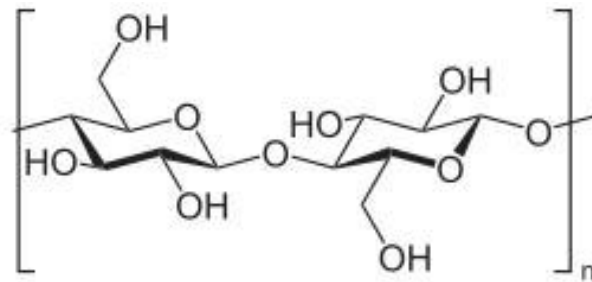# Polyurethane foams from renewable and sustainable polyols

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Thesis to obtain the Master of Science Degree in

Materials Engineering

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"Less is more." Ludwig Mies van der Rohe

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Resumo

O âmbito desta tese insere-se na produção de espumas de poliuretano com polioís provenientes da madeira. O objectivo é encontrar a melhor combinação de propriedades adequadas a espumas de poliuretanos com o máximo de teor de polioís, provenientes da liquefacção de madeira, de forma a proporcionar o decréscimo do preço e produção de uma espuma amiga do ambiente. Primeiramente, o trabalho experimental iniciou-se com a optimização da reacção de liquefacção de madeira. Esta parte foi efectuada com diferentes tipos de catalisadores procurando o melhor rendimento e o catalisador mais barato a nível industrial. Seguidamente foi feita a extracção dos polioís com o objectivo de eliminar as moléculas de açúcar presentes após a quebra das ligações nas moléculas de celulose, lignina e hemicelulose através de despolimerização. Os polioís foram caracterizados através do valor OH e ácido e pela técnica de espectroscopia ATR-FTIR. Na segunda parte desta tese foram obtidas espumas que apresentaram bons resultados comparadas com espumas comerciais que incluem polioís provenientes de combustíveis fosseis. A formulação destas espumas deve ser melhorada, no entanto os resultados mostram ser possível a utilização de madeira liquefeita para a produção industrial de espumas com um custo mais baixo.

Palavras-chave: liquefacção, madeira liquefeita, extracção, polióis, catalisadores, espumas de poliuretano

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 of 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.

Resumen

El fin de este proyecto es la producción de espumas de poliuretano con polioles de madera licuificada. El objetivo es encontrar la mejor combinación de las propiedades adecuadas para las espumas de poliuretano con un contenido máximo de polioles de madera licuificada, para disminuir el precio y hacer que la espuma sea ambientalmente amigable. En primer lugar, el trabajo experimental se inició con la optimización de la reacción de licuefacción de la madera. Esta parte se llevó a cabo con diferentes tipos de catalizadores con el fin de encontrar los mejores resultados de rendimiento y el catalizador más barato a nivel industrial. Lo siguiente fue realizar la extracción de los polioles con el fin de eliminar las moléculas de azúcar presentes en la madera licuificada, como consecuencia de la ruptura de los enlaces en la celulosa, la lignina y la hemicelulosa mediante la despolimerización. Los polioles se caracterizaron con la determinación del valor OH y el valor de ácido y la técnica espectroscópica ATR-FTIR.

En la segunda parte de este trabajo se obtuvo las espumas de poliuretano. Estas espumas mostraron buenos resultados comparándolas con las espumas comerciales que son producidas a partir de polioles de combustibles fósiles. La formulación de las espumas debe ser mejorada, sin embargo, los resultados muestran que es posible el uso de los polioles de madera licuificada para producir espumas de forma industrial con un menor coste.

Palabras clave: madera licuificada, licuefacción, extracción, polioles, catalizador, espuma de poliuretano.

Resum

La fi d'aquest projecte és la producció d'escumes de poliuretà amb poliols obtinguts de la liqüefacció de fusta. L'objectiu és trobar la millor combinació de les propietats adequades per a les escumes de poliuretà amb un contingut màxim de poliols de fusta per disminuir el preu i fer que l'escuma sigui ambientalment amigable. En primer lloc, el treball experimental es va iniciar amb l'optimització de la reacció de liqüefacció de la fusta. Aquesta part es va dur a terme amb diferents tipus de catalitzadors amb la finalitat de trobar els millors resultats de rendiment i el catalitzador més barat a nivell industrial. El següent va ser realitzar l'extracció dels poliols amb la finalitat d'eliminar les molècules de sucre presents en la fusta liquada, com a conseqüència de la ruptura dels enllaços en la cel·lulosa, la lignina i la hemicel·lulosa a través de la despolimerització. Els poliols es van caracteritzar amb la determinació del valor OH i valor d'àcid i la tècnica espectroscòpica ATR-FTIR.

En la segona part d'aquest treball es van obtenir les escumes de poliuretà. Aquestes escumes van mostrar bons resultats comparant-les amb les escumes comercials que són produïdes amb poliols de combustibles fòssils. La formulació de les escumes ha de ser millorada, no obstant això, els resultats mostren que és possible l'ús dels poliols provinents de la fusta per produir escumes a nivell industrial amb un menor cost.

Paraules clau: liqüefacció de fusta, poliols, extracció, catalitzador, escuma de poliuretà.

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Abbreviations

2EH	2-ethylhexanol
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
B8871	polyether-modified-polysiloxane-copolymer
BH	Base Holes
CC	Cell collapse
CR	Crumbling
CSK	Cutting shrinkage
DEG	Diethylene glycol
DMDEE	2,2-dimorpholinodiethylether
DME	Dimethyl Ether
DP45	Tetrabromophthalate ester
FSK	Froth Shrinkage
GB	Glass Bubbles
LPG	Liquefied Petroleum Gas
MDI	Dipheylmethane diisocyanate
MPG	Monopropylene glycol
NCO	Isocyanate group
OCF	One component foam
OH	Hydroxide group
OU	Outflow
PU	Polyurethane foam
SBH	Side base holes
SEM	Scanning electron microscopy
SK	Shrinkage in mould
TCPP	trichloropropylphospate
TEP	triethyl phosphate
V&P	Voids and Pin Holes

Chapter 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 obtaining of a product which can be used to produce materials and fuels.(Ma et al. [2012]) The most familiar and accessible biomass lignocellulosic feedstocks are wood, algae, municipal solid waste, sewage sludge and scraps from paper.(Pan [2011])

1.1 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.(McKendry [2001a])

1.1.1 Thermochemical conversion

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

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 some 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. As gasifying agent 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 Fischer–Tropsch Synthesis. (McKendry [2001b])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.(Balat et al. [2009a])

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 352°C and 452°C. Low temperatures and high residence times favour 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 60–75 wt.% of liquid bio-oil, 15–25 wt.% of solid char, and 10–20 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.(Balat et al. [2009b]) There are four essential features of a fast pyrolysis process:

1. Very high heating and heat transfer rates are used, which usually requires a finely ground biomass

feed.

2. A carefully controlled pyrolysis reaction temperature is used, often in the 427–502°C range.

3. Short vapour residence times are used (typically less than 2 seconds).

4. Pyrolysis vapours and aerosols are rapidly cooled to give bio-oil.

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 catalyst 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. (Panwara et al. [2012])
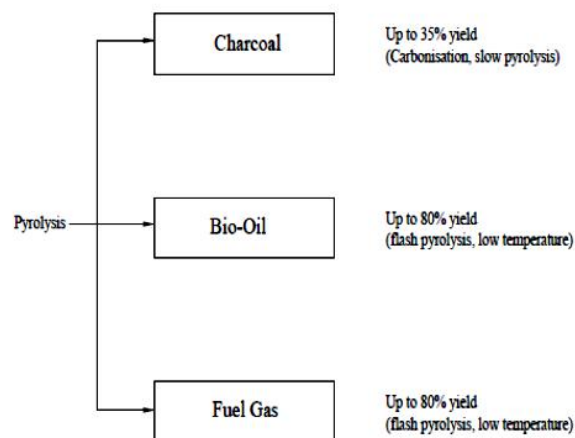
Figure 1.1: Products from pyrolysis. Source: Energy production from biomass (part 2): conversion technologies.Peter McKendry

Liquefaction

Lignocellulose is a complex, macromolecular polymer composed through the cross-linking of C–O and C–C 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 performed. (Ma et al. [2012]) 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 180ºC, or without catalyst at higher temperatures ranging from 180 to 250ºC. Recently, also other solvents, such as cyclic carbonates,lower alcohols and dioxane were examined and used successfully for the liquefaction of woody biomass.(barbary M. Hassan and Shukry [2007]) 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. (Min et al. [2011])

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. (Wang and Chen [2007])

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

1.2   Wood: chemical characteristics

Wood biomass is comprised of C, H, O and N, and also little quantities of Ca, K and Mg. A typical analysis of dry wood yields on a weight percentage: carbon (52%), hydrogen (6.3%), oxygen (40.5%) and nitrogen (0.4%). The components of lignocellulosic biomass include cellulose, hemicellulose, lignin, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds.
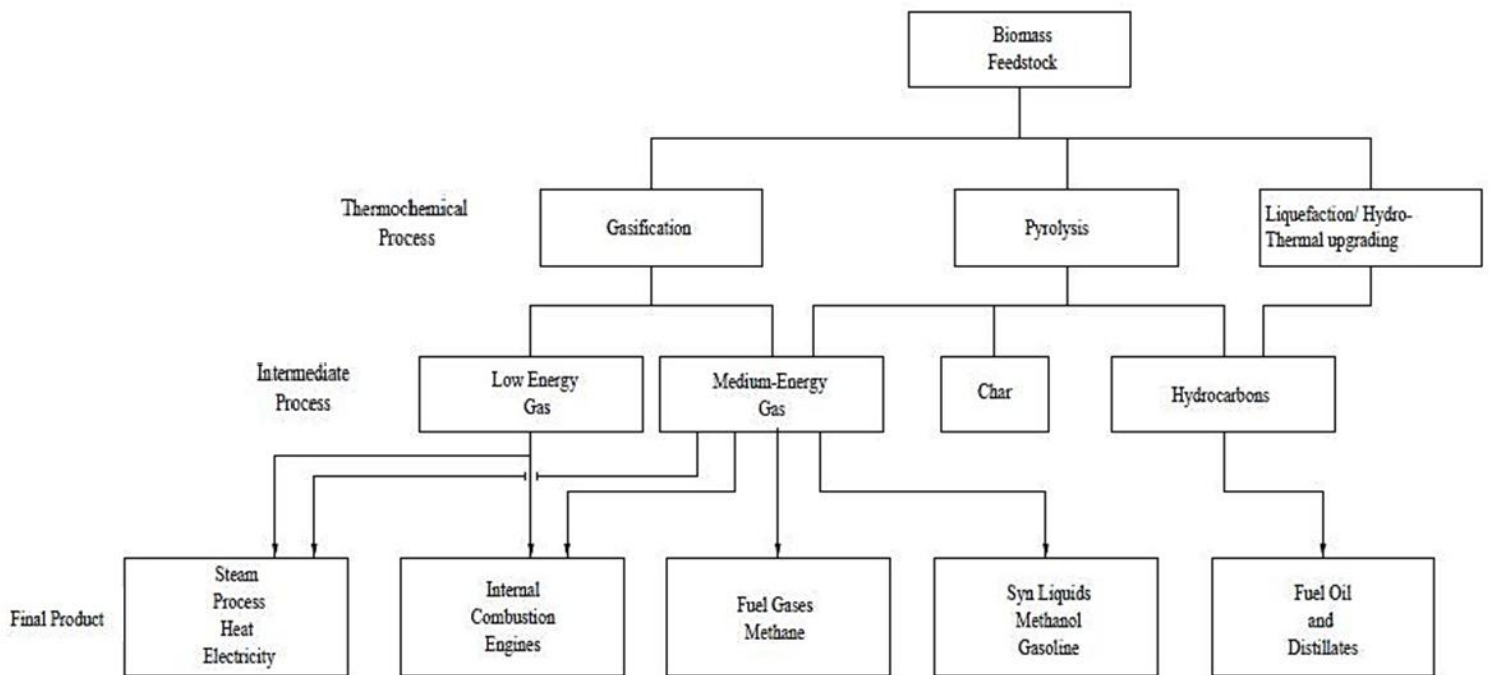
Figure 1.2: Thermochemical processes. Adapted from "Energy production from biomass (part 2): conversion technologies". Peter McKendry

The proportions of the three main components are: cellulose (40-45%, in hard and softwoods), hemicellulose (15-35% in hardwoods and 20% softwoods) and lignin (17-25% in hardwoods and 25-35% in softwoods). These components decompose into small molecules during the liquefaction process. Hardwoods or deciduous woods have a higher proportion of cellulose, hemicelluloses, and extractives than softwoods, but softwoods have a higher proportion of lignin. (Balat et al. [2009b])

Cellulose is the major chemical in wood, it is a linear polymer composed of repeating glucose units. Cellulose is a remarkably pure organic polymer, consisting of units of glucose held together in a giant straight chain molecule.These glucose 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. (Demirbas [2009])

 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 length than cellulose, and the molecular structure is slightly branched. In addition, the polymer chains of hemicelluloses have short branches and are amorphous. Because of the amorphous morphology, hemicelluloses are
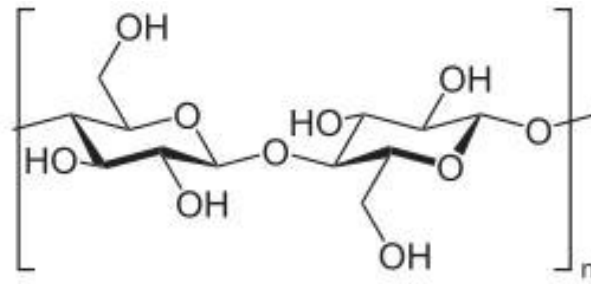
Figure 1.3: Schematic illustration of building units of cellulose.

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. (Demirbas [2009])

Lignin is a chemical compound that is most commonly derived from wood and is an integral part of the
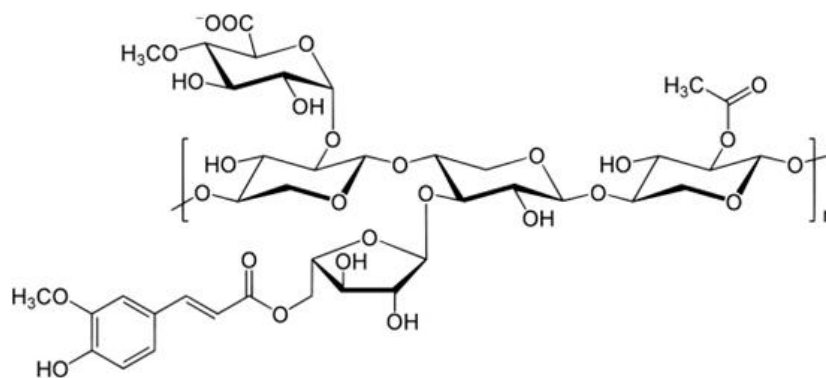
Figure 1.4: Schematic example of one possible xylan structure (xylan are a group of hemicelluloses).

cell walls of plants. It is one of most abundant organic compounds on Earth after cellulose and chitin. Lignin is a complex, high molecular weight (in excess of 10.000 amu) polymer built of hydroxyphenylpropane units. Lignin 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 hardwood and with galactoglucomannans in the case of softwoods. (Demirbas [2009])

1.3   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 were laid in
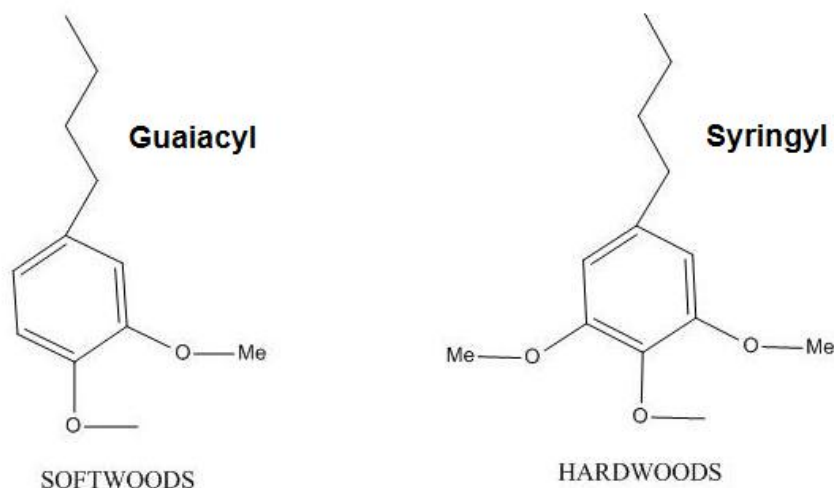
Figure 1.5: Schematic illustration of building units of lignin.

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

1.3.1 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.

Types of Polyurethane

Flexible Polyurethane Foam: Flexible polyurethane foam is used as cushioning for a variety of consumer and commercial products, including bedding, furniture, automotive interiors, carpet underlay and packaging. Flexible foam can be created in almost any variety of shapes and firmness. It is light, durable, supportive and comfortable.

Rigid Polyurethane Foam: Rigid polyurethane and polyisocyanurate (polyiso) foams create one of the world's most popular, energy-efficient and versatile insulations. These foams can significantly cut energy costs while making commercial and residential properties more efficient and comfortable. To maintain uniform temperature and lower noise levels in homes and commercial properties, builders turn to rigid polyurethane and polyisocyanate foam. These foams are effective insulation materials that can be used in roof and wall insulation, insulated windows, doors and air barrier sealants.

Coatings, Adhesives, Sealants and Elastomers: The uses of polyurethanes in the coatings, adhesives, sealants and elastomers (CASE) market offer a broad and growing spectrum of applications
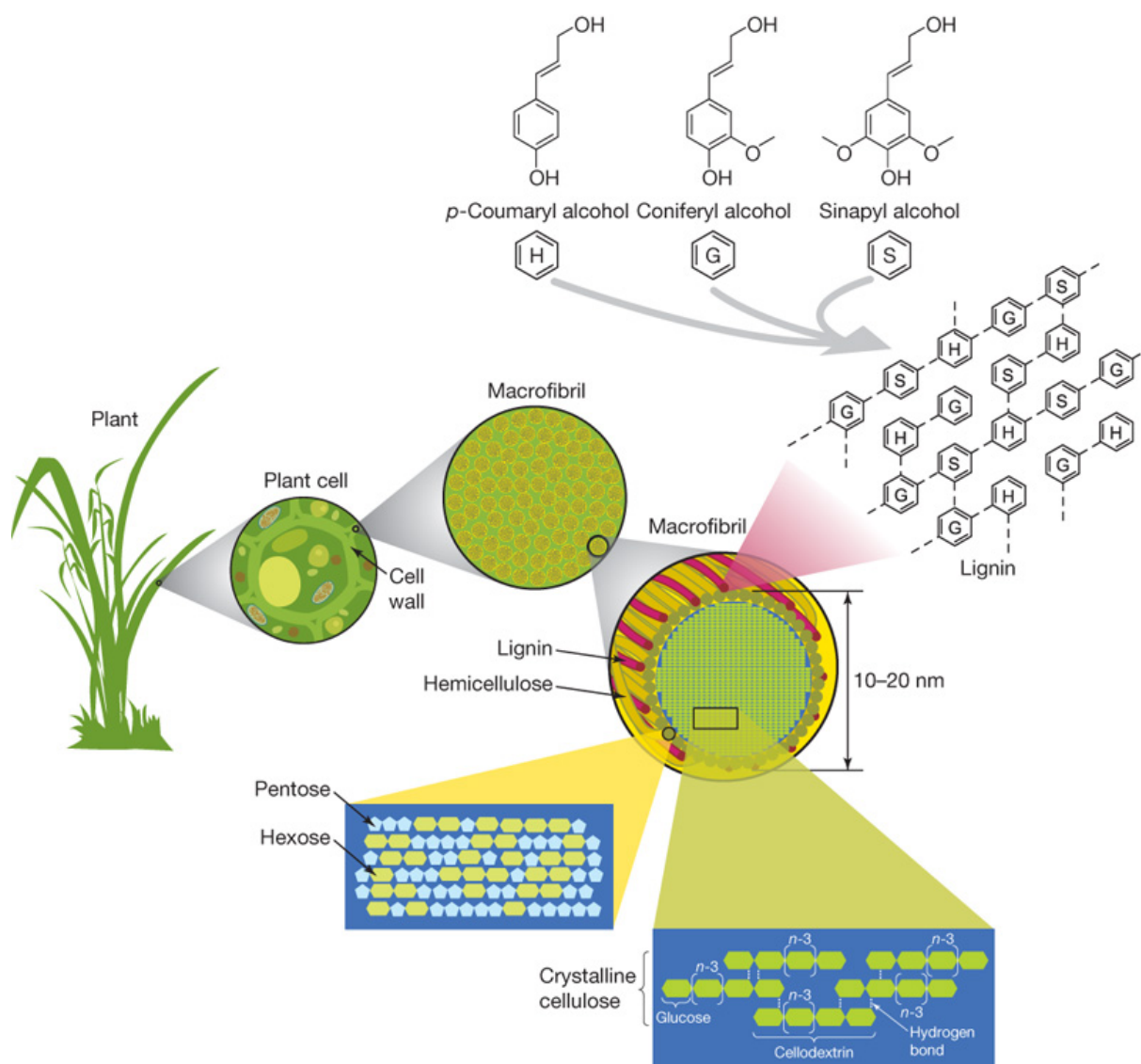
Figure 1.6: Structure of lignocellulose. Source: Genomics of cellulosic biofuels. Nature 454, 841–845 (2008).

and benefits. Polyurethane coatings can enhance a product's appearance and lengthen its lifespan. Polyurethane adhesives can provide strong bonding advantages, while polyurethane sealants provide tighter seals. Polyurethane elastomers can be moulded into almost any shape, are lighter than metal, offer superior stress recovery and can be resistant to many environmental factors.

Thermoplastic polyurethane: Thermoplastic polyurethane (TPU) offers a myriad of physical property combinations and processing applications. It is highly elastic, flexible and resistant to abrasion, impact and weather. TPUs can be coloured or fabricated in a wide variety of methods and their use can increase a product's overall durability. TPU is an elastomer that is fully thermoplastic. Like all thermoplastic elastomers, TPU is elastic and melt-processable. In addition, it can be processed on extrusion, injection, blow and compression moulding equipment. It can be vacuum-formed or solution-coated and is well suited for a wide variety of fabrication methodologies. TPU can provide a considerable number of physical property combinations, making it an extremely flexible material adaptable to dozens of uses

such as construction, automotive and footwear.

Reaction Injection Moulding: Car bumpers, electrical housing panels and computer and telecommunication equipment enclosures are some of the parts produced with polyurethanes using reaction injection molding (RIM). Adding design flexibility, the polyurethane RIM process produces parts that are usually not achievable using typical injection molding processes, such as thick- and thin-walled parts, encapsulated inners and foamed cores. In addition to high strength and low weight, polyurethane RIM parts can exhibit heat resistance, thermal insulation, dimensional stability and a high level of dynamic properties. Automotive, construction, appliance, furniture and recreation and sporting goods are a few of the markets and applications using RIM technology.

Binders: Polyurethane binders are used to adhere numerous types of particles and fibres to each other. Their primary areas of use are in the manufacturing of wood panels, rubber or elastomeric flooring surfaces and sand casting for the foundry industry. The highest volume application for polyurethane binders is in the manufacture of Oriented Strand Board (OSB). These wood panels are used in structural sheathing and flooring, manufactured housing, joists and beams and shop panels. The production of rebound foam used under carpet primarily uses polyurethane binders and chemicals to bind the scrap foam, which is often flexible polyurethane foam, into the flooring underlay.

Waterborne Polyurethane Dispersions: Waterborne polyurethane dispersions (PUDs) are coatings and adhesives that use water as the primary media. With increasing federal regulation on the amount of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) that can be emitted into the atmosphere, PUDs are being used in more industrial and commercial applications. (Denny [2014])

(a) Production 2012   (b) Global production 2012
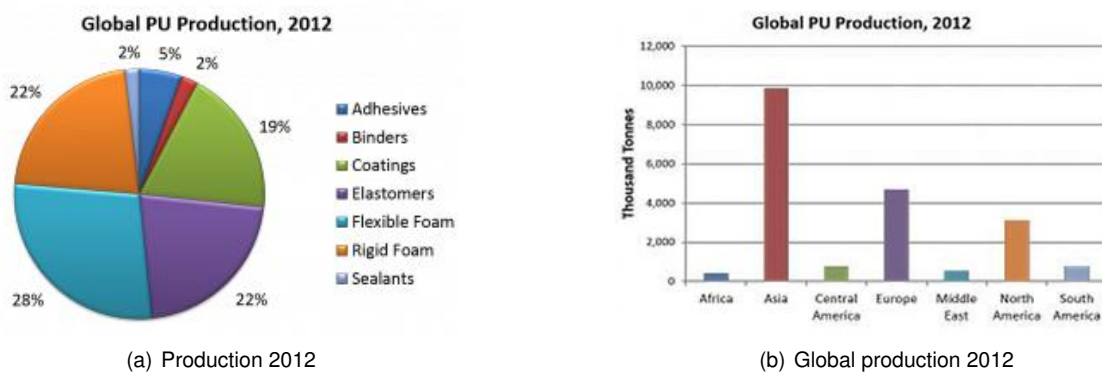
Figure 1.7: PU market. Source: utech-polyurethane.com

1.3.2 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 polymers. 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).
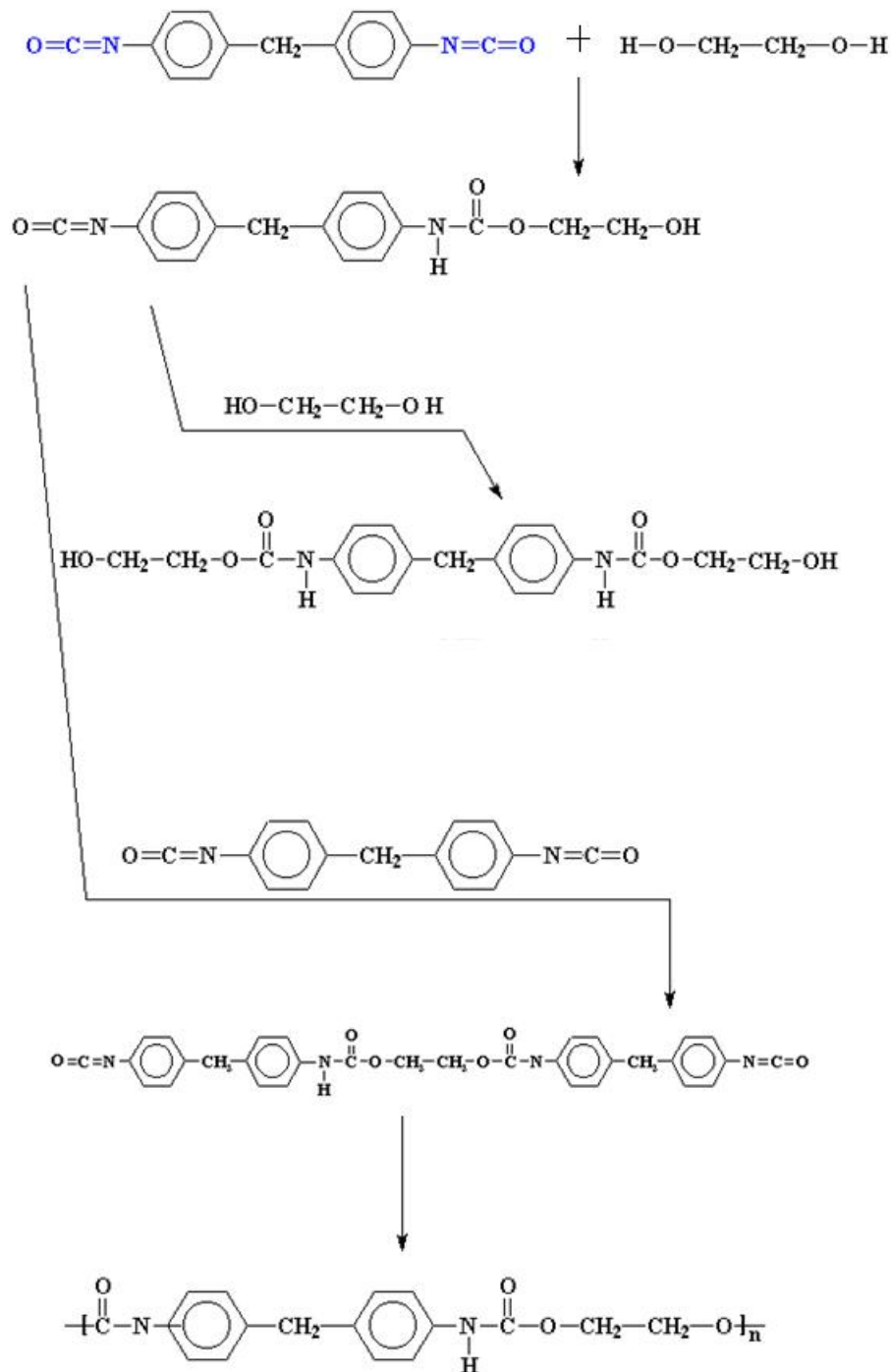
Figure 1.8: Scheme of the polyurethane reaction. Adapted from "Química y tecnología de macromoléculas", escuela de ingenierías industriales.

The mechanism of the reaction showed in the figure 1.8 begins with when the H from the polyols lightly positive charge (the O attract their electrons) forms and hydrogen bridge with the N of the isocyanate groups(NCO). The O from polyol have a partial negative charge and the C from the isocyanate have a partial positive charge. Oxygen gives a couple of electrons to C forming a new bond. After that

there is a O with positive charge and N with negative charge. This N reacts with the H from an alcohol group. The result after that is an urethane dimer (the urethane group is –NH–CO–O–). In one border the urethane group has an -OH group and in the other has -NCO. Then the dimer can react with another dimer, monomer or oligomer until become a polyurethane with a big molecular weight. In this reaction there are not subproducts, then is a polymeric addition. When the -NCO reacts with H_2O from the environment, the reaction is a polymeric condensation because there are CO_2 molecules as subproducts. (Hernando [2006])

The polymerization process builds polymeric chains, the polymers, with diverse size from different molecular weights. When the monomers provide two functional groups the polymeric structure is linear. In case that one of the monomers has more than two functional groups, the final structure is branched. If the structure is linear the PU is flexible, when the structure is branched the PU is rigid.

1.3.3 Polyurethane foams

Flexible foams are the largest market segment polyurethanes and can be obtained in block or moulded. 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 with different properties and applications, but 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. (Cinelli et al. [2013])

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. (da Silva [2005])

1.4 Motivation

The main objective of this project is to find the way and formulation to produce the best polyurethane foam for isolation uses with the maximum contents of polyols from liquefied wood. 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.

Chapter 2

Experimental: obtaining of liquefied wood

2.1 Reagents

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

2.2 Pretreatment

At least 12 hours before of doing the reaction is necessary to do the swelling. It consists in impregnate the wood spraying 2 ml/50g wood of solvents (in the same proportion as in the reaction)or liquefied wood. The aim of the pretreatment is to swell the cells and make easier to the catalyst arrive to the whole structure of the wood. It proceeds specially on the lignin and the cellulose. This procedure have been studied in previous tests performed by the group.
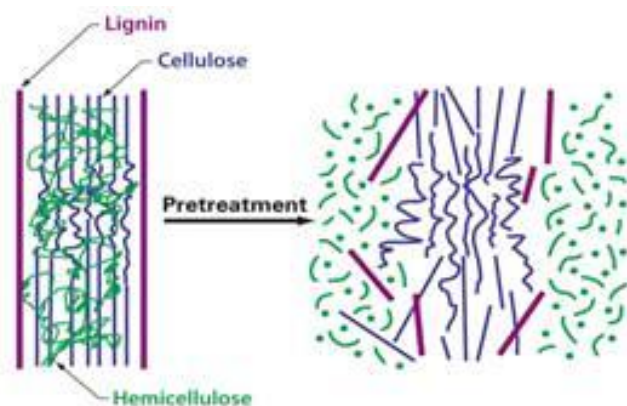
Figure 2.1: Wood cells during pretreatment. Adapted from "Pretreatment: the first chemical treatment in the wood to biojet/co-product conversion", NARA website.
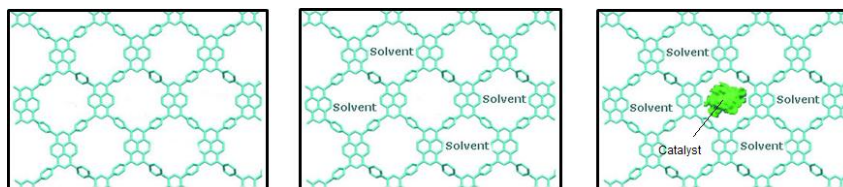
Figure 2.2: Swelling process.

2.3 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 (figure 2.3); the wood/solvent mixture and the catalyst were placed in the reaction flask. The proportion of wood and solvent were for 1g of wood 1g of DEG and 2g of 2EH, and different proportions of catalyst were used. For 100g of wood 100g of DEG and 200g of 2EH are used. For this quantity of wood the amounts of catalyst used are showed in the table 2.1, the percentage are calculate respect the total mass (total mass of solvents plus wood).

Table 2.1: Mass of catalyst used

% catalyst	mass catalyst (g)
0,1	0,4
0,5	2
1	4
3	12

The flask was put on a heating mantle and preheated at 160ºC. The liquefaction was conducted under constant stirring and reflux until it finished. After the reaction, the product was leave to cool until 80ºC. (A.1)

The resulting reaction mixture filtered in a kitasato apparatus (figure 2.4) until colourless filtrate was obtained. The residue was washed with acetone and methanol. The liquefied residue collected, was dried in oven at 120ºC to until constant weight was verified, for the determination of the liquefaction yield (α) in mass terms.

$$\alpha = (1 - \frac{W_f}{W_i}) * 100 \tag{2.1}$$

In the expression W_f is the final weight, after dried the residue and W_i is the initial weigh of the wood. During the reaction time, the samples for the study of the different catalyst were get in different intervals of time from the exit in the bottom of the reactor.

2.4 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

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A – Thermo par
B – Solid dropping funnel
C – 5 socket reactor Lid
D – Reactor clamp
E – O-ring
F – Stirring shaft
G – Wide-necked reactor
H – Heating Mantle
I – Condenser
J – Dean-Stark separator
K – PTFE flexible connector hose
L – Overhead stirrer
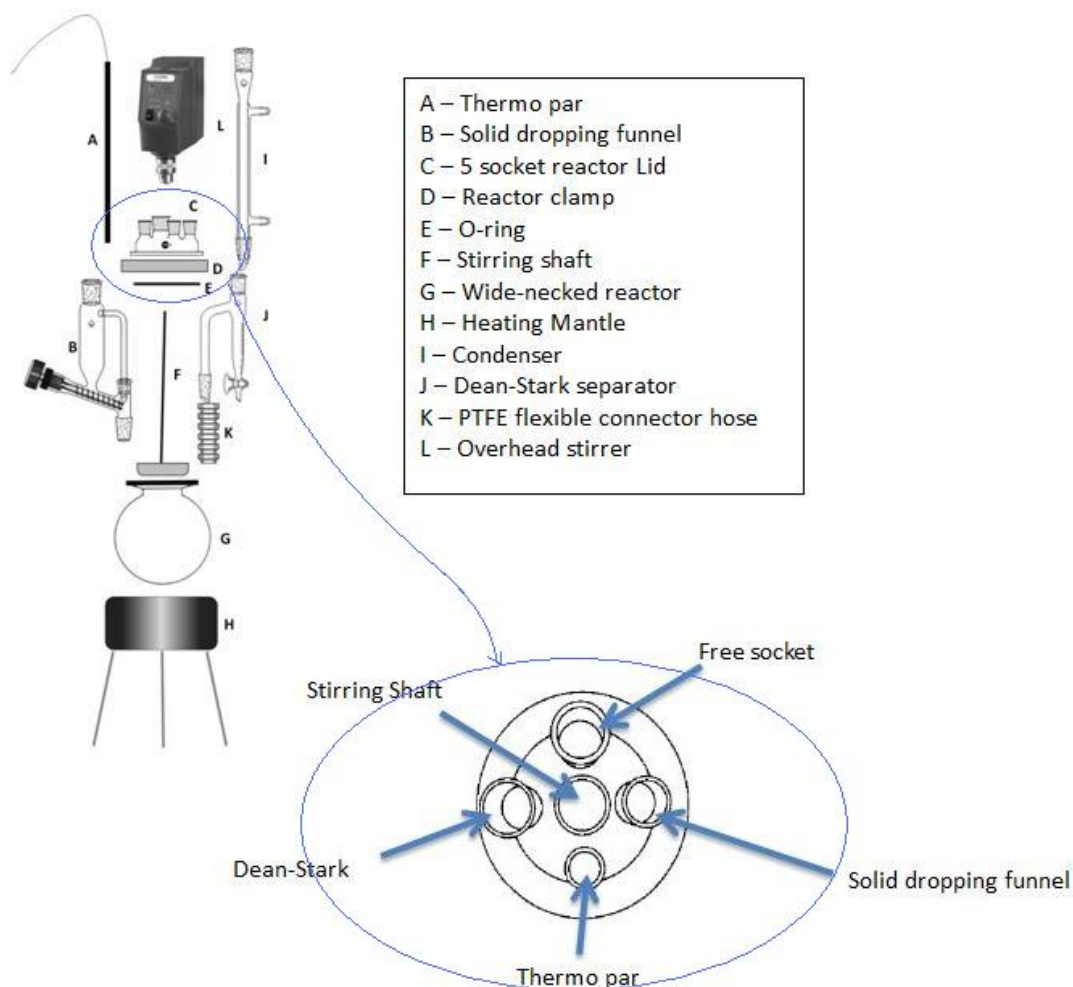
Figure 2.3: Experimental arrangement.
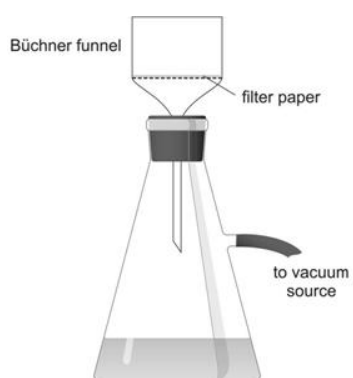
Figure 2.4: Kitasato apparatus.

out in a decanter flask where the liquefied wood with more or less the same quantity of water was mixed and stirred to ensure the sugars dissolve in the water. Waiting, two phases appear: on the top the polyols (the dark phase) and on the bottom the aqueous phase (sugars solved in water).

Chapter 3

Experimental: obtaining of polyurethane foams

3.1 Experimental One component foam technology

The one component foams foaming process has generally 4 stages as shown in figure 3.1.

Figure 3.1: Schematic diagram of foaming process.

In the first stage the aerosol can was filled with a mixture of polyol blend, isocyanate and blowing agents (low boiling point gases). The pre-polymerisation reaction occurs inside the can. At the second stage, the liquid prepolymer leaves the can and expands to a low-density froth due to the evaporation of the blowing agents. The blowing agents are used to form gas bubbles in the pre-polymerizing reaction mixture. They cause a higher solubility between components inside the can. They also act as propellants causing the pre-polymer to exit the can. Third stage starts when the froth is exposed to the air, it cures by the reaction with moisture in the air or from the substrate, resulting carbon dioxide production that gives a second expansion of the froth. The last stage results in the fully cured foam.

Three different compositions of foams were done as indicated in the tables 3.1, 3.2 and 3.3. The component A has the polyol from wood and the component B has the isocyanate.

The chemicals of these different formulations of the foams have the next functions:

- TCPP, TEP and DME act as viscosity reducers.

- TCPP, TEP, Safron 6605 and DP45 are flame retardants. In general terms, flame retardant additives incorporate phosphorous, organohalides or both halogen and phosphorous.

- DP45 acts also as plasticiser.
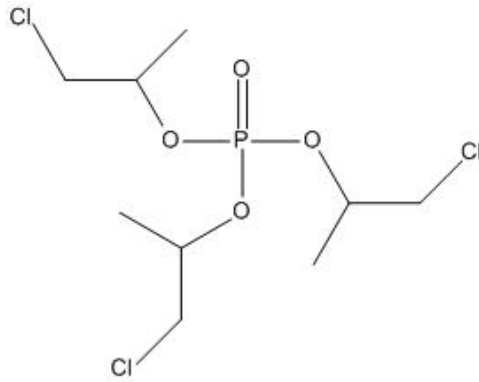
Figure 3.2: Molecule of TCPP.
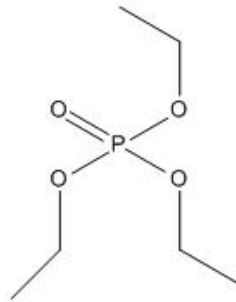
Figure 3.3: Molecule of TEP.

- B8871 is a sulfactant with a function of cell opener.

- DMDEE, represented in figure 3.4, is catalyst in the polymeric reaction.
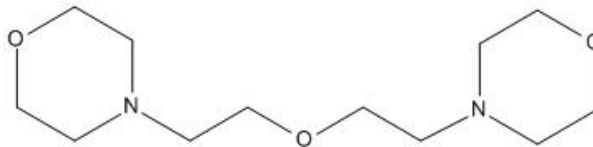
Figure 3.4: Molecule of DMDEE.

- 2EH reacts with free molecules of the isocyanate.

- Voranol 1010L is a polyether polyol.

- MPG is a chain extender.

- GA13 VTA is a prepolymer mixture.

- Propane and Iso-butane (LPG mix) and DME are the blowing agents and propellants. Besides, they serves as cooling agent for the short-term stabilization of the foam before the start of the hardening reaction. Usually the combination of polar and apolar blowing agents gives optimal solvency power. Blowing agents should be toxicology and ecologically safe.

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Table 3.1: Composition foam A

Component A			Component B			Gas		
name	**mass (g)**	**%**	**name**	**mass (g)**	**%**	**name**	**mass (g)**	**volume (ml)**
wood polyol	8,46	3,83	GA13 VTA	168,95	76,44	propane	12,2	24
Voranol 1010L	9,2	4,16				isobutane	28,6	50,6
2EH	22,3	10,09				DME	17,5	26
TCPP	7,87	3,56						
B8871	3,82	1,73						
DMDEE	0,41	0,18						
total	279,2 g	306,0 ml						
total without gas	221,0 g	205,3 ml						

Table 3.2: Composition foam B

Component A			Component B			Gas		
name	**mass (g)**	**%**	**name**	**mass (g)**	**%**	**name**	**mass (g)**	**volume (ml)**
wood polyol	12,94	5,84	GA13 VTA	173,25	78,23	propane	12,2	24,1
2EH	22,87	10,33				isobutane	28,6	50,7
TCPP	8,07	3,64				DME	17,5	26,1
B8871	3,92	1,77						
DMDEE	0,42	0,19						
total	279,8 g	306,0 ml						
total without gas	221,5 g	205,1 ml						

Table 3.3: Composition foam C

Component A			Component B			Gas		
name	**mass (g)**	**%**	**name**	**mass (g)**	**%**	**name**	**mass (g)**	**volume (ml)**
wood polyol	12,47	5,17	GA13 VTA	139,06	57,58	propane	12,2	24
MPG	0,53	0,22	TDI TX	8,92	3,69	isobutane	28,5	50,6
2EH	9,05	3,75				DME	17,4	26
Safron 6605	49,51	20,5						
TEP	7,55	3,13						
DP45	8,17	3,38						
B8871	5,65	2,34						
DMDEE	0,6	0,25						
total	299,6 g	306,0 ml						
total without gas	241,5 g	205,5 ml						

Chapter 4

Experimental: Techniques of characterization

4.1 Characterization of liquefied wood

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.

4.1.1 Acid and OH values

Hydroxyl value: is defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid taken up on acetylation of one gram of a chemical substance that contains free hydroxyl groups. It is a measure of the content of free hydroxyl groups in a chemical substance, expressed in units of mass of potassium hydroxide (KOH) in milligrams equivalent to the hydroxyl content of one gram of the chemical substance. This value is calculated with the equation 4.1. In this expression *blank* is the volume of KOH solution in ml used to do the blank titration, *v KOH* is the volume in ml of the KOH solution used to do the titration of the sample *mSample* is the mass of the sample in grams, 56,1 is the molecular weight of KOH and 0,5 is the normality of the KOH solution.

$$V_{OH} = \frac{(blank - v_{KOH}) * 0,5 * 56,1}{m_{Sample} + V_{Acid}}$$

(4.1)

Acid value: Is a measure of the amount of carboxylic acid groups in a chemical compound. It is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance.This value is calculated with the equation 4.2. In this expression *v KOH* is the volume in ml of the KOH solution used to do the titulation of the sample, *mSample* is the mass of the sample in grams, 56,1 is the molecular weight of KOH and 0,1 is the normality of the KOH solution.

$$V_{Acid} = \frac{v_{KOH} * 0,1 * 56,1}{m_{Sample}}$$

(4.2)

4.1.2 SEM of wood

Scanning electron microscopy (SEM) observations of wood powder and liquefaction residue, 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.

4.1.3 Attenuated total reflectance-Fourier transform infrared (ATR-FTIR)

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

ATR-FTIR is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation. It provides good quality data in conjunction with good reproducibility.

ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave which extends into the sample. The penetration depth into the sample is typically between 0.5 and 2 micrometres, with the exact value being determined by the wavelength of light, the angle of incidence and the indices of refraction for the ATR crystal and the medium being probed. The number of reflections may be varied by varying the angle of incidence. The beam is then collected by a detector as it exits the crystal. Most modern infrared spectrometers can be converted to characterize samples via ATR by mounting the ATR accessory in the spectrometer's sample compartment. This evanescent effect only works if the crystal is made of an optical material with a higher refractive index than the sample being studied. Otherwise light is lost to the sample. In the case of a liquid sample, pouring a shallow amount over the surface of the crystal is sufficient. For the technique to be successful, the following two requirements must be met:

- The sample must be in direct contact with the ATR crystal, because the evanescent wave or bubble only extends beyond the crystal 0.5 μ - 5 μ.

- The refractive index of the crystal must be significantly greater than that of the sample or else internal reflectance will not occur – the light will be transmitted rather than internally reflected in the crystal. Typically, ATR crystals have refractive index values between 2.38 and 4.01 at 2000 cm^{-1}. It is safe to assume that the majority of solids and liquids have much lower refractive indices.

4.2 Characterization of polyurethane foams

4.2.1 Quick tests

The three different compositions were evaluated by the research centre of the company Greenseal. The properties of a foam can be analysed through the Quick tests. The foam samples for this test have to be obtained through two different dispensing procedures: Foam bead on paper and on mould. The rating is given visually and during the froth spray, during curing process and after cured foam. The tests are doing

in two different temperature conditions: 23ºC and 5ºC (the temperature must be the same inside the can and in the environment). The quick tests for the liquid mixture inside the can evaluate the shaking rate, for the froth after dispensing evaluate the froth shrinkage and the froth outflow and for the cured foam evaluate the surface structure, the cell structure, the curing streaks, the base holes, the glass bubbles, the crumbling, the voids and pin holes, the cell collapse, the side base holes, the curing shrinkage and the cutting shrinkage. The quick tests of each property are explained bellow. The curing period is also related to the temperature and relative humidity at which the froth is curing. (da Silva Dionisio [2009])

Shaking rate

In order to start the test, is necessary to shake the can to mix the prepolymer and the gas inside. The shaking rate evaluation is subjective and the score is given to the initial shake. Higher shake, higher score.

Froth shrinkage

This property is evaluated during dispensing and while the froth is curing.

Froth outflow

The froth outflow can be evaluated by seeing if the foam has expanded towards the lines drawn shortly after dispersing, and if it has covered them. It is necessary too, to check the shape of the foam, to see if it presents the usual semicircular shape or it has flattened. If the lines covered and the foam has a flattened shape, the foam presents froth outflow. This is an important property because is necessary to have low viscosity inside the can to assure good output, but after dispensing the froth it should be stable and give no outflow.

Surface structure

The surface structure of the foam can be smooth or irregular (frothy).

Cell structure

The cell structure of the foam is related to the size and distribution of the cells in the sample. These cells must not be very large and should present homogeneous distribution throughout the sample.

Curing streaks

The curing streaks appear when there are problems during the curing of the froth. They causes coarser cells characterized by their weakness and lack of flexibility. This problem appears usually in the centre of the foam, where takes longer for the humidity to penetrate.

Base holes

Base holes are an important phenomenon that occurs when the froth is in contact with the porous surface (e.g. paper) and the layer does not densificate (there is no pressure development). This is due to the high boiling blowing agents like butanes and iso-butanes are captured and remain into the porous structure. The evaporation of these gases causes the appearance of base holes, by dissolving the fresh froth on the surface of the foam in contact with the porous substrate. The lower viscosity of the froth the bigger risk of base holes, because is more gas captured on the froth. Base holes affect adhesion properties, making them worse. where takes longer for the humidity to penetrate.

Glass bubbles

Glass bubbles can be visually identified by the shiny look of the foam surface. They appear when there is a bad gas combination in the prepolymer giving poor physical properties. Gas is rapidly evaporating out of the fresh extruded froth bead. The quick evaporation of the low boiling gases such as DME and propane does not cause the glass bubbles, but the higher boiling point gases such butane and iso-butane do. They dissolve the cells at the surface of the foam and make cell coalescence. Usually glass bubbles are more pronounced at low can temperature, due a slower evaporation of the gases.

Crumbling

Crumbling occurs when there is friable cells in the foam. It can be evaluated by pressing the foam with the finger (after different periods of time). If the foam presents crumbling by pressing, a cracking sound can be noticed. It is more notorious when the curing takes place at low temperatures, because with lower temperatures crystallize the free NCO groups, retarding the cure reaction. At lower temperature there is also less humidity in the air, and it retards more the reaction cure. Two different kinds of crumbling can appear:

- Foam cured at ambient temperature: if foam has crumbling it remains in the time.

- Foam cured at low temperature (considering low temperature under 5°C): the crumbling disappears with time (hours or days).

During the measurement of the crumbling, due to the pressure, cell membranes touch each other and curing streaks or cell collapse can be originate. That is the reason why this test is made in a different bead.

Voids and pin holes

Voids and pin holes (small voids) are created due to small gas accumulations, which can not be homogeneously mixed into the prepolymer by manual shaking. The better the solubility of gases in the prepolymer, the lesser gas accumulations exist. Not enough shaking of cans could cause voids in the foam. The presence of the voids make the physical properties worse.

Cell collapse

Cell collapse can be detected by the presence of curing streaks (at early stage) or in the worst case, by the presence of large void spaces in the foam. The cell collapse in the foam make its structure weaker. This phenomenon is more critical with foam on mould than with foam on paper, due to the curing conditions are more severe in the mould. It occurs because the froth is curing too slowly due to a combination of low moisture level, low temperature and too hydrophobic prepolymers.

Side base holes

To check the side base holes, it is necessary to remove a piece of paper on the side of the bead. The presence of side base holes is showed by the low adhesion between the foam and the paper due to the quantity of holes. The froth expansion happens in the mould, while curing, producing a densification of the froth against the walls of the mould. But as occurs in base holes, the gas is trapped in the irregularities of the substrate, dissolving the froth (because of the DME as blowing agent), but the difference is the location in the side of the bead. A slower curing of foam, increases the possibility of side base holes, since the pressure development of the froth against the side walls is slower and allows to capture gas to dissolve the froth. In general in the mould the base holes rating is better than the side base holes. The gases are accumulated in the corner of the mould avoiding holes in foam while curing.

Curing shrinkage

The curing shrinkage is evaluated when the cured foam bead is removed from the horizontal mould. It must be checked if the foam fully fills the compartment (in the mould). In case the foam does not fill it, it is considered to have curing shrinkage. It is usually checked after one day and can not be confused with the shrinkage after the foam is fully cured (dimensional stability). The curing shrinkage happens due to the low pressure developed inside the froth during the cure process, promoting in this way shrinkage from initial bead thickness.

Cutting shrinkage

This is a simple test in which a cylindrical shaped bead is cut off longitudinally when foam has already cured (the foam is hard). The cells in the foam should not be destroy while the knife is passing by the foam. After that one bead sample is analysed visually to check if there is shrinkage, usually after 24 hours. The rating can be done by comparison. There is also available more accurate procedure calculating the angle between the two halves of the foam. This phenomena is related with dimensional stability in dimension size. Usually, cutting shrinkage is higher in mould and at low temperatures, due to the slower diffusion of the gases and a bigger quantity of trapped gas sprayed in mould.

4.2.2 SEM of foams

Scanning electron microscopy (SEM) observations of foams samples, were also (as the liquefied wood residue) 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.

Chapter 5

Results and discussion

5.1 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.

5.1.1 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.

$$\bar{PM} = \frac{f * 56100}{V_{OH} + V_{Acid}} \tag{5.1}$$

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

Table 5.1: Average molecular weight calculated from VOH and V acid

PM	f	VOH	Vacid
406,6	2,5	**340,13**	**4,77**

Results found in literature (Hu et al. [2011],Jin et al. [2010],Xu et al. [2013]): the results for polyols from liquefied wood suggest bigger hydroxyl value 1093–1323 mg KOH/g and acid value determinate was 7.3–8.0 mg KOH/g. In this thesis the hydroxyl value is much more low because the 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 to much hydroxyl groups confer more rigidness 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.

5.1.2   ATR-FTIR, Attenuated total reflectance Fourier transform infrared spectroscopy
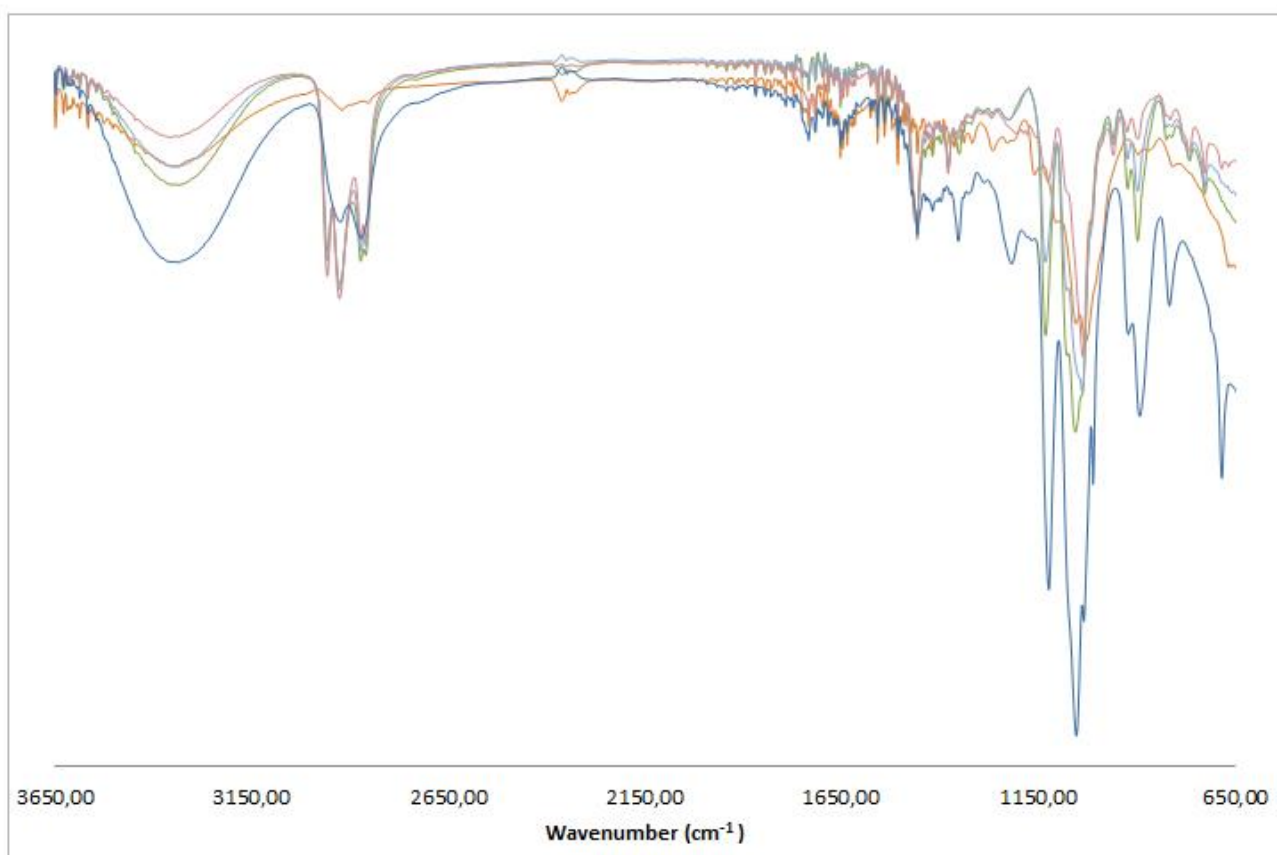
wavenumber (cm-1)	bond
1150	CO
1450	CH_2
1710	$C = O$
2900	CH
3300	OH

Legend:
— sovents
— wood
— liquified wood
— wood polyols
— wood sugars

Figure 5.1: 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. This technique was employed to investigate the functional groups of the obtained products from the liquefaction reaction (liquefied wood, polyol and sugars) and the reagents (solvents and wood). The figure 5.1 shows the results from the ATR-FTIR. In all the samples appear the principal peaks at 1050 cm^{-1} attributed to the $-CO$ stretching

vibrations, around 2900 cm^{-1} typical of $-CH$ stretching vibrations and around 3300 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 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 them break a hidrogen atom join to the oxygen becoming $-OH$ group. The absorption band at 1710 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 cm^{-1}. It is remarkable that the sample from the wood sugars has bigger peaks at 3300 cm^{-1} (-OH) and especially at 1050 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.

5.1.3 Study of different catalysts for the liquefaction

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

Table 5.2: Resume of catalysts results

Catalyst	%	Time (max. conversion)	Conversion	Time Swelling	Price of ton
1	0,5%	20 min	93%	25 min	$1000-1500/ton
	3,0%	20 min	89%	24h	
2	0,1%	25 min	95%	24h	$1000/ton
	0,5%	40 min	96%	24h	
	3,0%	15 min	99%	24h	
3	0,1%	40 min	98%	24h	$400/ton
	0,5%	35 min	96%	24h	
	3,0%	15 min	99%	24h	
4	3,0%	No reaction happened		24h	$5000/ton

How is showed in the table 5.2, conversion results were obtained with low quantities of catalyst 2 catalyst 3. They are the cheapest catalysts, also showed in table 5.2. 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 5.2 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 best conversion of the two catalysts seems be the one from the catalyst 2 for 0,5% of concentration and for 0,1% is the one form the catalyst 3. 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. (Peng et al. [2010]) 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. .
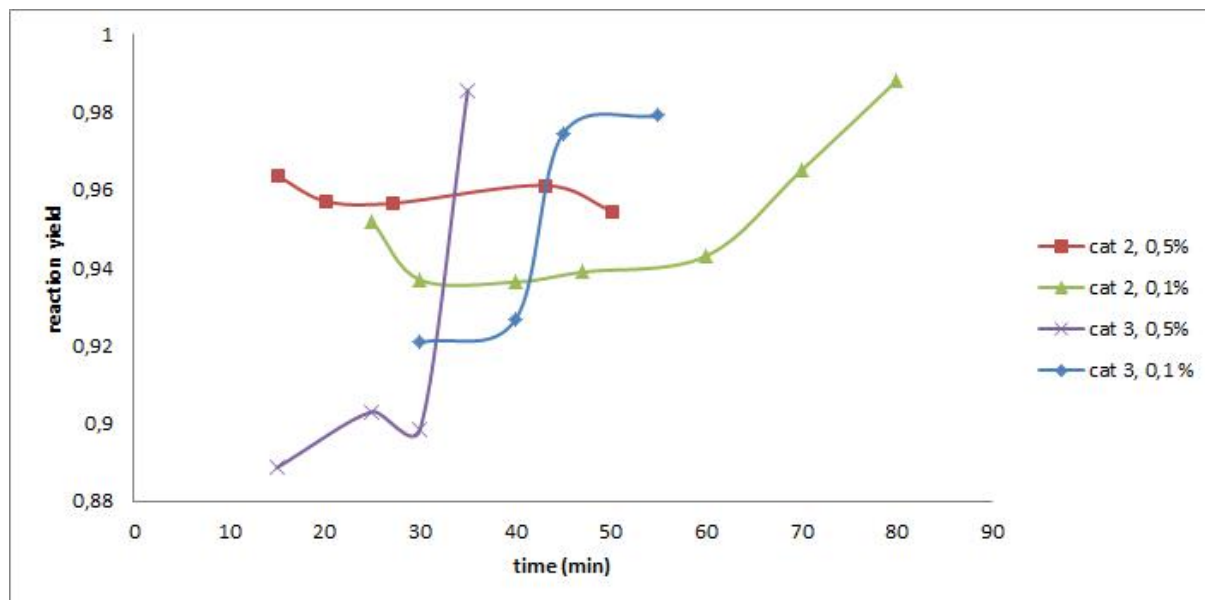

Figure 5.2: Conversion results of catalysts 2 and 3.

5.1.4   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 5.3 shows the SEM micrographs of extracted pine wood prior to the reaction and of the residue after the reaction. In the SEM images is showed the row wood and the residue from reaction with catalysts 2 and 3 with x100, x500 and x1500 magnification. 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. Between the two different catalysts (the two best of all of the catalysts tried) there is no so much difference in the residue, that can be explained by the fact that the yield of the reaction is very similar between them. The big difference is 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 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%.

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	x100	x500	x1500
Row wood			
Cat3 0,1%, 25 minutes			
Cat3 0,5%, 30 minutes			
Cat2 0,1%, 30 minutes			
Cat2 0,5% 25 minutes			
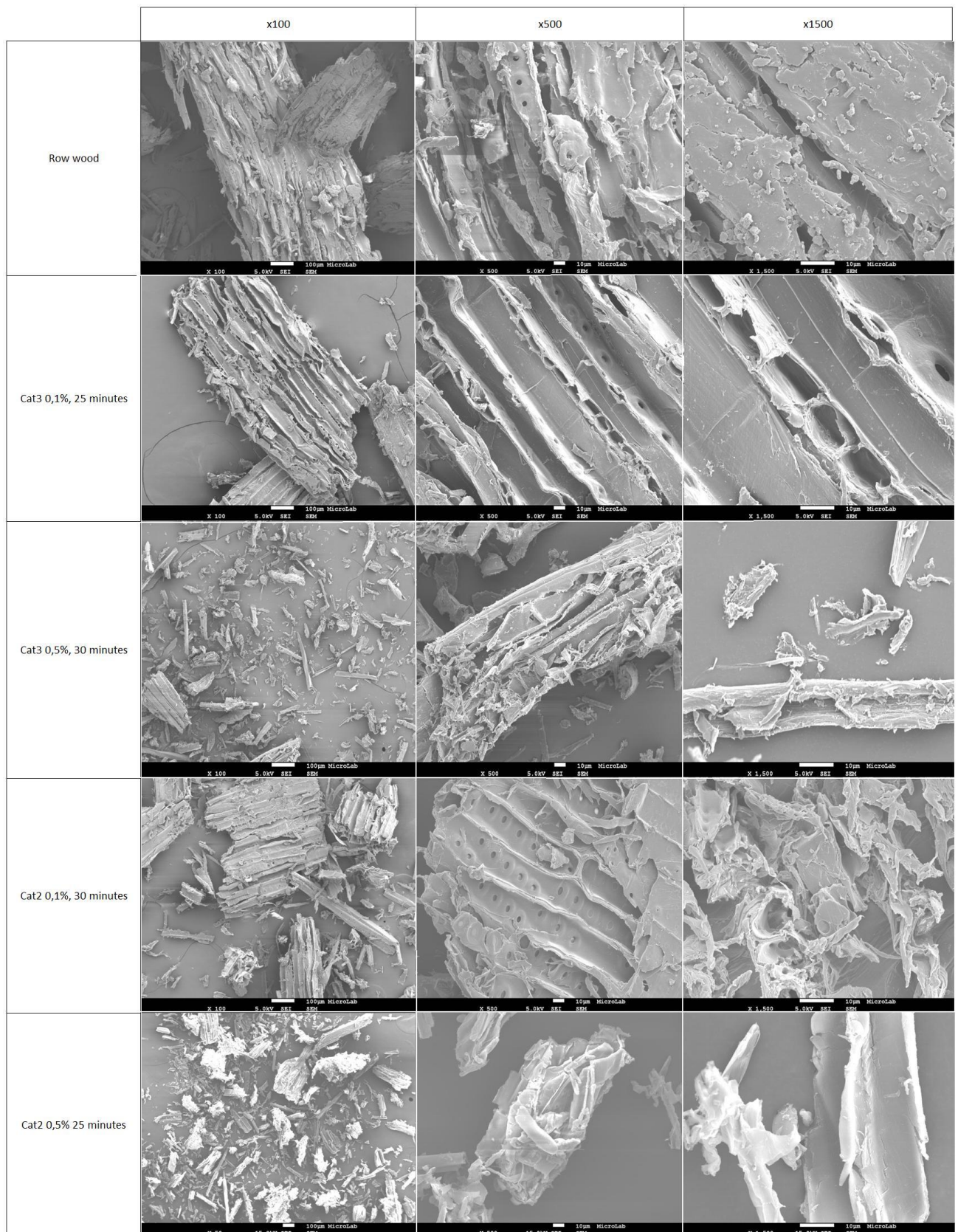
Figure 5.3: SEM pictures of residues from reactions with catalysts 2 and 3 compared with row wood.

	x100	x500	x1500
cat 2 0,1%, 25 minutes			
cat 2 0,1%, 80 minutes			
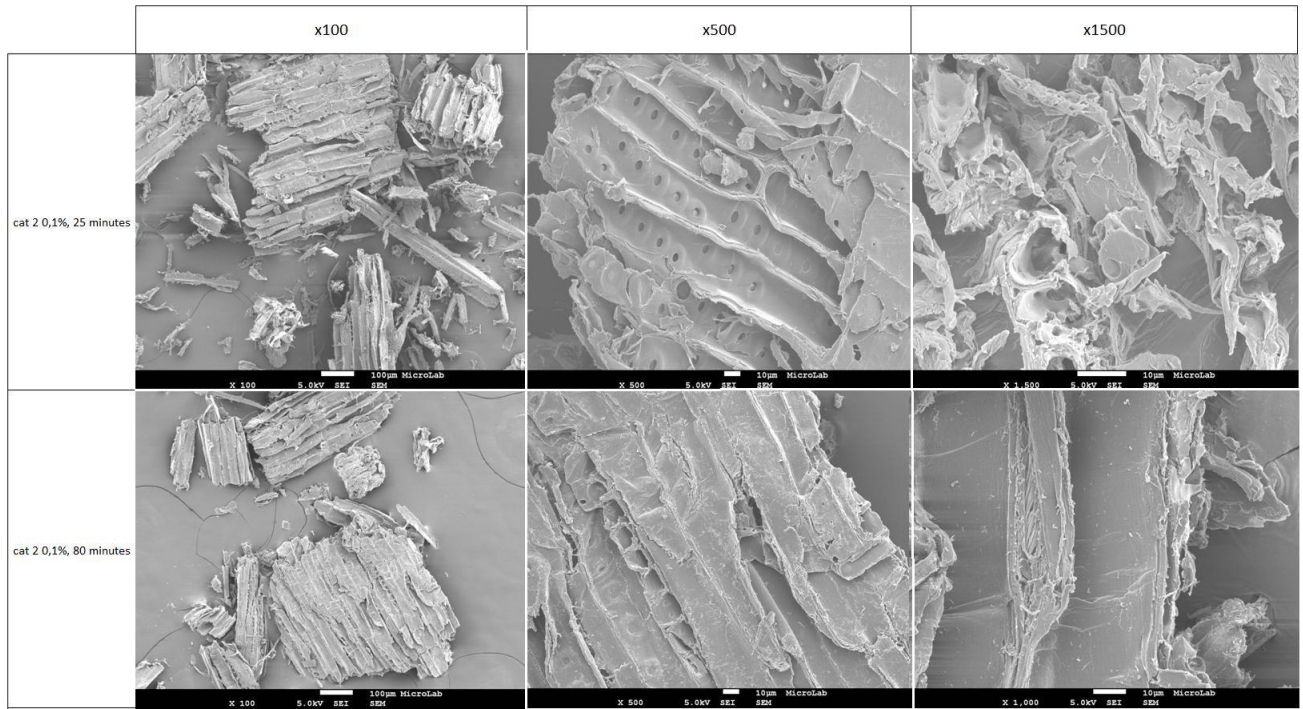
Figure 5.4: SEM pictures of residues from reactions with catalyst 2 of different times.

	x100	x500	x1500
cat 3 0,1%, 30 minutes			
cat 3 0,1%, 55 minutes			

Figure 5.5: SEM pictures of residues from reactions with catalyst 3 of different times.

Like in the case of the difference of concentration, after more time of reaction the particles of the wood's residue are smaller as is possible to see in figures 5.4 and 5.5 and also more degraded.

5.2   Characterization of polyurethane foams

During and after the obtaining of the foams, they were studied and characterized. (A.2)

5.2.1   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: 23°C and 5°C (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 (23°C) and a low temperature (5°C). The quick tests for the liquid mixture inside the can evaluate the shaking rate, for the froth after dispensing evaluate the froth shrinkage and the froth outflow and for the cured foam evaluate the surface structure, the cell structure, the curing streaks, the ba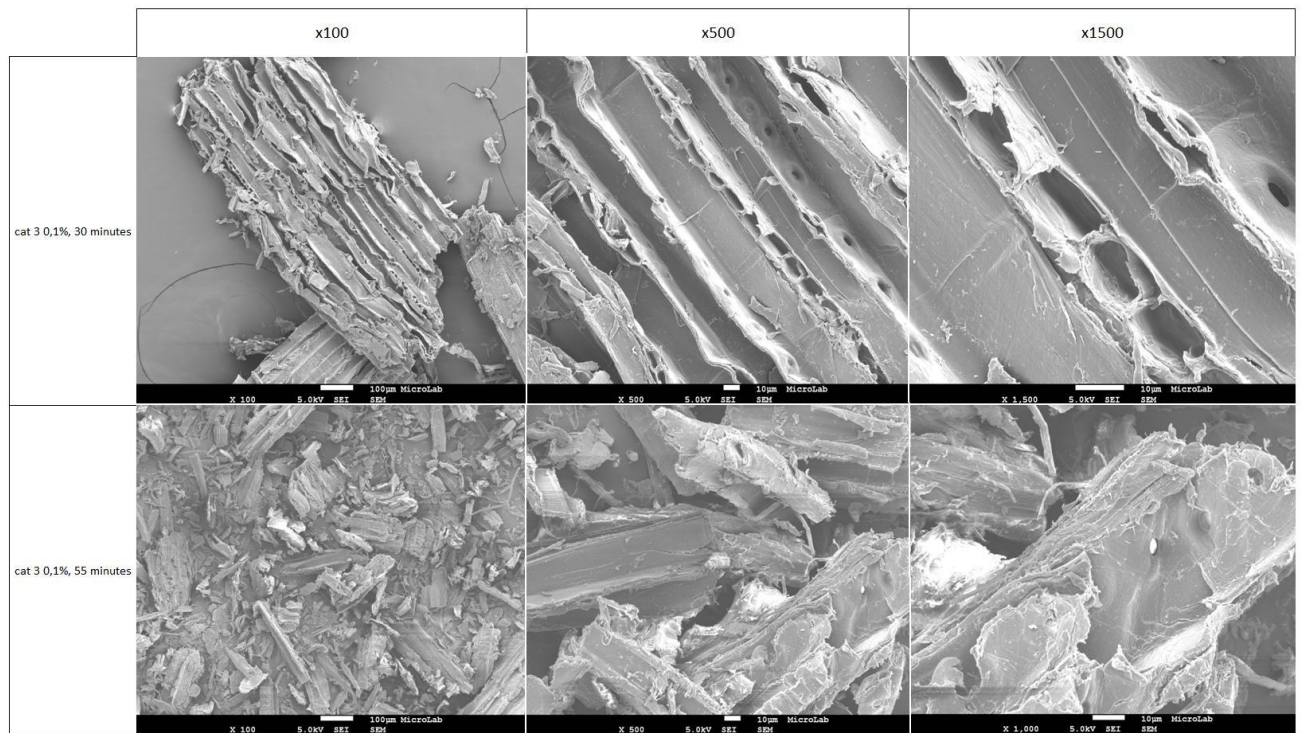se holes, the glass bubbles, the crumbling, the voids and pin holes, the cell collapse, the side base holes, the curing shrinkage and the cutting shrinkage. The results of the quick test are showed in the figure 5.6. The properties of the three formulations are quite similar. But the formulation C has the best properties, probably because as showed at the table 3.3 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 In the figure 5.6 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. As explained in section 5.2 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 5.7 appear the different foams, produced at two different temperatures (5 and 23°C). In them is possible see that the more appreciable defect are the base holes, specially in the foams produced at 23°C. This problem are bigger in foams B and C. The foams produced at 5°C present less defects.

5.2.2   Output test

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 can during a certain time which is usually 10 seconds. 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). This test is performed at a
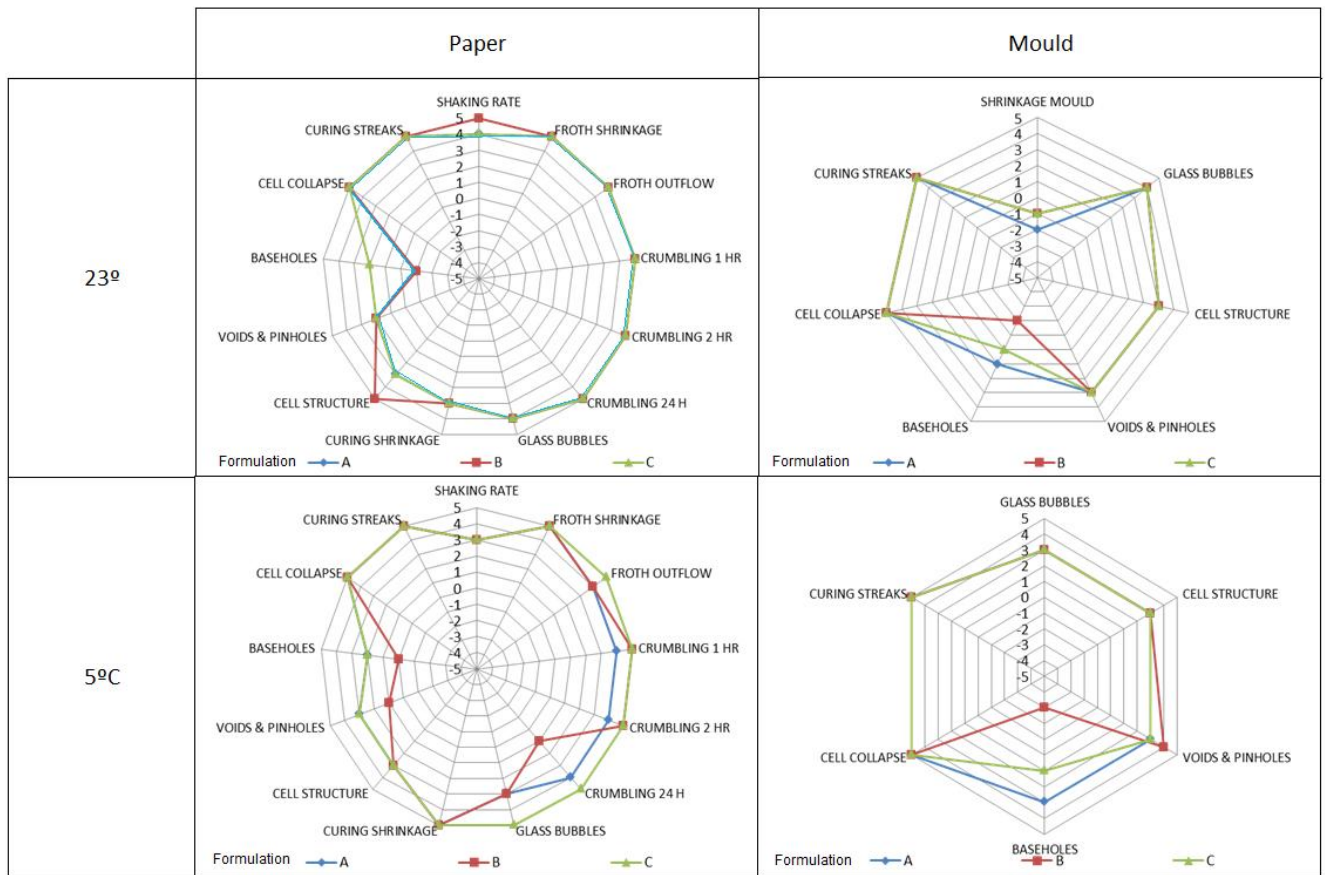
Figure 5.6: Benchmarking performed between formulations.

Figure 5.7: Pictures of the different foams.

can/curing temperature of 5/5ºC, which is the worst case scenario. The output rate depends strongly on the viscosity. The higher the viscosity of the prepolymer of polyurethane products, the lower the will be
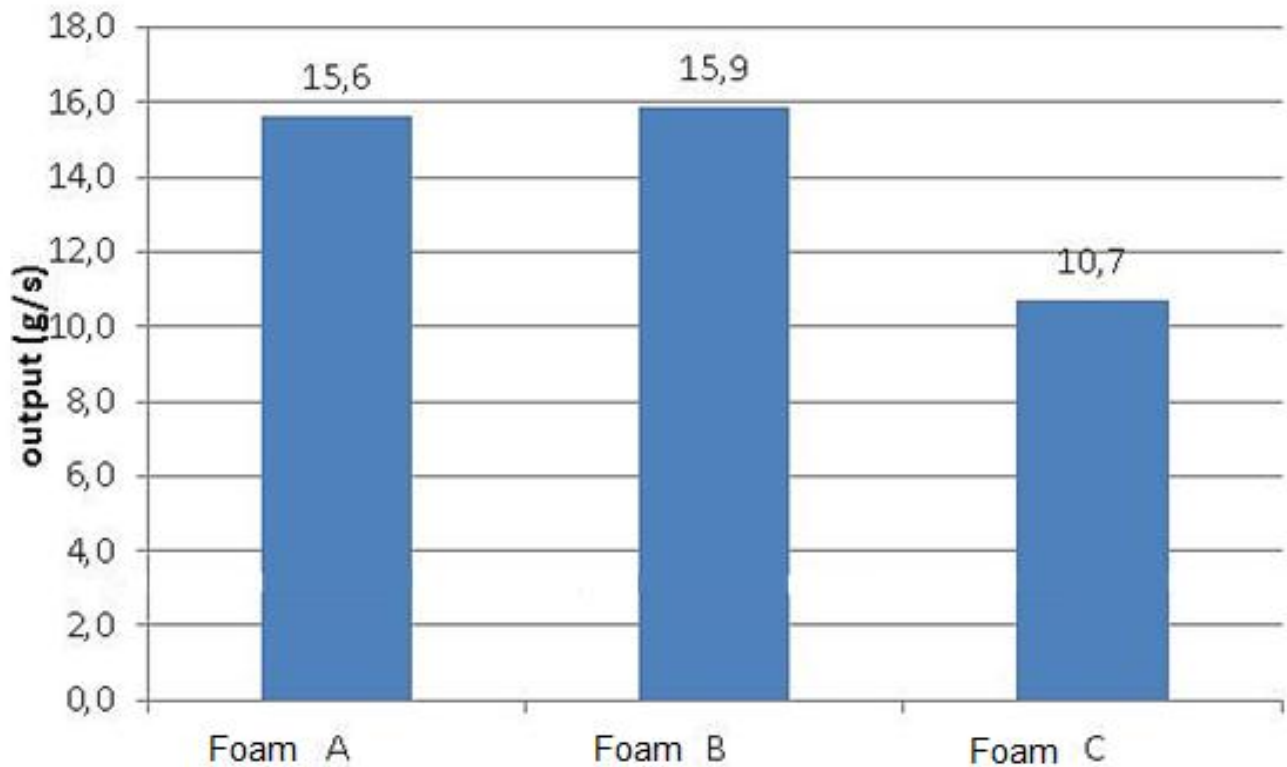
Figure 5.8: Output results at 5ºC.

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 5.8,formulation C has the lowest output rate (is the most viscous) due to its composition with more additives of high molecular weight.

5.2.3 Foam structure (SEM)

SEM images of polyurethane foam samples are shown in figure 5.9. It can be seen that the bio-polyols 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 5.6 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).
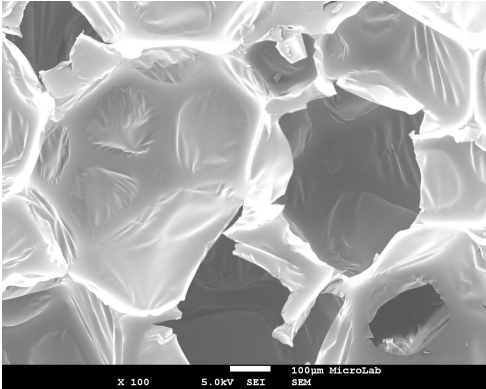
(a) Foam A x100
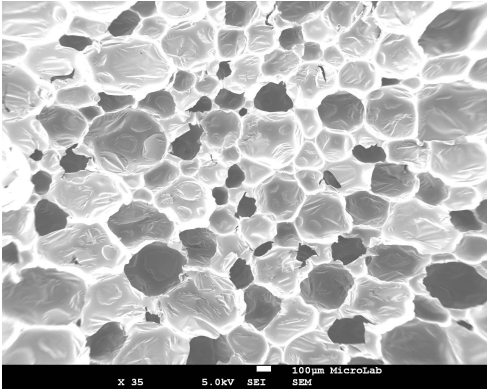
(b) Foam C x 35
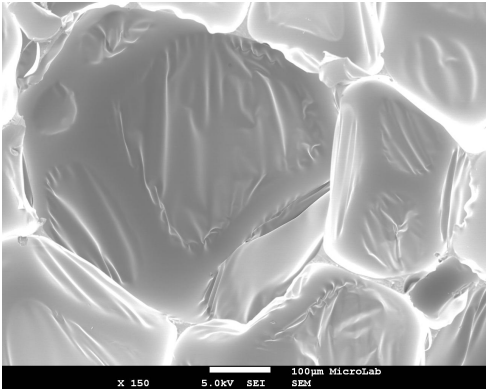
(c) Foam A x150
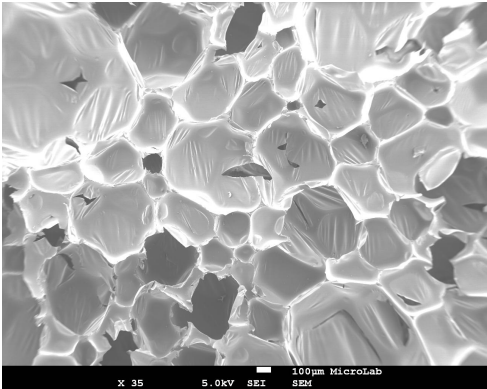
(d) Foam B x35
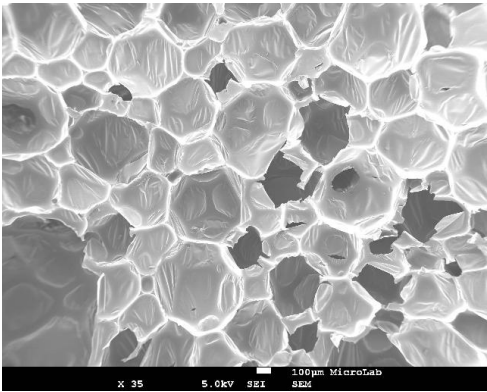
(e) Foam A x 35

Figure 5.9: SEM images of Foams.

Chapter 6

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 liquefaction solvents and with different type of catalysts. This reaction has attracted a lot of attention because is carried at atmospheric pressure and low temperature with only one step. Once the necessary amount of polyols were obtained, three different polyurethane foams were produced by the 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.

6.1 Achievements

The principal achievement of this project 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 environmentally conscious 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 (and interesting to do it in an industrial scale) because the catalyst is the most expensive reagent.

6.2 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). And also to obtain foams with more percentage of wood polyols, that means more percentage of reagent from a green origin and more biodegradability of these foams. Related with the biodegradability, it 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.

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Appendix A

Appendix

A.1 Experimental arrangement

Figure A.1: Picture of the experimental arrangement.

A.2 Table of foams properties

Qualification

Property	5	4	3	2	1	0	-1	-2	-3	-4	-5
Shrinkage mould								A mould 23ºC			
						B mould 23ºC					
								C mould 23ºC			
Glass bubbles		A paper 23ºC, A mould 23ºC	A paper 5ºC, A mould 5ºC								
		B paper 23ºC, B mould 23ºC	B paper 5ºC, B mould 5ºC								
	C paper 5ºC	C paper 23ºC, C mould 23ºC	C mould 5ºC								
Cell structure			A mould 23ºC, A paper 23ºC, A mould 5ºC, A paper 5ºC								
	B paper 23ºC		B mould 23ºC, B paper 5ºC, B mould 5ºC								
			C paper 23ºC, C mould 23ºC, C paper 5ºC, C mould 5ºC								
Voids and pinholes			A paper 23ºC								
			A mould 23ºC, A mould 5ºC, A paper 5ºC								
		B mould 5ºC	B mould 23ºC	B paper 23ºC	B paper 5ºC						
			C paper 23ºC								
			C mould 23ºC, C paper 5ºC, C mould 5ºC								
Baseholes		A mould 5ºC	A paper 5ºC	A mould 23ºC		A paper 23ºC					
						B paper 5ºC	B paper 23ºC	B mould 23ºC	B mould 5ºC		
				C paper 23ºC, C paper 5ºC	C mould 5ºC	C mould 23ºC					
Cell collapse	A mould 23ºC, A paper 23ºC, A mould 5ºC, A paper 5ºC										
	B paper 23ºC, B mould 23ºC, B paper 5ºC, B mould 5ºC										
	C paper 23ºC, C mould 23ºC, C paper 5ºC, C mould 5ºC										
Curing streaks	A mould 23ºC, A paper 23ºC, A mould 5ºC, A paper 5ºC										
	B paper 23ºC, B mould 23ºC, B paper 5ºC, B mould 5ºC										
	C paper 23ºC, C mould 23ºC, C paper 5ºC, C mould 5ºC										
Shaking rate		A paper 23ºC	A paper 5ºC								
	B paper 23ºC		B paper 5ºC								
		C paper 23ºC	C paper 5ºC								
Froth shrinkage	A paper 23ºC, A paper 5ºC										
	B paper 23ºC, B paper 5ºC										
	C paper 23ºC, C paper 5ºC										
Froth outflow	A paper 23ºC	A paper 5ºC									
	B paper 23ºC	B paper 5ºC									
	C paper 23ºC, C paper 5ºC										
Crumbling 1h	A paper 23ºC	A paper 5ºC									
	B paper 23ºC, B paper 5ºC										
	C paper 23ºC, C paper 5ºC										
Crumbling 2h	A paper 23ºC	A paper 5ºC									
	B paper 23ºC, B paper 5ºC										
	C paper 23ºC, C paper 5ºC										
Crumbling 24h	A paper 23ºC	A paper 5ºC									
	B paper 23ºC			B paper 5ºC							
	C paper 23ºC, C paper 5ºC										
Curing shrinkage	A paper 5ºC	A paper 23ºC									
	B paper 5ºC	B paper 23ºC									
	C paper 5ºC	C paper 23ºC									

Figure A.2: Summary of foams properties.