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## **Crude Glycerol Valorization**

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Thesis to obtain the Master Degree in

### **Petroleum Engineering**

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**October 2019**

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Declaro que o presente documento é um trabalho original da minha autoria e que cumpre todos os requisitos do Código de Conduta e Boas Práticas da Universidade de Lisboa.

#### Declaration

I hereby declare that the present document is an original work of my authorship and that it meets all the Code of Conduct and Good Practice requirements of the University of Lisbon.

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## Abstract

The objective of this thesis was to valorize the crude glycerol. This was achieved focusing on the monoglyceride to create a new resin. To produce this resin a two-step process was developed. The first step consisted on reacting the monoglyceride (result of the reaction between waste cooking oil and crude glycerol) with Unidyme18, obtaining a high molecular weight polyester. The reaction was monitored by determining the acid value of the product. The second step focused on the production of the non-petroleum-based resin achieved by breaking the terminal C-OH bonds of the polyester by adding toluene diisocyanate and liquefied biomass.

After adding the biomass, the monoglyceride was also added to the polyester resulting in an apparent decrease of viscosity. With the resin produced, it was possible to develop different formulations of particleboards, composed by two layers: one internal and another external. To produce these particleboards, it was used pine wood. From all the formulations developed, only the ones containing polymeric methylene diphenyl diisocyanate were select to be tested in an industrial facility.

Although the secondary intention was to obtain a new fuel or fuel additive at the end, the primary objective of adding new value to the crude glycerol was achieved, with a process that uses by-products with low commercial value, creating a product with considerable potential.

**Keywords:** Crude Glycerol, Waste Cooking Oil, Resin, Monoglyceride, Particleboards

## Resumo

O objetivo deste trabalho era a valorização do glicerol crude. Este foi alcançado utilizando monoglicérido para criar uma nova resina. Para produzir esta resina foi desenvolvido um processo de duas etapas. O primeiro passo consistiu na reação do monoglicérido (produzido com óleo de cozinha usado e glicerol crude) com o Unidyme18, obtendo-se um poliéster de alto peso molecular. A reação foi monitorizada através da determinação do valor ácido do produto. O segundo passo focado na produção da resina que não é à base de petróleo foi alcançado quebrando as ligações C-OH terminais do poliéster adicionando o diisocianato de tolueno e biomassa liquefeita.

Depois de adicionar a biomassa, o monoglicérido também foi adicionado ao poliéster, resultando numa diminuição da viscosidade aparente. Com a produção desta resina, foi possível desenvolver diferentes formulações de aglomerados. Estes painéis eram compostos por duas camadas: uma interna e outra externa. Na sua produção, foi utilizada madeira de pinho. De todas as formulações desenvolvidas, apenas as que continham metileno difenil diisocianato polimérico foram selecionadas para serem testadas numa indústria.

Apesar do objetivo secundário ser obter um novo combustível ou aditivo, o objetivo principal de dar novo valor ao glicerol crude, com um processo que utiliza subprodutos de baixo valor comercial, foi alcançado, criando um produto com elevado potencial.

**Palavras-Chave:** Glicerol Crude; Óleo de cozinha usado, Resina, Monoglicérido, Aglomerados

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## Abbreviation Index

ATR – Attenuated Total Reflection  
DA – Dimer Acids  
DG – Diglyceride  
DTG – Derivative of Thermogravimetric curve  
FAME – Fatty Acid Methyl Ester  
FFA – Free Fatty Acids  
FTIR – Fourier Transform Infrared  
G – Glycerol  
GPC – Gel Permeation Chromatography  
KF – Karl Fischer  
MG – Monoglyceride  
MMT – Montmorillonite  
PHA – Polyhydroxyalkanoates  
PMDI - Polymeric Methylene Diphenyl Diisocyanate  
TDI – Toluene Diisocyanate  
TG – Triglyceride  
TGA – Thermogravimetric Analysis  
U18 – Unidyme18  
WCO – Waste Cooking Oil

## Chapter 1 – Introduction

The dilemma food versus fuel (raw materials being seeds, grains and sugars) remains unclear and unresolved, even nowadays. The use of agricultural, commercial, industrial and/or domestic waste (with biological nature) as raw materials can, however, minimize this concern. The primary source of energy that can provide large quantity of energy is still from burning fossil fuels and coal, but their usage comes with great consequences, like the release of greenhouse gases to the atmosphere. The accumulation of these gases presents danger for all mankind, leading to urgent changes in national policies worldwide.

We live in an era “ruled” by fossil fuels, it defines our economies and our society. We can see it in almost every item used nowadays. Its primary function is to be converted into fuel, gasoline for cars, jets and to generate heat and electricity, but it’s also used to produce items essential for our lives, such as, plastic, medicines, materials for electronic devices, etc. Our society is settled on fossil dependency and without considerable changes there will be a depletion of its reserves.

More and more countries are currently investing time and money in research of new alternative energy sources that will allow the decrease of the volume of fossil fuels that goes into the energy sector.

Renewable energy sources are clean and inexhaustible, they differ from fossil fuels in their diversity, abundance and in the fact that they can provide energy with zero or almost zero emissions of air pollutants and/or greenhouse gases. The continuous development of different renewable energy systems will resolve problems like, local energy and water supply, low living standards, ensuring sustainable development of remote regions and many others. Renewable energy sources show great potential, but also some problems like seasonal variations dependency (solar, wind). For this case the solution is careful planning and further studies, developing more complex structures, optimized methods resulting in better and cleaner technology.

However, there is something that over the years is continuously growing, the produced waste. This is a consequence of mankind existence, where its presence implicates the production of waste. With the growth of population, larger cities were built, and with technologic advances new materials are created every day, replacing older ones and all of this generates large amounts of waste. Normally when dealing with waste disposal, the cheaper route selected to deal with it, is usually incineration and send it to a landfill. This is a very “short” vision approach which represents the state of the economy, and their simple and linear model of “take, make and dispose”. But this policy is not compatible with the vision of a healthier and sustainable future, meaning that we don’t have a circular economy.

Circular Economy, Figure 1, is a regenerative system that is based on the valorisation of end life products focusing on the principles of reuse, repair and recycling.

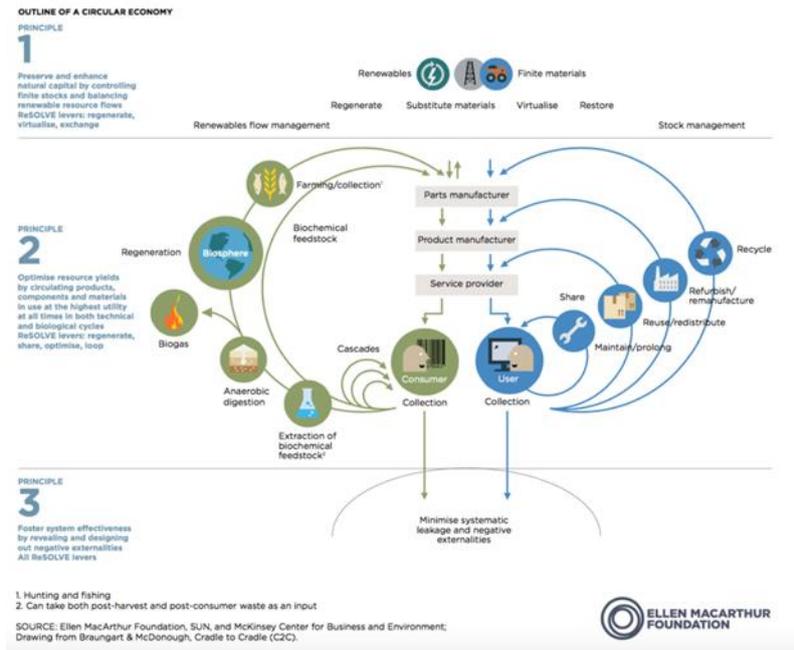


Figure 1 - Circular economy scheme [1]

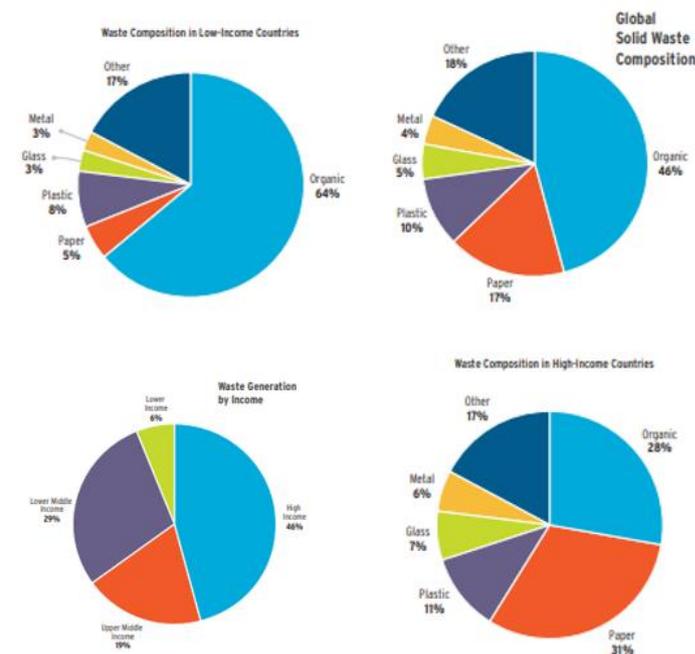


Figure 2 - Waste distribution and composition of different countries [2]

The classification of a waste (hazardous or non-hazardous) is essential and will determine the best route and its destination in order to protect our environment and ourselves. As humanity evolved, the type of waste and its complexity also evolved. While in the past the predominant waste was organic, nowadays there is an increase of metal waste and more complex wastes such

as plastic, electrical, paper, industrial and so on. Even so, organic waste remains the predominant type and the most generated by developed countries, as shown in figures 2 and 3.

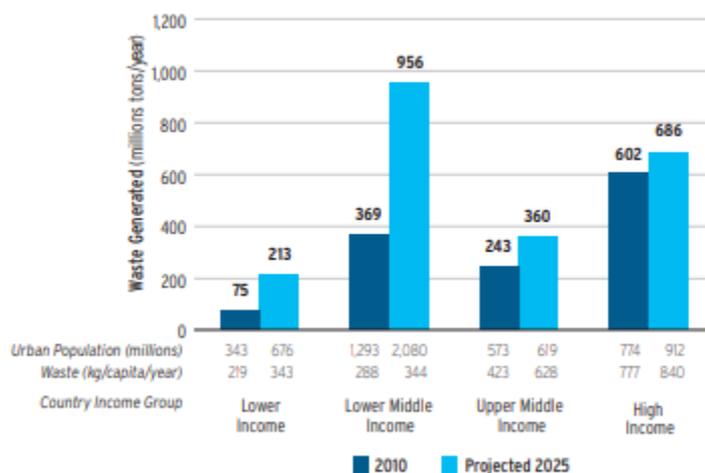


Figure 3 - Amount of waste produced by income [2].

Waste cooking oil (WCO) is a domestic waste produced all over the world. Legislation<sup>1</sup> doesn't allow to simply dispose it directly into the sewer, making its collection by specified companies a requirement for destroying it properly. This type of domestic waste has been nowadays used as raw material in biodiesel production. However, industrial processes need new oils for the process to succeed, making it a problem for the food vs fuel dilemma.

To solve this problem, this work was based on the change in the initial feedstock, changing it to WCO with the crude glycerol, allowing to obtain a commercial product from low value materials.

The resulting compound of the reaction of the WCO with the crude glycerol was a monoglyceride (MG). This compound has a lot of applications mainly as a surfactant [3], in food-processing industry for the stabilization of both water-in-oil (e.g., margarine) and oil-in-water (e.g., artificial cream) [4], and to enzymatic digestion of lipids in human milk disrupt enveloped viruses [5].

The MG prepared showed to be an added-value material several applications, as it will be presented in further chapters. MG was included in the production of the polyester as one of the reactants; in the production of the non-based petroleum resin as one of the three components, resulting in the reduction of the resin viscosity; and in the preparation of the resin for the production of the particleboards, in order to reduce the resin viscosity. In the production of the polyester both MG and a dimer acid (Unydime18) are used. The purpose of using the dimer acid

<sup>1</sup> The collection and disposal of waste oils in the European Union is regulated by Regulation (EC) No 1013/2006 of the European Parliament and of the Council of 14 June 2006 on shipments of waste and Council Directive 1975/439/EEC of 16 June 1975 on the disposal of waste oils (75/439/EEC).

is to allow its reaction with the MG terminal OH bonds breaking them and allowing the formation of new high carbon chain compound, essential for the resin.

## 1.1. Objective

The objective of this thesis was to develop a process for the valorisation of crude glycerol (by-product of the biodiesel production). Initially the intention was to convert this by-product into a fuel or a fuel additive. However, due to several limitations such as legislations for new fuels, there were three aspects that needed to be addressed before this transformation. These aspects pointed by biodiesel industries were:

- Developing a process with only waste cooking oil (WCO) in the feedstock to modify their biodiesel production line, eradicating problems due to the food vs fuel dilemma;
- Valorisation of the crude glycerol, empowering it to achieve new markets, increasing its market price;
- Applying all developed processes in the line without major changes.

These three guidelines were transformed into this thesis objectives.

## 1.2. Outline of thesis

In the second, third and fourth chapters a review is made to present the glycerol, dimer acid and WCO. Each of these chapters start with a little introduction to the component, followed by a few examples of studies already made regarding them. The fifth chapter is about the experimental methods (reactions) developed. In this chapter all the reactions are fully described, which equipments were used in different reactions, how much material was used and also what were the operation parameters of the reactors. In this chapter it is mentioned the formulation used to produce the particleboards.

The sixth chapter is a brief introduction to the experimental methods applied to do an elementary analysis to the compounds used, such as the methods employed to analyse the resulting products of each reaction. In this chapter it also mentioned how the tests to the particleboards were performed such as the description of all the apparatus used during the course of this thesis.

In the seventh chapter, the results are presented, followed by their discussion. The results are presented in order of the method used. In the last chapter, chapter eight, the final conclusions and overall comments of the work done accompanied by an global outlook on the possible future research and work that can still be done around this project.

## Chapter 2 – WCO (Waste Cooking Oil)

WCO can be considered a non-edible waste due to the chemical reactions that occur during the frying process so it must be destroyed. Its estimated to be produced worldwide around 29 million tons per year [6].

It can be very challenging to analyse the WCO, most of the cases the origin can be considered unknow due to fact that it is a complex and heterogeneous waste and not a single type of oil but often a mixture of two or more oils. Another aspect of the WCO is the different type of residue present, consequence on the type of food that was cooked in it. The frying process of the food certainly leaves some residues inside the oil and with the reutilization of the oil, those residues can also be decomposed.

Currently the most used method to deal with this waste is by an incineration process (Figure 4). The incineration facilities can be equipped with turbines that can use the steam form from the destruction of this waste to generate energy in the form of electricity. Although this can be considered a valid route, the waste introduced is getting destroyed rather than being reused (principle of circular economy). [7]

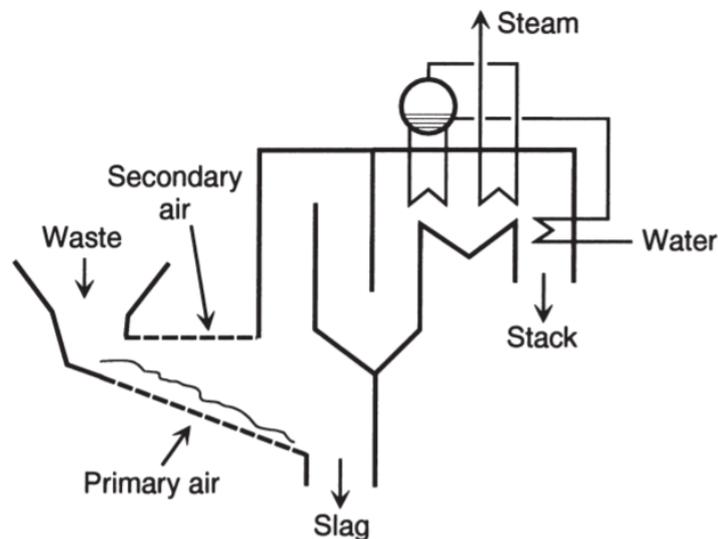


Figure 4 - Simplified solid waste incinerator schematic [7]

There have been several studies devoted to the reutilization of the WCO converting into a new product with commercial value, eliminating the cost of disposal. Although almost 90% of Europe WCO is used to produce biodiesel, it generates low conversion yields due to the high

concentration of free fatty acids (FFA), representing major drawbacks in its reutilization as a raw material.

## 2.1. Production of materials from waste oils

### 2.1.1. Bioplastics

An alternative for plastic has been the topic of several studies. Recently polyhydroxyalkanoates (PHAs) (Figure 5) have drawn attention as an alternative for non-degradable plastic with the potential to form a biodegradable and biocompatible alternative.

In the work of Pezzella and co-authors, the conversion of the FFA present in the WCO was studied by a microbial fermentation process to PHA biopolymer. An *Escherichia coli* strain was produced exclusively to convert FFA into PHA.

A pre-treatment was required to reduce the content of non-lipid carbon sources that prevent the FFA microbial conversion. In the end a WCO with half of the FFA content was retrieved that could be used in the biodiesel production generating more yields. The yield of this conversion to PHA was quite low, suggesting the study of more strains to improve it. [8]

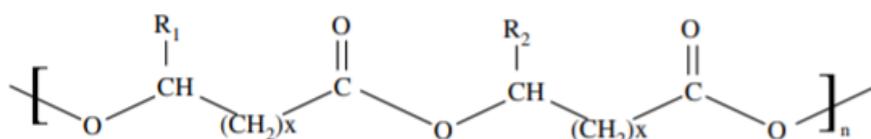


Figure 5 - Structure of PHA [8]

### 2.1.2. Biolubricant

A two-step process was created, capable of converting WCO into a biolubricant using *C. rugosa* lipase-mediated hydrolysis to generate FFA from the WCO followed by Amberlyst 15H esterification of FFA with octanol, producing octyl ester that will be the bio lubricant.

The maximum yield of lubricant was produced with the following operation conditions: FFA molar ratio = 3:1, at 80°C, 2 g of catalyst and a desiccant (preferably silica gel powder) of 50% weight of FFA. The conversion to ester was confirmed via FTIR spectroscopy [9].

### 2.1.3. Soaps

In 1988, Shimizu K. was able to convert WCO into liquid soap. To achieve this he used an amine derivative (alkanol amine) with an alkyl amine and an alkylene amine in conjunction with a surface-active agent. To produce the alkanol amine soap, a saponification was done to the fatty acids of the WCO at high temperature over a long period of time. The resulting substance was controlled by measuring the pH level and composition. The resulting liquid soap can be diluted with water to be employed for laundry use, house cleaning, polishing and others [10].

#### 2.1.4. Biodiesel

Biodiesel can be made from any fat or vegetable oil by transesterification. In this process glycerol is removed from the fat or oil. Either primary (i.e. straight or virgin) oils or secondary (used) oils can be used with no discernible difference in the product. Biodiesel is also known as FAME (fatty-acid methyl ester). Figure 6 shows the process of converting WCO into biodiesel fuel.

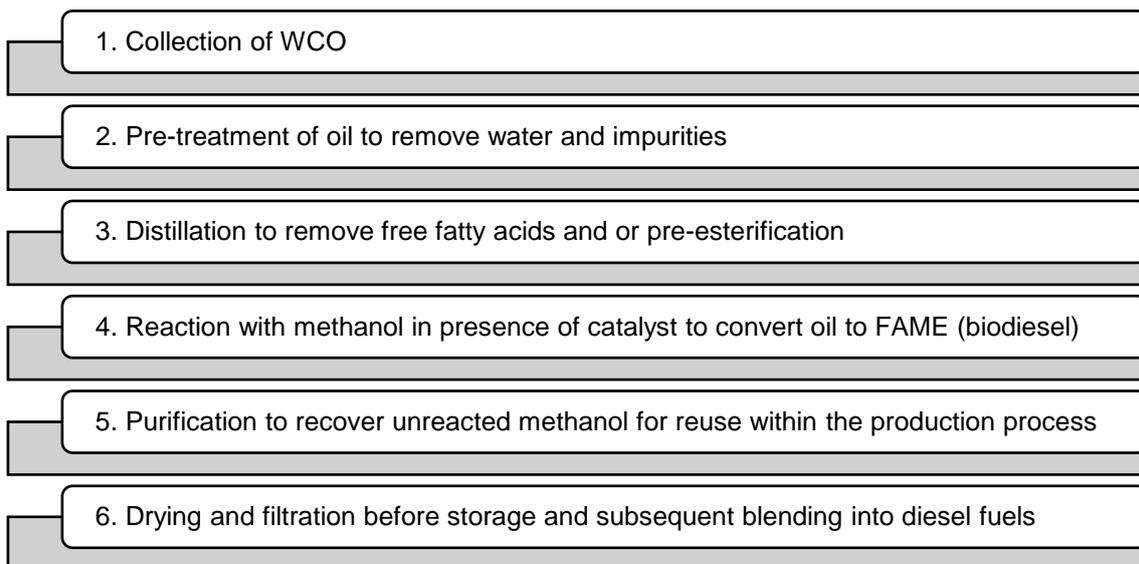


Figure 6 - Conversion of WCO into Biodiesel [11]

The use of fatty waste materials to produce biodiesel will promote a higher cetane number fuel than the one produce from vegetable-based oils, getting cleaner energy and more efficient combustion in diesel engines. Fats are more prone to congealing at lower temperature, due to high levels of saturates, making them more suitable for generating fuels than for example cars or planes, and for other situations [11].

## Chapter 3 - Glycerol

Glycerol (Figure 7) is a simple polyol compound. It is a colourless, odourless, viscous liquid that is sweet-tasting and non-toxic. It was discovered in 1779 when a Swedish chemist was doing an experiment with olive oil with alkaline material. In 1823 another chemist discovers that glycerol was formed by the saponification of oil. The biggest discover related with glycerol was when Alfred Nobel in 1866 discovered dynamite, making glycerol a very important compound for industry [12].

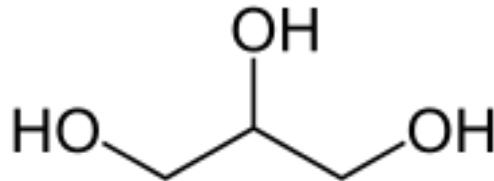


Figure 7 - Glycerol structure [13]

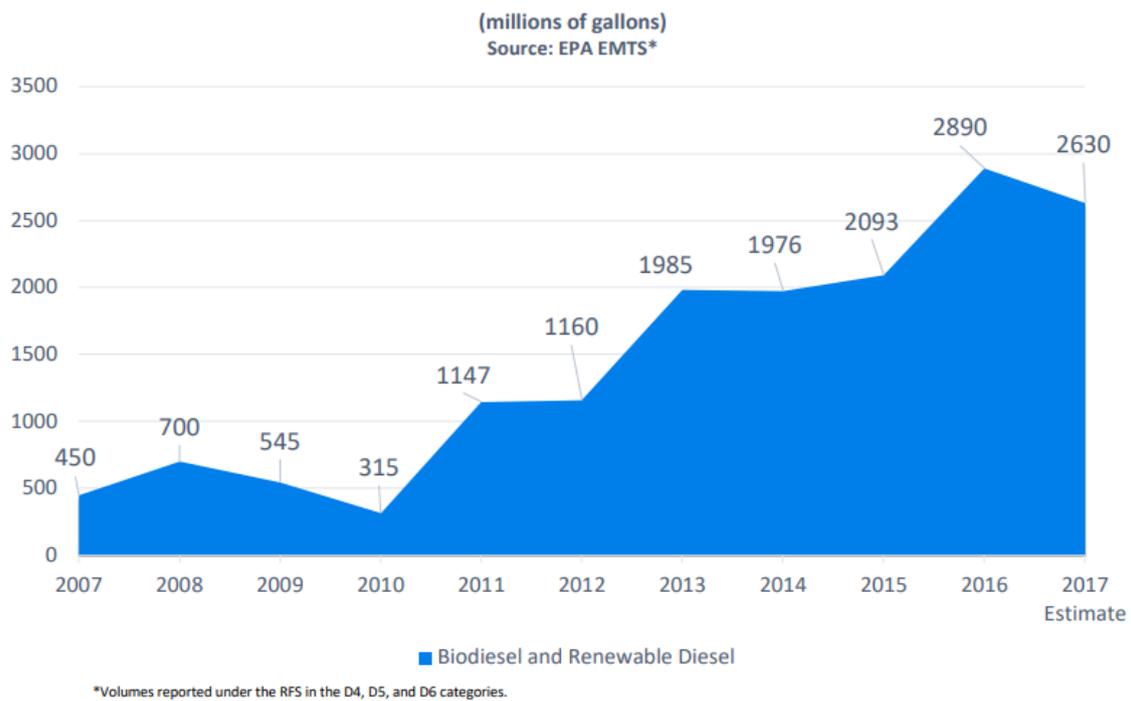


Figure 8 - U.S. Biodiesel and Renewable Diesel Market [14]

Due to the high growth of biodiesel production (Figure 8), glycerol, a major by-product from its transesterification is also produced in great quantity, resulting in an oversupply and a drop in its price.

Currently glycerol shows a large list of applications, as showed in figure 9. It is more used in pharmaceuticals and base chemical industry, [15][16], but also to produce food and cosmetics due to its nontoxic, edible and a biodegradable characteristic.

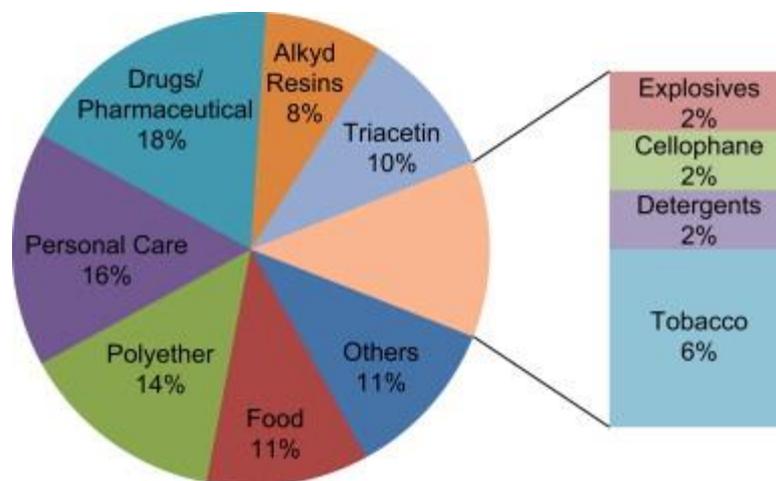


Figure 9 - Glycerol current applications [17]

In terms of energy production, glycerol also shows very interesting sets of routes. Glycerol is mainly used to produce hydrogen [18], due to the technological advances made in the industry. Most of these processes are thermochemical:

- Steam reforming;
- Auto-thermal reforming;
- Aqueous-phase reforming;
- Supercritical water reforming;
- Partial oxidation gasification;

Steam reforming is the most used process to obtain hydrogen. [19]. The process involves two main steps. The first step consists in the splitting of the hydrocarbon molecule in presence of water and the second one the water and water-gas shift (WGS) reaction. From those sets of reaction there is also other products produced like carbon dioxide and monoxide [18], [20].

As it's known, carbon monoxide is highly toxic, but has a very important role in the chemical industry, mainly as a reducing agent. It is also important in the production of organic, inorganic and some intermediate chemicals, making it a very valuable compound. There is also another method capable of producing hydrogen from glycerol, combining dark fermentation with an anaerobic digester. This method faces many challenges, starting with its implementation in an industrial plant.

Despite these several possible routes this technology is not mature yet, as it is condemned to produce insufficient amounts of hydrogen to be feasible on its own. Another important consideration is the presence of impurities in the crude glycerol that can act as poison to the catalyst affecting its performance [21]. [22].

### 3.1. Glycerol as a raw material

#### 3.1.1. Production of oxygenated compounds from glycerol

Glycerol cannot be used directly as a fuel due to its high oxygen content that will affect the combustion performance causing fuel degradation. However, it is possible to produce hydrocarbon fuels and additives from it, Figure 10. Hydrocarbon fuels are fundamental in the global energy chain. In the work of Weiyin and others, a catalyst zeolite in a two-bed reactor was capable to produce gasoline-range alkyl-aromatics (mainly C<sub>8</sub>-C<sub>10</sub>) [15]. The yield obtain was around 60% for the two-bed reactor in comparison to a single-bed reactor with a yield of 30%-40% [23] and using alcohols as solvents the yield decreases to 25% [24].

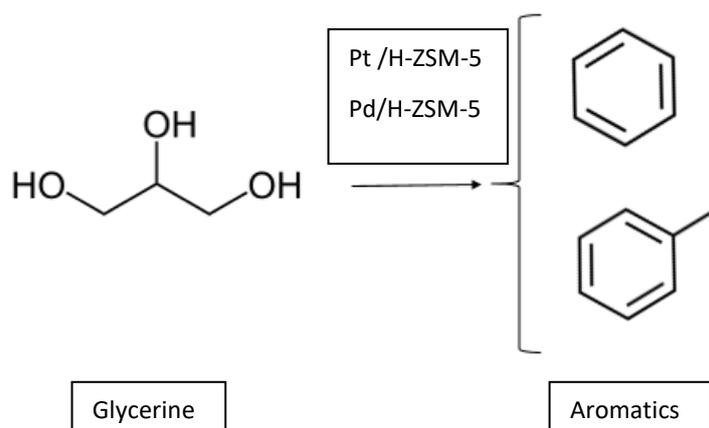


Figure 10 - Glycerol to aromatics reaction

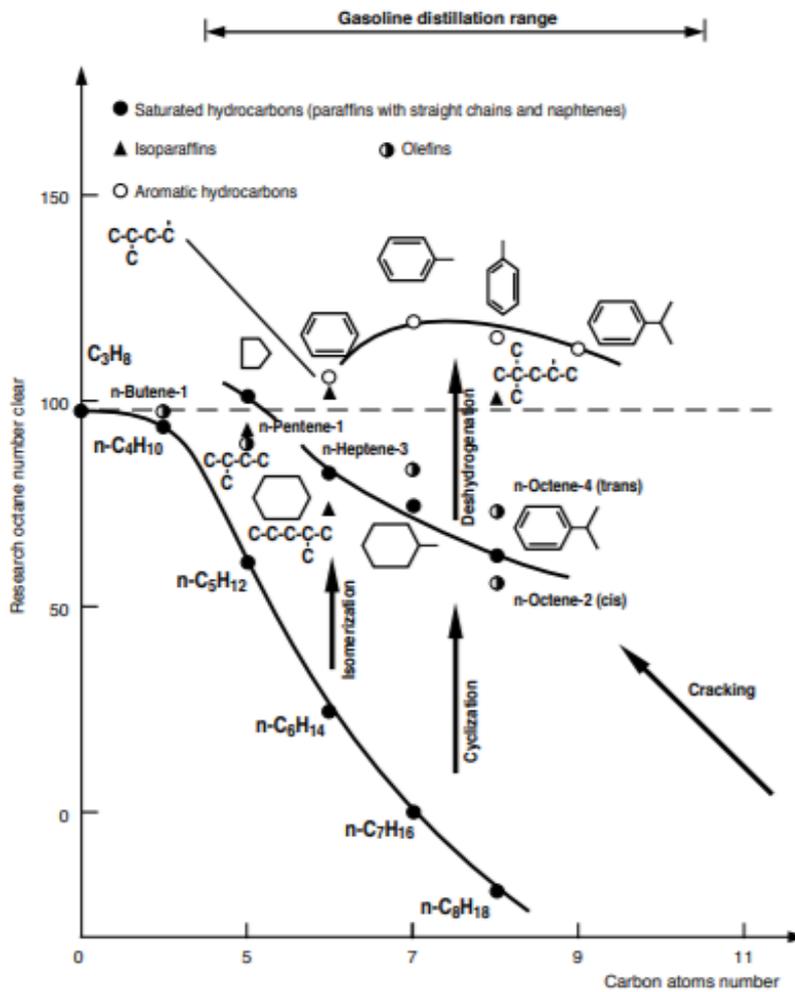


Figure 11- Octane Index Number of different components [25]

As we can see from the figure 11 the aromatics show a high-octane number, being capable of being more compressed, when reached the limit the force or the energy release will be much higher [26].

It's also possible to obtain oxygenated compounds from glycerol. Some oxygenated compounds can be used as additives to improve the properties of several fuels, such as diesel, biodiesel and gasoline [27], [28], [29]. The most common additives are alcohols (ethanol and methanol) [30] or alkyl (MTBE, ETBE, TAME and TAEE). Adding additives, it reduces the density and the viscosity of the fuel, increases the octane or cetane reduces particle emissions and carbon monoxide production [28]. Several routes can be taken to produce these oxygenated additives, but the one with the highest conversion percentage is combining glycerol and aldehydes (90%) (Figure 12).

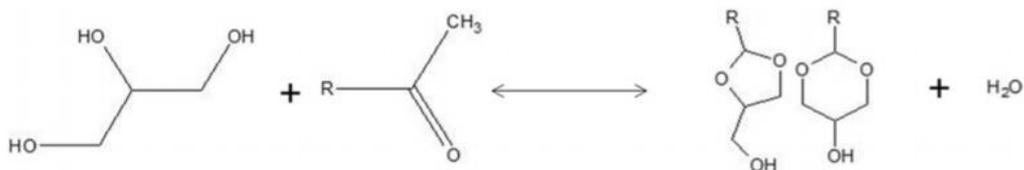


Figure 12 - Reaction between glycerol and aldehydes [27]

### 3.1.2. Production of Solketal from glycerol

Solketal (Figure 13) is a derivative compound that can be obtained from glycerol and can be used as an additive for gasoline and /or biodiesel. Solketal is usually used in the synthesis of mono- (MG), di- (DG) and triglycerides (TG) by ester bond. The free hydroxyl groups of solketal can be esterified with a carboxylic acid to form the protected monoglyceride, where the isopropylene group can then be removed using an acid catalyst in aqueous or alcoholic medium. [31]

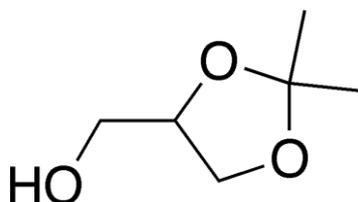


Figure 13 - Solketal structure [21]

Solketal is produced by condensation reaction of glycerol and acetone in the presence of an acid catalyst. Solketal can produce an important derivative compound, benzyl solketal ether, by the etherification of the Solketal and a benzyl alcohol. Benzyl solketal ether is an oxygenated compound that can be used as a fuel additive.

As is shown in figure 14, although the total conversion cannot be reached because water is formed as a by-product, the higher conversion (82,7%) of glycerol to solketal was achieved with the highest acetone to glycerol molar ratio, 1:6, Figure 15. [31].

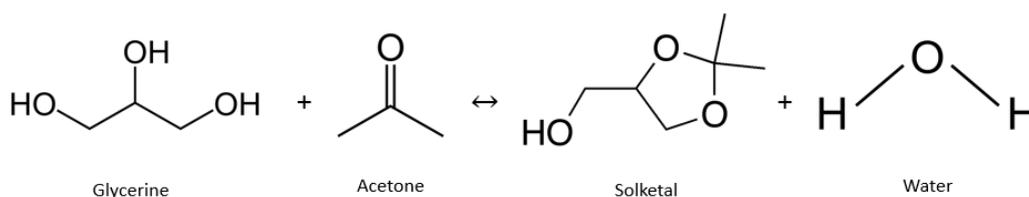


Figure 14 - Solketal synthesis reaction

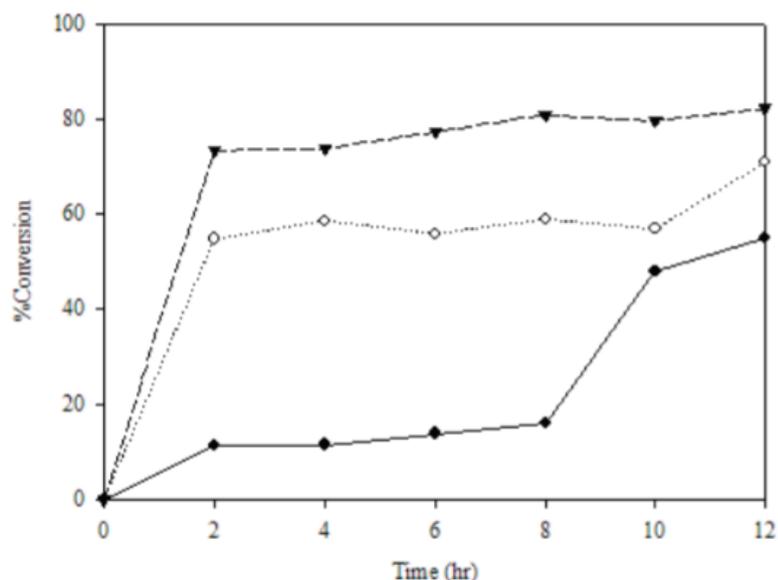


Figure 15 - Conversion of glycerol to Solketal by using acid catalyst at different time: (◆)1:2 molar ratio of glycerol to acetone, (○)1:4 molar ratio and (▼)1:6 molar ratio [32]

In the previous work the temperature was up to 110°C, the 2.2%wt *p*-toluenesulfonic acid is added to start the reaction for 12 hours. The studies of Shanbhang and co-authors [33], showed that using a different catalysts and different concentrations it's possible to achieve higher glycerol to solketal conversions at lower temperatures. They were able to synthesize solketal from glycerol and acetone with various types of Brønsted solid acid catalyst (Figure 16) such as:

- Amberlyst-15 [34];
- Montmorillonite K-10 [34]
- Zeolite beta [34];
- HUSY [34];
- Zeolite ZSM-5 [34];
- *p*-toluenesulfonic acid [34];
- SO<sub>3</sub>H-SBA-15 [35];
- Sulphonated carbon-silica composite [36];
- Silica-induced heteropolyacids [37].

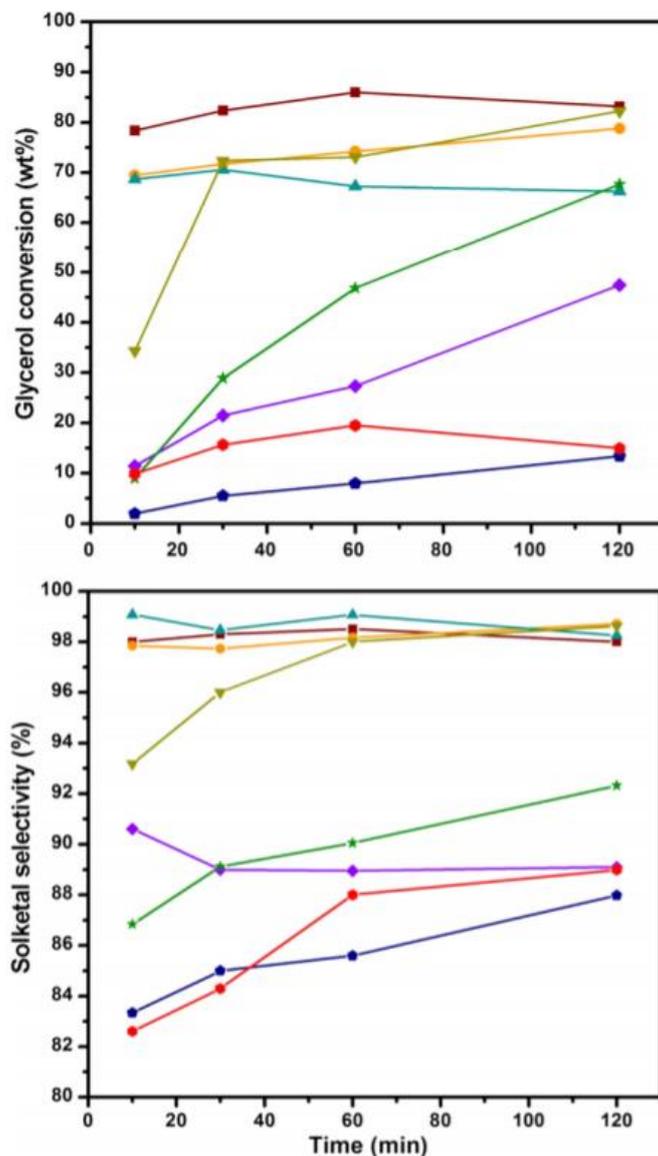


Figure 16 - Glycerol acetalization with acetone using various solid acid catalysts. Reaction conditions: catalyst amount = 5 wt% referred to glycerol, acetone/glycerol mole ratio = 2, room temperature. H-Beta-1 (■), H-Y (●), Amberlyst-15 (▼), CsHPW (▲), Montmorillonite K-10 (◆), MoO<sub>3</sub>/SiO<sub>2</sub> (▲), H-ZSM-5 (hexagon), H-Mordenite (pentagon) [33]

From all the catalysts, the H-Beta zeolite showed the better results in lesser time (1h) and with a glycerol conversion of 86% and 98,5% of solketal selectivity. With the best catalyst selected, solketal was produced using the H-Beta zeolite but now with lower crystallite size. At figure 17 is possible to see that using a catalyst with lower crystallite size highly improves the glycerol to solketal conversion and slightly his selectivity.

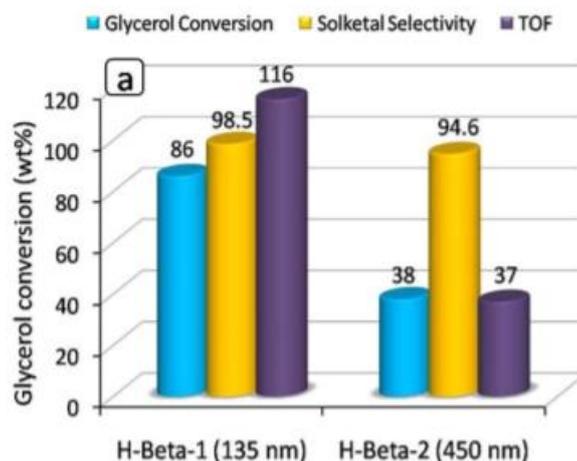


Figure 17 - Catalyst performance of H-Beta catalyst with two different crystallite size [33]

### 3.1.3. Glycerolysis of Fatty Acids

Fatty acids are aliphatic, straight chain of monocarboxylic acids. The broadest definition includes all chain lengths, but most natural fatty acids have even chain lengths between C4 and C22 (Figure 18).



Figure 18 - Structure of fatty acids

Glycerolysis of fatty acids and oil is very important industrially because it produces monoglycerides and diglycerides. These products and their derivatives have many applications, such as:

- Surfactants and emulsifiers;
- Cosmetics;
- Pharmaceutical products.

The reactions between the glycerol and the fatty acids need to occur between the range of temperatures 210-260°C and in the presence of an inorganic catalyst. The reaction itself is reversible because there's alcohol or water formed, and there is formation of monoglycerides, diglycerides and some triglycerides [38].



Some studies focused in the glycerolysis of fatty acids with other catalyst. A work using potassium hydroxide catalyst was able to reach a 50-55% of conversion to monoglycerides [39].

Another report used an alkaline catalyst in a two-step reaction. First, they reacted the fatty acid with the glycerol in the presence of the alkaline catalyst and then adding more catalyst with an organic solvent, it increased the conversion to MG [40]. The work of Kassem and others reported that zinc as catalyst also has a good conversion to MG [41].

## Chapter 4 - Dimer Acids

Dimer acids, Figure 19, are characterized as been a yellow/light or yellow, viscous, non-toxic, transparent liquid. Their primary usage is in the synthesis of polyamide resins and hot melt adhesives, but can also be used as surfactants, as fuel oil additives as lubricants [42], [43], [44] and many others.

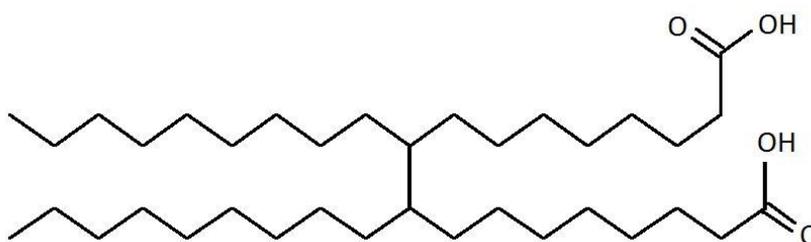


Figure 19 - Dimer fatty acid structure

Dimer acids are also referred in the literature as dimerized fatty acids. Dimer fatty acids (DA) are very important industrial chemical derived from renewable and natural oleic acids such as:

- Rapeseed oleic acid;
- Soya oleic acid;
- Cottonseed acid;

Dimer acids are considerable low-cost, renewable, easy to obtain and cleaner source of energy making it a focus of attention from the scientific community in this last years and can prepare by mixing two unsaturated fatty acids. Dimer acids can react like reagents with hydroxyl groups to produce bio-polyols [45] [46].

### 4.1. Dimerization of Unsaturated Fatty Acids with Montmorillonite

There are currently two process: homogenous catalysis and heterogeneous catalysis. The traditional process is the homogeneous catalysis which uses a catalyst alkali or alkaline metal salts, Lewis and Bronsted acids. In another process, the heterogeneous catalyst makes the reaction more overall attractive, because it is more environmentally friendly, more abundant, less expensive and easier to separate from the end products. The heterogeneous catalysis can be clay or clay materials like kaolinite or montmorillonite (MMT). Despite montmorillonite being the most commonly used clay mineral due to is abundance in nature and highly beneficial properties

(high cationic exchange capacity, high specific surface area and large aspect ratio) bentonite clay is currently the only catalyst used industrially to produce dimer acid.

The advantages of using MMT as catalyst is that it can produce two kinds of acid centers, Brønsted acid and Lewis acid. The Brønsted acids can produce carbocations of conjugated linoleic acid that will promote the dimerization of unsaturated fatty acids and the Lewis acids promote the conversion of unconjugated to conjugated linoleic acid. The downside of using MMT is the hydrophobicity of it that prevents the dispersibility in the unsaturated fatty acids leading to less efficient reaction [47].

In the studies of Feng and co-workers [47], dimer acids were produced using different types of MMT catalyst, O-MMT (one step) and T-MMT (two-step) being the unmodified the Mg-MMT, characterization of the specific surface area texture, morphology, surface acidity and dispersibility. As it possible to see in Table 1, the modified MMT catalysts gave better results than the unmodified catalyst, producing higher yields of dimer acids.

Table 1 - Basal distance and yield of dimer acids from the different MMT catalyst

MMT	20°	Basal distance (nm)	Selectivity of dimer acids (%)	Yield of dimer acids (%)
Mg-MMT	5.97	1.48	73.10	32.69
O-MMT	2.33	3.80	72.19	50.86
T-MMT	2.31	3.82	72.77	68.03

## 4.2. Synthesis of Nylon 6 with Dimer Acid

In the study of Huang and others [48], a long carbon chain dimer acid is introduced into a nylon 6 structure and is copolymerized with different structural amines to produce amorphous nylon 6. The major problem with this product is that it has a great water absorption capability due to its hydrophilic group, causing an increase of density, decreasing the stability of the product. The authors mention the huge demand for high optical transparency polymers for applications in optical films and food packaging.

Table 2 - Transparency and water absorption of Nylon 6 with different copolymerization components [48]

Polymer	Transparency (%)	Haze (%)	Water Absorption 24 h (%)	Water Absorption 48 h (%)
COM	87.50	32.0	1.07	1.31
COX	85.80	39.4	1.51	2.13
COC	87.90	52.4	1.29	1.62
COH	81.90	75.0	1.57	2.21
COI	87.30	39.4	1.30	1.62
COMM	88.80	29.2	1.24	1.42

From all different copolymerization components COM (synthesized by Caprolactam (C), dimer oleic acid (OA) and 4,40-Methylenebis(cyclohexylamine) (MCA)) and COMM (synthesized by Caprolactam (C), dimer oleic acid (OA), and 4,40-Methylenebis(2-methylcyclohexylamine) (MMCA)), Table 2, the COMM polymer gave the best results in terms of transparency, haze and water absorption so it was study the effect of that polymer with different concentrations, Table 3.

Table 3 - Composition of Nylon 6 containing dimer oleic acid [48]

Polymer	PA6 molar ratio	Acid molar ratio	Base molar ratio	Molecular Weight
COMM1	CPL, 98%	OA 1%	MMCA 1%	38621
COMM3	CPL, 94%	OA 3%	MMCA 3%	37552
COMM5	CPL, 90%	OA 5%	MMCA 5%	37421
COMM7	CPL, 86%	OA 7%	MMCA 7%	35223
COMM10	CPL, 80%	OA 10%	MMCA 10%	34226

Table 4 - Transparency and water absorption for Nylon 6 with different concentrations of octadecadienoic acid and 4,4 methylenebis (2-methylcyclohexylamine) [48]

Polymer	Transparency (%)	Haze (%)	Water Absorption 24 h (%)	Water Absorption 48 h (%)
COMM1	67.8	89.6	2.35	2.84
COMM3	76.9	84.6	1.78	2.61
COMM5	84.7	73.5	1.52	2.32
COMM7	87.1	41.9	1.22	1.84
COMM10	88.8	29.2	1.24	1.42

Table 4 shows that with the increased of the acid molar ratio (copolymerization ratio) for COMM there's also an increased in some properties (transparency and water absorption). It's possible to

see that 10% of copolymer ratio gave the most wanted results, the transparency increases and the haze decreases, mainly due to the increase in the methyl side chain and the cycloalkyl group and the water absorption decreases as the content of the bicycloalkyl group increases [48].

### 4.3. Polyurethane fertilizer based from dimer acid

In this work an acid-based polyurethane coated fertilizer (PUF) was prepared, Figure 20. First, they used the dimer acid to synthesize biopolyol which was used to prepare the modified polyurethane fertilizer (MPUF). The major feature that lead to the used of dimer acid, was to obtain an end-product from a renewable source and its biodegradability, which enables future projects without worrying with the environmental impact.

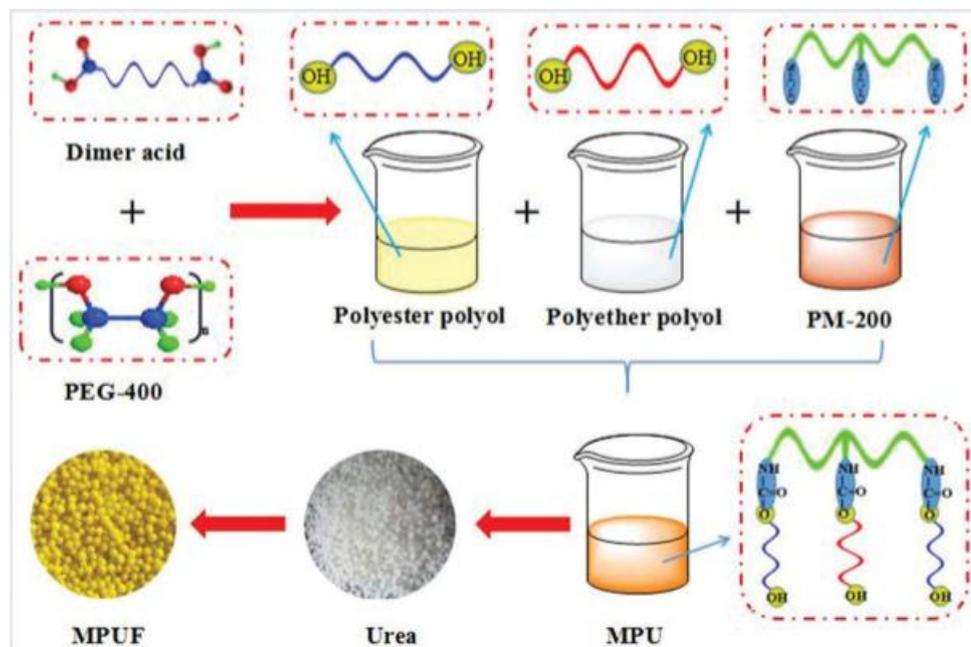


Figure 20 - Diagram of the fabrication process of MPUF (modified polyurethane fertilizer) [49]

The polyurethane produced from the dimer acid had denser structure (when compared to regular/conventional produce polyurethane), increased cross-linking density, contact angle and the thermal stability, Figure 21, decreased coating porosity and slowed water absorption rate [49].

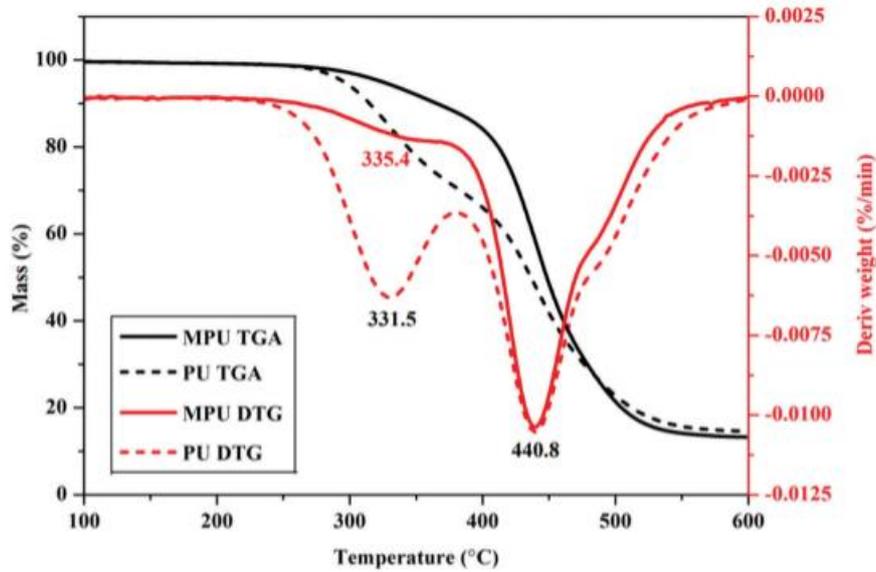


Figure 21 - TGA curve and its derivative (DTG) of PU and MPU [49]

#### 4.4. Rigid polyurethane foam based from dimer acid

Polyurethane foams have excellent thermal insulating properties, low apparent density, great mechanical properties, high weight-carrying capability and good resistance to different weather conditions. Due to their vast set of properties, polyurethane foams are mostly used in industries like:

- Building construction;
- Automotive;
- Bedding;
- Furniture;
- Cosmetic;

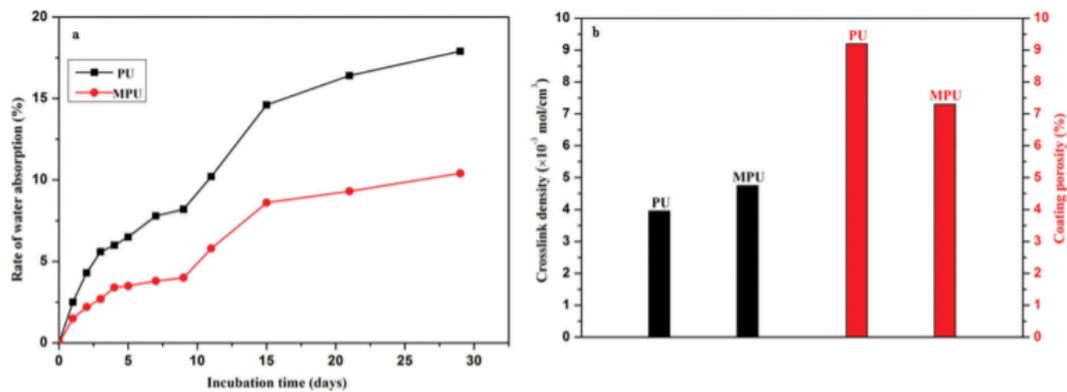


Figure 22 - Water absorption, porosity and crosslink density of PU and MPU [49]

Normal polyurethane foams are prepared using a petroleum based polyol in the presence of a blowing agent, surfactants and a catalyst. Using a petroleum base product is a big problem due to decreasing petroleum resources. Also, the environmental impact in the price of the product will be dictated also by the current price of petroleum, causing serious problems that can make the production economically unvailable [50].

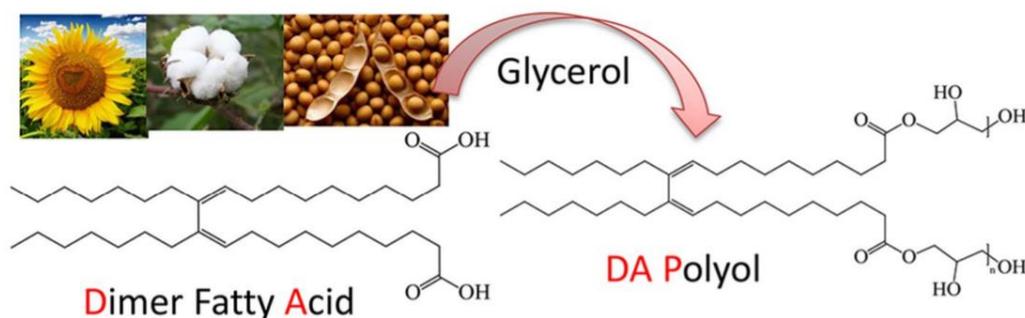


Figure 23 - Representation of the synthesis of dimer acid polyol [50]

To reverse this a bio-alternative most be found. In the report of Jinchun et al, it was used a dimer fatty acid based polyol (DAP) that was synthetized via esterification of a dimer acid and glycerol, Figure 23. As mentioned before, dimer acids can be produced by using renewable and natural materials. In this work a rigid polyurethane foam was produced from the dimeic acid based polyol. Comparing the dimer acid based foam with the petro based foam, the apparent density and the compressive strenght decreased, thermal conductivity didn't change, water resistance improved, water absorption decreased more than a half. Meaning that biopolyol can be a good alternative for petrochemical poly [50].

## Chapter 5 - Experimental Methods

Figure 24 shows a schematic diagram of all the processes develop in this thesis.

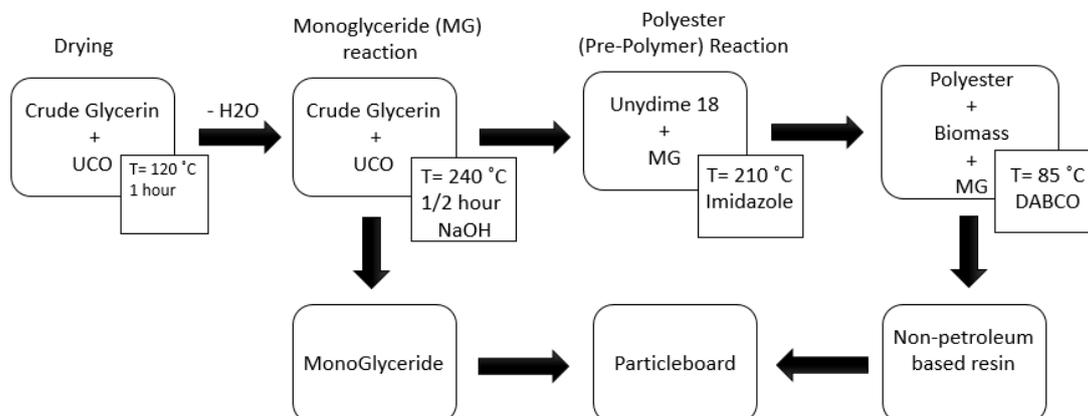


Figure 24 - Workflow diagram

### 5.1. Preparation of Monoglyceride (MG)

The MG was synthesized according to the following steps and report [51]. Firstly, the reaction was prepared in a smaller scale so it could be optimized. For a 2 l reactor, 245 g crude glycerol, 900 g of used oil and 0.9 g of sodium hydroxide (0.1 wt% of oil) were placed in a four-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet, Figure 27. The mixture was subjected to a 120 °C pre-heat treatment for approximately 1 hour to remove potential existing water. After the pre-treatment the temperature was raised to 240 °C with 250-300 rpm. The reaction was finished when a sample taken from the mixture and added with ethanol ( $\frac{3}{4}$  ethanol and  $\frac{1}{4}$  sample), giving a brown-yellow transparent and homogenous solution, Figure 25, 26. After optimizing the reaction, a scale-up was performed to a 10 l reactor using the same conditions of operation and quantity of reactants (proportionally). Both 2 l and 10 l the reaction time needed to produce the MG was around 30 min.



Figure 25 - MG produced at different steps of the reaction



Figure 26 - MG mixed with ethanol at different steps of the reaction



Figure 27 - MG production assembly

## 5.2. Preparation of Polyester (Pre-Polymer)

The pre-polymer polyester was prepared in a 2 l three-necked round bottom flask equipped with a mechanical stirrer and a nitrogen inlet by mixing the product from previous reaction with 880 g of MG, 660 g of Unidyme18 (U18) and 5-10 g of imidazole as a catalyst. The mixture was heated to 210-230 °C with 250-300 rpm. The reaction was finished when we reached a desirable molecular weight that can be calculated using the method and procedure described in chapter 6.3.

## 5.3. Resin reaction

During the project 3 types of formulations were produced. The first formulation, RX#1, was to test if the conditions of operations were adequate to produce the high MW polyester. The other two differed in the reactant used and in the addition of other components to deal with the high viscosity obtain.

- The RX#1 formulation was the first to be tested, the resin was prepared by Polyol 8000 (high molecular low viscosity polyether 6000—20000 with properties such as low viscosity) and TDI into three-necked round bottom flask equipped with a mechanical stirrer and a nitrogen inlet with a temperature of 85°C. After adding the TDI the viscosity of the mixture started to rise with time. Afterwards the wood biomass was added to the reactor generating the glue. The proportions of these formulations are 30% polyol to 70% biomass.
- The second formulation, RX#2, uses the same process and proportions as the previous one but instead of using polyol 8000 it uses the product of the reaction of the MG with the dimer acid (U18), polyester.
- The last formulation, RX#3 (Figure 28), also uses the same procedure and parameters as the last two but it incorporates another component, MG, that is added after mixing the biomass with the polyester. The parameters for this formulation are 30% polyester, 50% biomass and 20% MG.



Figure 28 - Liquefied biomass without solvent (left) and resin RX#3 (right)

#### 5.4. Production of Particleboard

The plywood was the final application for the produced glue, in two different steps. The first step involved mixing the glue with another product, MDI. The plywood products are composed by 3 layers (one internal and two external layers). The internal layers are composed by 208 g of pine fine wood and 20g of RX glue. Before mixing the glue with the wood it is necessary to wet the wood with 2.5%-10% (wt of wood) of MDI and mixing the resin with 2.5%-10% (wt of resin) of MDI.

After preparing the mold as shown in the schematic, it was placed in the heated press at 200°C for 10 minutes at a pressure of 10 bar. After that, the pressure is released gradually over the period of another 10 minutes.

## Chapter 6 - Characterization Methods

### 6.1. FTIR-ATR

The FTIR (Fourier-Transform Infrared), Figure 29, is a technique used to obtain an IR spectrum (can be emission or absorption) of a solid, liquid or gas, those spectrums can provide crucial information essential for the determination of the molecular composition of the samples.

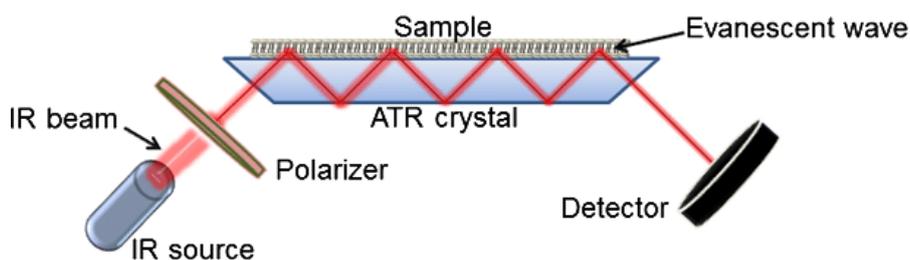


Figure 29 - Schematic representation of a FTIR-ATR system [52]

ATR stands for attenuated total reflection, when the IR beam goes through the ATR crystal it guarantees that the beam will reflect at least once off the surface of the sample that is in contact with the crystal (as it shows in Figure 30). As a result, an evanescent wave that propagates throughout the sample, to this wave occur it's necessary that ATR crystal is made from an optical material with high refractive index, higher than the sample material, so that the beam is retain in the crystal and doesn't propagate to the sample. The different functional groups present in the samples will have different vibration frequencies when subjected to an impulse of energy, in other words different dipolar moments when excited allowing their identification. The spectrums were obtain using an ABB FTLA 2000-100 spectrometer with the software F. Menges "Spectragryph – optical spectroscopy software", Version 1.2.9, 2018.



Figure 30 - FTIR-ATR equipment

## 6.2. Thermogravimetric Analysis (TGA)

The TGA is performed in an instrument known as a thermogravimetric analyser, it consists of a precision balance with a sample pan both located inside a furnace. The function of this apparatus is to measure the variation of mass of the sample with temperature over time, the temperature is programmable, and it can be defined to increase at a constant rate. Also, it's possible to select different types of atmospheres inside the furnace, ambient air, vacuum, inert gas, etc.

The data retrieved from a TGA Hitachi STAT7200 (Figure 31) is used to generate a graphic known as TGA curve, where it represents the percentage of mass in function of the temperature or time. For a better interpretation of the TGA curve is used made a first derivative graphic, known as dTG curve, which allows for a better visualization of the inflection points. In the end, the TGA is used to study/characterize the thermal behaviour of a material and defined decomposition/degradation pattern [53].



Figure 31 - TGA equipment

## 6.3. OH value and Acid Value

### OH value

The OH value or the hydroxyl value is the value in milligrams of KOH necessary to neutralize the acetic acid in 1 g of sample. In the end the OH value is the number of free hydroxyl molecules present in the sample expressed in milligrams of KOH.

- **Catalyst solution**

1% (4-n,n-dimethylaminapyridine ((DMAP) in THF) (1 g in 100 ml)

- **Acetylation solution**

12,5% acetic anhydride in THF (125 ml in 1000 ml)

### **Procedure**

- 1- Weight 1 to 2 g of sample and dissolve in 40-50 ml THF
- 2- Add 10 ml to the catalyst solution
- 3- Add 10 ml to the acetylation solution
- 4- Stir for 10 min
- 5- Add 2 ml of distilled H<sub>2</sub>O
- 6- Stir for 30 min
- 7- Titrate using KOH 0,5N (in ethanol) and as an indicator thymolphthalein (1% in THF)
- 8- Repeat all the above steps without the sample, White test.

### **Acid Value**

The acid value is the minimum quantity necessary of KOH (mg) to neutralize the existing amount of acid present in 1 g of sample.

### **Procedure**

- 1- Weight 1 to 2 g of sample and dissolve in 40-50 ml THF
- 2- Titrate using KOH 0,1N (in Ethanol) and as indicator Thymolphthalein (1% in THF)

#### Acid Value calculation

$$\text{Acid Value} = \frac{C \times MW \text{ solution} \times \Delta V}{m \text{ sample}} = \frac{0,1 \times 56,1 \times \Delta V}{m \text{ sample}} \quad (4)$$

#### OH value calculation

$$OH\ value = \frac{C \times MW\ sample \times (\Delta V_{white} - \Delta V_{sample})}{m\ sample} + Acid\ Value \quad (5)$$

$$OH\ value = \frac{0,5 \times 56,1 \times (\Delta V_{white} - \Delta V_{sample})}{m\ sample} + Acid\ Value \quad (6)$$

$$MW = \frac{56100 \times functionality}{Acid\ Value + OH\ value} \quad (7)$$

Where  $C$  is the concentration of titrant,  $MW$  is the molecular weight of the sample,  $\Delta V$  variation of the volume,  $m$  is the mass of the sample.

#### 6.4. Moisture Analysis by Karl-Fischer (KF)

Karl-Fischer titration is a chemical analysis method used for the determination of the water content/moisture content in a sample. There are two types of KF analysis the Coulometric and Volumetric. Coulometric Karl Fischer (Figure 32) is used when working with small samples (few grams) with low moisture level (around 1% or less). For larger samples with higher moisture content is preferring to use the Volumetric Karl-Fischer can large samples will fill quickly the Coulometric measuring cell.



Figure 32 - Coulometric Karl-Fischer titration

## 6.5. Gel Permeation Chromatography (GPC)

GPC (Figure 33) is a SEC type technique that aims to separate dissolved molecules in a gel-packed column according to their size in solution, higher molecular weight materials while pass faster throughout the column than the lower molecular weight materials. In the figure 34 shows how a GPC is composed, the mobile phase is more than GPC column with a stationary phase of porous particles, the pore size is previous selected according to the molecular weight of the sample. The pump is a key element to the process because it provides the necessary pressure and flow rate so can the samples go through the column. There can be different types of detectors attach to the it, UV, refractive index, IR, density, etc., normally they are equipped with two different detectors in this case were UV detector than a refractive index detector. The output of GPC is a chromatogram that will allow to determine the molecular weight.

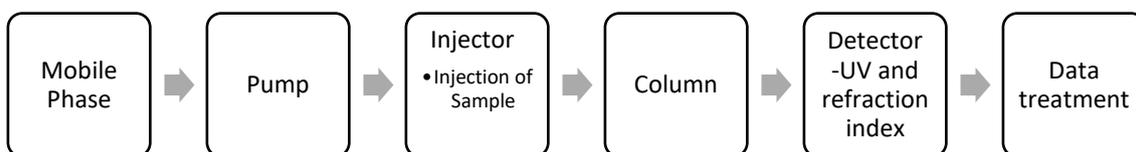


Figure 33 - GPC schematic workflow



Figure 34 - GPC equipment

## 6.6. Particleboard tests

The particleboard produced were sent to an industrial facility, different tests were made to see if they were according with the specifications to be produced in industry, Appendix I. The following tests were done to five different particleboard which one with different resin formulation.

### 6.6.1. Traction test

The traction test consists on using a small sample of the Particle board and glue it to two pieces of metal that will connect to the traction machine (Goodbrand GBX, Figure 35), then after defining the slope of the force, the machine will start pulling the sample at two ends (Figure 36) and will pull apart the particle board. The purpose of this test is to see how much force is necessary to reap the particleboard and where does it happen, in the internal layer or external layer.



Figure 35 - Traction equipment



Figure 36 - Result of the traction test

### 6.6.2. Swelling

The Swelling test is a very simple test to apply; it consists in introducing a sample of the particleboard inside a thermostatic bath (Figure 37) at room temperature during 1h. The purpose of this test to see how much water is adsorbed by the sample and measured by the increased thickness.



Figure 37 - Grant thermostatic bath

### 6.6.3. Moisture content



Figure 38 - Comparison of the pre-swelling particleboard with post-swelling particleboard

To determine the moisture content existing in the samples of particleboard, Figure 38, samples were measured and place in an oven at 105°C for one hour after it the samples are measured again. To calculate moisture content, it was used the following equation.

$$\%Moisture = \frac{W_{inicial} - W_{final}}{W_{final}} \times 100 \quad (8)$$

## Chapter 7 - Results and discussion

### 7.1. FTIR-ATR

Figure 39 shows four analysis to two types glycerol samples, since the sample of the crude glycerol was store in a large container a sample form to top and bottom was taken to see it had any contaminate.

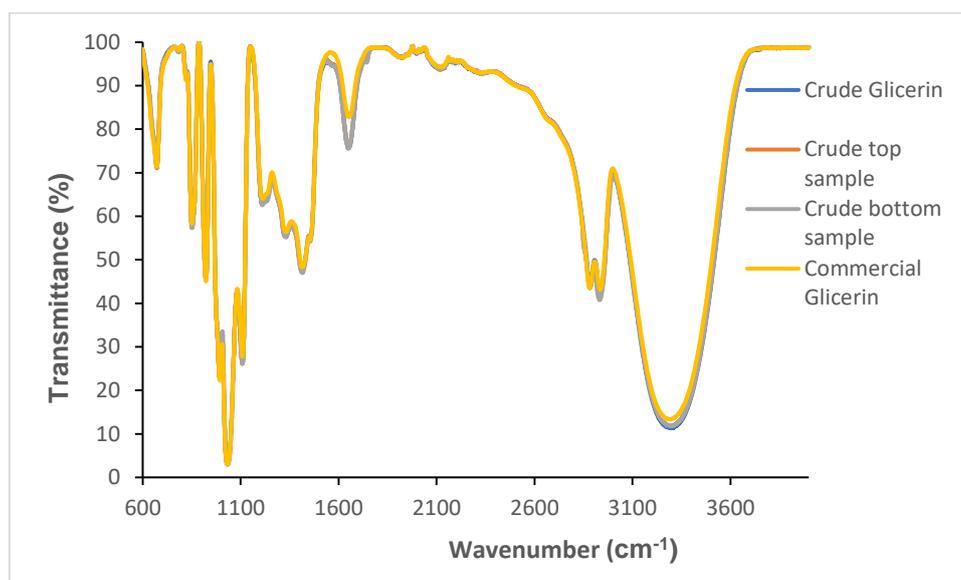


Figure 39 - FTIR-ATR analysis of crude glycerol vs pure glycerol (85%)

As it is possible to see, between 3000-3500  $\text{cm}^{-1}$  a very intense band that corresponds to the alcohol intermolecular bonding (O-H) stretching, between 2800-2900  $\text{cm}^{-1}$  a medium peak relative to the C-H alkane stretching, the 1600  $\text{cm}^{-1}$  is associate with possible existence of water and around 1100  $\text{cm}^{-1}$  relative to the C-O stretching of the primary alcohol. This analysis it's a great indicator because it shows that the crude glycerol does not differ too much from the commercial making it viable to use in the reaction.

Until the final reaction to obtain the MG, many reactions were made where the quantity of the reactants were different other times the reaction parameters and sometimes both. The optimize reaction was the reaction designates as reaction MG F, the procedure of this reaction is described in the experimental procedure chapter.

F0 is the sample taken when the reactor reached the 240°C, when the desire temperature was achieved and F1 is a sample taken when the reaction ended.

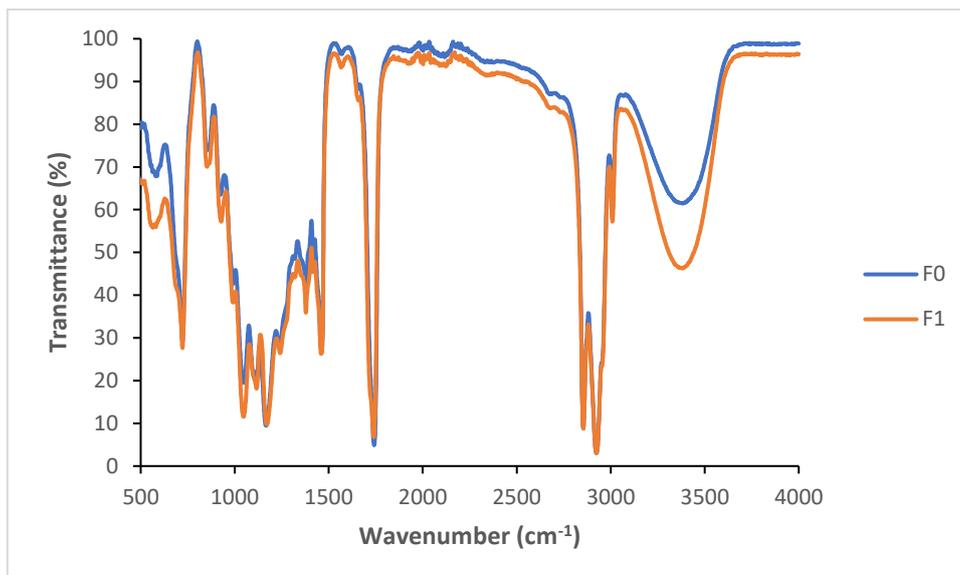


Figure 40 - FTIR-ATR of the MG prepared at beginning of the reaction (F0) and at the end (F1)

The figure 40 shows the FTIR spectrum of the MG F0 and F1, at first look they look very similar but F0 shows smaller bands so the analysis will be the same for both, around 3000-3500  $\text{cm}^{-1}$  there's a very intense band that corresponds to the alcohol intermolecular bonding (O-H) stretching, 2900-3000 a medium band from the C-H stretching of the alkane, the 1740-1720 band is related with C=O stretching of the aldehyde and the last band, the 1085-1050 with the C-O stretching of the primary alcohol. By analysing the F0 FTIR shows that the time that takes the reactor to reach the 240°C there's already formation of the MG (it shows the corresponding bands) and comparing F0 with F1 it's possible to conclude that no secondary product is forming.

## 7.2. Thermogravimetric Analysis (TGA)

The following TG analysis were made to study the behaviour of crude glycerol with the commercial glycerol to see how much they differ from one to another, using a Hitachi STA7200 with Standard Analysis with EMA function, version 1.0.2 (Build 2), Hitachi High-Tech Science Corp. 2018. The parameters used for analysing both samples were 10  $^{\circ}\text{C}/\text{min}$  with a flux of nitrogen of 200  $\text{ml}/\text{min}$  and the temperature range was of 25-600  $^{\circ}\text{C}$ .

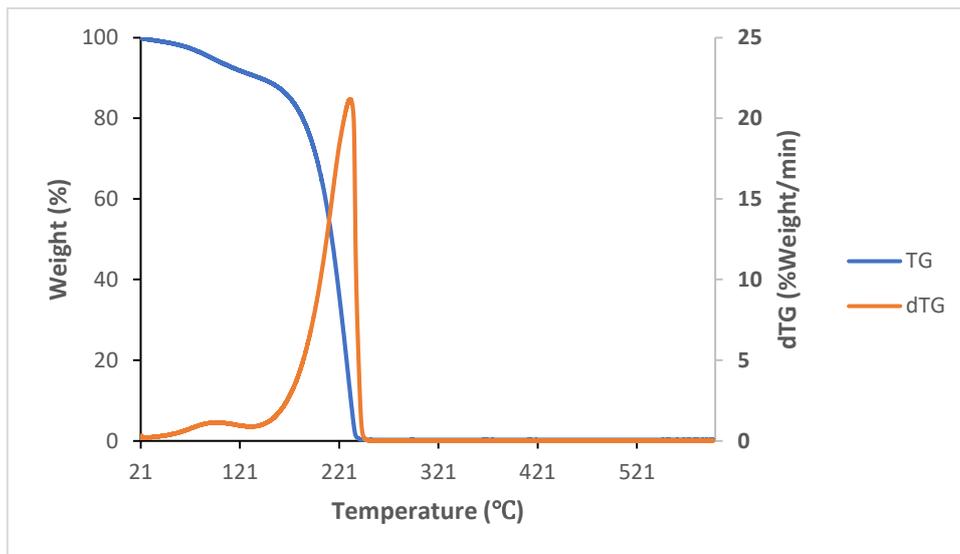


Figure 41 - TG analysis of commercial glycerine

From figure 41 it is possible to see two zones where the weight loss occurs. The first one occurs around 60 to 100 °C and the weight loss is approx. 8%, this weight lost may be correspondent to some existing water present in the sample and some more volatile components. Between 140 and 234°C it is possible to see a zone where the major weight loss occurs around 87%, maybe due to the breaking of the molecular bonds.

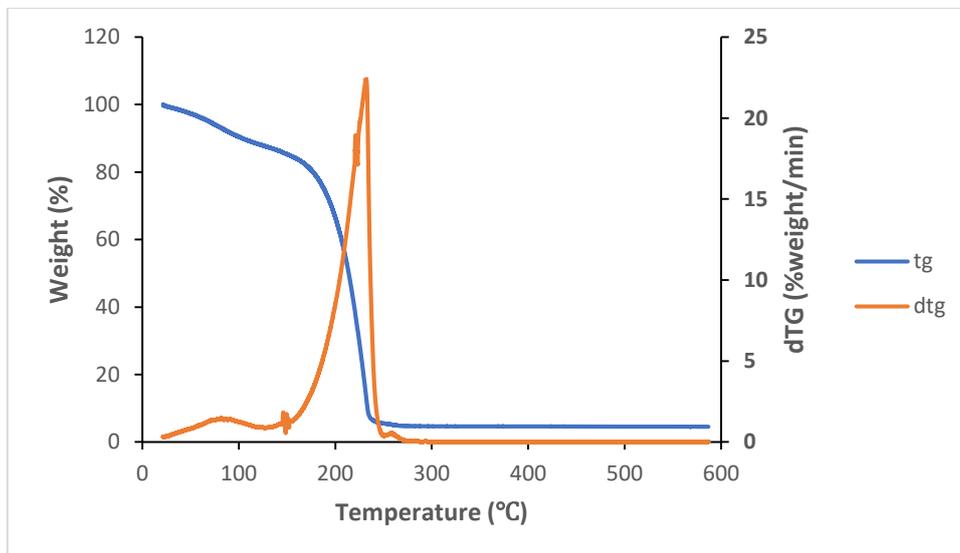


Figure 42 - TG analysis of crude glycerine

Comparing the TGA of crude glycerol (Figure 42) with the TGA of commercial glycerol (Figure 41) is possible to see similar weight loss zones, 60-100 °C there's a first peak visible in the dTG,

the weight loss is due to the water and some volatile components present in the sample, around 160 to 232 °C it is shown the zone where the highest weight loss occurs possible due to the breaking of the molecular bonds of the sample.

### 7.3. OH value and Acid Value

The initial polyester formulation used 1160 g of MG to 1321 g of dimer acid (U18) and 30 g of catalyst (imidazole), as it shows in figure 43, the final acid value obtain was of 19. To obtain this value it took 23 hours, which is a considerable time, and the result was not that great with a final OH value of 34 and the molecular weight of the polyester 2400.

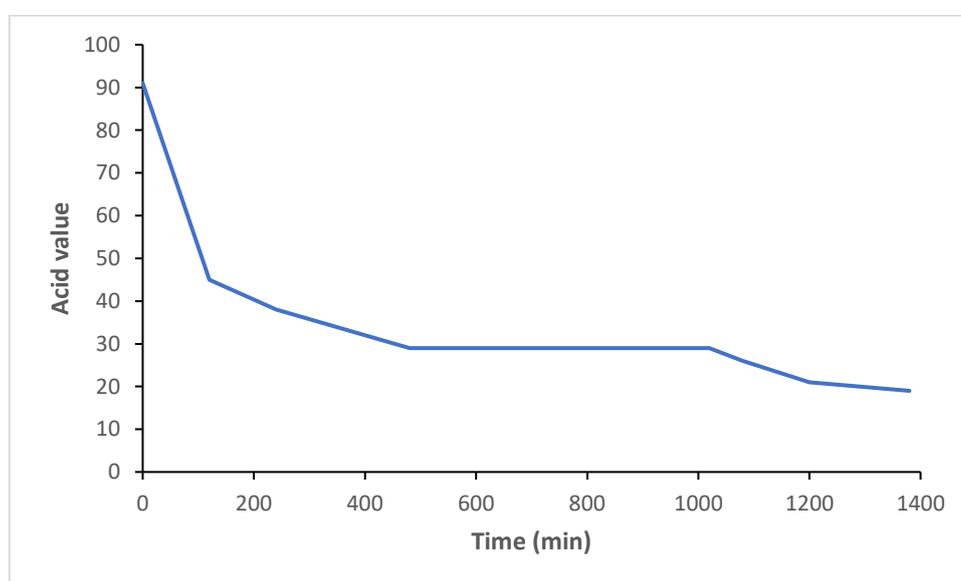


Figure 43 - Acid value for the initial polyester formulation

The final polyester formulation produced contained 880 g of MG to 660 g of dimer acid (U18) and it was used as catalyst 5-10 g of imidazole. Comparing the graphics, it is clear to see that the initial acid value was lower in the final formulation, due to the excess of MG in the solution. The initial quantity of MG initially used was 480 g, the addition of 100 g of MG was done at the following times: 840, 1200, 1320 and at 1740 minutes. The final polyester obtained an OH value of 29, due to the excess of MG there was still some that didn't react, and the final acid value was of 6 (Figure 44) and molecular weight 3611. The OH and acid values were obtain using equations (4), (6) and (7).

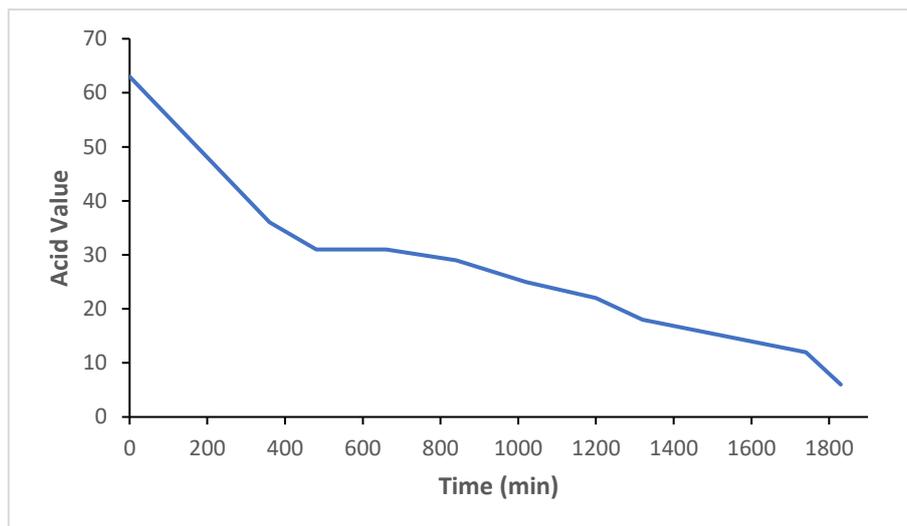


Figure 44 - Acid value for the final polyester formulation

#### 7.4. Moisture Analysis by Karl-Fischer (KF)

The volumetric Karl Fischer analysis was used for determination the moisture content of the crude glycerol. The result of KF shows that the sample had 127153,6 ppm that is approximately 12,7% of water. With the result of this test, a pre-heating step was introduced into the MG production reaction with the purpose to extract much of the water introduced into the reactor. If the water is not removed, it represents a risk to the reaction generating bursts inside the reaction.

#### 7.5. Gel Permeation Chromatography (GPC)

The GPC apparatus was calibrated with a standard polymer of polystyrene, which indicates that the GPC column is better suited to analyse linear molecules than non-linear such as the MG. This aspect will have a great affect in the results when comparing with the literature. Other consequence of the use of incorrect column is shown in the equation MW calibration curve, in these two study cases the equation should be the same but is slightly different one form another.

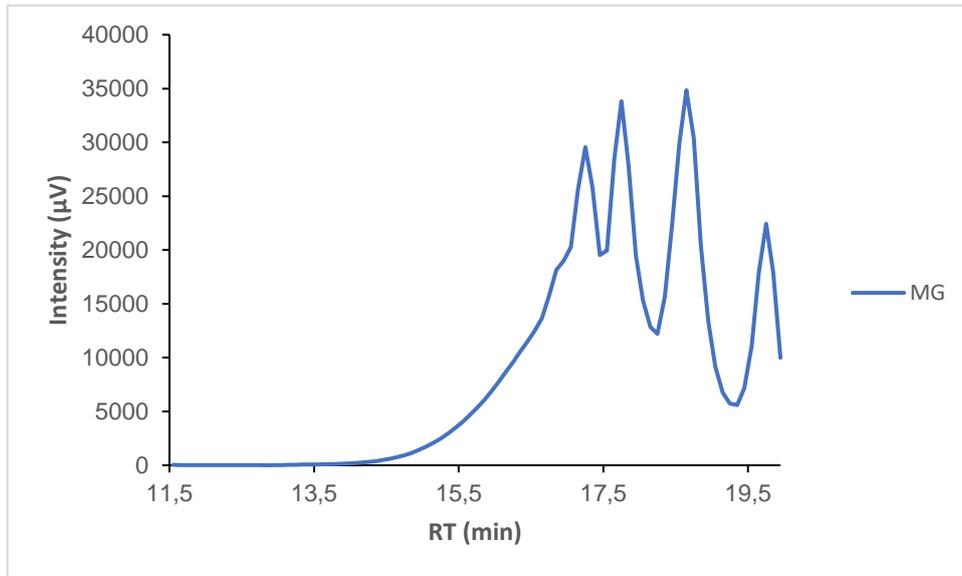


Figure 45 - GPC analysis of the resulting MG

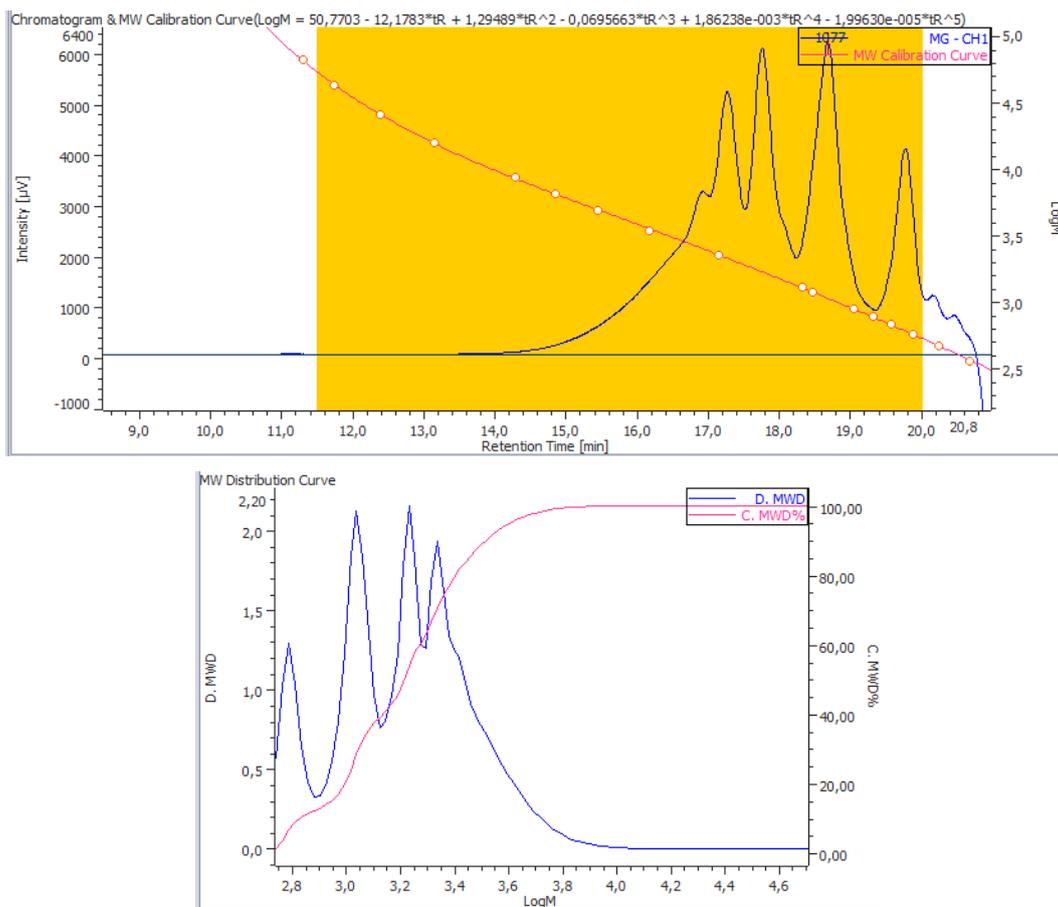


Figure 46 - MG MW calibration curve (top) and cumulative MW distribution curve (bottom)

The calibration curve used to calculate the molecular weights of the different peaks depending on the respective retention times is the following:

$$\text{Log}(MW) = 50.7703 - 12.1783RT + 1.29489RT^2 - 0.0695663RT^3 + 1.86238 * 10^{-3}RT^4 - 1.99630 * 10^{-5}RT^5 \quad (9)$$

Where  $RT$  is the retention time in the GPC column.

As mentioned before, substituting the retention time value of the peaks in the equation 9 and figure 45 and 46 it gives the respective molecular weights. The compounds were determined by what was expected the MG reaction to produce, since the objective was to break the TG into DG and then into MG so they exist in the final product, also the reaction uses used oil so its predicted that there still some residue also present. Its known that the TG was a higher MW than the DG and MG and that the DG MW is higher than the MG. Using the principle of functionality of the GCP column, it is expected that the TG will have lesser retention time than the DG and MG.

Table 5 - Peak determination of MG GPC

RT	MW	Compound
16.9	2550.864	n.i.
17.3	2113.718	TG
17.8	1662.626	DG
18.7	1062.524	MG

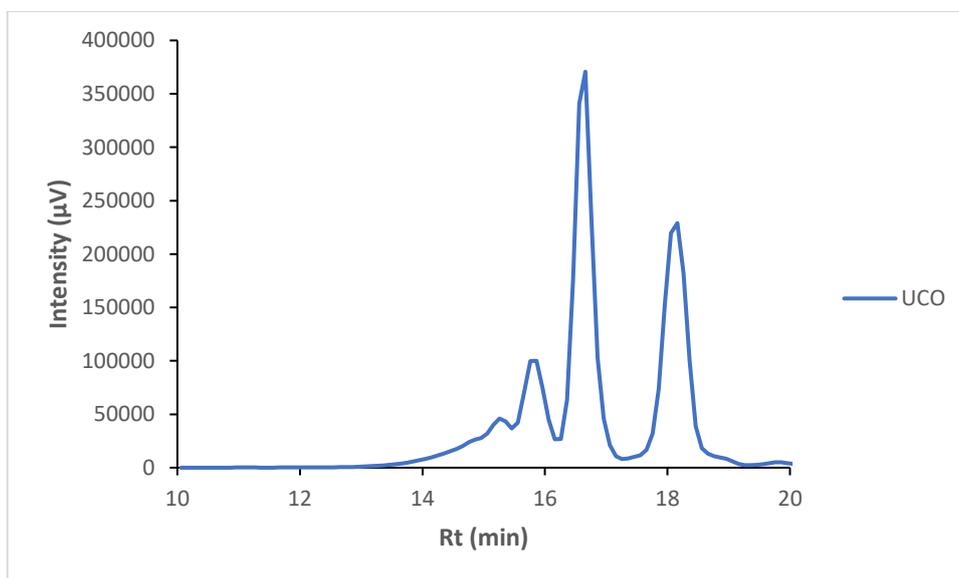


Figure 47 - GPC analysis of the resulting WCO

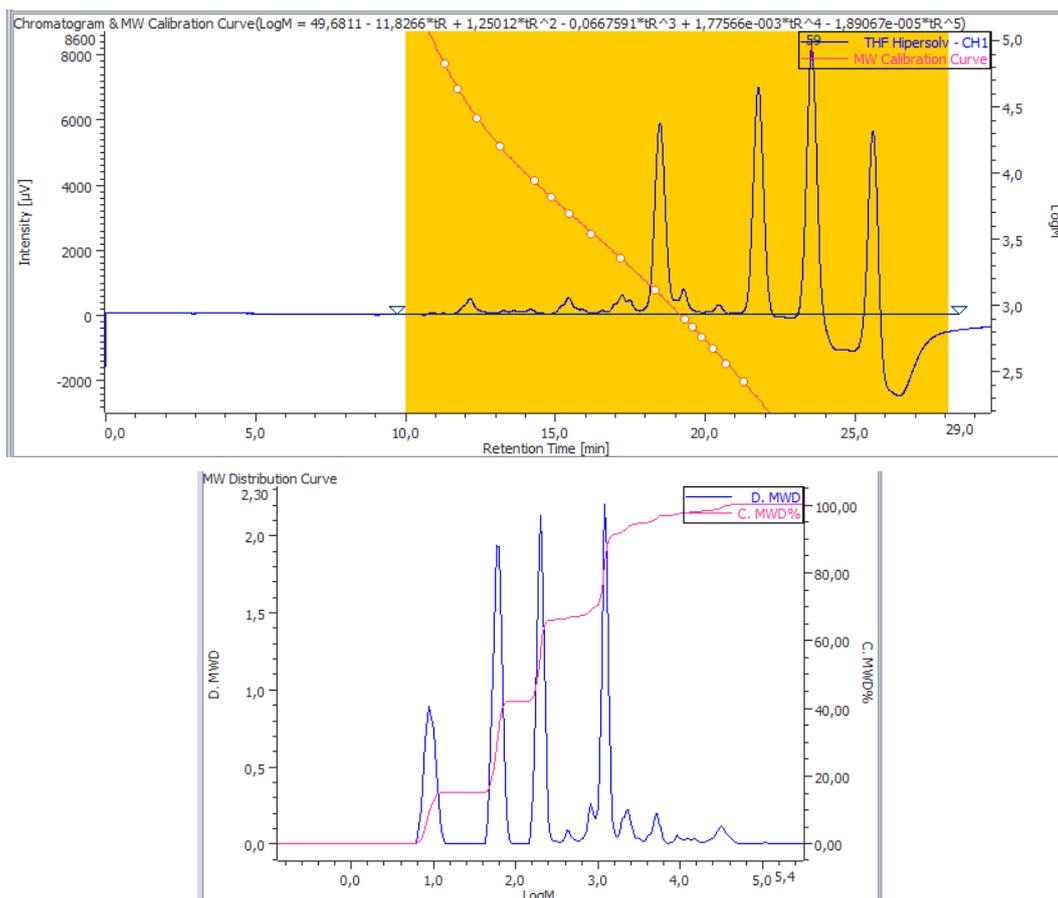


Figure 48 - WCO MW calibration curve (top) and cumulative WCO distribution curve (bottom)

The calibration curve, figure 48, used to calculate the molecular weights of the different peaks, figure 47, depending on the respective retention times is the following:

$$\text{Log}(MW) = 49.6811 - 11.8266RT + 1.2512RT^2 - 0.0667591RT^3 + 1,77566 * (10^{-3}) * (RT^4) - 1,89067 * 10^{-5}RT^5 \quad (10)$$

Table 6 - WCO MW of the GPC peaks

RT	MW	Compound
<b>15.28</b>	5346.18	n.i.
<b>15.8</b>	4214.87	n.i.
<b>16.63</b>	2895.43	n.i.
<b>18.1</b>	1435.20	n.i.

It's impossible to determine the composition of the WCO, table 6, but comparing the results from the two GPC analysis it is possible to conclude that the heavier molecules will break forming lighter molecules generating the TG, DG and the MG.

## 7.6. Particleboard test results

Numerous formulations were developed, but only the formulations containing PMDI were subjected to a physical analysis test. All the particleboards that did not contain PMDI when leaving the heating press (after a period for cooling) the boards did not show rigidity and would break easily when subjected to a small strength.

Table 7 - Particleboards specifications table

Particleboard	Initial Thickness (cm)	Formulations
#1	14.41	4% PMDI in the wood
#2	14.64	4% PMDI in the wood & resin
#3	14.98	5% PMDI in the wood & resin
#4	11.00	3% PMDI in the wood and resin
#5	12.00	1.5% PMDI in the wood and resin

Table 8 - Particleboard density results (\*taken from Appendix I)

Particleboard	Density (g/cm <sup>3</sup> )	Required value*
#1	678	650 - 700
#2	690	
#3	648	
#4	760	≈ 700
#5	782	

Table 9 - Particleboard traction result (\*taken from Appendix I)

Particleboard	Traction (N/mm <sup>2</sup> )	Required value*
#1	0.3	≥ 0,35
#2	0,63	
#3	0.725	
#4	0.20	≥ 0,40
#5	0.23	

Table 10 - Particleboard swelling results (\*taken from Appendix I)

Particleboard	Swelling (%)	Required value (%)
#1	24	≤ 8
#2	6	
#3	18	
#4	52	
#5	53	

Table 11 - Particleboard moisture results (\*taken from Appendix I)

Particleboard	Moisture content (%)	Required value (%)
#1	24.7	8 ± 3
#2	6.15	
#3	18.3	
#4	2.8	
#5	3.6	

As mentioned before, many formulations produced very fragile particleboards so they were immediately excluded. Comparing the results of Table 8 to 11, from the five particleboard produced, only two had the specifications required. The #1 particleboard failed the traction test and the swelling test, the #4 and #5 particleboard showed very similar results, but they failed to meet the required value.

The particleboards that showed promising results were the ones containing PMDI in both the wood and resin. Both passed the traction test ( $traction \geq 0.40 \text{ N/mm}^2$ ), the density of both boards is according with the specifications but the #3 particle board adsorbed more water having a value of 18% and its required to have  $\leq 8\%$ . The only test that met all the requirements was the #2 particleboard.

## Chapter 8 – Conclusion

Looking at the results obtained, the FTIR-ATR validated the alternative to use crude glycerol instead of its pure version in the process. Also, in the FTIR-ATR of the MG reaction it's possible to visualize the peaks that could correspond to molecular bonds of the MG.

With the GPC analysis of the MG, it was possible to ensure that there was a conversion of TG into MG, but the results also showed that there was still presence in the product some TG and DG, meaning that the reaction itself was not 100% efficient.

Although the GPC apparatus was not properly calibrated to analyse non-linear molecules, the results obtained showed that there is a reduction of the MW. The WCO GPC figure 47 with MG GPC figure 45 and that MG GPC analysis is possible to see three peaks that correspond to the unreacted TG and the other to the DG and MG.

The moisture analysis Karl-Fischer revealed an important essential information for the planning of the process, the analysis of the crude glycerol revealed a high content of water, indicating that a pre-treatment (drying) should be implemented before beginning the MG production reaction to ensure that no water would be inside the reactor when heating to reaction temperature.

To obtain the polyester with high MW ended up being a challenge, because the reaction in question is a reversible reaction. The montage used was not properly equipped to produce such product. In the exits of the reactor it was possible to see water condensation even with a high nitrogen flux. This event was observed due to the smaller diameter of the reactor heads, in a reaction that would require to extract the maximum quantity of water.

From all the particleboards, the #2 was the formulation that obtain the better result, according with the specifications present in Appendix I. The presence of PMDI in the formulation of the particleboards end up being fundamental, because it gave rigidity to it. The formulation produced without PMDI were too much flexible and broke easy, the presence of the PMDI will mean an additional cost to the production.

The objective of this thesis was to valorize the by-product of biodiesel production (crude glycerol). This valorization was not achieved by developing a new fuel or fuel additive but by creating a compound from those two wastes, a monoglyceride. The development of the MG process will valorize not only the biodiesel process but also the crude glycerol, promoting the increase of this market value. The creation of a non-petroleum based resin can be another via of valorization of the prior process referred and it also promotes the study and researching of new non-petroleum based materials so that the demand of petroleum gets lower and more petroleum could be available for the production of energy and less for the production of material. The inclusion of the WCO directly promotes the circular economy but also it does not increase the dilemma of Food vs Fuel.

Although this thesis is complete, there is still much work to be done. For future work this project would benefit with testing the efficiency of different catalyst in the production of the MG and trying to develop a process that would directly implement the MG in the production of the fuel/ fuel additives.

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# APPENDIX I

Specification table for the pine particleboard given by the industry for comparison with the produced in this work.

		ESPECIFICAÇÕES PARA AGLOMERADO DE MADEIRA												
Propriedades físico/mecânicas		Teste ref*	Periodicidade	Espessura (nominal, mm)										
				8	10	12	15	16	18	19	22	25	28	30
Comprimento	(mm)	EN324-1	T	± 5										
Largura	(mm)	EN324-1	T	± 5										
Espessura	(mm)	EN324-1	T	± 0,3										
Esquadria	(mm/m)	EN324-1		± 2										
Densidade	(Kg/m <sup>3</sup> )	EN 323	T	730 ± 5%	710 ± 5%	700 ± 5%	650 ± 5%	620 ± 5%			615 ± 5%			
Humidade	(%)	EN322	T	R ± 3										
Tração	(N/mm <sup>2</sup> )	EN319	T	≥ 0,40			≥ 0,35			≥ 0,30		≥ 0,25		
Tensão / Flexão	(N/mm <sup>2</sup> )	EN310	D	≥ 13			≥ 13			≥ 11,5		≥ 10		
				Face	(N)	≥ 470								
Parafuso	Face	6	D	≥ 420										
	Trapo		(N)	≥ 1300										
Resistência da superfície	(N)	EN311	D	≥ 1300										
Inchamento em água	(%)	EN322	T	≤ 8										
Conteúdo de formaldeído	E1	EN120	D	≤ 8										
	E2		(mg/100g)	> 8 e ≤ 30 mg/ 100 g de painel seco										

Corpo com os requisitos de classe E1 (limitado segundo a EN 120) definidos na Norma Europeia EN 312:2010

Legenda:

T - Ensaio efectuado em todos os tempos

D - Ensaio efectuado diariamente

R - Ensaio efectuado regularmente

Estes valores físico- mecânicos cumprem a classificação P2 definida pela norma europeia EN 312:2010. Painéis de aglomerado de partículas para aplicações de interior

(incluindo mobiliário) para utilização em ambiente seco (tipo P2)

## APPENDIX II

Characteristic sheet of the crude glycerol use in the production of MG and in the particleboards formulation from the production of biodiesel.

ESPECIFICAÇÃO DE VENDA PARA:		Pág. 1 de 1	
		E - 38	
GLICERINA		Edição	Data
		04	05/07/2018
Elaborado: RQF	Revisto: DF	Aprovado: DF	

### 1. Objectivo

A presente especificação determina os limites das características da Glicerina.

### 2. Descrição

Glicerina – subproduto proveniente da reação de transesterificação de metanol com óleos vegetais e/ou óleos alimentares usados (UCO).

### 3. Características

Água (% m/m) (Método interno)	Máx. 10
Glicerina (% m/m) (Método interno)	Min. 82
Metanol (% m/m) (Método interno)	Máx. 0,1
M.O.N.G (Matter Organic Non-Glycerol) (% m/m) (Método interno)	Máx. 1,5
Cinzas (das quais 80% são NaCl) (% m/m) (Método interno)	Máx. 7

### 4. Utilização prevista

Produto destinado a ser utilizado para fins técnicos (não adequado para uso alimentar).

### 5. Condições de Transporte e Armazenamento

Transporte em cisterna, isotank ou flexibag. Armazenar em local limpo, seco e ao abrigo do calor.