

Crude Glycerol Valorization

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Abstract

The objective of this thesis was to valorise 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 added 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 Glycerin, Used Cooking Oil, Resin, Monoglyceride, Particleboards

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 is 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 grate potential, but also some problems, some of them are affected from seasonal variations (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. Waste is a consequence of Mankind existence, where is Man there is waste. With the growth of population, larger cities were built, 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 incinerated and send 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 is a regenerative system that’s based on the valorization of end life products focusing on the principles of reuse, repair and recycling.

type of waste and complexity also evolved, while in the past the predominant waste was organic, nowadays there is an increase of metal waste and more complexed wastes such as plastic, electrical, paper, industrial wastes and so on. Even so, the organic waste remains the predominant and that more developed countries generated more waste, as showed in figure 2 and 3.

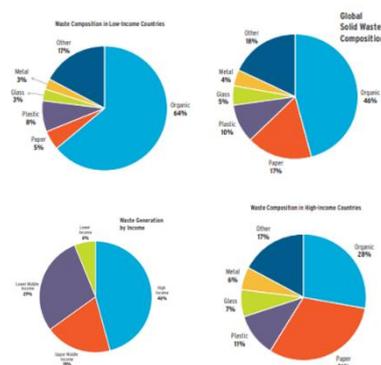


Figure 2 - Waste distribution and composition of different countries [2].

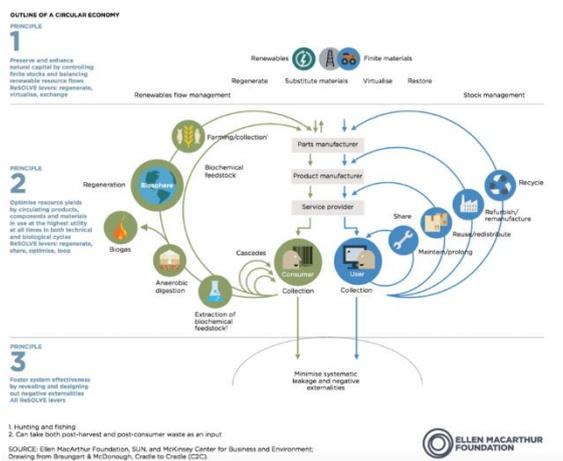


Figure 1 - Circular economy scheme [1].

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 evolve the

¹ 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

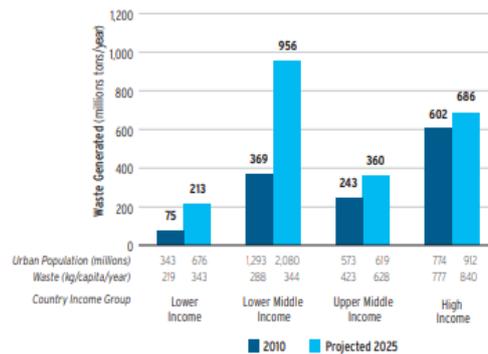


Figure 3 - Amount of waste produced by income [2].

Unused cooking oil (UCO) is a domestic waste produced all over the world. Legislation¹ doesn’t allow to simply dispose it directly into the sewer, making it’s the collection by specified companies a requirement for destroying it properly. This type of domestic waste has

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).

been nowadays used as raw material in biodiesel production. However, industrial processes need new oil as well 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 is 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], Mg generated enzymatic digestion of lipids in human milk disrupt enveloped viruses [5].

The produced MG showed to be an added-value material for all this process, was it will show in further chapters, MG will be included in every step developed. In the production of the polyester, the Mg is one of the reactants of the reaction, in the production of the non-based petroleum resin is used as one of the three components, resulting in the reduction of the resin viscosity. The last application of the MG is when preparing the resin for the preparation of the particleboards, MG can be added to the resin to reduce its viscosity. In the production of the polyester both Mg and a dimer acid (Unydime18) are used. The purpose of using the dimer acid is to allow its reaction with MG terminal OH bonds breaking them and allowing new, forming a high carbon chain compound essential for the resin.

2. Experimental Methods

The following diagram, **Figure 4** is illustrative of the global process developed.

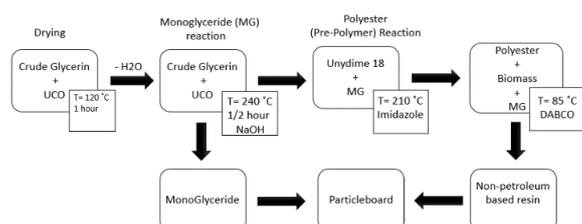


Figure 4 - Workflow diagram

2.1. Preparation of Monoglyceride (MG)

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 2L reactor, 245 g Crude Glycerol, 900 g of used oil and 0.9 g of Sodium hydroxide (0.1 wt% of oil), it was used a four-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet. 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 (¾ Ethanol and ¼ Sample) gave a brown-yellow transparent and homogenous solution. After optimizing the reaction, a scale –up was perform to a 10L reactor using the same conditions of operation and quantity of reactants (proportionally). Both 2L and 10L the reaction time need to produce the Mg was around 30 min.

2.2. Preparation of Polyester (Pre-Polymer)

The pre-polymer polyester was prepared in a 2L three-necked round bottom flask equipped with a mechanical stirrer and a nitrogen inlet by mixing the product from previous reaction, 880 g, X mol of MG with 660 g, X mol of Unidyme18 (U18) with 5-10 g of Imidazole as 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 3.3.

2.3. Resin reaction

During the project 3 types of resin formulations were produce, the first formulation the Rx#1 was to test if the conditions of operations were adequate for the production of the high MW polyester. The other two one differs in a reactant use and the other its added another component 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 was 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 will start to rise with time, then its added wood biomass to the reactor generating the glue. The proportions of this formulation is 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, again uses the same procedure and parameters as the last two but it incorporates another component, MG that is add after mixing the biomass with the polyester. The parameters for this formulation is 30% Polyester, 50% Biomass and 20% MG.

2.4. Production of Particleboard

The plywood will be the final application for the produce glue, there is two different steps. The first steps involve mixing the glue with another product, MDI. The plywood produces is composed by three layers (one internal and two external layers). The internal layers is composed by 208 g of pine fine wood and 20g of Rx glue, before mixing the glue with the wood 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, its put 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 time of another 10 minutes.

3. Characterization Methods

3.1. FTIR-ATR

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 5**). As a result, a 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

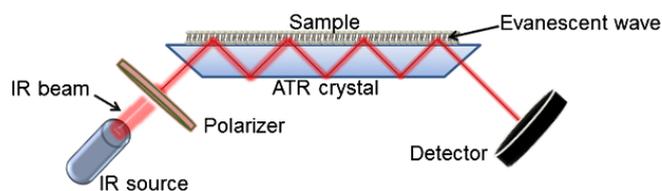


Figure 5 - Schematic representation of an ATR-FTIR system [6]

moments when excited allowing their identification. The spectrums were obtain using a ABB FTLA 2000-100spectrometer with the software F. Menges "Spectragryph – optical spectroscopy software", Version 1.2.9, 2018.

3.2. 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 it 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 is used to generate a graphic known as TGA curve, where is represent 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 utilize to study/characterize the thermal behaviour of a material and defined decomposition/degradation pattern [53].

3.3. OH value and Acid 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.

Procedure:

- Acid Value

Weight 1 to 2 g of sample and dissolve in 40-50 ml;

- THF Titulate using KOH 0,1N (in Etanol) and as indicator Thymolphthalein (1% in THF);

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

- OH value

- Weight 1 to 2 g of sample and dissolve in 40-50 mL THF;
- Add 10 mL to the catalyst solution (1% (4-n,n-dimethylaminopyridine ((DMAP) in THF) (1 g in 100 mL));
- Add 10 mL to the acetylation solution (12,5% acetic anhydride in THF (125 mL in 1000 mL);
- Stear for 10 min;
- Add 2 mL of distillate water;
- Stear for 30 min;
- Titulate using KOH 0,5N (in Ethanol) and as a indicator Thymolphthalein (1% in THF);
- Repeat all the above steps without the sample, White test.

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

$$\text{OH value} = \frac{0,5 \times 56,1 \times (\Delta V_{\text{white}} - \Delta V_{\text{sample}})}{m \text{ sample}} + \text{Acid Value} \quad (2)$$

$$MW = \frac{56100 \times \text{functionality}}{\text{Acid Value} + \text{OH value}} \quad (3)$$

3.4. Moisture Analysis 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 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 more

adequate to use the Volumetric Karl-Fischer can large samples will fill quickly the Coulometric measuring cell.

3.5. Gel Permeation Chromatography (GPC)

GPC 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 X 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 determining the molecular weight.



Figure 6 - GPC schematic workflow

3.6. Particleboard tests

The particleboard produce were sent to an industrial facility, different test were made the see if they were according with the specifications to be produce industry, ANNEX I. The following tests were apply to five different particleboard which one with different resin formulation.

3.6.1. 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) then after defining the slop of the force, the machine will star pulling the sample at two ends and will pulled 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 of external layer.

3.6.2. Swelling

The Swelling test is a very simple test to apply; it consists in introducing a sample of the particleboard inside a thermostatic bath (Grant) 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.

3.6.3. Moisture content

To determine the moisture content existing in the samples of particleboard, 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.

$$\%Moisture = \frac{W_{inicial} - W_{final}}{W_{final}} \times 100 \quad (4)$$

4. Results and discussion

4.1. FTIR-ATR

In the Figure 6 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 as any contaminate. The reason why the comparison of the “pure” commercial glycerol with the crude.

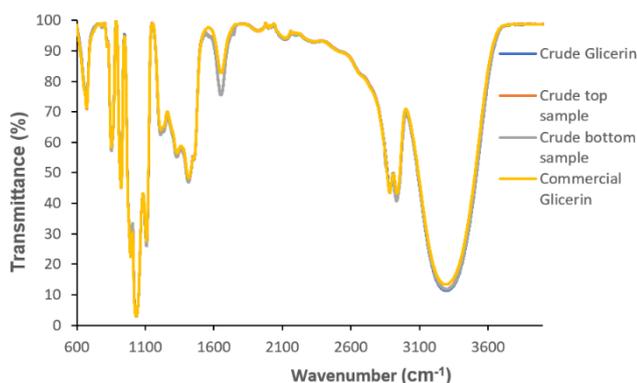


Figure 6 - FTIR-ATR ANALYSIS OF CRUDE GLYCEROL VS PURE GLYCEROL (85%)

As is possible to see, in figure, between 3000-3500 cm⁻¹ a very intense band that corresponds to the alcohol intermolecular bonding (O-H) stretching, between 2800-2900 cm⁻¹ a medium peak relative to the C-H alkane

stretching, the 1600cm⁻¹ is associate with possible existence of water and around 1100 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 were 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.

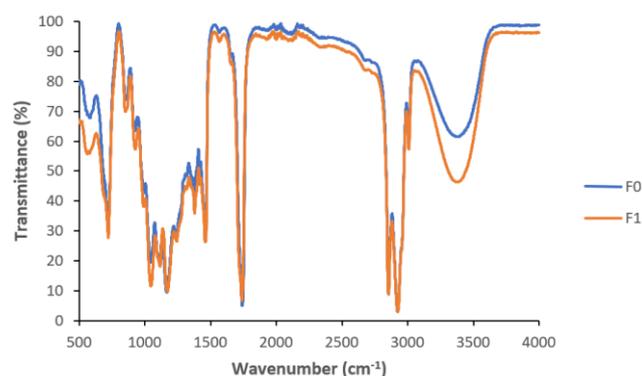


Figure 7 - FTIR-ATR spectrum of the produce MG at beginning of the reaction (F0) and at the end (F1).

F0 is the sample taken when the reactor reached the 240°C, when the desire temperature was achieve and F1 is a sample taken when the reaction ended. The Figure 8 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 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.

4.2. 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 °C/min with a flux of nitrogen of 200ml/min and the temperature range was of 25-600 °C.

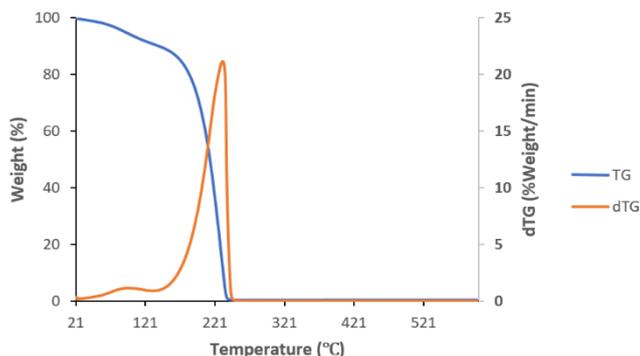


Figure 8 - Commercial Glycerine TG analysis

From Figure 8 is possible to see two zone were 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 is possible to see a zone where the major weight loss occurs of around 87%, maybe due to the breaking of the molecular bonds.

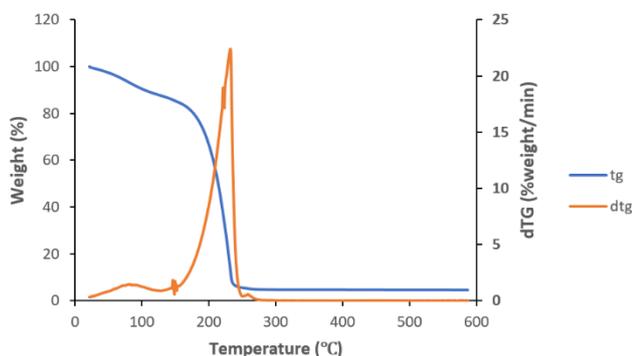


Figure 9 - Crude Glycerine TG analysis

Comparing the TGA of Crude Glycerol (Figure 9) with the TGA of Commercial Glycerol (Figure 8) 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 is show the zone where the highest weight loss occurs possible due to the breaking of the molecular bonds of the sample.

4.3. Acid and OH 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 10, 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 giving and the molecular weight of the polyester was 2400.

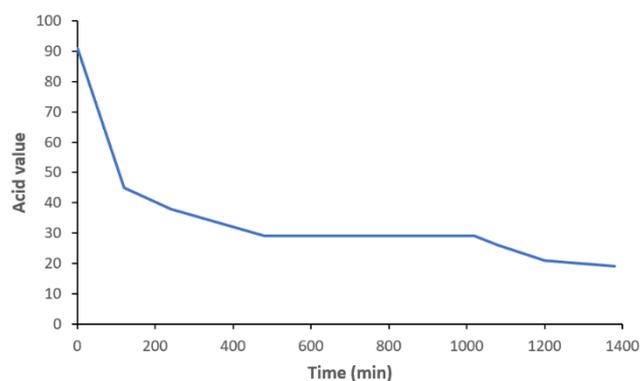


Figure 10 - Initial Polyester formulation Acid value curve

Final polyester formulation used contained 880 g of Mg to 660 g of dimer acid (U18) and 5-10 g of Imidazole. Comparing the graphics in clear to see that the final formulation that the initial acid value was lower, due to the excess of MG in the solution. The initial quantity of Mg initially used was of 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, figure 11, obtained a OH value of 29, due to the excess of Mg there's still some that didn't react, the final acid value was of 6 and molecular weight 3611.

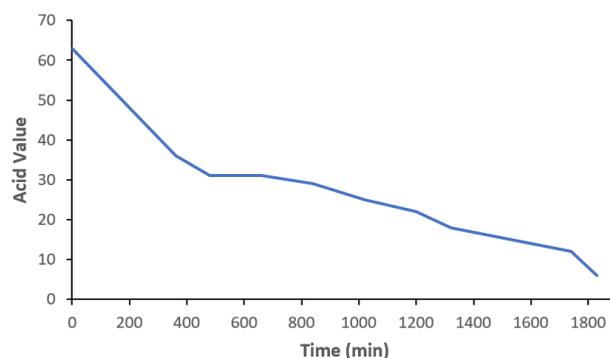


Figure 11 - Final Polyester formulation Acid value curve

4.4. Moisture Analysis Karl-Fischer (KF)

The Volumetric Karl Fischer analysis was used for determination the moisture content of the Crude Glycerol, the result of KF show 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 introduce into the reactor. If the water is not removed, it represents a risk to the reaction generating bursts inside the reaction.

4.5. 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.

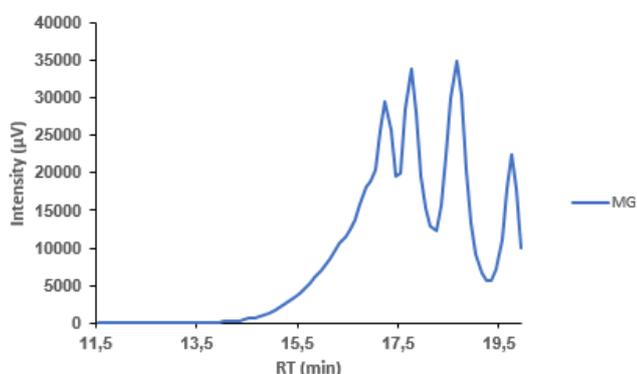


Figure 12- GPC analysis of the resulting MG

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

Where RT is the retention time in the GPC column.

As mention before, substituting the retention time value of the peaks, figure 12, in the calibration curve, eq.5, 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 GPC column is expected that the TG will have lesser retention time (RT) than the DG and MG.

Table 1 - MG GPC Peak determination

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

$$\text{Log}(MW) = 49.6811 - 11.8266RT + 1.2512RT^2 - 0.0667591RT^3 + 1,77566 * (10^{-3}) * (RT^4) - 1,89067 * 10^{-5}RT^5 \quad (6)$$

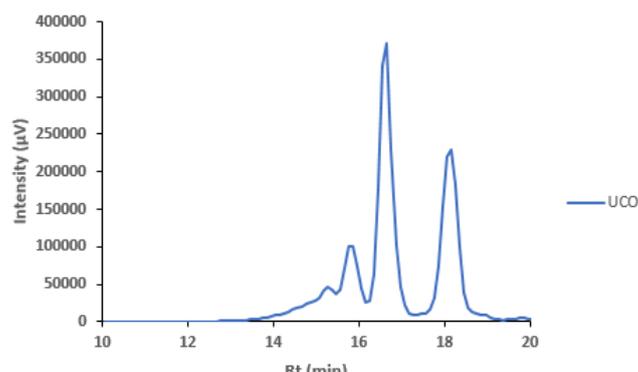


Figure 14 - GPC ANALYSIS OF THE RESULTING WCO

Table 2 - WCO MW of GPC peaks

RT	MW	Compound
15.28	5346.18	n.i.
15.8	4214.87	n.i.
16.63	2895.43	n.i.
18.1	1435.20	n.i.

It's impossible to determine the composition of the WCO 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.

4.6. Particleboard tests

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 3 - Particleboard spec table

Particle board	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	3% PMDI in the wood and resin
#5	12	1.5% PMDI in the wood and resin

Table 4 - PARTICLEBOARD DENSITY RESULTS (*TAKEN FROM APPENDIX I)

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

Table 5 - PARTICLEBOARD TRACTION RESULT (*TAKEN FROM APPENDIX I)

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

Table 6 - PARTICLEBOARD SWELLING RESULTS (*TAKEN FROM APPENDIX I)

Particleboard	Swelling (%)	Required value (%)
#1	24	≤ 8
#2	5.5	
#3	18	
#4	52	
#5	53.4	

Table 7 - PARTICLEBOARD MOISTURE RESULTS (*TAKEN FROM APPENDIX I)

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

As mention before many formulations produce very fragile particleboards so they immediately excluded, comparing the results of **Table 4 to 7**, from the five particle board produce only two had the specifications required. The #1 particleboard fail the traction test and the swelling test, the #4 and #5 particle board show very similar results, but they fail the meet the required value.

The particleboards that show promising results were the ones containing PMDI in both the wood and resin. Both obtain pass 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 ≤ 8%. The only test that met all the requirements was the #2 particle board.

5. Conclusions

Looking at the results obtained, the FTIR-ATR validated the alternative to used 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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