyether polyols in the synthesis of new rigid foams for use in boiler insulation.

It was found that, in addition to the transesterification reaction between PU and DEG, other side reactions also occur, such as glycolysis of urea groups, hydrolysis reaction and thermal degradation, which produced some by-products such as carbamate, aromatic amines CO_2 and unsaturated compounds. Datta and Rohn [22] employed 1,6-hexanediol (HDO) and potassium acetate (KAc) for the decomposition of PUFs with the aim of reusing the glycolysates in the synthesis of PU elastomers.

All these studies have served to prove the feasibility of the process, but it is still not economically viable, since a molar excess of DEG is needed and its price is only slightly lower than the price of recycled polyol [18]. For this reason, another glycolysis agent with better economic efficiency is being sought. De Lucas et al., [23] studied the possibility of using crude glycerol, a residue from biodiesel production, as a novel, sustainable and economical glycolysis agent in the process of recovering polyols from waste PU foams. But it was not until later, that they demonstrated its feasibility [24]. PUF foam waste was treated and a polyol with low by-product content was obtained. This polyol, after being properly purified, was used as a replacement for crude polyol in the production of new PUFs, showing that it could replace up to

25 wt.% of the virgin polyol stream. Subsequently, this method was used for the recycling of viscoelastic foams, and similar results were obtained *[25]*. The high dielectric constant of glycerol is responsible for the higher yield of glycolysis.

Simon et al., *[26]* used stannous octoate as a catalyst in the presence of DEG. According to the results obtained, a glycol/PUF mass ratio of 1.125:1 would be the optimum when the catalyst/glycol concentration was 1.3 wt.% at 189 °C. This same group demonstrated the improved performance of this catalyst when crude glycerol was used as an agent.

Recently, Zn-Sn-Al hydrotalcite has been introduced as a heterogeneous catalyst for depolymerization of PUF waste. DEG was chosen as the transesterification agent, and the recovered polyol can be used as feedstock in the manufacture of PUF foam *[27]*.

One of the problems of split-phase glycolysis is to obtain a bottom phase with a large excess of glycol, for this reason, a series of investigations were carried out to revalorize this phase and it was demonstrated that, through distillation at low pressures (about 50 mbar), it was possible to recover part of the polyol used to reuse it again in the glycolysis process without any problems *[28]*. The isocyanate derivatives generated in glycolysis are found in the distillation column residue, which were considered hazardous waste up to that time. This distillation column residue was characterized, and due to its properties, was employed as a rigid polyol initiator, replacing the commonly used one based on toluene diamine (TDA). All the synthesized polyols showed similar characteristics to the virgin polyol demonstrating the feasibility of using the vacuum residue as initiator. Split-phase glycolysis has been developed for conventional flexible foams *[11]*, for HR foams *[24]* and for viscoelastic foams *[25]*.

1.3.2.   PUR foam

The glycolysis process of PUR foams consists in the treatment with a low molecular weight glycol that provides a single-phase of low viscosity and high number of hydroxyls. This product can be reused as a substitute for rigid polyether polyol in the synthesis of new PUR foams or even in the adhesive synthesis industry. However, in general, glycolysis of PUR foams does not give a recovered product of high quality and defined composition *[18]*.

Glycolysis for PUR foam was first described using DPG as cleavage agent and KAc as catalyst. A single-phase product was obtained which could be used in the synthesis of new PUR

foam *[3].* Xue et al., *[33]* performed the glycolysis process of PUR foam residues, using DEG as glycol and MEA as catalyst. The product obtained was used as a hardener for epoxy adhesives.

To treat PUR foam waste from refrigerators, Mooroka et al., *[34]* carried out glycolysis using DEG and barium oxide (BaO) as catalyst. They stated that up to 10 wt.% of the obtained glycolate can be added to the virgin polyol to produce new PUR foams with thermal conductivities and compressive strengths like those of standard foams.

Although recently, Zhu et al., *[35]* reported glycolysis reactions of PUR foams from refrigerators, obtaining higher yields by using EG instead of DEG. They also observed that catalytic efficiency of NaOH was higher than that of triethanolamine (TEA) or BaO. They described as optimal reaction conditions a PU:EG ratio of 1:1, a catalyst concentration in the glycolysis agent of 1 wt.%, a reaction temperature of 198 ºC and a reaction time of 2 h. They valued the recovered glycolysates as rigid polyol substitution up to 10 wt.% respect to the total amount of polyol in the new foaming recipes.

1.3.3.   Elastomers

Initially, the glycolysis of elastomers based on polyether polyols and MDI was described *[19].* They employed EG, PG, triethylene glycol (TEG) and poly (ethylene glycol) (PEG) as glycols and DEA as catalyst. The reaction temperature described was 170-180°C, with a glycolysis agent: PU residue ratio of 2:1 and a DEA:EG ratio between 1:1 and 1:9. A split-phase mixture was obtained in which upper liquid phase was polyol. Later, the same research group claimed that the obtained glycolysates could be used as components in the synthesis of PU adhesives *[29].* Wang et al., *[30]* described the glycolysis of PU elastomers based on MDI and polyether polyol. DEG and EG were used as low weight glycols, while ethanolamine (EA) and lithium acetate were used as catalysts. The degradation reactions were carried out at 160-190 °C. They found that, using a 9:9:2 ratio of DEG/EG/EA by weight, the decomposition products were completely separated into two layers, where the top layer was the polyether polyol

1.4. INDUSTRIAL SCALE OF PU GLYCOLYSIS

So far, the most important processes for chemical recycling of PUs have been discussed, however, most of these processes have not reached industrial and commercial scale, and even in some cases the level of technology readiness is as low as laboratory level.

Single-phase chemolysis plants are operating in Italy (shoe soles), Austria (elastomeric foam), Germany (Reaction Injection Molding, RIM) and the United Kingdom (Flexible slab stock) *[5]*. The product obtained is a mixture of different types of polyols, glycolysis agents and isocyanate derivatives with a high number of hydroxyls with very limited reusability alternatives. These single-phase blends can only replace virgin polyols in semi-rigid foam formulations, but not in PUF ones *[18]*. However, split-phase glycolysis processes that produce higher-phase polyols with much better characteristics have only been developed on a pilot plant scale. Therefore, it can be stated that the lower the quality requirements of the glycolysates and polyols recovered for their applications, the more implemented the process is.

The following is a description of the main glycolysis processes implemented at pilot plant or industrial scale; distinguishing between single-phase and split-phase methods.

1.4.1.   Single-phase

-Pilot Scale:

The Italian company EniChem is dedicated to the production of new RIM PU products. So, it designed a pilot plant to treat wastes of this nature to reconvert them into new RIM PU. The process was developed by Modesti and Simioni using DPG as the cleavage agent, with a DPG: RIM waste ratio of 1:1, a reaction temperature of 200 ºC and an organometallic catalyst that favors the glycolysis reaction over the secondary ones *[36]*. The final product obtained is a single-phase glycolate with such a high hydroxyl number value that at that stage of development it could hardly be used in the synthesis of new RIM PUs with suitable standard characteristics. In fact, the only application described for this product without further processing is the preparation of PUR foams for home insulation. EniChem was able to manufacture new RIM PUs using up to 50 wt.% of recovered product with respect to the total amount of polyol used.

-Industrial scale

Regra, located in Germany, developed a glycolysis process for the treatment of shoe soles, with the final objective of obtaining a recovered product capable of being used in the synthesis of new shoe soles. On the other hand, Aprithane, also located in Germany, carried out a glycolysis process of PUR foams and obtained a single-phase product that was successfully used in the synthesis of new PUR foams. Both glycolysis plants ceased their activity, as these glycolysis processes are far from being cost-effective due to the use of traditional and expensive glycolysis agents *[37]*.

Troy Polymers has developed a single-phase glycolysis process for PUs foams, with which it can treat blends of foams based on either polyether and polyester or TDI or MDI. The process consists of two stages. In the first stage, the glycolysis reaction takes place at a temperature between 180 and 210 ºC and using KOH as catalyst. In the second stage, a propoxylation process is carried out considering the single-phase glycolysates obtained in stage 1 as initiators of the polyols. The Troy Polymers process yields polyols that can be used in the manufacture of new PU specialties *[38]*. Troy Polymers is currently marketing two polyols, InfiGreen 320 for HR foam synthesis and InfiGreen 420 for PUR foam synthesis. InfiGreen 320 can be successfully applied as a substitute for bulk flexible ether polyol up to 10 wt.% in the manufacture of new HR foams. Most of the mechanical properties vary with the presence of InfiGreen 320. Nevertheless, they are all within the specified ranges for automotive seat production. As for InfiGreen 420 polyol, it has been used as the only polyol component in the synthesis of new PUR foams and since 2002 it has been applied in the manufacture of PUR foams for the automotive sector *[39]*.

1.4.2.   Split-phase

-Pilot Scale

ICI - Huntsmann has developed a split-phase glycolysis process using DEG as glycolysis agent and an organometallic compound as catalyst. The type of PU waste treated was HR and MDI-based PUF foams. The process consists of three steps *[40]*: First, PU waste is pre-treated with the aim of increasing the density of the PU waste, obtaining pellets with a density of 500 kg/m^3 instead of 35 kg/m^3, which was the initial density of the HR foam. Then, they react for 3 h at 200 ºC with the glycolysis agent at a shearing agent: PU mass ratio of 1.5:1. The final product

was divided into two phases. The lower one consisted of the excess glycol, while the upper phase consisted of the partially impurified recovered polyol. To increase the purity of polyol, the process incorporated a purification unit consisting of a clean DEG extraction and a subsequent evaporation module to recover the glycol. The recovered purified polyols were used as a substitute for raw flexible polyether polyol in the manufacture of new PUF foams. In fact, the plant was designed to recycle 100 kg of PU using 150 kg of DEG [40]. Nowadays, the pilot plant exists, but is no longer in operation due to the unprofitable economics of the process.

-Industrial Scale:

Split-phase glycolysis processes have not yet reached industrial scale due to the excess of cutting agent required to ensure proper phase separation and their high price. Therefore, considering that most of the glycolysis processes are not currently operational for economic or quality reasons, except for Troy Polymers [39]. Therefore, the implementation of improvements in the economics and efficiency of split-phase glycolysis processes should provide us with a viable process. In addition to conventional chemical recycling processes for PUs, several industrial-scale processes consisting of an association of several technologies are being developed in recent years. Rampf Ecosystems and H&S Anlagentechnik are the most important companies currently operating in this sector:

In the Rampf Ecosystems process, the PUR residues are broken down into small pieces (5 mm) and continuously introduced into a depressurized reaction vessel, in which there are different reagents and catalysts depending on the type of PU. This vessel operates at 200ºC, with constant agitation to favor the splitting of the PU molecular chains. This process lasts 7 hours, and the liquid product is a mixture of polyols and low molecular weight urethane. The liquid is filtered, and the residue consists exclusively of unwanted materials. These are easily disposed of by incineration. Finally, the recycled polyol produced is fed into storage tanks. The final product obtained by the Rampf process is known as RECYPOL and can be used alone or blended with new polyol to produce PUR foams. The cost of obtained polyol by this process is about 0.95-1.16 €/kg compared to 1.80 €/kg for a conventional polyether polyol, which represents a cost reduction [41].

On the other hand, H&S Anlagentechnik has developed a recycling process that distinguishes two types of processes depending on the type of PU foam treated. In this technology, PUF foam waste is reacted with a mixture of carboxylic acids and basic polyol

(2,000-6,000 g/mol; 36-56 mg KOH/g; 600-3,000 cp). The recovered polyols obtained show good reactivity and do not contain primary aromatic amines which are hazardous and not acceptable in bedding and upholstery foams. However, it is crucial to note that H&S has an important operational limitation to obtain these recovered products with low hydroxyl number and consequently, suitable for the synthesis of new PUF foams. The H&S process requires separation of the residues in case of essential chemical differences, e.g., MDI and TDI foam, conventional and HR foams, etc. For this reason, H&S recommends this type of recycling for post-production waste. Nevertheless, without a selective collection process, the recovered product has a high hydroxyl number and could only be applied in the synthesis of PUR foams, replacing up to 50 wt.% of conventional raw rigid polyether polyol *[5]*.

H&S recommends this recycling route (without waste separation and sorting) for post-consumer mattresses recycling. As discussed above, H&S has also developed a chemolysis process for PUR foam waste recycling. This process consists of a glycolysis with DEG in the presence of a catalyst with the objective of improving the process kinetics. The optimum conditions described by H&S are a catalyst concentration in the glycolysis agent = 11 wt.% and a mass ratio of the glycolysis agent to the PU foam are 1,3:1. In the case of H&S recovered rigid polyols, the manufacturing costs of recycled polyol are about 30% lower than the original polyol market price and could replace up to 30 wt.% of the crude rigid polyether without any influence on the physical and mechanical properties of the PU foam *[42]*.

However, both the Rampf and H&S process presents a very important operational limitation, as both processes require sorting of the residues in case of essential chemical differences, to obtain high quality recovered products with low hydroxyl number and, consequently, suitable for the synthesis of new PUF foams.

2. OBJECTIVES

PU is the sixth most manufactured plastic polymer in the world, therefore, it would be very beneficial for everyone to find a sustainable way to manage its waste. Currently in Spain there is no defined recycling route for this waste and it is usually left stored in landfills because it is considered a non-hazardous waste. Therefore, the following objectives have been set:

- To carry out a bibliographic study of the types of PU foam recycling. We are looking for a method that offers us a process where waste or by-products from other processes can be used to improve its economic viability.

- Situation of PU foam waste management in Spain.

- Basic design. From the bibliography, data from other experiences will be used to select and dimension the equipment.

3. PUF FLEXIBLE WASTE MANAGEMENT IN SPAIN

Currently, due to its versatility and good properties, PU is one of the most manufactured polymers worldwide *[18].* It is a fact that it has a low biodegradability and due to its commercial success, a lot of waste is generated, and its treatment is an environmental challenge. These wastes comprise waste from the manufacturing process, EoL products, and post-consumer products. The latter represent a major problem as they are often contaminated or deformed and therefore more difficult to reuse. On April 19, 2018, a new regulation was adopted indicating when a foam manufacturing waste is considered a by-product *[43].* Until then, industries that synthesized PU had to pay a waste manager to treat the production waste and the introduction of this directive benefited the industries as they could sell these wastes as by-products.

Solid waste management is governed by the "Lansink Ladder", which determines a generally accepted hierarchy of waste treatment methods and was the basis for the hierarchy in force since Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 *[44].* This hierarchy establishes a priority order in waste legislation and policy. However, it admits the possibility of omitting some steps, if necessary, for technical, economic, or environmental reasons. Until a few years ago, landfills were the exit route for PU waste, however, the massive tightening of environmental laws following the mandates of European policies on waste management, causes a new waste management route based on recycling *[5].*

In 2018, in Spain, 2.5 million tons of post-consumer plastic waste were collected. Of this, 41.9% went to a recycling process, 38.8% ended up in landfill and 19.3% was used to recover energy. Between 2006 and 2018, plastic waste volumes have doubled, but the amount sent for recycling has increased *[5].*

In our country, collection systems are considered as the set of means that facilitate the collection of waste under municipal jurisdiction, from the point of contribution where the holder disposes of it to the first destination, either a warehouse or a facility to carry out a recovery or disposal treatment. Waste can be collected by *[45]:*

- Surface or underground containers: This system is the most used. It consists of placing containers of different types on the public highway, depending on the characteristics of the fraction to be collected and the urban planning of the area. To bring the waste, citizens must go to the collection points. These containers are emptied by the corresponding collection services following schedules and frequencies adapted to the filling levels of the containers, depending on the generation of each fraction and in some cases also depending on the characteristics of the material itself, such as the odor of organic matter.

- Door to door: This system consists of delivering the waste to the municipal collection service in front of the door of home or business according to a weekly schedule for each fraction collected and at a stipulated time. This system can be used to collect all domestic and commercial fractions. This system is widely used for specific commercial collections. The results of separate collection achieved in municipalities with this system are generally superior to other mechanisms, both in terms of quantity collected and quality of separation. The application of this system is highly recommended in areas of low population density where the identification of each person's waste is easier, but it can also be developed in denser areas with more vertical construction through the collection of communal containers in multi-family dwellings. This type of collection makes it possible to identify the waste generator.

- Pneumatic: The pneumatic waste collection system consists of a series of waste collection boxes connected by subway pipes to the collection point from where the circuit is aspirated. The collection boxes can be located either inside the dwellings, in communal areas inside the buildings, or in outdoor public areas. The waste poured into the collection boxes falls by gravity to the valves installed at lower levels, where it is temporarily accumulated until the suction process is carried out.

- Clean point or green point: these are selective collection and storage centers, mainly for municipal waste that is not collected at the household level, with the objective of facilitating the correct management of non-ordinary fractions. These facilities are mainly for the use of private individuals and small businesses. Three types of waste are accepted at these points: recyclable, reusable, and hazardous waste. These clean points can be fixed or mobile.

- Specific collection: In addition to the clean point services, there are different waste fractions that have specific collections. Some of materials that are collected in this way are: batteries, pharmaceuticals, used vegetable oils, textile waste and pruning and vegetable waste.

In most of Spain and specifically in Catalonia, the waste separation model is based on 5 fractions *[45]:* glass, paper-cardboard, light packaging, organic fraction, and residual waste. In the case of light packaging and glass, the government contracts external companies to manage this waste. "Ecovidrio" is the company in charge of glass management; "Ecoembes" is the company in charge of packaging management.

Although part of society has become aware of the environmental risk posed by poor waste management, it is still normal and common to find different types of PU, ranging from mattresses to refrigerators, on the streets. This is a big problem, for this reason, it is possible that in a few years, to avoid that they accumulate in an uncontrolled way in the public road, the generators of waste are identified at the time of depositing them in the containers and then charge them, according to the quantity and quality of the waste generated.

Within the management of municipal waste, landfill is the last possibility contemplated within the management hierarchy according to the Waste Framework Directive and Law 22/2011, on waste and contaminated soils, therefore only those wastes that cannot be prepared for reuse, recycled, or recovered after undergoing prior treatment to reduce their volume or hazardousness, and thus generate the lowest possible contributions, should be destined to these facilities *[46]*. Controlled landfills are deposits in which the soil is totally impermeable, with leachate channeling systems and pipes that collect the biogas which is formed inside (and can be used for energy purposes). Currently it is totally forbidden to dump waste in an uncontrolled manner throughout the national territory, according to the previous law, to avoid problems such as water pollution, the generation of hazardous substances or being a possible source of fire *[45]*.

Royal Decree 1481/2001, of 27 December, which regulates the disposal of waste by landfill, classifies landfills into the following categories according to the topology of the waste to be deposited *[47]*:

- Landfill for hazardous waste,

- Landfill for non-hazardous waste, including municipal waste.

- Landfill for inert waste, non-hazardous waste that does not undergo significant physical, chemical, or biological transformations.

All this has made the waste treatment development a fundamental issue both at the scientific level and for the industrial sector, since it is of global interest to conserve natural sources and reduce the amount of waste disposed of in landfills. In case of PU, the product which most often ends up in landfills are foams and because they are formed by cellular structures that contain air molecules, their storage in landfills can be problematic because if a fire occurs, the foams would fuel the fire, and when combusted, would produce toxic gases *[18],* so an efficient way to recycle this waste instead of storing them in a landfill has been sought. The public awareness of environmental issues and current problems (such as climate change) has been decisive for the administrations to draft a legislation that aims to provide an efficient treatment of solid urban waste.

PU is not dangerous at the EoL (if it does not contain flame retardants), when it arrives at the waste sorting centers, it is sorted in the banal container. If we have more bulky waste, such as mattresses or refrigerators, these centers do not take care of the separation of materials, but a company comes to collect them. Once they arrive at the place of material separation, it is shredded to reuse as much as possible. When all the foam has been separated and there is not a high level of contamination to recycle it, a useful and quick recycling option for this material is to shred it and agglutinate it to form sandwich panels *[10].* This is one of the most used methods, although the waste is previously treated to reduce its volume and use it to obtain energy and send the remains to the landfill. This is because there's no defined industry for the recycling of this polymer in Spain, from which a higher quality product can be obtained, since the current processes are very expensive, and the initial properties of the waste are lost to manufacture materials with little added value.

Another alternative for managers of this waste is to send it to recycle plants in other European countries to be used to synthesize new PU. This alternative serves to give an outlet to the waste, but due to the large amount of waste that these plants treat, it is vital to be able to establish a recycling process in Spain to process our waste and if possible, those of other countries. Therefore, it is urgent to be able to revalue the waste because after its useful life it still has a lot of value.

There is currently a great deal of investment in the recycling of this material in Europe. Since 2015, industrial-scale or pilot plants for the chemical recycling of PUF foam have been planned or are being built in countries such as France, the Netherlands, Germany, and Belgium. For example, Dow Polyurethanes has been involved in the construction of Europe's first post-consumer PU foam chemical recycling plant in Semoy (France). Foam producer The Vita Group, which operates foam production plants throughout Europe, was the first to officially announce that it will use recycled chemicals from the plant to manufacture new PU foams. In September 2021, the Semoy plant officially opened *[9]*.

All this development has also reached Spain, as, Repsol announced that it plans to build the country's first plant for chemical recycling of PU foam at its Puertollano Industrial Complex *[48]*. The new facility is expected to be completed by the end of 2022. Once operational, the plant will be capable of processing around 2.000 Tn/year of PU foam. The recycled polyol will be included under the Repsol Reciclex 14 brand to be used in new foams synthesis *[9]*.

4. SELECTION OF PROCESS

Due to the need of countries to prevent PU waste from ending up in the landfill, many studies have been carried out to investigate those chemical recycling processes that offer the best results *[1,14,18]*. In these investigations, different conditions and agents have been used to try to find a process in which, from production waste or waste that has reached the EoL, a product can be obtained, in this case polyol, which can be used as a replacement for a certain part of polyol for the synthesis of new foams.

4.1. SELECTION OF RECYCLING METHOD

There are many ways to deal with PU waste, but all have much room for improvement. The most widely applied way to dispose of PU waste currently is by landfilling *[18];* however, it is environmentally damaging, land-consuming and in most cases, not economically justified. Another frequently used method is mechanical recycling because it is relatively cheaper, but it has many limitations as it offers products that have much lower prices than the original PU material. Chemical recycling requires relatively high temperatures and aggressive reagents and now, very few have been developed on an industrial scale due to its economic feasibility and low product purity *[11]*. Biological degradation requires moderate temperature and does not require any hazardous chemicals, but there is still a long way to go before it can be applied on an industrial scale *[18]*. It should be noted that biodegradation is quite promising due to a wide range of possibilities and modifications available.

Therefore, when selecting our process, chemical recycling has been chosen and energy reconversion methods have not been considered, since these processes are useful if it is not possible to recycle the waste chemically or mechanically. In reference to thermochemical recycling, it has been discarded due to the extreme conditions to which PU is reacted and because its economic and sustainable viability is very low, and they are only used when the waste cannot be treated and must be disposed *[6]*. On the other hand, mechanical recycling methods have been discarded, although they are a good measure to eliminate the waste, the

processed products lose properties with respect to those residues and with little economic value.

Among all the methods we found for chemical recycling, glycolysis is considered the most convenient way to recycle PU [19]. This method has been used as a polyol recovery method for PU waste and other plastic waste such as PET, which can be recycled in a similar way [18]. Glycolysis is a depolymerization reaction by glycols at high temperature. It may or may not be a catalytic reaction, but it has been found that the reaction time decreases with the introduction of a catalyst [26]. Amines, inorganic salts, inorganic acids, and phosphorus compounds are mainly used as catalysts. The resulting recycled polyol can be used as starting material in the synthesis of new PUFs with the aim of providing a final application for the products recovered from the glycolysis process. Undoubtedly, glycolysis is one of the most important processes, especially for PUR and PUF foams because it requires relatively mild reaction conditions and recovered polyols with properties like commercial polyol are obtained [6].

Initially, in the glycolysis process, PU waste is crushed, converted into small pieces, and then ground. This product is reacted with a glycol, usually DEG, in a reactor at a high temperature between 190-250ºC. It is a long process, between 1,5 to 7 hours for PUF and after the reaction a single-phase product is obtained or a split-phase product if a stoichiometric excess of glycol is used [11]. Currently, several industries have been developed that obtain a single-phase product, but it has been shown that the product obtained has a very low purity and is therefore not viable [36-42]. These processes produce polyols that can only replace virgin polyols in semi-rigid foams, but not in PUF foams.

In general, research is being done to find a process that results in a split-phase product, where the top layer contains the recovered polyol and after purification, can be used to synthesize new PUF foams [30]. Since the reaction conditions influence the quality of the product, many researchers have studied the mechanism, the effect of glycol, the type and concentration of catalyst, the temperature, the purification and the properties of the recycled polyol products and foams to find the optimal formula for split-phase glycolysis of PUF foams. For this reason, glycolysis agent selection and the type of catalyst to be used in our process is very important. It has been decided that our process will work with a split-phase product, i.e., we will work with an excess of glycol.

4.2. SELECTION OF GLYCOLYSIS AGENT

As mentioned above, many studies have been carried out to find the glycolysis agent since it is one of the major limitations when performing the two-step process, due to the need to overuse it. Over the years, different low weight glycols have been used in the glycolysis process of PU waste. Modesti et al., *[36]* described glycolysis reactions of PUF foams based on polyether polyol and TDI using EG and DPG. However, Wu et al., *[49]* was the first group to report the glycolysis of PUF foams using DEG. This was a breakthrough in this field, as DEG had the best results so far. However, Datta et al., *[50]* obtained good results in the glycolysis of PUF foam using EG, PG, BDO, 1,5-pentanediol (GP), HDO as glycols. On the other hand, Molero et al., *[12]* carried out a study to determine the optimum glycol to be used in the split-phase reaction of PUF foams. The foam used for that study was a conventional one based on polyether polyol, which, was reacted at a PU/glycol mass ratio of 1:1,5 with several low weight glycols: monoethylene glycol (MEG), DEG, MPG and DPG. As catalyst DEA was used in a mass to glycol ratio 1:6. MEG provided a slow degradation of the urethane chain, while DEG showed a good chain degradation capability requiring a shorter time to achieve its complete degradation and obtaining a polyol with properties like those of the virgin material. Consequently, DEG was the glycol selected as the most suitable for the split-phase glycolysis process. It is very important to remember that the split-phase glycolysis process allows recovering the polyol with higher purity than in case of single-phase processes because the upper layer is mainly formed by recovered polyol and the lower one by the excess glycolysis agent and reaction by-products *[12]*. To obtain phase partitioning, a large excess of glycol is required, for this reason, they have been scaled up to pilot plant but have not reached commercial scale because the operating cost is so high *[18]*. It is vital to be able to find an alternative glycolysis agent that reduces the operating cost to make the process viable. This agent must meet two conditions *[11]*:

- Contain hydroxyl group terminations to be able to produce the exchange with the ester group of the PU.

- Be insoluble with the polyol to be recovered to ensure an adequate glycolysis process in the cleavage phase.

With this objective, Molero et al., *[23]* investigated to find a substance that fulfilled these conditions. They studied the possibility of using crude glycerol as an agent, which is a low-value

by-product with a very different composition from purified glycerol as it usually contains several impurities, such as water, methanol, and fatty acids mainly. Considerable efforts have been devoted to find applications to convert crude glycerol into high value products to improve the economic viability of the biodiesel industry and overcome the environmental problems associated with the disposal of crude glycerol. Approximately, glycerol as a by-product in biodiesel production accounts for 10 wt.% of the total product, so it would be a matter of revalorizing two wastes, foam, and crude glycerol, to obtain a product that comes from ethylene oxide [52].

Initially, this agent fulfilled the first condition, since it contains 3 hydroxyl groups that can react with the ester group of the PU. The same group of researchers was dedicated to verifying the insolubility of this agent with the polyol and to verify the feasibility of the process using crude glycerol as an agent. For this purpose, they performed the whole glycolysis process using as agents' glycerol with 99% purity, crude glycerol with 80% purity and the most used agent, DEG [25]. The wastes were treated with an arbitrary diameter ranging from 5 to 25 mm of a PUF foam based on a viscoelastic polyether polyol with functionality 3 and TDI. The ratio of PU waste to agent was 1:1.5. Stannous octoate was used as a catalyst at a weight ratio of 1.3 wt.% to the glycolysis agent. The reaction was carried out at 190°C.

Next, we can see a Table 1 and Table 2 with the composition of each phase after the reaction using 3 types of agents.

Table 1: Recovered polyols concentration comparison in the glycolysis upper phase depending of the glycolysis agent used. (Table extracted from [23])

GLYCOLYSIS AGENT	Upper phase composition (wt%)				
	High M_n Polyol	Low M_n Polyol	Net polyol	Ratio High M_n polyol/Net polyol	Glycolysis agent
Diethylene glycol	51.92	9.39	61.31	0.85	11.75
Glycerol 99% PS	33.50	37.82	71.32	0.47	5.01
Crude glycerol	35.99	34.25	70.24	0.51	2.90

Bottom phase 150 min	% by weight	
	High Mn polyol	Low Mn polyol
Diethylene glycol	2.97	17.58
Glycerol 99% PS	0	1.74
Crude glycerol	0	1.76

A remarkable and very interesting advantage can be observed when crude glycerol is used with respect to other glycolysis agents. When this cleavage agent is used, the low molecular weight polyol contained in the viscoelastic remains, to a large extent, in the upper phase. However, in the glycolysis reactions performed with DEG, the upper phase mainly consisted of the high molecular weight polyol, while the concentration of the low molecular weight polyol was only 9.39 wt.% in this phase. This different behavior is due to the higher dielectric constant (ε = 42.5) of glycerol than of DEG (ε = 31.69), and therefore, the low molecular weight polyol of the viscoelastic formulation remains in the polyol phase since it is not polar enough to be solubilized by the crude glycerol phase as occurs when DEG is used [25]. Moreover, high molecular weight polyol is totally insoluble in this phase since the higher the molecular weight of a polyol, the lower the dielectric constant and, consequently, the lower its solubility in a very polar solvent such as glycerol [24]. On the other hand, glycolysis concentrations by-products and agents are also lower in the upper phase when the transesterification reagent used is crude glycerol instead of DEG, because of the higher dielectric constant of glycerol which causes a higher affinity of these undesirables for the bottom phase [1].

It can be observed in the Table 1 that using DEG the total percentage of polyol in the upper phase is lower than that of crude glycerol (61 wt.% in the case of DEG and 71 wt.% in the case of crude glycerol). This allowed to prove, on the one hand, the insolubility of polyol in the agent and on the other hand, the improvement of results of this new agent compared to the results of the best agent studied until then. On the other hand, it was found that the purity degree of glycerol does not have a direct influence since they give very similar results [25].

Once the two phases were separated, the hydroxyl number of the upper phase of reaction with DEG and crude glycerol was found to be 217.8 mg KOH/g and 257.1 mg KOH/g,

respectively. These rates are much higher than those of flexible polyether polyol (28-160 mg KOH/g) *[4]*. This is because in the glycolysis process several by-products, mainly aromatic amines, are generated because of side reactions, such as thermal degradation or hydrolysis reaction of PU foams *[11]*. These impurities together with the remaining glycolysis agent, which although this in a very small proportion, having the hydroxyl number higher than those of a flexible polyether polyol, provides a huge increase in the number of OH of the upper glycolysis phase compared to the number of hydroxyls of the crude polyol *[23]*. Therefore, to achieve a high quality recovered polyol, susceptible to be used as a replacement for a virgin one, it is crucial to remove most of the impurities from the glycolysis polyol phase.

Most of the investigations encountered the same problem, the high number of hydroxyls in the upper phase of glycolysis regardless of the type of PU foam treated. Therefore, further purification of the upper phase of glycolysis is a mandatory task, regardless of the type of foam to be treated and the glycolysis agent used. Consequently, to obtain a recovered polyol with optimal properties to be used as a substitute for a virgin one, it was shown that the best purification process is a liquid-liquid extraction *[53]*. The optimum conditions obtained to carry out the extraction process were with a solvent pH between 4 and 5, with a mass ratio of the polyol phase to the solvent of 1:1, a reaction time of 60 minutes and a temperature of 60 ºC. It was later shown that an increase in temperature leads to an increase in extraction efficiency, so it was determined that it was better to operate at 90ºC. This purification process has been developed mainly when DEG is used as an agent*,* where its OH number has been reduced up to 84 mg KOH/g, i.e., its rate has been reduced up to 3 times *[53]*. This was a consequence of the fact that the concentration of by-products and DEG was reduced with the extraction, going from 28 wt.% to 19.28 wt.% in three extractions: causing an increase in the net proportion of polyol, reaching 79.37% by weight *[25]*. In the case of crude glycerol*,* acidified demineralized water would be used as the extracting agent, with a pH between 4 and 5 *[23]*. Following the extraction step, a vacuum distillation could be added to remove all the water from the recycled polyol *[53]*. The residue of this distillation is the recovered polyol.

In Table 3 we can observe the hydroxyl number of the recovered polyol after the purification step. The number of by-products and crude glycerol have decreased, causing the OH number to decrease and therefore, the recovered polyol has properties like the virgin polyol *[25]*.

Table 3: Aproximate hydroxyl number calculation of the purified recovered polyol by means of GPC. (Table extracted from [23])

Refined 3	Content (wt%)	f	M_n	M_n * wt%/100	f * wt%/100	OH (mg KOH g^{-1})
Oligomers	19.29	3	4007	773.04	0.579	
High M_n Polyol	47.65	3	2134	1016.90	1.430	
Low M_n Polyol	29.39	3	723	212.49	0.882	
Byproduct 1	0.38	3.2	264	1.00	0.012	$OH_{number} = \dfrac{56100 \cdot f}{Mn}$
Byproduct 2	0.49	3.2	164	0.81	0.016	
Crude glycerol	0.12	3	103	0.13	0.004	
Byproduct 3	2.66	3.2	80	2.13	0.085	
				$M_n = \sum = 2006.51$	$f = \sum = 3.007$	$OH_{number} = 84.07$

Once a recycled polyol has been obtained, the three main variables that determine whether it can be used as a raw material are the hydroxyl number value, the functionality, and the average molecular weight. For polyols to be useful for the synthesis of PUF foam, they must have a molecular weight of 2,000-6,000, with a functionality of 2-3 and a hydroxyl number of 28-160 mg KOH/g. [51]. The recovered polyol falls within the range of these three parameters, thus demonstrating that a high-quality polyol is obtained that can replace part of the virgin polyol.

Once this was demonstrated, it was necessary to determine the amount of polyol that could be replaced by recycled polyol. It was shown that up to 25 wt.% of virgin polyols could be replaced without affecting the properties of the foams synthesized with this replacement [25]. Therefore, this process allows us to replace part of the virgin polyol stream.

On the other hand, Molero et al., [28] demonstrated that the bottom phase of glycolysis could serve as a replacement part of virgin polyol for the synthesis of PUR foams. This bottom phase of glycolysis mainly consists of excess of crude glycerol and various by-products of glycolysis, such as low weight carbamates and aromatic amines, which react with isocyanate [12]. To use this bottom phase for the synthesis of PUR foams, a vacuum distillation at 190 °C

must be performed to remove the by-products and reduce the number of hydroxyls *[11]*. The polyol for synthesizing new PUR foams is the residue of the distillation. This is mixed with virgin polyol to initiate the synthesis of new foams. The hydroxyl number of this polyol obtained is 759 mg KOH/g *[28],* which is in the range of values of virgin polyol (250-1,000 mg KOH/g). Therefore, the bottom phase of glycolysis has been successfully used in the synthesis of new PUR foams with a similar structure to conventional ones.

In summary, it has decided that our process will be a two-phases glycolysis process using crude glycerol as the solvent, at a temperature of 190ºC, with a ratio between PU waste and the agent of 1:1.5 and a reaction time of 150 min. Then the phases will be separated, and the upper phase will undergo a purification step consisting first of a liquid-liquid extraction with acidified demineralized water with a pH between 4 and 5 with a mass ratio of the polyol phase to the solvent of 1:1, a reaction time of 60 min and a temperature of 90 ºC. On the other hand, the bottom phase will not be discarded, but will be sent to a company that can perform the separation of the excess glycerol from the polyol for rigid foams and thus could be reused to synthesize new foams. Therefore, the bottom phase of glycolysis will be considered a by-product and not a waste.

Through this process we will be able to revalue two wastes, crude glycerol, and PU, to obtain two products with a large market (the two phases of glycolysis), since they are products of fossil origin, which have been obtained in a sustainable manner from wastes. Another interesting point of this process is its versatility, since this process has been developed, using crude glycerol, for PUF foams *[23],* both for HR *[24]* and for viscoelastic *[25],* and PUR foams *[54].* Therefore, although our process is intended for the recycling of PUF foams, it could be extrapolated to other types of foams because they have similar conditions. Now it only remains to determine the catalyst to be used.

4.3. SELECTION OF CATALYST

In glycolysis processes, the PU chain is degraded by successive transesterification reactions of the urethane bond with low molecular weight glycols with the aid of a catalyst. Several studies have been published on the glycolysis of PUs, where the major concerns are the formulation of a viable glycolysis process, the properties of the polyols obtained from the wastes and the purification of the resulting products *[18].* Among other reaction variables, the

choice of catalyst is an important factor affecting the properties of the recovered products as well as the time to reach complete degradation of the foam. Catalysts used in PU glycolysis include bases such as amines, hydroxides and alkoxides, as well as Lewis's acids [55].

In the literature, the general catalysts in transesterification reactions are Pb, Zn, Ca, Co, and Mn acetates, although in the case of transesterification of urethane bonds with glycols, only KAc and sodium acetate are used, resulting in high amine values in the resulting products [55]. Simioni et al., [56] used the catalysts used in the hydrolysis process to see their feasibility in the glycolysis process. Alkali hydroxides were used resulting in higher contents of undesired aromatic amines. Borda et al., [19] studied the reaction time dependence using DEA. They reported an improvement in the decomposition step although this resulted in an increase in the hydroxyl number. Recently, organometallic catalysts have been used in the glycolysis process. Among all the compounds, Simioni et al., [57] reported titanium n-butoxide ($Ti(OBu)_4$) as a selective catalyst for the transesterification of the urethane group.

To check which type of catalyst was the most suitable, Molero et al., [55], performed the glycolysis process with DEG as an agent, in a ratio of 1:1.5 and using DEA, $Ti(OBu)_4$, potassium octoate and calcium octoate as catalysts. It was found that using the octoates led a complete degradation of the polymeric chain in a shorter time and with a higher concentration of polyol compared to the most used catalysts, DEA. Moreover, another advantage is that the amount of octoate used represents only 15 wt.% of the DEA needed [26].

On the other hand, it was shown that potassium octoate increases the selectivity of the process by avoiding the hydrolysis reaction, which results in a lower content of primary amines and, therefore, a better yield with respect to $Ti(OBu)_4$. This research served to demonstrate that these new catalysts are a cheaper and improved alternative to the catalysts studied until then [26].

Finally, Simon et al., [55] wanted to prove that stannous octoate could be a good catalyst for two-step glycolysis. They found that it shows an adequate yield, producing a recycled polyol with a high quality in the shortest reaction time. It also has the advantage that it does not need to be removed from the polyol for using in foaming.

It is crucial to choose the temperature and catalyst concentration since, an increase in temperature and catalyst concentration increases the degradation rate, but also negatively affects the process by the extension of side reactions and the polyol phase contamination. High

ratios of glycolysis agent to PU foam shift the equilibrium towards glycol substitution, promoting phase partitioning which results in a polyol-rich phase. However, too large an excess of glycol would imply equipment with very high volume and higher amounts of bottom phase. Taking all this into account, a balance must be achieved between the speed of reaction, the polyol content in the upper phase and the properties of the recovered polyol *[20]*.

For our process, we need the catalyst that gives us the highest quality polyol in the shortest possible reaction time. Currently the catalyst that has given the best results is stannous octoate, so this will be our catalyst. The optimum reaction conditions for this catalyst are *[55]*:

- Catalyst concentration in the glycolysis agent: 1.3 wt.%.

- Mass ratio between glycolysis agent and PUF foam: 1:1.5

- Reaction temperature: 190°C

5. BASIC DESIGN OF FLEXIBLE PUF RECYCLING

To obtain a polyol capable of being used to synthesize new foams with suitable properties, it has been decided to apply a chemical recycling to treat PUF foam waste by means of the split-phase glycolysis process using an excess of crude glycerol, which is our glycolysis agent, being a reaction catalyzed with stannous octoate.

5.1. DESIGN BASIS

5.1.1. Plant location

It is necessary to find a strategic location that allows us to minimize the transportation expenses of first materials to the plant and the transportation of product and waste to its destination. To this end, it has been decided to locate the plant in the municipality of Abrera, mainly because once the recycled polyol is obtained, it will be sent to a manufacturer of PUF located in the same municipality, Celmus S.L. .This company is dedicated to the transformation and handling of plastic materials, where one of these materials is PU, which is mainly used in the automotive industry, packaging, and the manufacture of foams for mattresses *[58].*

5.1.2. Capacity

Due to the nature of the process and the research carried out, process will be carried out in batches. It has been decided to work in a discontinuous way because in this way we ensure a better quality and higher yield of recycled polyol.

This process is designed to manage part of PUF foam waste generated in Spain, specifically in Catalonia. This material is not well accounted for, and it is very difficult to find data

on the amount collected due to poor management by institutions, as much of this waste ends up in the landfill.

Finally, it was possible to obtain a design basis by contacting the company in charge of treating the mattress waste collected in the metropolitan area of Barcelona, "Reciclatges La Noguera". This company is dedicated to collect this waste and separate each of its pieces to send them to their corresponding destination. In the case of the foam extracted from the mattresses, this is sent to France so that they can take care of this waste.

As a basis for calculation, we have taken the annual amount of PUF foam from mattresses (from the metropolitan area of Barcelona), which is 440 T/year.

5.1.3.   Working conditions

To process all PU waste, it has been estimated that 1.2 Tn/day need to be treated. The entire process consists of the loading of raw materials to the unloading of the products and takes approximately 6.6 hours. It is assumed 365 working days to promote the feasibility of the process. It has been decided to make 3 batches per day, each one will occupy 8 hours, of which 6.6 will be dedicated to the process and the rest to the maintenance and cleaning of the equipment. Therefore, when each worker arrives at the plant, he will find all the equipment ready to operate and at the end of his shift he will have to leave everything prepared and ready for his colleague to carry out a new load.

Through data from other experiences, the material balance of the system has been determined [67]. The amount of PU to be treated per batch was set at 400 kg and maintaining the proportions mentioned in section 4.2. In this case, 600 kg of agent and 8 kg of catalyst will be used. Once the reaction time has elapsed, an upper phase of 269 kg is obtained, which after the purification stage, 245 kg of recycled polyol are obtained. In order to make the design we have assumed the times of each operation (Table 4). The only times specified were the reaction time and the extraction time.

Table 4 : Operation time for the equipment

Stages	TIME (MINUTES)
Introduce crude glicerol to R-1	10
Introduce catalyst to R-1	2
Heat mixture in R-1	20
Introduce PUF foam waste in R-1	60
Glycolysis reaction in R-1	150
Pumping the product to S-4	20
Phases separation in S-4	25
Pumping bottom phase to S-6	10
Pumping upper phase to S-7	10
Pumping water to S-7	10
Liquid-liquid Extraction in S-7	60
Pumping wastewater to S-9	10
Pumping recovered polyol to S-8	10
	Total= 397 min

So, to treat 440 Tn/year, 3 batches of 400 kg each will be carried out, which means a total of 1,095 batches per year.

5.1.4. Collection of raw materials

For the chosen process, we have crude glycerol as raw materials, waste PUF foam and catalyst. Our glycolysis agent is a by-product of biodiesel production, so it will be provided by a company dedicated to this production. "Ecomotion" is a company located in Montmelo, dedicated to biodiesel production for using as fuel *[60].* This company has a crude glycerol production of 3,000 Tn/year. This raw material does not need purification since the purity of this

material does not imply substantial improvements in obtaining the recycled polyol. Using 600 kg per batch, 657 Tn/year will be needed to develop our process.

On the one hand, we have the PU waste, which will arrive crushed and with the necessary size (between 5 and 10 mm) to carry out the process. These wastes will be collected by the company, "Reciclatges la Noguera", and they themselves will oversee reducing the size of the wastes so that they arrive at the factory with the desired size. The fact that they arrive already in operating conditions will allow us to avoid the expense involved in the collection and adaptation of these wastes. By making 400 kg batches, a total of 438 Tn/year will be processed.

On the other hand, we have the stannous octoate that will be used as a catalyst for glycolysis reaction. This raw material will be provided by the company "Todini Quimica Iberica S.L.", which distributes salts and oxides of non-ferrous metals *[61]*. For annual production requires 8.760 kg.

Finally, although it is not a feedstock, the process needs demineralized water to carry out the purification stage of the upper phase. The demineralized water will be provided by the company "Tpmultiaqua", located in Sant Quirze del Valles *[62]*. 294 Tn of demineralized water are needed per year. For this water to be used in the process, it must be acidified to obtain a pH between 4 and 5. To achieve this pH change, the company will be asked to provide us with this demineralized water already acidified.

5.1.5.   Destiny of the products

The whole process is designed to obtain a product obtained from two waste streams, PUF foam waste and crude glycerol. Using these raw materials, it is intended to obtain a recycled polyol with similar characteristics to virgin polyol to be used to synthesize new PUF foam. Through this process, a polyol with a hydroxyl index of 84 mg KOH/g *[25]* will be obtained, which will be sent to the "Celmus S.L.", plant located in Abrera. This company produces PUF foam with polyols with the standard hydroxyl index for this type of foam (28-160 mg/KOH). As we can see, our polyol would fall in this range, therefore this product will be sent to this company.

As a by-product we have the bottom phase of glycolysis, which has been shown that it can be used as a replacement for part of polyol stream destined for the synthesis of PUR foam *[28]*. The destination of this by-product is not very well defined because there is no industry

dedicated to separate crude glycerol from isocyanate, therefore, this by-product should be sent to a plant that synthesizes PUR foam with polyols with similar characteristics. Furthermore, it would be so beneficial for the plant to be able to mix glycerol, once it has been separated from initiator, with different vegetable oils to obtain polyol, as it is a very promising technology *[63]*. It has been discarded to perform the separation in our plant, because that would mean a recirculation of the glycolysis agent, which would help to reduce the amount of glycerol needed, but it has been demonstrated that once the glycolysis has been performed, the excess glycol from the bottom phase still has a lot of working capacity, therefore, once separated from the isocyanate it can be used for another function, since it is a substance with a lot of value and with a lot of market demand *[64,65]*.

Finally, we have as a residue of the process, the wastewater from the purification stage. This water is mainly used to extract the amines and the remaining amount of glycolysis agent, so it is necessary to send this water to a WWTP *[53]*. As the plant is in Abrera, the wastewater will be sent to the nearest WWTP, which is in the same municipality.

5.2. DESCRIPTION OF THE PROCESS

Through the studies of different researchers on split-phase glycolysis, this process has been developed to treat PUF foam wastes using crude glycerol as agent and stannous octoate as catalyst. These raw materials arrive at the plant under operating conditions; the waste with a diameter of between 5-10 mm; the crude glycerol with a purity of 80%; and finally, the stannous octoate with a purity of 100%.

Once they are in the plant, they are stored, in the case of crude glycerol and catalyst in liquid storage tanks (S-2 and S-3), and in the case of foam, in a silo (S-1). Initially, glycolysis agent and catalyst are introduced into the reactor. These components will be stored at ambient conditions. Once introduced into the reactor, they will be heated up to the reaction temperature (190ºC). Both the agent and the catalyst will be introduced into R-1 by two pumps (B-2 and B-3) from the bottom of each tank to the reactor to be mixed. Once the reaction temperature has been reached, the waste PUF foam is introduced by means of an Archimedes screw (B-1). An important factor is the fact that time 0 is taken as the exact time at which all the PU has been introduced *[11]*. Once everything has been introduced, it will be reacted for 150 min.

The reaction will be carried out in an isothermal jacketed stirred tank batch reactor. Inside the reactor we will find a PU: glycolysis agent ratio of 1:1,5 and with a catalyst concentration of 1.3 wt.% with respect to the glycolysis agent *[23]*. Once the reaction time has elapsed, the resulting mixture will be pumped, via B-4, from the bottom of the reactor to the separation tank (S-4). The product pumped to S-4 is at a lower temperature than in the reactor, approximately 100ºC. When the mixture reaches S-4, it is allowed to stand for 25 min so that the phases are well separated. Once the phases are separated, the same pump (B-5) is used to initially send the bottom phase to its storage tank (S-5) and then send the upper phase, which is where the polyol to be recovered is located, to its purification stage (S-7). The bottom phase is considered a reaction by-product which will be stored until it is sent to its destination. On the other hand, the upper phase will be sent to its purification stage, which consists of a liquid-liquid extraction with demineralized water with a pH between 4 and 5 and with an upper phase: water ratio of 1:1 at a temperature of 90 ºC; and an extraction time of 60 min *[53]*. After this stage, the recycled polyol will be pumped by B-7 to its respective storage tank (S-8). The wash water will be pumped to its storage tank by B-8.

As can be seen in Table 3, following this process, a recycled polyol is obtained with a hydroxyl number of 84 mg KOH/g, a functionality of 3 and a molecular weight of 2006 *[25]*. These values would fall within the ranges of each property within the values of commercial polyol.
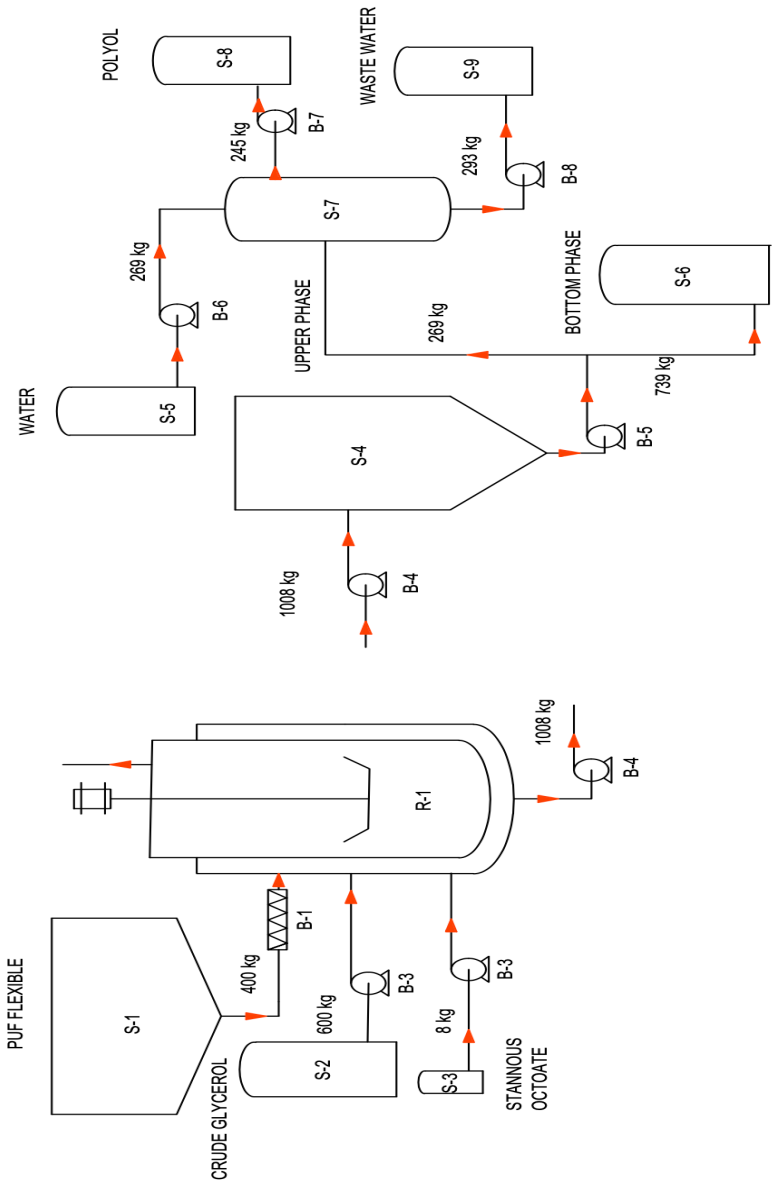
5.3. PROCESS DIAGRAM

Figure 1: Plant process diagram. Do it in Autocad

5.4. EQUIPMENT SELECTION

5.4.1.   Storage tanks

To carry out our process, a total of 6 storage tanks and a silo are required. This has been chosen because the tanks are intended to store liquids and the silo will be used to store PU waste. To size the equipment, it was assumed that the first materials will be received every 15 days, so it was sized for 15 days of production. This has been considered, except in the case of catalyst that due to the small quantity needed, the product will be supplied every 30 days. It has been so considered because it has been shown that stannous octoate, if stored under the right conditions, can maintain its properties for more than 30 days *[67]*.

For the 6 liquid storage tanks, the Tank Sto model of the Die Dietrich company has been selected (Figure 2).
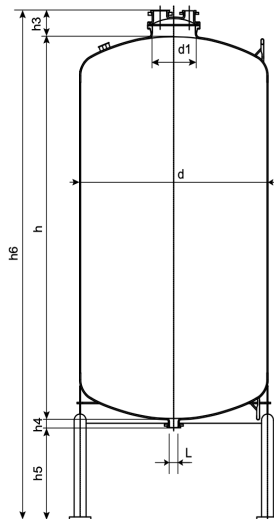
Figure 2: Tank STO. The De Dietrich web [68]

As liquids are stored, it has been decided that the tanks should be vertical with the outlet at the bottom because this benefits when pumping the fluid to its destination. This company will provide us with glass-lined steel tanks (DD3009 enamel) with high resistance to corrosion *[68]*. In the appendices we find the datasheet (APPENDIX 1: Table 4: Technical data sheet for Tank STO, the De Dietrich web).

In the case of silo, we decided to use the SCE610/11T45 model from Symaga (Figure 3) *[69].* The volume of each tank will be specified below.
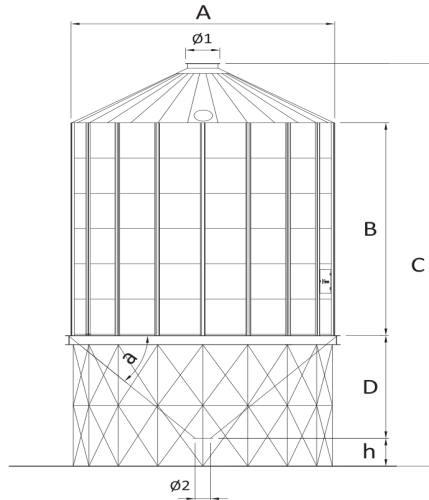
Figure 3: Silo SCE610/11T45.The Symaga web [69]

-Silo (S-1)

In this tank we find the PUF foam wastes, which are not considered hazardous products, since they are identified as industrial polymers *[4].* These PU wastes will be introduced into the reactor by means of an Archimedes screw (B-1). Considering the volume to be treated in 15 days (approximately 18 Tn), a silo with a capacity of 413,000 L has been considered. The safety measures to be considered are *[70]:*

- In case of fire, as it is a combustible material and causes, in its combustion, intense heat and dense smoke, it must be stored away from heat sources. Suitable fire extinguishers (water, dry powder, or liquid foam) should be available. If the foam comes into contact with the skin, the burned surface should be cooled with water without removing the foam. In the case that a person has inhaled combustion gases, he/she should be evacuated from the area and given medical attention.

- When handled, PUF foam at ambient temperature does not present any healthy risk. No special protective equipment or clothing is required for handling the foam, as it

does not irritate the skin, eyes, or respiratory system, except in processes where dust is produced. It does not require specific ventilation, if there is adequate ventilation.

In general, this material does not require any specific storage measures, so it can be stored under ambient conditions, since it is a material with good properties at room temperature *[4]*.

- Storage tank (S-2)

The next tank is used to store glycolysis agent, crude glycerol, to be fed by the B-2 pump to the reactor. The material to be stored usually contains various impurities, such as water, methanol, soap, and fatty acids. The tank will have a capacity of 25,000 L (Table 5). The safety measures to be considered are *[71]:*

- In case of fire, a fast-acting ABC/BC/B powder extinguisher should be used since water would expand the puddle if used. As a consequence of fire, CO and CO_2 are formed due to combustion.

- In the event of a spillage, the spilled product should be collected and pumped into an appropriate container, such as a bucket. Another option would be to collect the spilled liquid with absorbent material, such as sand or sawdust, and then clean the surface with plenty of water.

- For storing, it should be kept away from heat sources, oxidizing agents and strong acids and bases. It should be kept in a dry place with ventilation at ground level. It is very important that the tank is covered so that the product does not lose its properties.

- The accumulation of electrostatic energy during the product transport through the plant should be avoided.

To store the product in the best conditions, it is essential that it is kept in a totally hermetic container at a minimum temperature of 15ºC and a maximum of 60ºC, in a glass-lined tank to avoid corrosion. To avoid the accumulation of electrostatic energy, all the pipes and pumps in charge of transporting the product must be grounded. The tank chosen meets these specifications.

To avoid a product spillage that could affect other equipment, a passive mitigation system such as a bucket will be used to accumulate the spillage. To minimize the effects of a fire, appropriate extinguishers will be available as an active mitigation system.

Table 5: Capacity of Tank Sto for crude glycerol

Nominal capacity [L]	Total capacity [L]
25,000	25,600

-Storage tank (S-3)

To favor the glycolysis reaction, stannous octoate is used as a catalyst for the reaction, which will be stored in this tank until it is introduced into the reactor. The selected tank has a capacity of 1,600 L (Table 6). The most important safety measures to be considered are *[72]:*

- In case of fire, sand or dry chemical powder should be used. An inadequate method of extinguishing the fire is to spray directly with water. It is not a combustible material, although in case of fire it can give off irritating and toxic fumes and gases such as CO.

- Ignition sources should be avoided so that, in case of spillage, it does not cause damage to other equipment. Another factor to consider is that it is a hazardous substance for the environment, so it must be avoided that it ends up being spilled in the environment.

- When storing it, it should be kept in a clean, dry, and well-ventilated area. Furthermore, it should be protected from the sun to avoid loss of properties. Incompatible products with this material are oxidizing and reducing agents and amines.

Table 6: Capacity of Tank Sto for stannous octoate

Nominal capacity [L]	Total capacity [L]
1600	1680

Therefore, this material should be stored in a dark and cool place, away from sunlight. It should be kept in a completely airtight container made of glass-lined steel. As this is a hazardous substance for the environment, to minimize the possible effects, a bucket should be used to accumulate the possible spillage.

- Storage tank (S-5)

Once the phases are separated in S-4, the bottom phase is pumped to its respective storage tank (S-6). The selected tank will have a capacity of 25,000 L (Table 7). This bottom phase mainly consists of excess glycol and reaction by-products. Part of these by-products are the product of the isocyanate reacting with the crude glycerol [11]. This mixture, from a practical point of view, can be considered as an aromatic amine [28]. The hydroxyl value of this phase is 785 mg KOH/g [21] which can be used to synthesize PUR foams.

Table 7: Capacity of Tank Sto for bottom phase

Nominal capacity [L]	Total capacity [L]
25,000	25,600

This bottom phase must be stored in the storage tank until it is shipped to its destination. It must be kept hermetically sealed in a dry and well-ventilated place. The container must be sealed and in an upright position to avoid leakage. As this phase contains amines, these are very toxic, so the product should not come into contact with the humidity of the air. The product must be kept at a temperature between 0 and 25 °C and it is advisable to store it under an inert gas atmosphere [28]. This blanketing consists of replacing a certain volume of air in the tank with a neutral gas to prevent oxidation of the stored product. To achieve this process, the company Air Liquide [73] will provide the nitrogen necessary to maintain an inert atmosphere inside the tank. A nitrogen storage tank will be placed to be introduced continuously to maintain the blanketing of the tank.

-Storage tank (S-8, and S-9)

For this case, we have two storage tanks where water is to be stored. The two tanks will have a capacity (Table 8) of 16,000 L. For the first tank S-4, we find the acidified demineralized water so that it can be used as an extraction agent. This water will be sent to S-7 through B-6 to start the purification stage. This product is not classified as hazardous to the environment; however, its discharge should be avoided as it is a product classified as hazardous to health. To maintain the properties of water, it should be stored at a temperature between 15-25°C.

On the other hand, we find the S-9 tank, in which the water is stored once it has been used in the extraction process. In this tank the residue of our process is stored. This water, as it

carries with it the impurities of the upper phase of glycolysis, is contaminated. Because these impurities are very reactive, the tank must be stored hermetically in a cool, dry place. The safety measures of this tank are very similar to those of the S-6 tank but in this case the use of blanketing is not necessarily due to the small number of amines. The contaminated water will be sent to the Abrera WWTP for treatment.

Tabla 8: Capacity of Tank Sto for water

Nominal capacity [L]	Total capacity [L]
16,000	16,300

-Storage tank (S-8)

To store the product obtained for shipment to its destination, the company Celmus S.L., it will be stored in a tank with a capacity of 12,500 L (Table 9). The properties of this polyol have been shown in Table 3. The most relevant safety measures to be considered are *[75]:*

- In case of fire, all types of extinguishing media may be used except water, as it may spread the fire.

- In case of spillage, it must not be allowed to enter any sewage system, neither on land nor in water.

- Thermal decomposition may cause emissions of irritating and toxic gases and vapors such as CO and CO_2.

- Avoid contact with skin, eyes, and clothing when handling.

- The product is hygroscopic.

Therefore, the tank should be kept in a cool, dry place, always avoiding contact with water and air humidity, due to its hygroscopic nature. If the product is stored at a temperature of 15-25ºC, it is stable under ambient conditions.

Table 9: Capacity of Tank Sto for recovered polyol

Nominal capacity [L]	Total capacity [L]
12,500	12,650

5.4.2.   Pumps

To be able to transport both solids and liquids through our facilities, pumps are needed to transport these substances to their destination. In the case of the PUF foam, it has been decided to introduce it into the reactor by means of an Archimedes screw. In the case of liquids, 2 types of pumps will be used depending mainly on the fluid to be treated:

Table 10: Calculated flow rate of the pumps

Pumps	Flow rate [L/min]
B-1	133
B-2	48
B-3	3,2
B-4	28
B-5	28
B-7	27
B-8	29
B-9	25

Using the times (Table 4) together with the density of each product, it has been possible to calculate the flow rates of the pumps to be used (Table 10). To calculate the flow rates of the pump that has to send the reaction product, after phase separation, to its destination, the density of the upper phase was used as the density of a polyether polyol (1.010 g/cm^3), since it is the majority substance. For the bottom phase, the density of crude glycerol (1.261 g/cm^3) was used *[67]*. The specification sheets of the pumps can be found in Appendix 1:Datasheets.

- Gear pumps (B-2, B-3, B-4, B-5, and B-8)

These pumps were chosen because they were considered the best option for pumping these products. The products to be pumped have a low viscosity, therefore the Standard Chem Gear Pump of the company Witte pumps and technology has been chosen *[76]*. The model chosen is the CHEM 46,3-45-45 (Figure 4) pump, because it offers a range of flow rates that meet our needs.

Of all these pumps, the one which can cause most problems is the B-4, which is in charge of pumping the two-phase product from the reactor to the phase separation tank, since it would be the hottest fluid to be treated. Even so, the pump model chosen can work with fluids at a temperature of 300ºC). In the case of B-4, the fluid to be treated will be at a temperature lower than 190ºC, therefore this model meets our requirements.
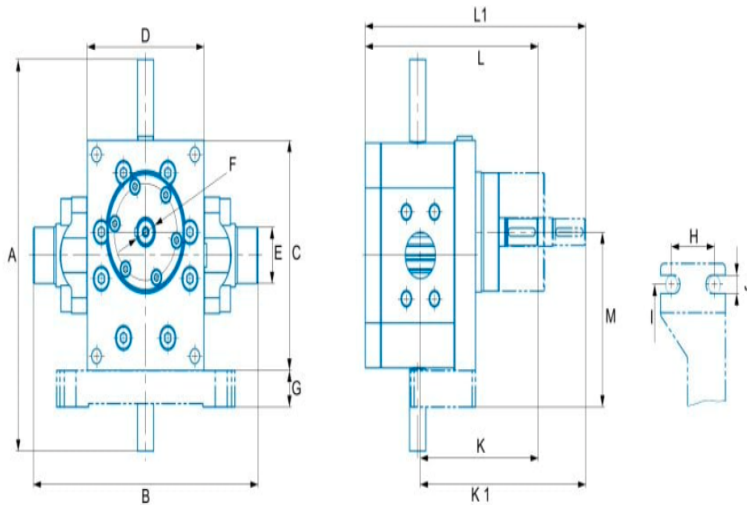
Figure 4: Standard Chem Gear Pump 46,3-45-45. Witte Pumps and Technology web [76]

-Centrifugal pumps (B-6 and B-8)

To improve the economic viability of the process, the B-6 and B-8 pumps must treat acidified demineralized water and wash water respectively, so it has been decided to use a simpler and more economical type of pump than the gear pumps. The B-6 pump is used to pump the water to the extraction stage. Once the extraction is finished, the B-8 will send the wash water to its storage tank S-9.

So, to meet our needs, it has been decided to use the DIN-FOOD 125-100-315 model of the INOXPA company (Figure 5) *[77]*.
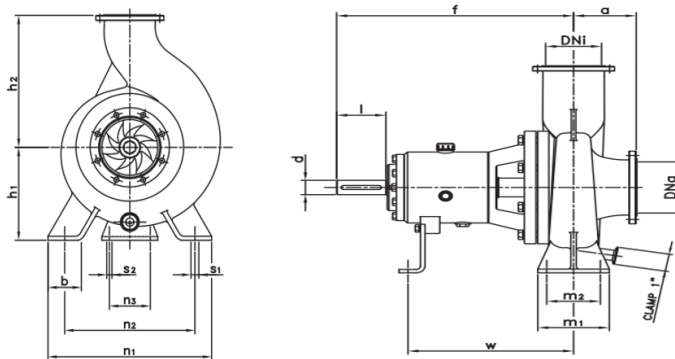
Figure 5: Gear DIN-FOOD 125-100-315. The Inoxpa web [77]

-Archimedes screw (B-1)

Due to the need to introduce the PUF foam waste into the glycolysis reactor, it was decided to use an Archimedes screw. This was considered because, to facilitate the dissolution of PUF foam in the medium reaction, the solid must be introduced at a low speed to favor the degradation of the foams *[18].* For this reason, this system of introducing foams into the reactor was chosen using the TARQ-1100 model of the company Hidrometalica (Figure 6)*.*

Figure 6: Archimedean screw TARQ-1100. Hidrometalica Web [78]

5.4.3.   Glycolysis reactor

When selecting the reactor, it is essential to know what happens inside it. Initially, the catalyst and the glycolysis agent will be introduced, and their temperature will be increased up to 190ºC. At this temperature, the PUF foam waste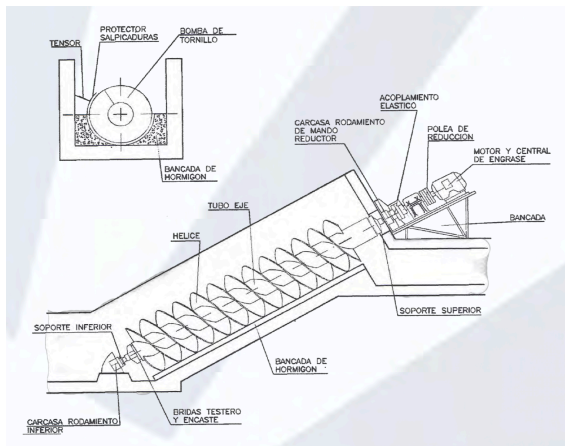 will be slowly introduced through B-1. The reactor is a batch stirred tank jacketed to keep the system isothermal, which means that we need a heating system to reach and maintain the desired temperature. It is operated at atmospheric pressure *[25]*. A thermal oil system has been chosen because it must work at a relatively high temperature but at a low pressure, therefore, this option has been considered as the most optimal. The design and selection of this system is crucial in the reactor design, since we need a system that allows us to maintain the temperature for 150 min and does not give us problems in terms of safety. So, a thermal oil system from Pirobloc will be selected *[79]*. It has been decided to use the thermal fluid boiler model - GFT line (Figure 7). The boiler will be placed vertically to minimize space. This thermal fluid system was chosen because it has a maximum design temperature of 350ºC, so our temperature (189ºC) falls within the operating range of the system.

Figure 7: Thermal fluid system. Model GFT line. Pirobloc Web [79]

Due to the complexity of the selection, we would ask this company to carry out a detailed study of our process and they would take care of all the specifications for the design of this installation.

The split-phase glycolysis process using crude glycerol as an agent has been studied by several researchers but has not yet been developed industrially. However, most of the studies

on this process provide similar results regardless of the type of foam used *[24,25,80]*. There have been no studies determining the order of glycolysis reaction with crude glycerol, but it has been determined for the process using DEG. Using this agent, glycolysis followed a kinetic model of order 2 and with an activation energy of 100.52 kJ/mol *[81]*. We can expect that the results obtained with crude glycerol would be very similar, so a reaction with order 2 kinetics will be assumed.

The reactor selected is OPX BE 8000 designed by De Dietrich with a capacity of 8000 L. Figure 8 shows the reactor in a drawing in which the specification sheet (APPENDIX 1: Table 5: OPX BE 8000 reactor technical data sheet. De Dietrich website) explains the value of each parameters shown in the picture.
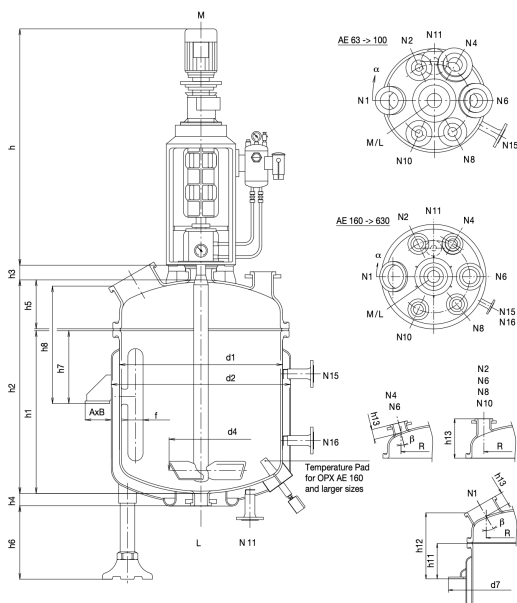
Figure 8: Reactor OPX BE 8000. De Dietrich web.

The reactor has 3 inlet streams and an outlet stream that exits at the bottom of the vessel. Inside the reactor, as gases, mainly CO_2 is formed, so it would be convenient to maintain an N_2 atmosphere to avoid the oxidation of CO_2 to CO *[19]*. Therefore, a nitrogen tank will be connected to keep the tank blanked. This nitrogen will be supplied by the same company that supplies it to store the recycled polyol, Air liquid *[73]*.

In summary, we have a jacketed stirred tank batch reactor with a thermal oil system to reach and maintain the temperature of 190ºC. It is fed with a stream of 400 kg PUF foam, a stream of 600 kg glycolysis agent and a stream of catalyst of 8 kg. Thus, a mass ratio of PUF foam/crude glycerol of 1:1.5 is maintained with a catalyst concentration of 1.3 wt% of glycolysis agent. The reaction time is 150 min, and the reaction will take place in an inert atmosphere. It is a reaction that follows a 2nd order kinetic model where the reaction product is a biphasic system composed of an upper phase where we find the recycled polyol with a series of by-products (mainly amines and part of the excess of glycol) and in the other phase we find the excess of glycol together with the isocyanate *[25]*. We obtain 1008 kg of reaction product, of which 269 kg correspond to the upper phase and 739 kg correspond to the bottom phase.

5.4.4.   Separation tank

From the reactor we obtain a biphasic mixture that is pumped by means of B-4 to the phase separation tank S-4. Once it reaches the tank, the mixture is left to settle for about 25 min to ensure that the phases are separated. For this purpose, the DCR-2400 model (Figure 9) from Hidrometalica *[82]* with a capacity of 1,600L was chosen.

This equipment will treat 1,008 kg, of which 269 kg correspond to the upper phase and the rest is the bottom phase. After 25 minutes, the B-5 will be in charge of sending, first, the bottom phase to its storage tank S-6, and then it will pump the upper phase to the purification stage S-7. The fact that the polyol we want to obtain is insoluble in the bottom phase assures us that if there is any problem at the time of pumping, we will not lose any of our desired product, the recycled polyol. If, on the other hand, part of the excess glycol remains in the tank after pumping the bottom phase and is carried over to the purification stage, this excess would be removed during extraction *[28]*.

To carry out the operation, the company will be asked to design the control system to ensure on the one hand the separation and quality of each phase, and on the other hand to guarantee that each phase has been completely pumped to its destination.
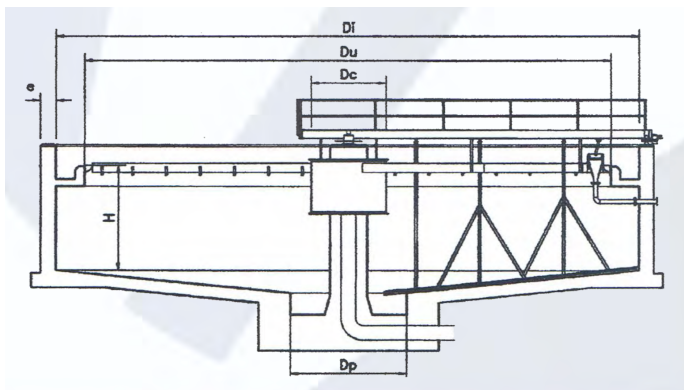
Figure 9: Decanter tank DCR-2400. The Hidrometalica Web [82]

5.4.5.   Liquid-liquid extraction

As mentioned above, after the glycolysis reaction an upper phase is obtained which cannot be used for the synthesis of new foams due to its high hydroxyl number. This high value is a consequence of having glycolysis agent residues in this phase causing the hydroxyl number to increase [25]. It is therefore necessary to remove all these unwanted products, or at least reduce the amount, to obtain a polyol capable of being used to synthesize new PUF foam. For this purpose, a liquid-liquid extraction is applied to the upper phase of glycolysis. It has been shown that the optimum conditions for this operation are [53]:

-   Acidified demineralized water with a pH between 4 and 5, since, at this pH, the -NH-groups corresponding to the amines and other by-products generated in the glycolysis reaction are protonated increasing their hydrophilicity and thus can be dragged into the water. A lower pH would cause an increase of polyol residues in the extract due to the increased solubility of the polyol in water.

-   The mass ratio between the solvent and the upper phase is 1:1 since a higher ratio would cause an increase in the volume of the equipment without significantly improving the extraction efficiency.

-   The extraction temperature of 90°C which is the maximum temperature that avoids excessive evaporation of the solvent.

Another important parameter is the number of stages necessary to obtain a refining with the right composition. It has been shown that from the third stage onwards, the composition of the refining is acceptable and adding stages would not substantially improve the composition *[53]*. The hydroxyl value of the upper phase before extraction is 257.1 mg KOH/g, and once 3 extraction stages are applied, the value drops to 84 mg KOH/g *[25]*.

After extraction, to facilitate the separation of water and recycled polyol, decantation is required. Initially it seems that applying some mechanical principle such as centrifugation or agitation would promote phase separation, but it was shown that applying these operations increased the operating costs but did not improve the separation process under the selected extraction conditions *[53]*.

Therefore, it has been considered that the best option for this extraction is to apply 3 extraction stages formed by the mixer-settler system due to the nature of the products to be separated. The selected extraction system is the Mixer-Settler (Figure 10) of the De Dietrich company *[83]*. Due to the importance of this stage, the manufacturer will be asked to design this purification system to obtain a recycled polyol with the best possible properties, complying with our operating conditions.

Figure 10: Glass-Lined Mixer-Settler. The De Dietrich Web

6. CONCLUSIONS

Through this work we have tried to visualize the current situation of PU recycling. It is a very valuable polymer and after its useful life it has the capacity to be recycled or reused. Little by little, it has been achieved that there is an industry in Europe capable of converting PU into its monomers. Currently in Spain, specifically in Catalonia, PUF foam waste from mattresses is sent to France.

It is great news that Repsol is going to build a recycling plant in our country, to treat part of waste stream from mattresses. This plant will be used to obtain a recycled polyol for the same company to synthesize new PUF foam. Perhaps if the plant is efficient, in a few years we can manage waste from other countries.

The design of these plants is mainly limited by the economy and by the fact of having to make an exhaustive selection of the waste to be treated, even so it has been considered that the best way to implement the chemical recycling of PUF would be to use the PU foam:

- Through the construction of a plant in an industrial park where the production of PUF foam is predominant. This plant would serve, initially, to treat PU production waste from these industries. The plant would be annexed to one of the PU producers so that once the polyol is obtained, that producer can market the recycled polyol. If this system works, this plant could also treat post-consumer waste.

- Another solution would be to build the process, but to treat very small volumes. If this process were cheap and efficient, perhaps it could be developed in all PUF plants so that, at least, they would be able to treat their own production wastes, and if they have a good waste screen, they could treat the post-consumer wastes of foams synthesized in that same plant. The split-phase glycolysis developed in this work would be a good solution for this case, since the two main components of PUF foam can be obtained from waste.

By means of split-phase glycolysis using crude glycerol as an agent, it is possible to obtain a polyol capable of reducing the costs of synthesis of new foams by making it possible to

replace a part of virgin polyol (up to 25 wt. % of recovered polyol). This process has not been developed at industrial level, but I hope that it will not take long time because it has been demonstrated in several investigations that it is a process that offers very good results and is versatile, since a large part of PU types can be recycled by this process.

Therefore, a plant has been designed to treat the PUF foam waste generated in the metropolitan area of Barcelona, for which the following equipment has been chosen:

- Reactor: the OPX BE 8,000 was chosen, with a capacity of 8,000L. To keep the reactor isothermal, the Pirobloc model GFT was installed as a thermal system.

- Storage tanks: 5 tanks and a silo have been selected; the one used for crude glycerol is STO model tank and has been selected with a capacity of 25,000 L; the same tank has been used to store the bottom phase; for the stannous octoate, the same model has been selected but with a capacity of 1,600 L; for the demineralized water and wastewater, a tank with a capacity of 16,000 L has been selected; to store the recovered polyol, a tank with a capacity of 12,500 L has been selected; For the demineralized water and wastewater, a tank with a capacity of 16,000 L has been selected; to store the recovered polyol, a tank with a capacity of 12,500 L has been selected; finally, the silo selected to store the PUF foam residues is the SCE610/11T45 with a capacity of 413,000 L.

- Pumps: 3 types of pumps have been selected; the gear pumps are the standard model CHEM 46.3-45-45; to drive the streams containing water, DIN-FOOD125-100-315 pump have been selected; finally, the TARQ-1100 model has been chosen as Archimedes screw pump.

- Extractor: The Glass-lined-Mixer-Settler extraction system from De Dietrich was selected.

- Decanter tank: The model DCR-2400 from Hidrometalica was selected.

Regarding the production plan, we know that 400 kg of waste are processed per batch. It has been decided to open 3 batches in one day, 365 days a year. This plan allows us to process 438 Tn/year of foam waste and produce 268 Tn/year of recovered polyol for the synthesis of new PUF foams. The total yield of the process is 99.5%.

For the practical application of any recycling method to be successful, it must be emphasized that the products resulting from these technologies must exhibit the unique

properties of PU. It is critical that future recycling of PU be considered during the product design phase of a new product, so it is more likely to be recycled at the end of its product life cycle. All these efforts to improve recycling technologies, together with the implementation of new design and collection concepts for these wastes, will undoubtedly lead to more PU recycling in the future.

REFERENCES AND NOTES

1. Yang, W., Dong, Q., Liu, S., Xie, H., Liu, L. & Li, J. (2012). Recycling and Disposal Methods for Polyurethane Foam Wastes. *Procedia Environ Sci,* 16, 167–175.

2. Magnin, A., Pollet, E., Phalip, V. & Avérous, L. (2020). Evaluation of biological degradation of polyurethanes. *Biotechnol. Adv.*, *39*, 107457.

3. Gama, N., Ferreira, A. & Barros-Timmons, A. (2018). Polyurethane Foams: Past, Present, and Future. *Materials* (Basel) 11,1841.

4. Akindoyo, J.O., Beg, M.D.H., Ghazali, S., Islam, M.R., Jeyaratnam, N. & Yuvaraj, A.R. (2016). Polyurethane types, synthesis, and applications-a review. *RSC Adv.,* 6,114453–114482.

5. ISOPA, 2015. The end.of-life of flexible foam from matresess and furniture. https://www.isopa.org/media/2763/flexible-foam-end-of-life-solutions.pdf (Accesed 27 Sep,2021)

6. Zia, K.M., Bhatti, H.N. & Bhatti, I.A. (2007). Methods for polyurethane and polyurethane composites, recycling, and recovery: *A review. React. Funct. Polym.,* 67, 675–692.

7. ISOPA (2001) Recycling and Recovering Polyurethanes: Regrinding. https://www.isopa.org/media/2617/reuse-and-reprocessing.pdf (Accesed Apr 30 ,2021)

8. ISOPA (2001) Recycling and Recovering Polyurethanes: Rebonded Flexible Foam. https://www.isopa.org/media/2606/flexible-rebonded-foam.pdf (Accesed Apr 30 ,2021)

9. ISOPA (2021). The end.of-life of flexible foam from matresess and furniture https://www.isopa.org/media/2763/EoL_Brochure_2021_EUROPUR.pdf (Accesed 2 Dec, 2021)

10. Kiss, G., Rusu, G., Peter, F., Tǎnase, I. & Bandur, G. (2020). Recovery of Flexible Polyurethane Foam Waste for Efficient Reuse in Industrial Formulations. *Polymers*, *12*, 1533.

11. Trzebiatowska, P.J., Beneš, H. & Datta, J. (2019). Evaluation of the glycerolysis process and valorisation of recovered polyol in polyurethane synthesis. *React. Funct. Polym. 133*, 119–130.

12. Molero, C., De Lucas, A. & Rodríguez, J.F. (2006). Recovery of polyols from flexible polyurethane foam by "split-phase" glycolysis: Glycol influence. *Polym Degrad Stabil* 91, (2), 221-228

13. Campbell, G.A. & Meluch, W.C. (1976) Polyurethane foam recycling -superheated steam Hydrolysis. *Environ. Sci.Tech* 10(2) ,1976,182-185.

14. Kanchanapiya, P.; Intaranon, N.; Tantisattayakul, T. (2021) Assessment of the economic recycling potential of a glycolysis treatment of rigid polyurethane foam waste: A case study from Thailand. *J. Environ. Manag. 280*, 111638.

15. Font, R., Fullana, A., Caballero, J., Candela, J. & Garciá, A. (2001). Pyrolysis study of polyurethane. J. *Anal. Appl. Pyrolysis* 58–59, 63–77.

16. Jomaa, G., Goblet, P., Coquelet, C. & Morlot, V. (2015). Kinetic modeling of polyurethane pyrolysis using non- isothermal thermogravimetric analysis. *Thermochim*. 612, 10–18.

17. Guo, X., Zhang, W., Wang, L. & Hao, J. (2016). Comparative study of nitrogen migration among the products from catalytic pyrolysis and gasification of waste rigid polyurethane foam. *J. Anal. Appl. Pyrolysis*, 120, 144–153.

18. Kemona, A. & Piotrowska, M. (2020). Polyurethane Recycling and Disposal: Methods and Prospects. *Polymers* (Basel) 12,1752.

19. Borda, J., Pasztor, G. & Zsuga, M. (2000). Glycolysis of polyurethane foams and elastomers*. Polym Degrad Stabil* 68 (3),419-423

20. Dos Santos, L.M., Carone, C.L.P., Dullius, J., Ligabue, R. & Einloft. (2014). Using different catalysts in the chemical recycling of waste from flexible polyurethane foams. *Polimeros* 23 (5),608-613.

21. Beneš, H., Rösner, J., Holler, P., Synková, H., Kotek, J. & Horák, Z. (2007). Glycolysis of flexible polyurethane foam in recycling of car seats. *Polym Adv Technol* 18,149–156.
22. Datta, J. & Rohn, M. (2007). Thermal properties of polyurethanes synthesized using waste polyurethane foam glycolysates. *J Therm Anal Calorim* 88,437–440.
23. Simón, D., Borreguero, A.M., De Lucas, A. & Rodríguez, J.F. (2015) Valorization of crude glycerol as a novel transesterification agent in the glycolysis of polyurethane foam waste. *Polym Degrad Stab* 121,126–136.
24. Simón, D., De Lucas, A., Rodríguez, J.F. & Borreguero, A.M. (2016). Glycolysis of high resilience flexible polyurethane foams containing polyurethane dispersion polyol. *Polym Degrad Stab* 133,119–130.
25. Simon, D., Borreguero, A.M., de Lucas, A. & Rodríguez, J.F. (2015). Glycolysis of visco- elastic flexible polyurethane foam wastes, Polym. *Degrad. Stabil.* 116, 23-35.
26. Simón, D., García, M.T., De Lucas, A., Borreguero, A.M. & Rodríguez, J.F. (2013). Glycolysis of flexible polyurethane wastes using stannous octoate as the catalyst: Study on the influence of reaction paràmetres. *Polym Degred Stabil 98* ,2013:144-149.
27. Morcillo-Bolaños, Y.D., Malule-Herrera, W.J., Ortiz-Arango, J.C. & Villa-Holguín, A.L. (2018). Polyurethane flexible foam recycling via glycolysis using Zn/Sn/Al hydrotalcites as heterogeneous catalyst. *Rev Fac Ing Univ Antioquia,* 77–85.
28. Simón, D., Borreguero, A.M., De Lucas, A., Molero, C. & Rodríguez, J.F. (2014). Novel polyol initiator from polyurethane recycling residue. *J Mater Cycles Waste Manag* 16,525–532.
29. Borda, J., Rácz, A. & Zsuga, M. (2002). Recycled polyurethane elastomers: a universal adhesive. J. Adhes. Sci. *Technol.* 16, (9), 1225–1234.
30. Wang, X., Chen, H., Chen, C. & Li, H. (2011). Chemical degradation of thermoplastic polyurethane for recycling polyether polyol. *Fiber Polym.* 12, (7), 857–863.
31. Datta, J. & Haponiuk, J.T. (2008). Advanced coating of interior of tanks for rising environmental safety - novel applications of polyurethanes. *Polish Maritime Research*,15(Special), 8-13.
32. Simioni, F., Bisello, S. & Tavan, M. (1983). Polyol recovery from rigid polyurethane waste. Cell. *Polym.* 2, (4), 281–293.
33. Xue, S., He, F., Omoto, M., Hidai, T. & Imai, Y. (1993). General purpose adhesives prepared from chemically decomposed waste rigid polyurethane foams. *Kobunshi Ronbunshu 50,* (11), 847–853.
34. Morooka, H., Nakakawaji, T., Okamoto, S., Araki, K. & Yamada, E. (2005). Chemical recycling of rigid polyurethane foam for refrigerators. *Polym. Prepr*. 54, (1), 1951.
35. Zhu, P., Cao, Z.B., Chen, Y., Zhang, X.J., Qian, G.R., Chu, Y.L. & Zhou, M. (2014). Glycolysis recycling of rigid waste polyurethane foam from refrigerators. *Environ. Techno*l. 35, (21), 2676–2684.
36. Modesti, M., Simioni, F., Munari, R. & Baldoin, N. (1995). Recycling of flexible polyurethane foams with a low aromatic amine content. *React. Funct. Polym*.26, 157–165.
37. Behrendt, G. & Naber, B.W. (2009). The recycling of polyurethanes (review). *J. Univ. Chem. Technol. Metall.* 44, (1), 3–23.
38. U.S. Patent No. 6,750,260. Process for Chemical Recycling of Polyurethane- containing scrap.
39. Troy Polymers,   http://www.troypolymers.com   (Accesed 12 Dec, 2021)
40. Zevenhoven, R. (2004). Treatment and Disposal of Polyurethane Wastes: Options for Recovery and Recycling. *Energy Engineering and Environmental Protection Publications, Espoo*. Report TKK-ENY-19.
41. Rampf. Layman's report LIFE ENV/D/000398 ''Large scale polyurethane recycling''.
42. H&S   Anlagentechnik,   https://docplayer.net/21139391-Your-specialist-for-pur-recycling-blending-storing.html (Accessed 19 Sep, 2021)
43. "Boletin Oficial del Estado" Nº95, 19 April 2018.
44. "Directiva 2008/98/CE del Parlamento Europeo y del Consejo"19 November 2008.
45. "Ministerio para la transición ecológica y el reto demográfico". https://www.miteco.gob.es/es/calidad-y-evaluacion-ambiental/temas/prevencion-y-gestion-residuos/flujos/
46. "Ley 22/2011 sobre residuos y suelos contaminados" ,28 July 2011.

47. "Real Decreto 1481/2001", 27 December 2001.

48. Repsol, New plant in Spain.https://www.repsol.com/es/productos-y-servicios/quimica/quimica-news/repsol-construira-puertollano-primera-planta-reciclado-poliuretano-espana/index.cshtml (Accesed 2 Jun ,2021)

49. Wu, C.H., Chang, C.Y., Cheng, C.M. & Huang, H.C. (2003). Glycolysis of waste flexible polyurethane foam. *Polym Degrad Stab* 80,103–111.

50. Datta, J. & Rohn, M. (2007). Thermal properties of polyurethanes synthesized using waste polyurethane foam glycolysates. *J Therm Anal Calorim* 88,437–440.

51. Simón, D., De Lucas, A., Rodríguez, J.F. & Borreguero, A.M. (2017). Flexible polyurethane foams synthesized employing recovered polyols from glycolysis: Physical and structural properties. J *Appl Polym Sci* 134,45087.

52. Tan, H.W., Abdul Aziz, A.R. & Aroua, M.K., (2013). Glycerol production and its applications as a raw material: a review. *Renew. Sustain. Energy Rev.* 27, 118–127.

53. Molero, C., De Lucas, A. & Rodríguez, J.F. (2006). Purification by liquid extraction of recovered polyols. *Solv Extr and Ion Exch* 24(5),719-730.

54. Simón, D., Rodríguez, J.F., Carmona, M., Serrano, A. & Borreguero, A.M. (2018). Glycolysis of advanced polyurethanes composites containing thermoregulating microcapsules. *Chem Eng J* 350,300–3.

55. Molero, C., De Lucas, A. & Rodríguez, J.F. (2006). Recovery of polyols from flexible polyurethane foam by "split- phase" glycolysis with new catalysts. *Polym Degrad Stab* 91,894–901.

56. Molero, C., De Lucas, A. & Rodríguez, J.F. (2009). Activities of octoate salts as novel catalysts for the transesterification of flexible polyurethane foams with diethylene glycol. *Polym Degrad Stab* 94,533-539.

57. Modesti, M. & Simioni, F. (1996). Chemical recycling of reinforced polyurethane from the automotive industry. *Polym Eng Sci;*36(17), 21738.

58. Celmus S.L., https://celmus.cat/es/ (Accesed 3 Dec 2021)

59. Nikje, M.M.A., Bagheri Garmarudi, A. & Idris, A.B. (2011). Polyurethane waste reduction and recycling: from bench to pilot scales. *Des Monomers Polym*; 14 (5),395421.

60. Ecomotion. https://www.ecomotion.de/eco/startseite/ (Accesed 30 Apr 2021)

61. Todini Quimica Iberica S.L.https://www.todini.com/es (Accesed 4 Dec 2021)

62. Tpmultiaqua,https://tpmultiaqua.com (Accesed 5 Dec ,2021)

63. Isikgor, F.H. & Becer, C.R., (2015). "Lignocellulosic Biomass: A Sustainable Platform for the Production of Bio-Based Chemicals and Polymers." *Polym. Chem*., 6 (25) 4497– 4559.

64. Ayoub, M. & Abdullah, A.Z. (2012). Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry, *Renew. Sustain. Energy Rev.* 16, 2671-2686.

65. Anitha, M., Kamarudin, S.K. & Kofli, N.T. (2016). The potential of glycerol as a value-added commodity, *Chem. Eng. J.* 295, 119–130.

66. WWTP Abrera.https://www.dam-aguas.es/portfolio-posts/edar-abrera/ (Accesed 3 Dec 2021)

67. Simon, D., (2017). Glycolysis Process for Polyurethane Waste Recycling.

68. De Dietrich, Products Portfolio Glass-lined Technology& Other Materials, http://modchem.com/wp-content/uploads/2019/06/DeDietrich-Glass-Lined-Technology.pdf (Accesed 3 Jun 2021)

69. Symaga, Storage silo. https://symaga.com/wp-content/uploads/2016/03/ficha-tecnica-silos-symaga.pdf (Accesed 2 June 2021)

70. Safety data sheet, mattresses, https://www.europur.org/images/MIDS_Flexible_Polyurethane_Foam_-_January_2020_-_Spanish.pdf (Accesed 5 Dec 2021)

71. Safety data sheet, crude glycerol https://www.regi.com/docs/default-source/sds-distribution/sds-200-us.pdf?sfvrsn=170aaac5_8 (Accesed 5 Dec 2021)

72. Safety data sheet, stannous octoate. https://www.alkanos.com.ar/wp-content/uploads/2019/09/49.-OCTOATO-DE-ESTAÑO.pdf (Accesed 5 Dec 2021)

73. Air Liquide, liquid nitrogen https://es.airliquide.com. (Accesed 10 Dec 2021)
74. Preparation and handling of amines   ,
    https://www.iquimica.unam.mx/images/iqseguro/007_Preparacion_y_manejo_de_aminas.pdf.
    (Accesed 10 Dec 2021)
75. Safety data sheet, polyol r3600 https://www.perstorp.com/en/products/polyol_r3600 (Accesed 3 Dec
    2021)
76. Witte Pumps and Technology, Gear pumps,
    https://www.wittepumps.com/fileadmin/photos/PDF/EN/Broschueren/WITTE_PB_CHEMIE_24Seite_E
    N_rev002_102019_low.pdf. (Accesed June 1, 2021)
77. Inoxpa centrifugal pumps, https://www.inoxpa.com/uploads/document/Fitxa%20tecnica/Components/
    Bombes/DIN%20FOOD/FT.DIN-FOOD.2_ES.pdf (Accesed June 2,2021)
78. Hidrometalica, Archimedes screw, https://www.hidrometalica.com/tornillo-arquimedes/ (Accesed June
    2,2021)
79. Pirobloc, "Sistema de aceite térmico",https://www.pirobloc.com/wp-content/uploads/2021/02/ficha-
    técnica-calderas-de-fluido-termico-ES.pdf , (Accesed 12 Dec ,2021)
80. Del Amo, J., Borreguero, A.M., Ramos, M.J. & Rodríguez, J.F. (2021) Glycolysis of Polyurethanes
    Composites Containing Nanosilica. *Polymers (Basel)*;13(9),1418.
81. Wang, Jingrong & Chen, Dajun. (2006). Studies on the Glycolysis Behavior of Polyurethane Fiber
    Waste with Diethylene Glycol. *J Polym Environ*. 14,191-194.
82. Hidrometalica, Decanter tank, https://docplayer.es/76462722-Decantador-por-gravedad.html.(Accesed
    2 June 2021)
83. De Dietrich, mixer-settlers,   https://www.dedietrich.com/en/solutions-and-products/extraction/liquid
    /liquid-extraction/mixer-settlers (Accesed 3 June 2021)

ACRONYMS

PU: Polyurethane

DEG: Di ethylene glycol

PUF: Polyurethane flexible foam

EoL: End-of-Life

TDI: Toluene diisocyanate

MDI: 4,4'-diphenylmethane diisocyanate

HR: High resilience

PUR: Polyurethane rigid foam

CASE: Coatings, Adhesives, Sealants, and Elastomeric applications

BDO: Butanediol

RIM: Reaction injection molding

RRIM: Reaction reinforced injection molding

CO_2: Carbon dioxide

MEA: Monoethanolamine

DEA: Diethanolamine

EG: Ethylene glycol

PMDI: Polymeric methylene diphenyl isocyanate

DPG: Dipropylene glycol

PG: Propylene glycol

HDO: 1,6-Hexanediol

KAc: Potassium acetate

BaO: Barium oxide

$Ti(OBu)_4$: Titanium n-butoxide

TEA: Triethanol amine

TEG: Triethylene glycol

PEG: Poly (ethylene glycol)

EA: Ethanolamine

GP: 1,5-Pentanediol

MEG: Mono ethylene glycol

APPENDICES

APPENDIX 1: DATASHEET

APPENDIX 1: Table 1: Technical datasheet for Silo SCE610/11T45, The Symaga web

CÓDIGO	A (mm)	B (mm)	D (mm)	C (mm)	CAPACIDAD (m³)
SCE610/11T45	6,100	12,580	2,940	18,110	413

APPENDIX 1: Table 2: Technical datasheet for Pump Din-Food 125-100-315. The Inoxpa web

Bomba	DNa	DNi	d	l	a	f	h_1	h_2	b	m_1	m_2	n_1	n_2	n_3	s_1	s_2	w
125-100-250	125	100	42	110	121	522	250	316	90	160	120	440	350	110	18	14	363
125-100-315						510	280	352				490	400				350
125-100-400					130		330	402	100	200	150	550	450		23		

Caudal máximo   *1000 m³/h*
Altura diferencial máx.   *90 mcl*
Presión máxima trabajo   *10 bar*
Tª máx. trabajo   *-10 ºC a +120 ºC (EPDM)*
                                    +140 ºC (SIP, máx. 30 min)
Velocidad máxima   *1750 rpm*

APPENDIX 1:Table 3: Technical datasheet for Standard Chem Gear Pump 46,3-45-45. Witte Pumps and Technology web

PUMP SIZE	A	B	C	D	E0	F0	G	H	I	J	K	K1	L	L1	M	WEIGHT
CHEM 46,3-45-45	234	244	176	134	60,3	24	25	75	170	14	148	186	228	265	13,5	26 kg

VISCOSITY
20 to 500 mPa s
TEMPERATURE
300°C
SUCTION PRESSURE
1 to 15 bar a
DIFFERENTIAL PRESSURE
16 bar
PUMP SIZES
10.2-25-32 (pumped amount: 0.15 to 36 l/min)

APPENDIX 1:TABLE 6: Technical datasheet for Decanter Tank DCR-2400, the Hidrometalica web

MODELO	Di	e	Du	Dc	Dp	H	Qm	Su	V
DCR-2400	24	0.35	23.10	2.30	4	2.60	587	419	1176.22

APPENDIX 1: Table 4: Technical data sheet for Tank STO, the De Dietrich web

Nominal capacity (litres)		1600	12500	16000	25000
Total capacity (litres)		1680	12650	16300	25600
Design pressure				)ar	
Main dimensions	d	1200	2000	2200	2600
	h	1700	4400	4700	5300
	d1	500	600	600	600
	a	1070	1780	2025	2375
	b	200	300	220	260
	e	800	3000	3400	3800
	f	450	700	650	750
	m	700	900	1050	1150
	h1	850	1250	1350	1550
	h2	1720	2520	2720	3120
	h3	250	270	270	270
	h4	90	100	100	100
	h5	500	600	600	600
	h6	2560	5370	5670	6270
Nozzles on cover	A	50	80	80	80
	B	80	100	100	100
	C	50	80	80	80
	D	100	150	150	150
Outlet nozzle	L	80	100	100	100
Weight approx. (DaN) without saddles or legs		660	2980	3580	5920

Design pressure	Design temperature
+3 bar	-25/+200 °C

APPENDIX 1:Table 5: Technical data sheet for Reactor OPX BE 8000. The De Dietrich Web

			OPX BE 8000
Nominal capacity		Litres	8000
Total capacity		Litres	9353
Half Coil capacity		Litres	322
Heating area (with half coil)		m²	16,4
Approx. weight without motor and supporting		daN	8600
Main dimensions		d1	2200
		d2	2300
		d5	850
		h1	3000
		h2	130
		h3	85
		hR	520
		f	180
Support System	Support ring	d7	2710
		h5 min.	475
		h6 min.	145
Nozzles on Vessel	M	DN	200
	L		150
	N1	DN/h13 R/β	600 / 150 800 / 30°
	N2	DN / h13 R / α	150 / 480 840 / 50°
	N3		150 / 480 840 / 77,5°
	N4		150 / 480 840 / 110°
	N5		300 / 530 800 / 145°
	N6		150 / 480 840 / 180°
	N7		300 / 530 800 / 215°
	N8		150 / 480 840 / 250°
	N9		150 / 480 840 / 282,5°
	N10		150 / 480 840 / 310°
Half Coil Nozzles	N12	DN / α	50 / 180°
	N11		50 / 225°
	N13		50 / 225°
	N14		50 / 225°
Drive		MDL Type	100
		h*	2200

	Design pressure	Design temperature
Inside	-1/+6 bar	-25/+200° C
Jacket	-1/+6 bar	-25/+200° C
Half Coil	-1/+30 bar	-25/+235° C