

# Polyurethane foams from renewable and sustainable polyols

Noemi Finez Acero  
noemi.finez@estudiant.upc.edu

Instituto Superior Técnico, Lisboa, Portugal

July 2014

## Abstract

The aim of this thesis is the production of polyurethane foams with polyols from liquefied wood. The objective is to find the best combination of appropriate properties to polyurethane foams with maximum content of polyols from wood liquefaction to decrease the price and make the foam environmentally friendlier. First of all, experimental work began with the optimizing of wood liquefaction reaction. This part was performed with different type of catalysts in order to find the best yield results and the cheapest catalyst at industrial level. Next was carried the extraction of the polyols in order to eliminate the sugar molecules present in liquefied wood, as consequence of the breaking of bonds in cellulose, lignin and hemicellulose through depolymerization. The polyols were characterized with the determination valor OH and acid value and the spectroscopic technique ATR-FTIR. In the second part of this thesis was obtained the foams which presented good results when compared with commercial foams and include polyols from fossil fuels. The formulation of the foams should be improve, but the results show that is possible the use polyols from liquefied wood for produce industrial foams with lower cost.

**Keywords:** liquefaction, liquefied wood, extraction, polyols, catalyst, polyurethane foams.

## 1. Introduction

Biomass is naturally occurring organic material that can be used as a renewable feedstock for the production of chemicals and fuels. The most abundant biomass is lignocellulosic, which is the major component of cell walls of plants and can be used as an alternative to fossil fuels. (Green Chem.[2013]) Nowadays some products made from fossil fuels are an emergent problem, as consequence of their nature and lower biodegradability. Conversion technologies refer to a wide array of state-of-the-art technologies capable of converting unrecyclable solid waste into useful products, such as green fuels and renewable energy, in an environmentally beneficial way. The aim of this thesis is utilizing liquefaction conversion technology to liquefied wood. This method gives the possibility for the obtention of a product which can be used to produce materials and fuels.([8]) The most familiar and accessible biomass lignocellulosic feedstocks are wood, algae, municipal solid waste, sewage sludge and scraps from paper.([15])

With the polyols obtained from the liquefied wood were produced polyurethane foams for isolation uses. These polyols are an environmentally conscious alternative to the depleting fossil resources and the catalytic transformation of the constituents of lignocellulose to this value added

chemical has attracted a lot of attention because it is presented as an environmentally attractive and energy efficient process compared to the currently used high temperature and energy consuming in gasification or pyrolysis technologies. Also the use of these polyols decreases the price of the foam and makes it more biodegradable. But it is necessary to take into account that the polyols have to satisfy some structural requirements in order to compete with petrochemical polyols, such as the right functionality and molecular weight.

## 2. Conversion technologies

Conversion technologies refer to a wide array of biological, chemical, thermal (excluding incineration) and mechanical technologies capable of converting different kinds of biomass into useful products and chemicals, green fuels such as hydrogen, natural gas, ethanol and biodiesel, and clean, renewable energy such as electricity. Utilization of conversion technologies can be used to transform solid waste which can reduce greenhouse gas emissions, reduce dependence of imported fossil fuels and enhance recycling efforts.([9])

### 2.1. Thermochemical conversion

Thermochemical biomass conversion includes a number of possible methods, such as, pyrolysis, gasification, and liquefaction, to produce fuels and

chemicals.

### 2.1.1 Gasification

Gasification converts biomass through partial oxidation into a gaseous mixture of syngas consisting of hydrogen  $H_2$ , carbon monoxide  $CO$ , methane  $CH_4$  and carbon dioxide  $CO_2$ . The oxidant can be steam,  $CO_2$  or their mixtures, with a small amount of air, and it is the main parameter affecting the syngas composition. Air is the most used gasifying agent, due to the great availability and no cost, but the large amount of nitrogen requires higher power on blowers and bigger equipment and especially lowers the heating value of the syngas produced. Pure  $O_2$ , avoiding the nitrogen content, increases the syngas heating value but also the operating costs due to the  $O_2$  production. Steam, due to the great availability and about zero cost of water, increases the heating value and  $H_2$  content of syngas, and can be produced using the excess of heat of the power plant. The syngas can be used in turbines and boilers or as feed gas for the production of liquid alkanes by FischerTropsch Synthesis. ([10]) Gasifiers can be divided into two main families, fixed bed (from which are derived the moving bed) and fluidized bed. Within the fixed bed gasifiers it is possible to distinguish updraft configuration when biomass move from the top and the gasifying agent from the bottom; downdraft configuration (concurrent), when the biomass and the gasifying agent move together from the top to the bottom of the reactor; crosscurrent when the biomass moves down and the agent is fed at right angles. ([12])

### 2.1.2 Pyrolysis

Pyrolysis is a thermal decomposition process that occurs in the absence of oxygen or when significantly less oxygen is present than required for complete combustion. The rate of thermal decomposition depends on biomass particle size and type, as well as, the heating rate, final temperature, reactor configuration and presence of impurities. Pyrolysis of biomass is a promising route for the production of solid (char), liquid (tar), and gaseous products as possible alternative sources of energy and chemicals. The yield of these products can be changed by selecting appropriate heating rates and pyrolysis temperatures. Production of liquid products is maximum at temperatures between 352C and 452C. Low temperatures and high residence times favor the production of char, while the higher temperatures and short residence times lead to high liquid production. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis. In the **conventional**

**pyrolysis** the biomass is heated slowly to produce char as a major product. At present, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence times. In **fast pyrolysis**, biomass is heated rapidly in the absence of oxygen, and it decomposes as vapours, aerosols, gases and char. Fast pyrolysis (more accurately defined as thermolysis) is a process in which the biomass is rapidly heated to high temperatures in the absence of air. If the aim is the production of mainly liquid and/or gaseous products a fast pyrolysis is recommended. Fast pyrolysis processes produce 6075 wt.% of liquid bio-oil, 1525 wt.% of solid char, and 1020 wt.% of noncondensable gases, depending on the feedstock used. If the purpose were to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. If the purpose were to maximize the yield of fuel gas resulting from biomass pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred. ([11]) The liquid bio-oil produced by fast pyrolysis has the considerable advantage of being storable and transportable, as well as the potential to supply a number of valuable chemicals that offer the attraction of much higher added value than fuels. The vapours and aerosols can be quickly condensed to liquid called bio-oil. The **flash pyrolysis** of biomass is a promising route with regard to the production of solid, liquid (bio-oil or bio-crude-oil) and gaseous products as possible alternate energy sources. Upgrading by lowering the oxygen content and removing alkalis by means of hydrogenation and catalytic cracking of the oil may be required for certain applications. Major problem of the present reactors for flash pyrolysis are the quality and the stability of the produced oil, strongly affected by char/ash content of bio-oil. Besides the known problems concerning solid particles in the bio-oil, char fines will catalyze repolymerization reactions inside the oil resulting in a higher viscosity. The flash pyrolysis of biomass inherently results in the production of pyrolytic water, which is one of the major drawbacks of the bio-oil produced. ([14])

### 2.1.3 Liquefaction

Lignocellulose is a complex, macromolecular polymer composed through the cross-linking of CO and CC bonds in its three primary constituents: cellulose, hemicellulose, and lignin. Through liquefaction, lignocellulosic components are brought to low molecular weight compounds with high reactivity that can be used in many useful potential applications. To separate the primary constituents and keep their respective structural units intact, cracking lignocellulose macromolecules can be per-

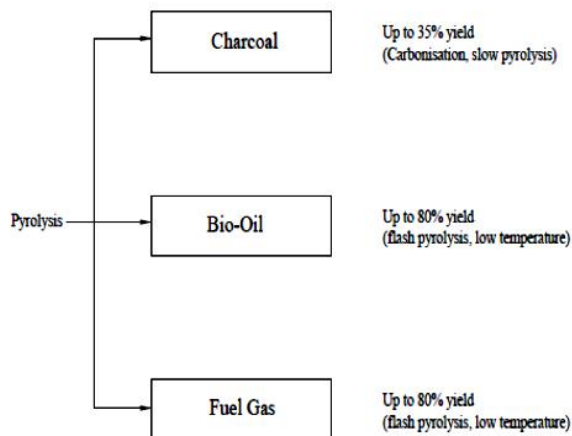


Figure 1: Products from pyrolysis. Source: Energy production from biomass (part 2): conversion technologies. Peter McKendry

formed. ([8]) Liquefaction technique can be done in the presence of organic solvents (phenols or polyhydric alcohols) using acidic or alkaline catalyst (organic or inorganic) at temperatures ranging from 120 to 180C, or without catalyst at higher temperatures ranging from 180 to 250C. Recently, also other solvents, such as cyclic carbonates, lower alcohols and dioxane were examined and used successfully for the liquefaction of woody biomass. ([4]) Catalytic liquefaction has attracted a lot of attention due to its simple operation, high production level and high energy conversion and because it is presented as an environmentally attractive and energy efficient process compared to the currently used high temperature and energy consuming gasification or pyrolysis technologies. That is the reason why in this project the conversion of the lignocellulosic biomass (wood) is produced by catalytic liquefaction.

Depending of the final use of the liquefied wood is chose the kind of liquefaction reaction, and the reagents. Is important to bear in mind that phenol is damaged to the environment. Also is important to make sure that the selected temperature of the reaction is compatible with the boiling point of the solvents. It is necessary to choose the time and the temperature of the reaction carefully, to obtain the biggest yield of liquefaction possible. As larger the time and temperature of the reaction are as larger the percentage of liquefaction is. But if the temperature is too high the spending of energy is bigger and part of the components from the liquefaction volatilize. Also if the temperature is too high starts a reaction of condensation of the liquefaction products. Both situations reduce the percentage of liquefaction. The residue from liquefaction products is the major factor in the evaluation of the efficiency

of lignocellulosic liquefaction. ([13])

#### 2.1.4 Uses of liquefied wood

In this moment there are a lot of interest in the production of liquefied wood because it can be use in different fields. The first one in be investigated was the use of the liquefied lignocellulosic biomass to obtain adhesives and other polymers, after that the efforts starting to focus to produce fuel. But it is even possible get products for the alimentary industry (sugars). The hydroxyl groups from liquefied wood components can be used as polyols to produce polyurethane foams, polyurethane resin precursors, phenolic resin and adhesives among the more important uses. The obtaining of the polyols from liquefied wood can be reproduced in the industry with low cost, then it means that they are an interesting substitute for polyols from petroleum, but the wood's polyols have to satisfy some structural requirements in order to compete with petrochemical polyols, such as the right functionality and molecular weight. ([5])

In this case the polyols obtained from liquefied wood were used to produce polyurethane foam.

### 3. Wood: chemical characteristics

Wood biomass is comprised of C, H, O and N, and also little quantities of Ca, K and Mg. The components of lignocellulosic biomass include cellulose, hemicellulose, lignin, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds. **Cellulose** is the major chemical in wood, it is a linear polymer composed of repeating anhydroglucose units. Cellulose is a remarkably pure organic polymer, consisting of units of anhydroglucose held together in a giant straight chain molecule. These anhydroglucose units are bound together by *beta*-(1,4)-glycosidic linkages. By forming intramolecular and intermolecular hydrogen bonds between OH groups within the same cellulose chain and the surrounding cellulose chains, the chains tend to be arranged parallel and form a crystalline supermolecular structure. Then, bundles of linear cellulose chains form a microfibril which is oriented in the cell wall structure. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Due its crystallinity is the less susceptible to the liquefaction. ([2])

**Hemicellulose** is the second major chemical species in wood. They are amorphous polysaccharides, such as xylans, galactoglucomannans, arabinogalactans, glucans, and galactans. The hemicelluloses, unlike cellulose, not only contain glucose units, but they are also composed of a number of different pentose and hexose monosaccharides. Hemicelluloses tend to be much shorter in

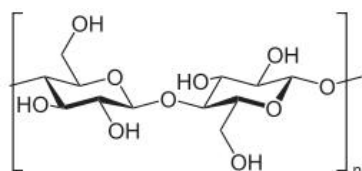


Figure 2: Schematic illustration of building units of cellulose.

length than cellulose, and the molecular structure is slightly branched. Because of the amorphous morphology, hemicelluloses are partially soluble or swellable in water. Hemicellulose act as the cement material holding together the cellulose micelles and fiber. Among the most important sugar of the hemicelluloses component is xylose. In hardwood xylan, the backbone chain consists of xylose units which are linked by *beta*-(1,4)-glycosidic bonds and branched by *alpha*-(1,2)-glycosidic bonds with 4-Omethylglucuronic acid groups. For softwood xylan, the acetyl groups are fewer in the backbone chain. ([2])

Lignin is a chemical compound that is most com-

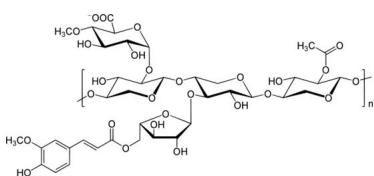


Figure 3: Schematic example of one possible xylan structure (xylan are a group of hemicelluloses).

monly derived from wood and is an integral part of the cell walls of plants. Lignin is a complex, high molecular weight (in excess of 10.000 amu) polymer built of hydroxyphenylpropane units. It is a completely different polymeric material, being highly cross linked and having phenolic like structures as the monomeric base. The molecule consists of various types of substructures that appear to repeat in random manner. The polysaccharide components of plant cell walls are highly hydrophilic and thus permeable to water, whereas lignin is more hydrophobic. The crosslinking of polysaccharides by lignin is an obstacle for water absorption to the cell wall Lignins are polymers of aromatic compounds. Lignin is covalently linked with xylans in the case of hardwoods and with galactoglucmannans in the case of softwoods. ([2])

#### 4. Polyurethane

Polyurethanes (PUs) are a very large family of materials. The reaction between isocyanate and hydroxyl compounds was identified in the 19 th century, the foundations of polyurethanes industry

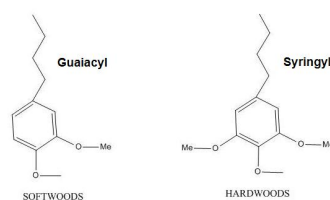


Figure 4: Schematic illustration of building units of lignin.

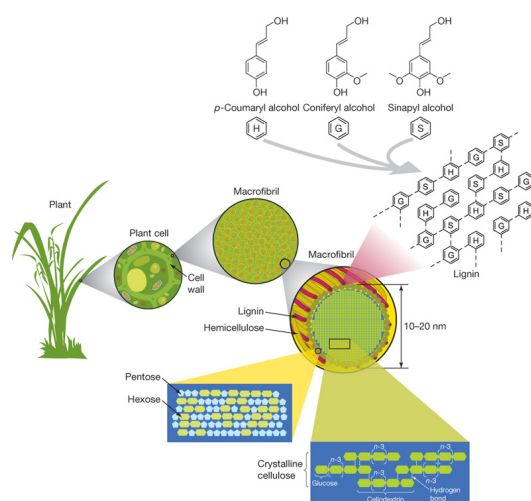


Figure 5: Structure of lignocellulose. Source: Genomics of cellulosic biofuels. Nature 454, 841845 (2008).

were laid in the en of the 30's; Otto Bayer and his coworkers at I.G. Farben in Leverkusen, Germany, first made polyurethanes in 1937.

#### 4.1. Polyurethane's market

The request for polyurethane is mainly generated by increasing demand from construction industry dominated by Asia. The product value chain starts with feed stock material until the end-use. The polyurethane market is segmented based on product types such as flexible foam, rigid foam, coatings, adhesives and sealants and elastomers; based on end-use as furniture and interiors, construction, automotive, electronics and appliances, footwear, packaging; and based on geography into Europe, North America, Asia Pacific and Rest of the World.([3])

#### 4.2. Polyurethane's chemistry

PUs come from the reaction between polyol (alcohol containing multiple OH groups) and isocyanate (NCO functional group). The result is a polymer with a multiple urethane groups (-NH-COO-). The principle of the polymer chemistry of the PU reaction is the extension of to di and polyfunctional isocyanates and hydroxyl compounds resulting in the formation of linear, branched or cross linked poly-

mers. The isocyanate reacts also with water (2:1), this is responsible of the foaming of urethane polymers in the production of foams by the liberation of carbon dioxide and the simultaneous formation of urea groups (during cure process).

#### 4.3. Polyurethane foams

Flexible foams are the largest market segment polyurethanes and can be obtained in block or molded. They can be produced with different densities and applied mainly in the production of mattresses and car seats. Rigid foams are the second most important market polyurethanes. They are used as thermal insulation in household appliances and in the building construction. Polyurethanes are a large family of polymers with very than they have in common the presence of repeating urethane groups in their molecular structure. They are prepared from the polyol component and isocyanates. Currently, for this application, only the production of polyol from renewable resources is reported. Although aliphatic di-isocyanates from dimerization of fatty acids are commercial, they do not have sufficient reactivity for application in foams, but they could be used for coatings and other applications. Thus, isocyanate for foams must be aromatic. But, polyols from different kinds of biomass, for example from wood, have an excellent chance for competing with petrochemical polyols in quality and especially in price of production. ([16])

##### 4.3.1 Types of production

There are two different ways to prepare the polyurethanes: one shot method and prepolymer method. The first one consists in the reaction of the isocyanate with the other components. In the prepolymer method, the isocyanate reacts at first with the polyol to make the prepolymer. After that the prepolymer reacts with the other components to obtain the final polymer. ([1])

## 5. Experimental

### 5.1. Reagents

Wood chips and sawdust from pine wood were used as a raw material. DEG, 2-Ethylhexanol from the chemical company Sigma Aldrich were used as a reagents.

In the reaction of PU foams B8871, DMDEE, TCPP, TEP, Safron 6605, DP45, DME, Voranol 1010L, MPG, GA13 VTA, TDI TX, Propane and Isobutane were used as a reagents.

### 5.2. Pretreatment

At least 12 hours before of doing the reaction is necessary to impregnate the wood spraying solvents or liquefied wood.

### 5.3. Liquefaction reaction

The liquefaction was carried in a wide-necked reaction flask, equipped with a multiple socket lid and starring head and proper stirring shaft, thermopar, a Dean-Stark separator/condenser and a solid dropping funnel; the wood/solvent mixture and the catalyst were placed in the reaction flask. The flask was put on a heating mantle and preheated at 160C. The liquefaction was conducted under constant stirring and reflux until it finished. After the reaction, the product was leave to cool until 80C. The resulting reaction mixture filtered in a kitasato apparatus until colourless filtrate was obtained. The liquefied residue collected, was dried in oven at 120C to until constant weight was verified, for the determination of the liquefaction yield ( $\alpha$ ) in mass terms.

$$\alpha = \left(100 - \frac{W_f}{W_i}\right) * 100 \quad (1)$$

In the expression  $W_f$  is the final weight, after dried the residue and  $W_i$  is the initial weigh of the wood.

### 5.4. Extraction

To produce polyurethane foams the sugars from the liquefied wood were extracted. This procedure allows to improve the reaction with the isocyanate to produce polyurethane. The extraction was carried out in a decanter flask where the liquefied wood with more or less the same quantity of water was mixed and stirred.

### 5.5. One component foam technology

The one component foams foaming process has generally 4 stages as shown in figure 6. Three different



Figure 6: Schematic diagram of foaming process.

compositions of foams were done.

### 5.6. Characterization

In order to do the characterization of the liquefied wood and its polyols, the following experimental test were realized: Acid value, hydroxyl number, ATR-FTIR, and SEM.

#### 5.6.1 Acid and OH values

The experimental method used to obtain acid and OH values is not explained because it is confidential.

$$V_{Acid} = \frac{vKOH \ 5,61}{mSample} \quad (2)$$

$$V_{OH} = \frac{(blank - vKOH) \ 0,5 \ 56,1}{mSample} + V_{Acid} \quad (3)$$

### 5.6.2 SEM

Scanning electron microscopy (SEM) observations of wood powder and liquefaction residue and polyurethane foam, were micrographed on a Hitachi S-2400 equipment, with a 15 kV beam. Samples were sputter coated with a thin layer of gold to avoid electrostatic charging during scanning.

### 5.6.3 Attenuated total reflectance-Fourier transform infrared (ATR-FTIR)

FTIR spectra were recorded on a Nexus-Thermo Nicolet spectrometer (64 scans and resolution of 4  $\text{cm}^{-1}$ ) in the 4000-400  $\text{cm}^{-1}$  range.

### 5.6.4 Quick tests

The three different compositions were evaluated by the research center of the company Greenseal. The properties of a foam can be analysed through the Quick tests. The foam samples were obtained through two different dispensing procedures: Foam bead on paper and on mould. The rating is given visually. The tests are done in two different temperature conditions: 23°C and 5°C.

## 6. Results and discussion

In this section are shown the results from the characterization of the obtained liquefied wood and polyurethane foams.

### 6.1. Characterization of polyols from liquefied wood

In order to do the characterization of the polyols obtained from the liquefied wood, the following experimental test were realized: Acid value, hydroxyl number, ATR-FTIR.

#### 6.1.1 Acid and OH value

The acid value and the hydroxyl number are obtained to calculate the average molecular weight. The hydroxyl number is also important to know the necessary amount of isocyanate. Higher OH numbers usually increase the cost of the formulation due to higher isocyanate consumption.

$$\bar{P}M = \frac{f \cdot 56100}{V_{OH} + V_{Acid}} \quad (4)$$

In the expression  $f$  is the functionality,  $V_{OH}$  is the hydroxyl value and  $V_{Acid}$  is the acid value. The functionality is considered 2,5 as a medium value between 2 (lineal structure of the molecules) and 3 (branched structure).

Results found in literature ([17],[18],[6]): the results for polyols from liquefied wood suggest bigger hydroxyl value 10931323 mg KOH/g and acid value determinate was 7.38.0 mg KOH/g. In this thesis the hydroxyl value is much more low because the

Table 1: Average molecular weight calculated from VOH and V acid

PM	f	VOH	Vacid
3605.769	2.5	34.408	4.488

extraction of the sugars was done. It is important to note that the molecules in biopolyols have plenty of primary hydroxyl groups, including sugar, which indicate these products should have good reactivity with isocyanate, however too much hydroxyl groups confer more rigidity to polyurethane foam. The physical and chemical properties of polyols further to extraction suggest that they have great potential for further reaction with isocyanate to produce foam applications.

### 6.2. ATR-FTIR, Attenuated total reflectance Fourier transform infrared spectroscopy

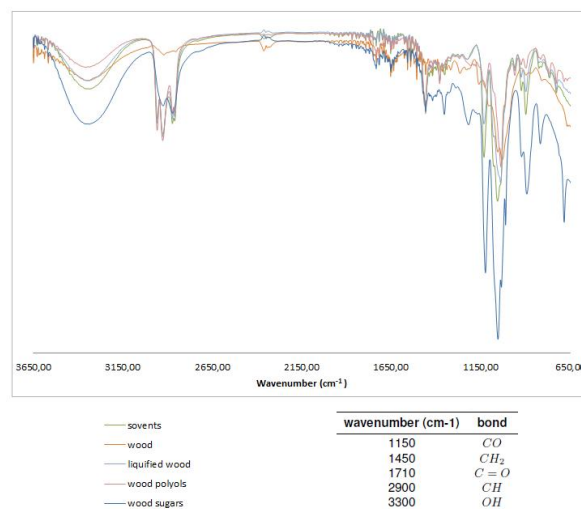


Figure 7: ATR-FTIR analysis of mixture of solvents, pine wood sawdust, liquefied wood from liquefaction, polyols and sugars from extraction of liquefied product.

The ATR-FTIR analysis of mixture of solvents, pine wood sawdust, liquefied wood from liquefaction, polyols and sugars from extraction of liquefied product. The figure 7 shows the results from the ATR-FTIR. In all the samples appear the principal peaks at 1050  $\text{cm}^{-1}$  attributed to the  $-CO$  stretching vibrations, around 2900  $\text{cm}^{-1}$  typical of  $-CH$  stretching vibrations and around 3300  $\text{cm}^{-1}$  which is the typical band arising from the  $-OH$ . All these functional groups are present in the liquefactions solvents (DEG and 2-Ethylhexanol) and products but the peak at 2900  $\text{cm}^{-1}$  does not appear in wood. The reason why they do not appear in wood is because most of atoms of carbon are



bonded between them in the macromolecules that constituted wood (lignin, cellulose and hemicellulose), and a lot of the oxygen atoms are bonded with double bonds to the chain, and when they break a hydrogen atom join to the oxygen becoming  $-OH$  group. The absorption band at  $1710\text{ cm}^{-1}$  is attributed to the stretching vibration of  $-C=O$  common for all soluble components of wood depolymerization. These esters were probably produced by a dehydration reaction between carboxyl groups of wood components in presence of the acid. Carboxyl groups are ordinarily present in hemicellulose and are also formed by oxidation of carbohydrates and lignin. Also, the spectra show some absorption bands which are characteristic for cellulose such as  $CH_2$  group absorption bands at  $1450\text{ cm}^{-1}$ . It is remarkable that the sample from the wood sugars has bigger peaks at  $3300\text{ cm}^{-1}$  ( $-OH$ ) and especially at  $1050\text{ cm}^{-1}$  ( $-CO$ ), because when the wood components bonds are broken a lot of this groups appear, specially when the cellulose breaks in sugars like glucose.

### 6.3. Study of different catalysts for the liquefaction

To optimize the liquefaction reaction, the reaction was carried out with 5 different catalysts and the kinetic of the reactions were compared.

The conversion results were obtained with low quantities of trichloroisocyanuric acid and aluminium chloride. They are the cheapest catalysts. Is very interesting for the industrial application to carry out the reaction with the lowest content of catalyst to get the liquefied wood as cheaper as possible, because the catalyst is the most expensive reagent.

In the figure 8 is showed the reaction yield versus the time of the two best catalysts, 2 and 3, studied with concentrations of 0,1% and 0,5%. The catalytic performance of catalyst 3 is correlated with the acidity of the reaction system due to it is strong lewis acid, and it form basic salts, resulting in the pH value of the solution becoming quite acidic. And this catalyst promoted the cleavage of lignin. ([7]) Is to bear in mind that if the time of the reaction is too much, the recondensation of a solid polymer starts, because repolymerization reactions of the intermediate products formed by the decomposition of lignin.

### 6.4. SEM applied to liquefaction of wood

The wood particles that remained after liquefaction were analyzed using SEM and compared them to the starting material in order to gain more information about the process. Figure 9 shows the SEM micrographs of extracted pine wood prior to the reaction and of the residue after the reaction. In

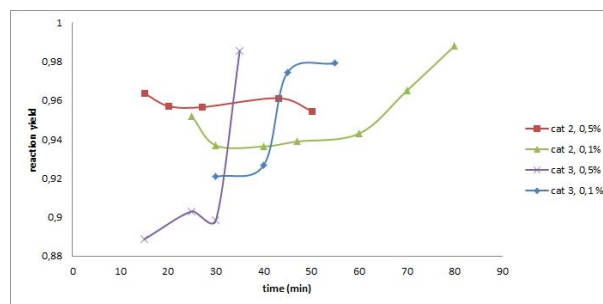


Figure 8: Conversion results of catalysts 2 and 3.

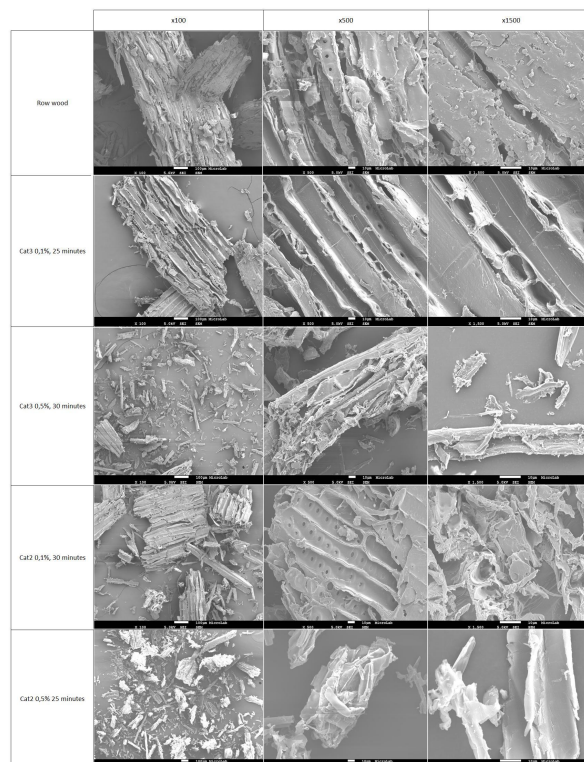


Figure 9: SEM pictures of residues from reactions with catalysts 2 and 3 compared with row wood.

the SEM images is showed the row wood and the residue from reaction with catalysts 2 and 3 with x100, x500 and x1500 augment. The micrographs reveal a substantial difference in wood particle composition and size. The starting material consisted in pine wood sawdust constituted by a mix of small particles, torn fibres, and intact wood parts. The residue appears to contain only irregular, powdery particles of wood fragments, perhaps mixed with some of the products of the polycondensation process that occur towards the end of the liquefaction processes. During the reaction the smallest particles and damaged fibres would undergo dissolution first, leaving behind only the most resistant undamaged parts of wood. There is a big difference between the different concentrations of the catalysts. In the

images with x100 augment is possible to appreciate that the particles are really much smaller after carry out the reaction with a 0,5 % concentration of catalyst than with 0,1%. With more augment it is possible see that the particles are much more degraded also with 0,5% of concentration. The degree of depolymerization with 0,5% of catalyst was substantially higher than with 0,1%.

### 6.5. Characterization of polyurethane foams

During and after the obtaining of the foams, they were studied and characterized.

### 6.6. Quick tests

The foam tested properties were evaluated according to a scale from -5 to 5 (being -5 the worst results and 5 the best). The rating is given visually and during the froth spray, during curing process and after cure foam. The tests were done in two different temperature conditions: 23C and 5C (the temperature is the same inside the can and in the environment). The tests are done in two different temperature conditions to see the effect of the temperature in the reaction, room temperature (23C) and a low temperature (5C). The results of the quick test are showed in the figure 10. The properties of the three formulations are quite similar. But the formulation C has the best properties, probably because has more kinds of additives and more quantity of them in its formulation. It has more quantity of surfactant (B8871) and also contents plasticizer (DP45); they reduce the defects related with the bubble coalescence. Almost all the evaluations of the properties of this foam's formulation are 3 or more. For one of the purpose of this project, to obtain foams with maximum as possible of alternative green reagents, the formulations B and C are the more interesting, because their percentage of polyol from wood is bigger and the properties of this first attempt were satisfactory. In the figure 10 is possible to see that the best results were obtained for cell collapse and the curing streaks in all the foams formulations, this properties are related with the velocity of curing of the froth. The worst results were obtained in base holes, specially for the formulation of foam B. It happens in contact with paper (porous surface) because the blowing agents are captured and remain between the paper's surface and the foam. Comparing the results between the properties of the foams on paper and on mould, the properties on paper are much better because in the mould there are less contact with air and a geometry restriction. In the pictures of the figure 11 appear the different foams, produced at two different temperatures (5 and 23C). In them is possible see that the more appreciable defect are the base holes, specially in the foams produced at 23C. This problem are bigger in foams B and C. The foams

produced at 5C present less defects.

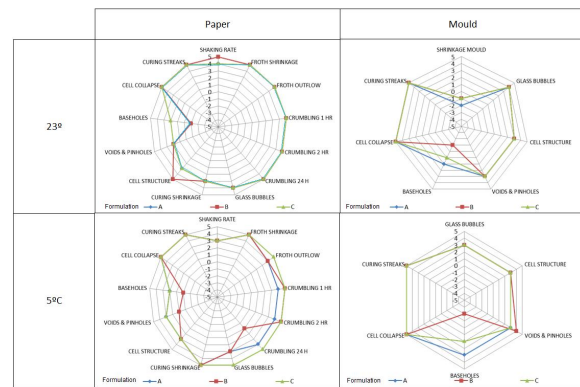


Figure 10: Benchmarking performed between formulations.



Figure 11: Pictures of the different foams.

#### 6.6.1 Output test

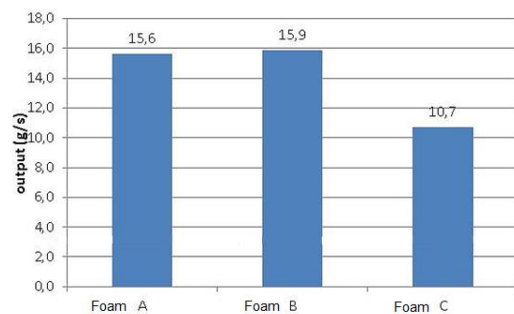


Figure 12: Output results at 5C.

The purpose of this test is to determine the output rate of the foam in mass/time. It consists of dispensing the foam through the applicator from the aerosol. Two different values are measured: the mass difference of the can before and after dispensing (released liquid) and also the mass of foam dispensed (released foam). The output rate depends strongly on the viscosity. The higher the viscosity of the prepolymer of polyurethane products, the lower the will be the output rate. A



viscous product has a lower rate of expansion. The viscosity depends on the canister temperature and the shelf life of the can. A cold and aged canister decrease the output rate. From the 3 foams formulations, as showed at figure 12, formulation C has the lowest output rate (is the most viscous) due to its composition with more additives of high molecular weight.

### 6.6.2 Foam structure (SEM)

SEM images of polyurethane foam samples are shown in figure 13. It can be seen that the biopolyols gave acceptable quality for preparation of polyurethane foams. In the SEM images of the cross section of the different polyurethane foams is showed how the obtained cells are. The pore surface was mostly regular and smooth, but with different size of cells (particularly in foam B). The size distribution is approximately 200-500 micrometres in diameter. The ideal structure is composed by homogeneous network of dodecahedra cells (honeycomb structure), where gas grows inside during the foam formation. This structure is the thermodynamically more stable. The quality of properties of the foams can be related with their microscopical cell structure. It is well known that the cell size of the rigid foam has an important effect on mechanical properties. The excellent honeycomb structure obtained during foam formation made it possible for a considerable amount of still air to be trapped, thus, leading to an increased passive insulation. According to figure 10 the best properties were showed by foam with formulation C. This formulation has the maximum score in most of the properties evaluated (specially on paper). In the SEM images is possible to appreciate that its cells are smaller and more homogeneous, and that means that there is more surface well distributed (it opposes more impediment as isolating).

## 7. Conclusions

It was shown that it is possible to convert wood into liquefied wood via acid liquefaction, at atmospheric pressure and moderate temperatures, in the presence of DEG and 2-Ethylhexanol as solvents and with different type of catalysts. After studying the liquefaction reaction with different catalysts it was found that the best options are trichloroisocyanuric acid and aluminium chloride, both of them with good yield of reaction and cheaper than others known in literature. Also was confirmed that is possible to carry out the liquefaction reaction with only 0,1% of catalysts, important fact because the catalyst is the most expensive reagent. Once the necessary amount of polyols were obtained, three different polyurethane foams were produced by the

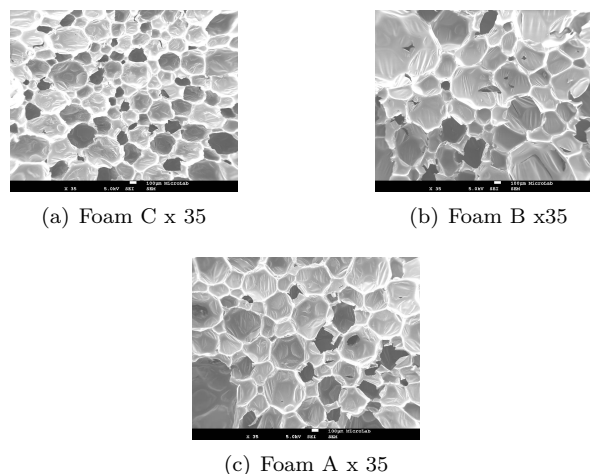


Figure 13: SEM images of Foams.

company Greenseal. The resultant foams have good properties, specially that related with cell collapse and the curing streaks. And they are more respectful with the environment.

### 7.1. Achievements

The principal achievement was to find the way and formulation to produce polyurethane foams for isolation uses with the maximum contents of polyols from liquefied wood. These polyols are an alternative to the depleting fossil resources and the catalytic transformation of the constituents of lignocellulose to this value added chemical because it is presented as an environmentally attractive and energy efficient process compared to the currently used high temperature and energy consuming gasification or pyrolysis technologies. Also the use of these polyols decreases the price of the foam and makes it more biodegradable. Another achievement of the present work were founding a good catalyst to improve the liquefaction reaction and make it cheaper.

### 7.2. Future Work

The results of the obtained foams show that is possible the use of the polyols from wood for produce the foams in industrial way from green sources, biodegradable and with lower cost that the ones produced with petrochemical reagents. But it is necessary to take into account that the polyols have to satisfy some structural requirements in order to compete with petrochemical polyols, such as the right functionality and molecular weight. Then the formulation of the polyurethane foams should be improve to satisfy more this requirements and enhance their properties, especially those that have the worst results like the presence of base holes (produced for the encapsulation of the blowing agents). Also the biodegradability should be studied the evolution of the foams during a long period of time to

make sure that is not an inconvenient to the final use of the foams.

### Acknowledgements

I would like to express my thanks to Professor Dr. Jão Carlos Moura Bordado to give me the opportunity to develop my dissertation in his department in the IST. I would like also to express my gratitude to my advisor Dr. Maria Margarida Pires dos Santos Mateus for encouraging my research. I am also grateful to the workers of Greenseal Research Center, who helped and advise me during the polyurethane foams production.

### References

- [1] A. L. D. da Silva. Sntesis, caracterizacin y propiedades de adhesin de adhesivos basados en quasi-prepolmeros de isocianato terminal, phd thesis, universidad de alicante, 2005.
- [2] A. Demirbas. *Green energy and technology. Biofuels*. 2009.
- [3] J. Denny. Polyurethane market, february 2014.
- [4] N. S. El-barbary M. Hassan. Polyhydric alcohol liquefaction of some lignocellulosic agricultural residues. *Industrial crops and products*, 27:3338, July 2007.
- [5] H.-Z. C. Hui Wang. A novel method of utilizing the biomass resource: Rapid liquefaction of wheat straw and preparation of biodegradable polyurethane foam (puf). *Journal of the Chinese Institute of Chemical Engineers*, 38:95102, 2007.
- [6] C.-Y. H. T. F. S. Junming Xu, Jianchun Jiang. Preparation of polyurethane foams using fractionated products in liquefied wood. *Journal of applied polymer science*, October 2013.
- [7] J. Z. J. Z. B. Z. Lincai Peng, Lu Lin and Y. Gong. Catalytic conversion of cellulose to levulinic acid by metal chlorides. *Molecules*, 15:5258–5272, August 2010.
- [8] Q. L. X. Z. W. M. Q. Z. Longlong Ma, Tiejun Wang. A review of thermalchemical conversion of lignocellulosic biomass in china. *Biotechnology Advances*, 30:859873, January 2012.
- [9] P. McKendry. Energy production from biomass (part 2): conversion technologies. *Bioresource Technology*, 835:4754, July 2001.
- [10] P. McKendry. Energy production from biomass (part 3): gasification technologies. *Bioresource Technology*, 83:5563, July 2001.
- [11] E. K. H. B. Mustafa Balat, Mehmet Balat. Main routes for the thermo-conversion of biomass into fuels and chemicals. part 1: Pyrolysis systems. *Energy Conversion and Management*, 50:31473157, September 2009.
- [12] E. K. H. B. Mustafa Balat, Mehmet Balat. Main routes for the thermo-conversion of biomass into fuels and chemicals. part 2: Gasification systems. *Energy Conversion and Management*, 503:31583168, September 2009.
- [13] M. H. A. Niu Min, ZHAO Guang-jie. Polycondensation reaction and its mechanism during lignocellulosic liquefaction by an acid catalyst: a review. *Forestry Studies in China*, 13:7179, 2011.
- [14] V. T. N.L. Panwara, Richa Kotharib. Thermo chemical conversion of biomass eco friendly energy routes. *Renewable and Sustainable Energy Reviews*, 16:1801 1816, February 2012.
- [15] H. Pan. Synthesis of polymers from organic solvent liquefied biomass: A review. *Renewable and Sustainable Energy Reviews*, 15:3454 3463, May 2011.
- [16] A. L. Patrizia Cinelli, Irene Anguillesi. Green synthesis of flexible polyurethane foams from liquefied lignin. *European Polymer Journal*, 49:11741184, April 2013.
- [17] Y. L. Shengjun Hu, Caixia Wan. Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw. *Bioresource Technology*, 103:227233, October 2011.
- [18] X. C. Q. L. Yanqiao Jin, Xuemin Ruan. Liquefaction of lignin by polyethyleneglycol and glycerol. *Bioresource Technology*, 102:35813583, October 2010.