

UNIVERSIDADE DE LISBOA
FACULDADE DE CIÊNCIAS
DEPARTAMENTO DE QUÍMICA E BIOQUÍMICA



Lignopolyol based one-component polyurethane foams

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Mário Filipe Lima do Vale

Dissertação orientada por:
Professor Doutor Carlos Alberto Nieto de Castro
Doutora Maria Margarida Pires dos Santos Mateus

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Abstract

Fossil fuels, such as natural gas, coal and oil are the base of all modern societies. They are used to produce energy that fuels all kind of industries and generates electricity. According to the OECD environmental outlook, the emissions are expected to grow 50% between now and until 2050, primarily due to a 70% growth in energy-related CO₂ emissions. In Europe, the chemical industry accounted for 14% of total greenhouse emissions in 1990.⁶ In an effort to tackle this global problem, efforts are being made by the chemical companies by developing more ecological products. One alternative carbon source to the fossil fuels is the production of multifunctional polyols from the plant biomass by a solvolysis liquefaction process. In this work, polyols were successfully produced by an acid liquefaction of eucalyptus bark, pine wood chips, cork powder and poplar wood chips, at 160°C and an ambient pressure, with conversion ratios of 58-91%, depending on the biomass. These new polyols, or lignopolyols, had an OH value of 193-303 mg KOH/g and a water content of 0,31-1,07%. The infrared spectra analysis concluded that they were an aromatic compound, with carbonyl and OH groups, which led to the conclusion that they must be derived from lignin and suberin.

After they were produced, the polyols from a base OCF formulation were progressively replaced by the lignopolyols in 5, 50 and then 100% parts per weight. The resultant rigid polyurethane foams had good outputs (over 3,5 g/s), an overall almost good quality and low quality degradation after 12 months of shelf life. The foam that presented the best results was the one based on the cork lignopolyol, having better quality than the control foam. However, all of them were very flammable submitted to an ignitibility test, even when a flame retardant was used.

To turn them into commercially viable one component foams, improvements in the formulations and further tests shall be done in future work. Flame retardant tests and the measurement of free monomeric MDI with HPLC shall be carried out.

Keywords: biomass liquefaction; lignopolyol; one component foam (OCF); polyurethane; foam evaluation.

Resumo

Num futuro muito próximo, está previsto um aumento drástico das emissões de CO₂ em todo o mundo. Segundo dados da OCDE, as emissões de CO₂ aumentarão cerca de 50% até 2050. Um dos grandes contribuidores são as emissões de fontes energéticas como os combustíveis fósseis. Para além disso, é uma fonte não renovável de energia e de matéria-prima para a indústria química, o que tem levado muitos cientistas a tentarem encontrar novas fontes que sejam mais renováveis e ecológicas, como a biomassa. Segundo a Diretiva Europeia 28/2009/EC a biomassa “consiste na “fração biodegradável” de produtos, resíduos e detritos de origem biológica provenientes da agricultura (incluindo substâncias vegetais e animais), da exploração florestal e das indústrias afins, incluindo a da pesca e da aquicultura bem como a fração biodegradável de resíduos industriais e urbanos”. Aproximadamente 70% da biomassa vegetal é composta por células vegetais. É estimado que por ano são geradas cerca de 200×10^9 toneladas no mundo inteiro de biomassa, ultrapassando largamente a produção anual de barris de petróleo. Mesmo que se só vá utilizar uma fração da biomassa, esta pode apresentar uma boa alternativa ao petróleo na área energética mas também na área da produção de químicos.

Um dos processos que tem sido alvo de desenvolvimento nos últimos tempos para a transformação da biomassa vegetal em produtos químicos é a liquefação. Este processo consiste na decomposição da celulose, hemicelulose e lenhina através duma reação de solvólise a temperaturas na ordem dos 160°C e a pressão atmosférica. O produto final primário será uma mistura de polióis com funcionalidade cerca de 2,5, com alto valor OH e baixo valor ácido, o que os torna adequados para a produção de espumas rígidas de poliuretano.

Neste trabalho polióis provenientes da casca de eucalipto (*Eucalyptus Globulus*), pinho (*pinus pinaster*), pó de cortiça e madeira de choupo foram diretamente introduzidos em formulações de espumas de um componente (*One Component Foams*, OCF) com o objetivo de substituir totalmente os polióis derivados do petróleo, criando um produto comercial mais ecológico e proveniente de fontes renováveis. Deste modo, o trabalho dividiu-se em duas fases: uma em que se liquefez e caracterizou-se os polióis derivados das madeiras, e outra em que foram gradualmente introduzidos numa formulação base OCF já comercial, verificando sempre as qualidades, envelhecimento e inflamabilidade das espumas obtidas.

Na liquefação foram utilizados um monol e um diol como solventes. Depois de adicionados à biomassa dentro do reator, a temperatura foi elevada até 160 °C e deixou-se reagir entre 1 e 2h, dependendo da biomassa. Depois de a liquefação ter ocorrido, os açúcares provenientes da celulose e hemicelulose são removidos através de extração líquido-líquido com água. A importância deste passo é elevada, pois se não forem removidos, o valor OH dos pólios será demasiado elevado e as espumas resultantes serão quebradiças. Para além disso, também é muito importante remover a maior quantidade de água possível dos polióis, pois uma elevada quantidade de água dentro das latas faz com que ocorra uma reação de expansão precoce e a pressão interna aumente, aumentando o risco de rebentamento. As quantidades utilizadas foram 70g para o pó de cortiça, 50 gramas para a casca de eucalipto e 85 gramas para a madeira de choupo, sendo os tempos de reação 2h, 1-2h e 1h-1h30min e as conversões 67-79%, 60-66% e 83-91%, respetivamente. As conversões da biomassa proveniente do eucalipto foram inferiores devido ao facto de esta ser uma casca, e portanto possuir um teor em lenhina substancialmente maior que as restantes. Os valores OH variaram entre 193 e 303 mg KOH/g e os conteúdos de água entre 0,35% e 1,07%. A análise do espectro de infravermelho permitiu concluir que o composto produzido é um álcool aromático com grupos carbonilo, provando assim ser um derivado da lenhina e da suberina.

A introdução de cada um dos polióis provenientes da biomassa vegetal em formulações de espuma rígida de poliuretano de um componente foi feita de forma gradual, começando com 5%, 50% e por fim 100% em partes por peso, substituindo por fim completamente os polióis da formulação base. A substituição foi feita utilizando um ficheiro de excel existente na empresa, denominado de *Foamcalc*, onde os ajustes poderão ser feitos automaticamente. Depois de cada formulação estar pronta e devidamente ajustada, foram enchidas uma lata para cada poliól. No enchimento da lata três componentes gerais são adicionados: um componente A, composto por uma mistura dos polióis, catalisador, *crosslinker*, plastificante e surfactante; um componente B composto por um prepolímero de isocianato e um componente C composto por uma mistura de gases propulsores. O primeiro componente a adicionar à lata será o componente B. O prepolímero de isocianato é produzido *in situ* pela própria empresa utilizando um isocianato comercial. De seguida, é preparado o componente A adicionando todos os seus constituintes, tendo o cuidado de não adicionar primeiro os mais viscosos (para não colar no fundo) nem os de menor quantidade (para garantir que se integram completamente na mistura). De seguida, são misturados mecanicamente e adicionados à lata. Por fim a lata é selada e os gases são introduzidos através da válvula de saída, utilizando uma

estação de enchimento adequada. Depois de agitar vigorosamente durante 1 minuto a lata é deixada a repousar durante 12h. Durante este período ocorre a reação de polimerização entre o poliól e o prepolímero de isocianato. Passado este tempo, é colocada em repouso novamente mas a 5°C durante 4h, dando-se início depois aos testes de avaliação da espuma.

Nos testes de avaliação, é determinada a taxa de débito, em g/s, e a espuma líquida é pulverizada em papel e em molde a 5 e 23°C, onde é depois dada uma classificação de -5 a 5 a vários parâmetros visuais, como a quantidade de buracos presentes na base ou no interior da espuma curada. Uma espuma será qualificada como sendo de boa qualidade se a taxa de débito for superior a 3,5 g/s e se nenhum dos seus parâmetros tiver uma pontuação abaixo de 3. Nesta fase, as substituições até 100% foram efetuadas com sucesso em todos os polióis derivados da biomassa vegetal, e todas as espumas avaliadas nesta fase obtiveram uma classificação quase boa, sendo a baseada no poliól de pinho a melhor com apenas um valor abaixo de 3 na substituição a 100%, sendo melhor até que uma espuma de controlo baseada num poliól derivado do caju. Visto que a introdução foi um sucesso, o teste de envelhecimento acelerado foi realizado em todas as formulações. Neste teste a qualidade da espuma é avaliada a 0, 6 e 12 meses, por isso foram produzidas 3 latas por cada formulação, incluindo a de controlo. Uma lata foi logo avaliada no dia seguinte, e as outras duas foram colocadas numa estufa a 45°C durante 26 e 52 dias, de modo a obter um envelhecimento acelerado de 6 e 12 meses, respetivamente. Passado esse tempo, as espumas foram avaliadas utilizando o mesmo método referido anteriormente e a deterioração de qualidade foi avaliada. Ao contrário da fase anterior, as espumas que apresentaram melhor resultado foram as baseadas nos polióis derivados do pó de cortiça.

Para uma espuma ser comerciável, não só terá que passar no teste de qualidade, mas também terá que ser B2 (não muito inflamável) e possuir menos de 1% de monomérico livre. Deste modo, testes de resistência à chama foram realizados de acordo com a parte 1 da norma DIN-4102, utilizando as formulações com 100% polióis derivados da biomassa vegetal mas com 5g de retardante de chama. Contudo, os resultados foram negativos em todas as formulações, incluindo a formulação base e a de controlo. A percentagem de monomérico livre foi impossível de determinar devido ao facto de não haver equipamento disponível na altura.

Em suma, a introdução dos polióis derivados da biomassa foi um sucesso, produzindo espumas com qualidade quase boa e que não deterioram muito ao longo do tempo. Porém,

como trabalho futuro será necessário melhorar as formulações, realizar estudos de resistência à chama com novos e variados retardantes de chama e medir a percentagem de monomérico livre de modo a que se tornem comerciáveis.

Palavras-chave: liquefação da biomassa; poliól derivado da biomassa vegetal; poliuretano; espumas de um componente (OCF); avaliação da espuma.

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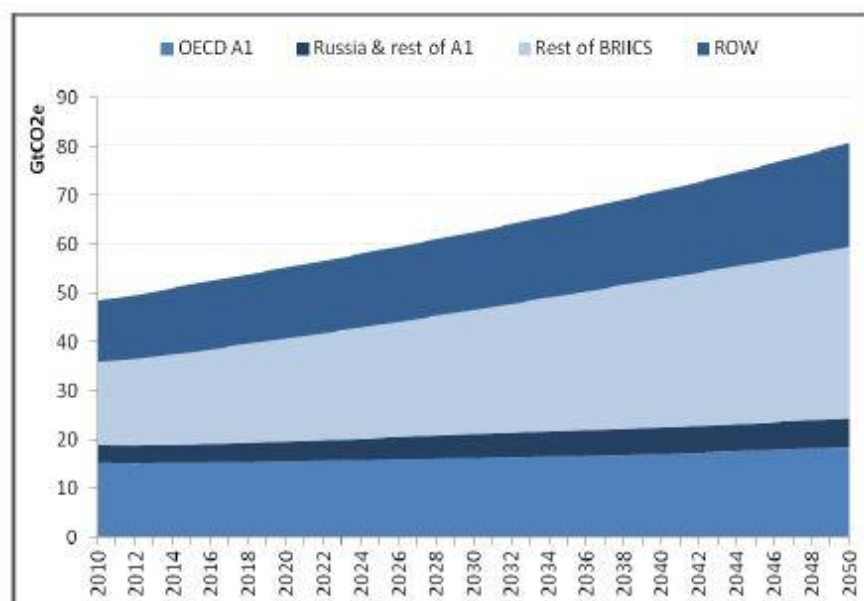
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1 Introduction

Fossil fuels, such as natural gas, coal and oil are the base of all modern societies. They are used to produce energy that fuels all kind of industries and generates electricity. Composed mainly of carbon, hydrogen and oxygen, they are the result of the deposition, under specific conditions, of organic material over a million years. Coal and gas are mainly used in power generation and oil, more specifically his distillates, are mainly used as transport fuel. Other uses include heat generation in buildings and in the chemical industry sector. However, fossil fuels are a finite resource and they can cause irreparable damage to the environment, is mishandled. Much debate has been occurring in the past years related to the finiteness of oil reserves, where some authors claim that we are already in the peak of oil and others say the peak will occur in a near future or will not occur at all.^{1,2} Another problem are the greenhouse gases, mainly CO₂, resulting from the combustion and refining of this fuel, which are released to the environment. In order to illustrate it, the following graph shows the evolution of greenhouse gas emissions in CO₂ equivalents by region:



Note: GtCO₂e = Giga tonnes of CO₂ equivalent
ROW = Rest of the World

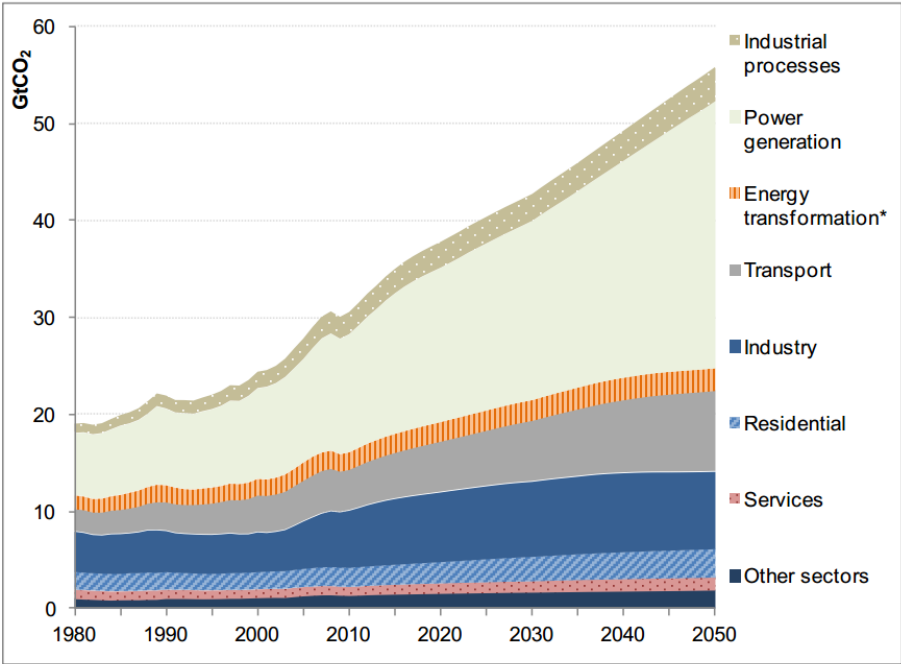
Figure 1 - GHG emissions by region (in GtCO₂e): baseline scenario.¹

Note: GtCO₂e = Giga tonnes of CO₂ equivalent; ROW = rest of the world

¹ Source: OECD Environmental Outlook Baseline; ENV-Linkages model.

According to the OECD environmental outlook, the emissions are expected to grow 50% between now and until 2050, primarily due to a 70% growth in energy-related CO2 emissions.³ The actual concentration of CO₂ in atmosphere is 400 ppm, which put us below the 450 ppm limit, but still too near. This concentration limit is important because if it remains below it, there is a 50% chance of stabilizing the climate at 2 °C global average temperature increase, which is still high but can be a good starting point for the stabilization of the climate. If no greenhouse emissions restriction policies are immediately applied in a global scale, it would cause irreversible damage to the environment. The greenhouse gases concentration would rise to 685 ppm in 2050, which is well above the 450 ppm mark. This will raise the temperature 3-6 °C above the pre-industrial average temperature by the end of the century, causing severe damage to the environment like precipitation patterns alteration, glaciers melting, sea-level rise and intensification of extreme weather events, like tornadoes and storms.^{4,5}

To further develop this topic, the image below shows the emission of CO₂ of each sector globally:



Note: The category “energy transformation” includes emissions from oil refineries, coal and gas liquefaction.

Figure 2 - Global CO2 emissions by source.⁵

Looking at the graph it’s clearly that the industrial processes are the largest contributor to the CO₂ emissions. In Europe, the chemical industry accounted for 14% of total greenhouse emissions in 1990.⁶ In an effort to reduce this value, it was developed cleaner and safer

technologies, waste recycling processes and new products to safeguard the environment and to increase energy efficiency of the processes, reducing its greenhouse emissions by 54% until 2012.⁷ Rigid polyurethane foams were one of the contributors to this reduction, because they are an excellent insulator and were easily applied in house insulating, increasing their energy efficiency and reducing greatly the greenhouse gas emissions caused by house heating and cooling. However, if it is possible to substitute some components of the foams for others that require less energy to produce, it will increase the energy efficiency of the process, and thus reducing even more the greenhouse gas emissions. One of the promising alternatives is the biomass derived chemical compounds.

In the following chapters it will be discussed what's the biomass and how can it be used to produce polyols, some history background of the polyurethane foams, its markets and how they are made. Then the biomass derived polyols will be inserted in a formulation in an attempt to produce biomass based polyurethanes.

1.1 The Forests as a renewable chemical source

Forests and wooded land cover more than 40% EU land area. Mainly, they provide wood, but also non-wood products, like food, resins, medicinal or cosmetic reagents and cork. In Portugal, about one third of its land area is covered by forests, which 50% of it is available as wood supply.

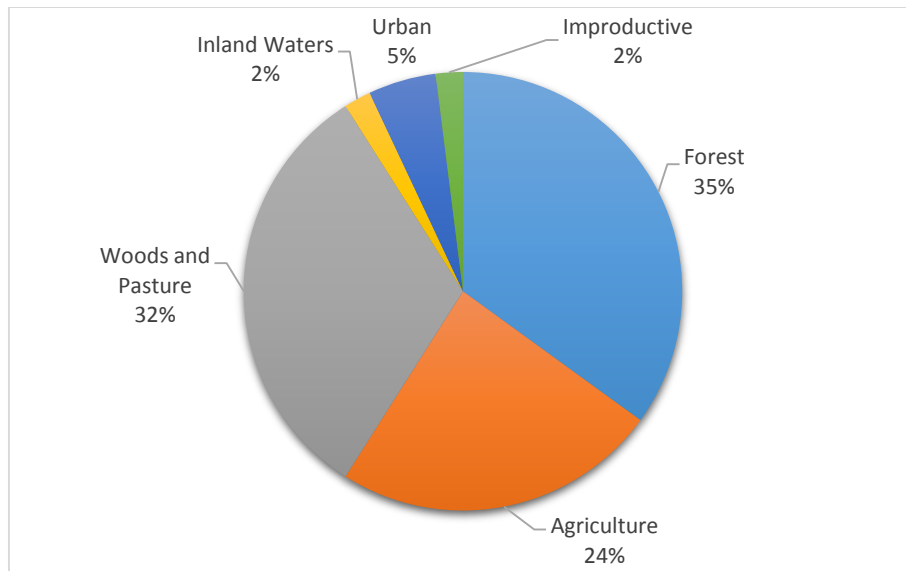


Figure 3 - Areas of land use distribution for Portugal in 2010.⁸

According to figure 4, it's safe to assume that this wood supply is mainly composed by blue gum, maritime pine and the cork oak tree.

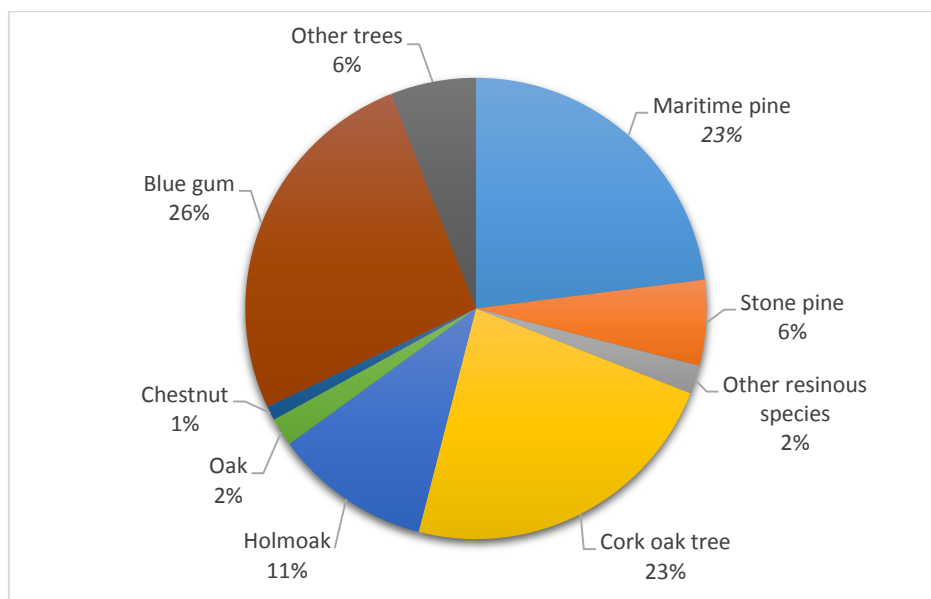


Figure 4 - Distribution of the total area by tree species.⁸

As renewable energy sources like solar, wind and hydroelectric, are the major alternatives of fossil fuels, so is biomass the major alternative hydrocarbon source of crude oil. In general terms, biomass it's all the biological material derived from recently living organisms that can be transformed to produce sustainable chemicals and fuels. In the past years, in response to the non-sustainability of oil supplies and the rising of CO₂ emissions, a global first attempt was made to launch a bio-based economy running on vegetable oils and sugars derived from starch or sucrose. However, these accessible products were in direct competition with the food chain, which directly or indirectly increased the effect of another big problem in the world: the hunger. As an alternative, the scientific community began to look upon a very abundant biomass source that was being devalued at the time: the plants.⁹

Plant biomass is the wood and bark of the trees. Approximately 70% of this biomass is composed of plant cells, which contains lignocellulosic matter. These matter can serve as the main source for the production of bio-based versions of common chemicals and polymers. The estimated annual amount of biomass generated globally is between 10 and 200x10⁹ tons, which, besides being a renewable resource, largely surpasses the annual production of oil barrels (4.0x10⁹ tons¹⁰). It is true that not all of this biomass could be used to produce bio-based materials, but this shows that even a small fraction of it can be a very good alternative source to fossil oil.

1.1.1 Biomass Sources

The sources of plant biomass for the production of alternative chemicals could be the same as used for the production of energy, such as, the residues of forest and agricultural industries, dedicated crops and even the residues that result from forest cleaning process.

1.1.1.1 Forest Industry Residues

Forest industry is defined by all the industry sectors that use and transforms all kind of wood into increased value materials. Its economic value really depends on the country. Portugal, according to the next figure, has a large area of forest

The percentage of the land use of forest and woody regions may be a positive factor for the production of these chemicals. Based on figure 3, Portugal has more than half of its land covered by woody regions, like forest and woods, having the potential to be a producer of plant biomass derived chemicals.

As already said above, the sources for the production of bio-based chemicals are expanding and changing to the industrial wastes. The industries that produce biomass residues are the ones that rely on wood. These can be the woodworking, paper pulp production and cork transformation industries.

In Portugal, 6% (682 508 t) of the residues produced in 2013 in all economic sectors were non-hazardous wood residues. The main producer of these residues is the paper and paper pulp production industries, as shown in the graph below:

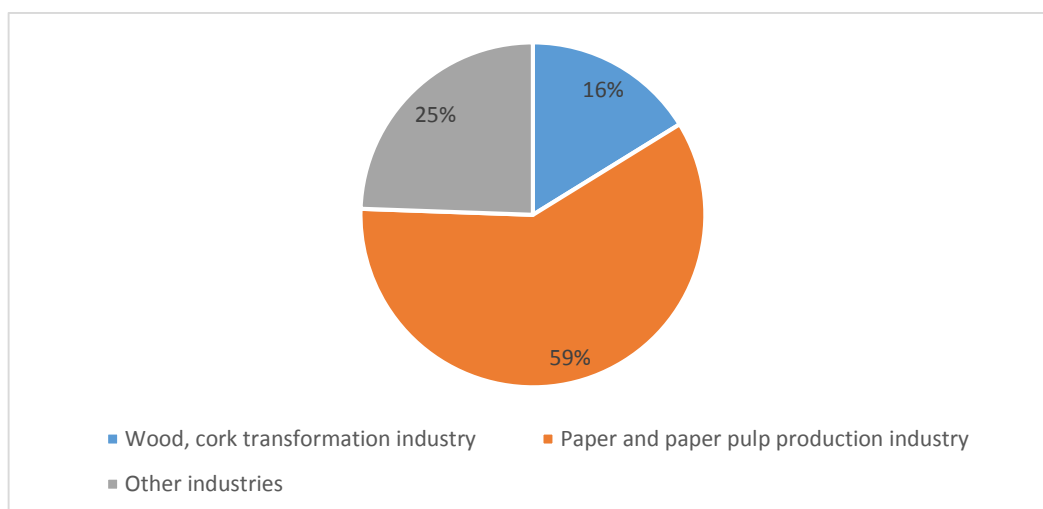


Figure 5 - Main producers of non-hazardous wood residues in Portugal in the year 2013. Source: Instituto Nacional de Estatística (INE).

1.2.1.1 Forest cleaning residues

Since 1980 until 2013, Portugal is the country with more number of fires registered and the third country with more burnt area in the all the Southern Member States of European Union, which consists of Spain, France, Italy and Greece. In 2013, Portugal shared a 52% of the total burnt area and 54% of the total number of fires registered in these countries. These alarming numbers are a result of the combination of its large woody area, inefficient anti fire policies, bad undergrowth wood managing and cleaning, few fire combat vehicles and bad preparation of the fireman personnel. However, some of these factors can be future advantages for the production of biomass derived chemicals. All the residues obtained in the cleaning of the undergrowth bushes can be a big source of biomass for the future liquefaction plants. Moreover, the terrain occupied by unclean pasture and forest can be converted into energy crops, which could provide more plant biomass, not only for producing energy, but for the production of bio-based chemicals.¹¹

1.2 Biomass Liquefaction Process

One of the emerging processes used to transform biomass into valuable chemicals is the liquefaction. In a few words, this process uses the solvent to break the biomass molecules into smaller ones, which can be used to produce alternative materials that normally came from petroleum, such as polyesters¹² and polyurethanes.¹³⁻¹⁹ This process was already studied in wood^{12,20}, agricultural residues^{15,16,18,19,21} and cork.^{22,23} The biomass materials may come from the wastes of their associated industries. Turning them into new improved materials increases its value and contributes to the preservation of the environment.

Succinctly, the biomass liquefaction process it's a solvolysis reaction, which means that the biomass is decomposed by the solvent into smaller molecules. The solvents used are polyhydric alcohols, like polyethylene glycol (PEG) or glycerol, and the catalysts are a strong acid or base, like sulphuric acid or sodium hydroxide. In the acid-catalyzed the reaction temperature is 110-160 °C, but in the based-catalyzed the temperatures are much higher (250 °C). However, all the reactions are made at atmospheric pressure. In the end a mixture of different polyols rich in hydroxyl groups is produced. This mixture can be used directly to produce polyurethane foams.²²

Chemical composition of biomass is a determinant factor in the final yield of the reaction. Normally, biomass is composed of lignin, cellulose and hemicellulose, were all of them are highly functionalized materials rich in hydroxyl groups, which are important in the liquefaction process.¹⁷ Another chemical compound present in almost every plant biomass is the suberin. Normally it's present in very low quantities, but in cork it's the most abundant compound, which gives it very special physical properties.

Because of their different structures, these chemical compounds will be liquefied at different stages of the process. Usually, the first compounds to liquefy are the ones who have a disorganized structure like cellulose, hemicellulose and lignin. These compounds liquefy rapidly in the first moments of the liquefaction because of the great accessibility to the solvent. In contrast, crystalline cellulose liquefies at later stages of the liquefaction, due to its well packed structure that is less accessible to solvents, turning it the rate-limiting reaction step. Theoretically, a biomass that has less crystalline cellulose should liquefy more rapidly.¹⁷

1.2.1 Cellulose

Cellulose is present in approximately 40-45% of dry wood, making it the most abundant organic compound in biomass and on Earth. It is an homopolysaccharide of β -D-glucopyranose units which are linked together by (1,4)-glycosidic bonds. They exist in the form of aggregates with highly ordered (crystalline) alternated with less ordered (amorphous) regions. These aggregates are known as microfibril, which in turn builds into larger fibrils and then cellulose fibres. These fibres are the major component of the cell wall, giving structure and strength to the plant. Without it, there wouldn't exist lumber, paper or cotton fabric.²⁴

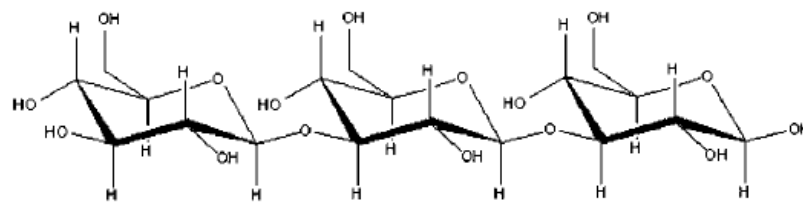


Figure 6 - Molecular structure of cellulose.²⁵

1.2.2 Hemicellulose

In general terms, hemicellulose is a heteropolymer of polysaccharides present in 20 to 30% of dry weight of wood, turning it the second most abundant organic material on plants and Earth. It is present in the primary and secondary cell wall, and its main function is to strengthen the cell wall by interacting with cellulose fibres and lignin. In the figure below, it is possible to see this interaction:

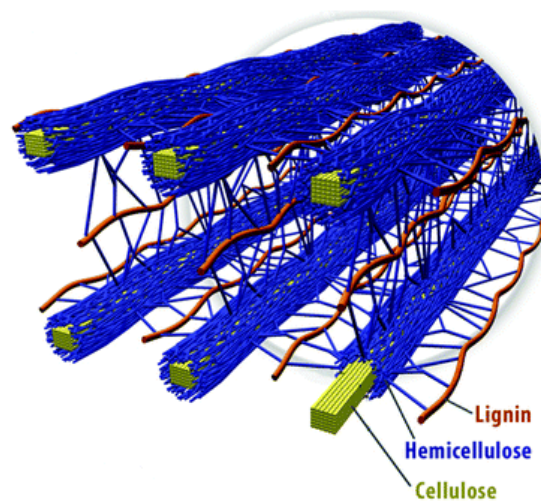


Figure 7 - Cellulose, hemicellulose and lignin spatial arrangements in the cell walls of lignocellulosic biomass.²⁶

Its chemical composition consists of long chains of a variety of pentoses and hexoses, varying from softwood to hardwood plants.^{27–29}

1.2.3 Lignin

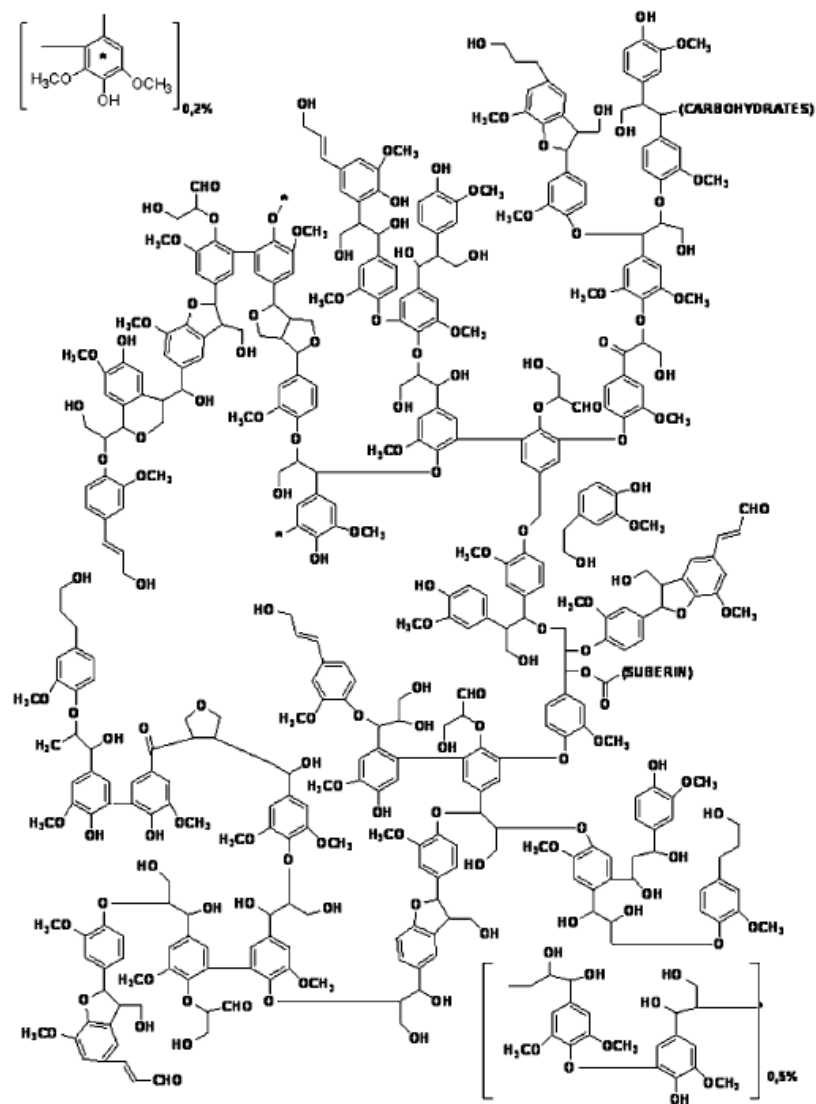


Figure 8 – Molecular structure model of lignin in the cork tree.²⁵

Lignin are the encrusting structural materials that embed cellulose in the wood. It can be divided into three types, related to its plant family: softwood (gymnosperm), hardwood (angiosperm) and grass (graminaceous) lignin. The chemical composition of the lignin of each plant family will vary. Coniferyl alcohol is the main component of softwood lignin, whereas coniferyl and sinapyl units are the building blocks of hardwood lignin. The lignin of grass plants are mainly composed of *p*-coumaryl alcohol units.²⁹

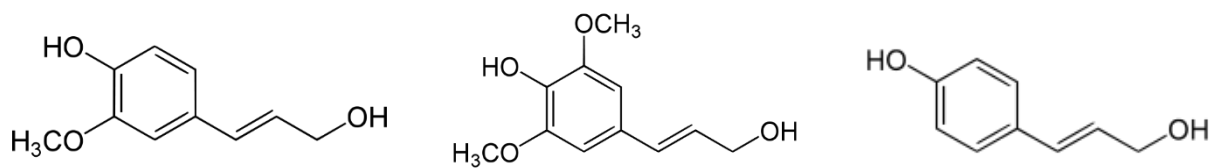


Figure 9 - Coniferyl (left), sinapyl (center) and p-coumaryl alcohol.

Although the model shown in figure 5 is from the cork bark (hardwood) lignin, it was proven by UV microscopy that lignin is a highly aromatic copolymer of different phenylpropane units. These units are joined about two thirds by C-O-C (ether) and one third of C-C linkages. They also have many functionalized groups like methoxyl, phenolic hydroxyl, and some aldehyde groups.²⁴

1.2.4 Suberin

Suberin is a biopolymer found more commonly in the outer bark of trees. It is named after the *Quercus Suber*, cork tree, in which 40% of its outer bark cell walls are composed by it. Suberin has two different polymeric domains: one aromatic composed of polyphenols linked via glycerol to another domain composed of polyaliphatic long chain molecules.

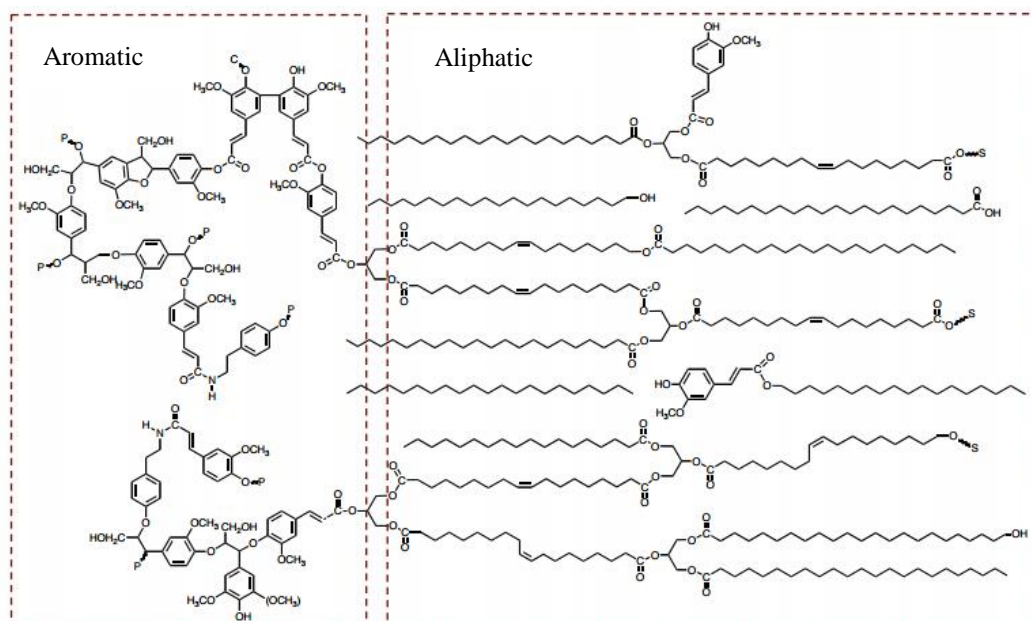


Figure 10 - Suberin molecular structure.⁴⁶

The main function of suberin in plants is to be a physical barrier, in order to prevent water loss from the tissues as well as providing pathogenic protection.³⁰

1.3 Polyurethane

A polymer is a macromolecule which consists of identical constitutional repeating units, also called structural units or monomers. If the monomers are chemically identical they form a homopolymer, but if they are different they are called heteropolymers. Depending on the chemical structure of the monomers, polymers can assume a linear, branched or even a 3D structure. Polyurethane is any copolymer with a characteristic urethane linkage between his two monomers. A urethane linkage is defined as an amide and ester group in the same carbonyl group, and it was discovered in 1849 when Wurtz and Hoffmann studied the reaction between isocyanate and a compound with alcohol groups.^{31,32}

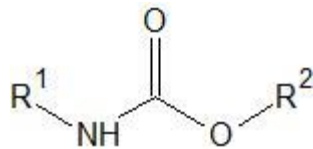


Figure 11 - Urethane linkage.

After some applications where discovered in 1937, the industrial production began, giving birth to one of the most versatile copolymers available in the market. They can be adhesives, coatings, elastomers, sealants and foams.³¹

1.3.1 Chemistry

The reaction that Wurzt and Hoffmann discovered was a simple addition reaction between an isocyanate and an alcohol, with hydrogen displacement. It is exothermic and is normally catalysed by bases. Approximately one hundred years later, Otto Bayer extended this reaction to polyfunctional isocyanates and alcohols, bounding them together successfully in long molecule chains. This was the birth of polyurethanes. The more commonly used process is the one that consists of a reaction between a mono or bifunctional alcohol, like a polyol polyether or polyol polyester, with a di or polyisocyanate group:



Figure 12 - Urethane polymerization reaction.

Besides reacting with the polyols, the isocyanates can react with every other compound that have mobile hydrogens like water, secondary and primary amines, carboxylic acids, and many others.

1.3.2 Applications

Polyurethane is a very versatile polymer. Just modifying the polyols and isocyanates, many applications can be made. The more common are foams and elastomers.

1.3.3 Foams

Foams are ramified polyurethane chains. They can be divided in two groups: rigid and semi-rigid. The use of polyols with high functionality and low molecular weight it's fundamental to produce rigid foams. The low molecular weight assures a small sized crosslink chains, giving the rigid characteristic after the curing process. Also, the high functionality of polyols combined with the highly reactive MDI, makes the reaction very fast, which in turns causes a rapid viscosity growth. This rapid growth don't let the expansion gas be released, which helps the growth and confers a closed cell structure to the foam, which is very important in thermic insulation applications. In fact, in terms of price and possible temperature range, rigid polyurethane foams are one of the best insulation materials in the market, and it can be used in the construction and electronics industry to insulate buildings and fridges, for example.³¹

The semi-rigid foam has two densities: one lower near its surface and one denser in the middle, giving them a very soft, sponge-like appearance. This is achievable using a cold mould and a low boiling point expansion gas. When the reaction begins inside the mould, its exothermic characteristic makes the temperature rise and the gas to evaporate, expanding rapidly and conferring a lower density. However, near the extremities, the mould is at a lower temperature than the inside. This causes the foam to expand more slowly, giving it a higher density. These foams are used in the automobile and furniture industries.³¹

1.3.3.1 Elastomers

Elastomers are linear polyurethane foams. They are prepared using one kind of a high molecular weight, in between 1000 and 2000, polyether or polyester diol. Sometimes, to extend the chain even further, a small molecule, like a glycol or amine, reacts with the isocyanates. Because of its relative high elasticity, resistance and durability they are primarily used to produce shoe soles.³¹

1.3.3.2 Market

After the discovery of polyurethane by Otto Bayer, many patents were filled after. It's presumed that they were flexible foams resulting from isocyanate-water reactions. After the end of World War II, the company for which Bayer worked, I. G. Farben, was closed due to complicity in war crimes (exploitation of slave labour and production of nerve gas). However, two globally well respected and large producers of polyurethane remain until today: Bayer AG and BASF SE. They are the main producers of all kinds of polyurethanes in Europe. In all the markets of the three major types of polyurethanes, that is rigid, semi-rigid and elastomers, the Asia and Pacific region countries dominate the volume of production and consumption, detaining near half of the market. The second in line is Europe, Middle East and Africa combined and then its North America region. This is explained by the fact that Asia is the location two developing super potencies, China and India, which have a market driven by industries that are very dependent of polyurethanes, such as construction, electronics and automotive. Furthermore, these fact combined by the low-cost environments of these countries, are shifting the attention of the big companies of the other regions to change their production factories to Asia.^{33,34}

Globally, the high versatility of polyurethanes made the world consumption increase from 2 million tons in 1980 to 10 million tons in 2004, proving that the market has a big potential for investors.³¹ Moreover its production is expected to raise until 2020:

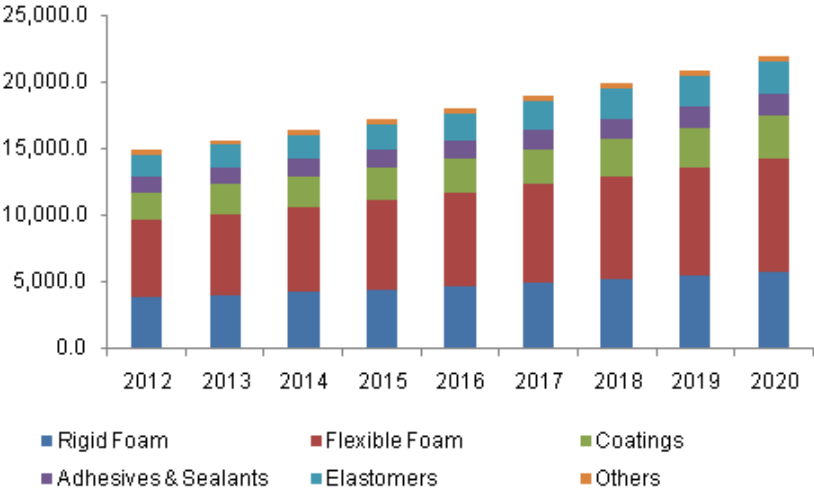


Figure 13 - Polyurethane market analysis by product and segment forecasts to 2020.³⁴

1.4 One Component Foam (OCF)

One component polyurethane foam (OCF) are self-adhering, self-expandable product. Because of this, they have gained increasing popularity in the recent years in adhesive, sealants and insulating applications due to its versatility, easy applicability and manufacture. They are called “one component” because all the reagents are mixed in a single container, normally a can, but generally they have many compounds.

Several foam preparation methods can be used as shown below:

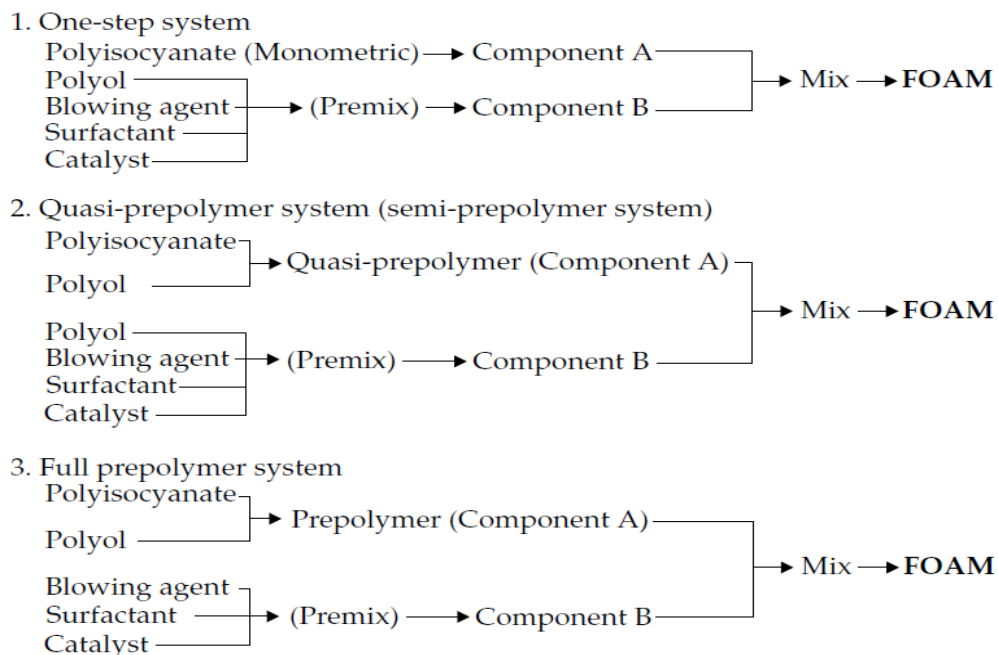


Figure 14 - Foam preparation methods.³⁵

The main difference between these methods is the manner which how the isocyanate and polyol are mixed. In the one-step method, the polyol plus additives and the isocyanate are mixed all together in one step and in 1:1 ratio (polyol and isocyanate). In the preparation of the full prepolymer system, all the polyols and isocyanates are previously reacted together before being mixed with catalyst and additives, and in the quasi-prepolymer system, some of the polyol is previously mixed, with excess isocyanate before adding the chain extenders polyols, catalyst and additives. Both of these prepolymers methods generate compounds with free NCO groups. The one shot process provides an easy, fastest and most economical manufacturing technique, and it's often used in the flexible foams production. On the other hand, two-step methods, like the full or quasi prepolymer, gives control of the toxicity,

reactivity, structure and the properties and quality over the final product by the manufacturer. This is the main reason why this method is used in the rigid polyurethane foam production, where the control of every property is crucial for foam optimization and to produce good quality foams.³⁵

OCF are sold in the form of pressurized cans with a “pre-polymerized” compound inside. This pre-polymerised compound is made according to the quasi-prepolymer method previously explained inside a pressurized can alongside a low-boiling gas mixture. There, the polymerization reaction (or gelation) occurs between a mixture, called “component A”, containing catalyst, a chain extender polyol and additives, and a “component B” composed of an isocyanate pre-polymer. In this reaction, the ratios are defined to yield a pre-polymerised product with free NCO groups (see figure 13).³⁶

To obtain polyurethane foam the user has only to spray the pre-polymerised product onto a surface, hole or fissure and wait for it to cure. In the curing process the free NCO groups will readily react with the humidity present in the air forming an unstable carbamine acid that will rapidly decompose into a primary amine, releasing CO₂ in the process.³⁶

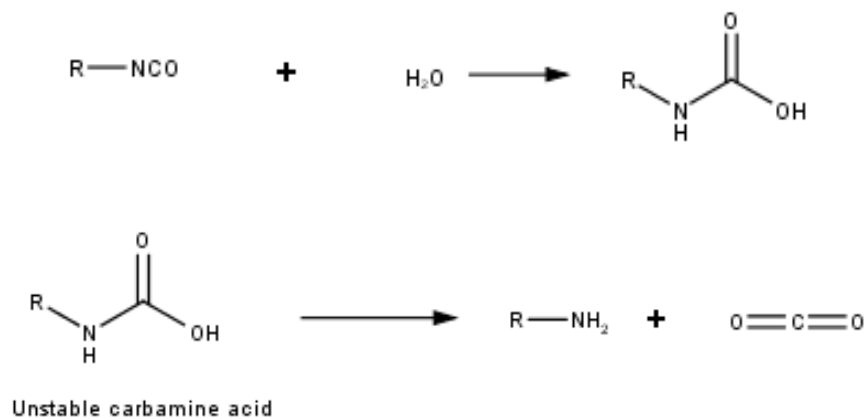


Figure 15 - Blowing reaction.

This CO₂ will act as the blowing agent and will expand the foam, doubling its original size. That’s why the fissures and holes should be half filled with the froth when it is being applied.

The primary amines will then react with the free NCO groups forming an urea link.

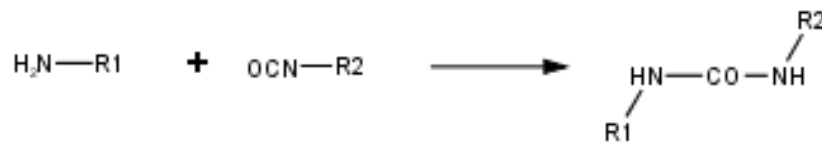


Figure 16 - Urea formation reaction.

Since this reaction is very fast, it will directly compete with the first expansion reaction and will be dependent of it at the same it. With di-isocyanates, like MDI, this reaction will yield linear groups, but with tri and higher functionalised isocyanates it will form a three dimension network.^{31,36}

As the froth starts to become thicker, the air humidity will gradually diffuse slower to the inside parts of the froth. As this happens, biuret condensations, formed by the reaction of the urea groups with the remaining free NCO groups of the pre-polymerised compound, will slowly become predominant at the point of eventually replacing the former reactions.³⁶

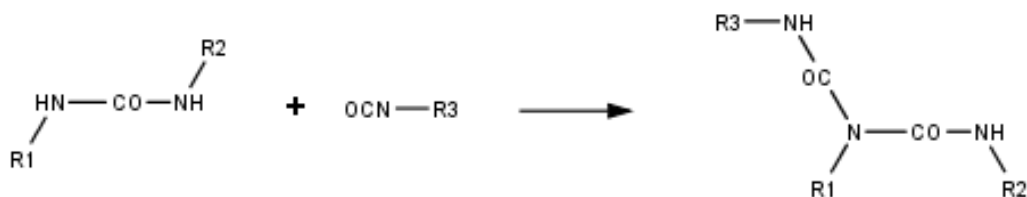


Figure 17 - Biuret formation reaction.

Because biuret formation occurs only at later stages of the curing process, a strong three dimensional network is already formed, so the rate of reaction will be controlled by diffusion. Only the shortest and most mobile chains containing free NCO-groups, like monomeric MDI, will be able to diffuse and react with the urea groups. This process will further harden the foam, until the process is finished.³⁶

2 Experimental Procedure

2.1 Biomass liquefaction process

As said above, the biomass acid liquefaction process generally consists of a solvolysis reaction under ambient pressure and temperatures between 110-160°C. The most common reagents used are polyethylene glycol (PEG) or glycerol and catalyst is sulphuric acid. In this work a new method was applied. The solvent used was a mixture of diethylene solvent A and solvent B in 1:3 mass ratio. The catalyst used was 3% in biomass weight of acid catalyst A.

After placing the biomass into the reaction vessel, the first reagent to be placed was solvent A, followed by solvent B and the acid catalyst which was previously diluted in it. Then the reaction was heated until the 160°C and the temperature was maintained for at least one hour. The final reaction time and temperature it's not fixed and can vary from biomass to biomass. Sometimes the reaction starts at lower temperatures, which stops the temperature rise, and needs more than one hour to complete, so it's very important to adapt the reaction to every biomass type.

After the reaction was finished, it was left to cool until it reached 80°C, after which one litre of water was added and mixed for a time in order to dissolve all the sugars contained in the final product. This step was very important because, based on previous experiences, these sugars will have a negative impact on the rigid polyurethane foams, turning them more brittle due to their high OH value. Next, the sugary water was filtrated under vacuum with a filter paper and a kitasato apparatus. After repeating this step two more times, the remaining black liquid, which was a mixture of lignopolyols and solid biomass residue, was removed from the reaction vessel by the underneath tap and filtered again trough the kitasato apparatus but now with a previously weighted large pore filter paper. In order to extract even more lignopolyols, the solid residue is washed with 500 mL of methanol and then 500 mL of acetone. In the end, all solid residues retained in the filter papers were then dried in a stove and weighted for the calculation of the conversion ratio.

The biomass conversion ratios of the liquefactions were calculated using the following formula:

$$\text{Biomass conversion ratio (\%)} = \left(1 - \left(\frac{m_r}{m_t} \right) \right) \times 100$$

m_r - mass of the residue after extractions;

m_t – total final mass;

Before storing, the lignopolyols are then placed in a rotary evaporator in order to remove the methanol, acetone and water.

2.2 Acid and OH value determination titrations

The acid number or value is the necessary milligrams of potassium hydroxide required to neutralize one gram of an acidic substance. This is a measure of the acid groups present in a substance and is the first step for the determination of OH value. The method used in this work was based in the ASTM D 974 and DIN 51558 norms. First, 0,30g lignopolyol was dissolved in 6 ml of Tetrahydrofuran (THF). Because of the particular dark coloured solution due to the lignopolyols, the potentiometric titration method was made with an Hanna instruments HI11310 electrode. This method consisted of titrating the lignopolyol with a 0,1N KOH solution in increments of 0,1ml at a time and taking note of the potential observed, until pH 14 was achieved. Then, a titration curve is trace with the obtained data. The turning point is easily determined as the highest peak point in the first derivative curve.

Finally, the following formula was applied in order to determine the acid number:

$$AV = \frac{V_{KOH} \times C_{titrant} \times 56,1}{m_{sample}}$$

AV - Acid value in mg KOH/g;

V_{KOH} – amount of titrant needed for the titration of the acetylated sample in mL;

$C_{titrant}$ – concentration of titrant in N;

m_{sample} - mass of the titrated sample in grams;

The acid value will be included in the determination of the OH value of the lignopolyols.

Similar to the acid value, the OH or hydroxyl value is the necessary milligrams of potassium hydroxide required to neutralize one gram of acetic acid formed by the acetylation of one gram of a chemical substance that contains free hydroxyl groups. The method used in this work was based on the ASTM D 1957 and ASTM E222-10. First, 0,30g lignopolyol was dissolved in 6 ml of Tetrahydrofuran (THF). Then, 1,6 ml of a catalyst solution composed of 1% of Dimethylaminopyridine (DMPA) in volume dissolved in THF, and 1,6 ml of an acetylating solution composed of 12,5% in volume of acetic anhydride dissolved in THF, were added to the lignopolyol solution and left to react for 10 min in agitation. In this reaction, the OH groups of the lignopolyols are acetylated, producing acetic acid:



Figure 18 - Acetylation reaction.

After the afore mentioned time elapsed, 0,30 mL of water was added in order to stop the acetylation by reacting with the remaining unreacted anhydride acetic, turning it into more acetic acid and left in agitation for 30 min. Finally, the acetic acid was titrated with a KOH 0,5N solution using the same potentiometric titration method for the determination of the acid number. After the determination of the turning point with the first derivative of the titration curve, the following formula was applied:

$$HV = \frac{(V_{blank} - V_{KOH}) \times C_{titrant} \times 56,1}{m_{sample}} + AV$$

HV - Hydroxyl value in mg KOH/g

V_{blank} – amount of titrant needed for the titration of the blank solution in mL

V_{KOH} - amount of titrant needed for the titration of the acetylated sample in mL

$C_{titrant}$ – concentration of titrant in N;

m_{sample} - mass of the titrated sample in grams;

AV – acid value of sample in mg KOH/g;

The amount of titrant needed for the titration of the blank solution was determined using the previous procedure but without lignopolyol.

2.3 Foam formulation development and can preparation

Foam formulation and development were done with an excel worksheet named *Foamcalc*, owned by Greenseal Research. In this worksheet the chemicals that were to be filled into the can were divided into three main groups called “components”: component A, which was a mix of lignopolyol and additives, component B, which was the isocyanate prepolymer, and component C, which were all the gases. In the first step, the lignopolyol’s hydroxyl values, densities, molecular masses, functionalities and water contents were added to the existing database in the worksheet. After a base formulation was selected, the lignopolyol was directly inserted into the component A group, with a number of parts given by the following formula:

$$p_l = p_T \times \frac{s}{100}$$

p_l – parts of lignopolyol;

p_T – total parts of polyol;

s – degree of substitution in percentage;

The parts of the other polyols in the new formulation were calculated with the following formula:

$$p_n = \frac{p_l \times p_b}{p_T}$$

p_n – parts of the given polyol in the new formulation;

p_l – parts of lignopolyol;

p_b – parts of the given polyol in base formulation;

p_T – total parts of polyols plus lingopolyol;

It is needless to say that this formula only applies to substitutions on a degree below 100%.

The figure below shows an example where the base formulation was 50% substituted in parts by cork lignopolyol:

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Figure 19 - Replacement of 50% in parts of base polyols by cork lignopolyol.

If the insertion of new compounds or changing the parts of any existing compound, causes a change in the NCO:OH ratio of the formulation, it should be changed to its original value by increasing or decreasing the isocyanate prepolymer parts. This could be easily achieved using Excel “goal seek” feature. Finally, the percentage of gas in the can, the volume of the can and the amount of them to be filled were defined in the worksheet and all the quantities of compounds were automatically calculated. All the worksheets are displayed in appendix 1.

Next, the process of filling the can began by weighting the component B and adding it to all the cans in the quantities determined by *Foamcalc*. Then all the compounds in component A were weighted and added together in a dry cup. In order to ensure complete homogeneity in the mixture, the compounds that were more viscous and present in greater amounts were added first. After mixing the component A for some time and with the extra care to avoid the formation of bubbles, it was added into the can where the component B was already present. If some flame retardant was to be added, it should be after this step. Finally, the gases (component C) are added through the burets in the gas filling station.



Figure 20 - Gas filling station.

With this gas filling station, the process was very fast and easy to do. After the can was tightly sealed, the burets were filled with the respective gases by pressing the valves until the volume previously determined by the *Foamcalc* worksheet. Then, the can was pressed and tilted in order to open the valve, and the gas was pushed into the can with nitrogen. In the end, the can was shaken and left to rest for at least 12 hours at ambient temperature, in order to ensure that all reactions could be completed in time for the evaluation.

2.4 Foam evaluation

When the reaction inside the can was complete, the foam could be evaluated using any or both of the following two types of test series: the quick tests and the foam evaluation. Both of them consisted of visually rating some properties, from a scale -5 to 5 in order to evaluate the overall quality of the foam in all its states (liquid, froth and fully cured foam) (see appendix 2). All the measured foam properties are summed up in the following table:

Table 1 – General overview of quick test.

	Properties	Stage
	Shaking rate	Liquid mixture inside the can (Quick test)
	Output*	Froth after dispensing (Quick test)
Paper	Froth shrinkage Froth outflow Crumbling after 1 hour Crumbling after 2 hours Crumbling after 24 hours	
	Curing shrinkage/Warping Glass bubbles Cell structure Voids & Pinholes Base holes Cell collapse Curing streaks	
Mould	Shrinkage mould Glass bubbles Cell structure Voids & Pinholes Base holes Cell collapse Curing streaks	

The quick test only rated the properties of the liquid inside the can and the curing froth. The foam evaluation consisted of rating the properties inherent only to fully cured foam. As it was presented in the table above, these properties were measured from top to bottom. In the following chapters, each of these properties and the general procedure to measure them will be explained.

2.4.1.1 Shaking rate

After the foam reacted in the can, it was placed in the fridge at 5°C for at least 4h, in order to cool the liquid inside. Then the can was shaken and a rating was given, where -5 means the liquid inside was very viscous and the 5 it was like water. This property has to be measured in the first initial shakes, since the viscosity increased by each shake due to increasing homogeneity between the gas and liquid phases.

2.4.1.2 Output

After the shaking rate was evaluated, the foam was sprayed at previously weighted paper in a $\pm 0,01$ precision balance for a determined time. This time was not fixed and it should be inversely proportional to the quantity of froth that's exiting the nozzle. When spraying, the back trigger of the gun should be fully pressed in order to ensure the maximum possible output. In the end, the output was calculated by doing the ratio of the quantity of dispensed froth, in grams, per elapsed time, in seconds.

2.4.1.3 Froth shrinkage and froth outflow

During the first minute after dispensing the froth it was important to check and rate the alteration of its shape. If it shrunk in size, froth shrinkage had occurred and a value under 5 was given, depending on its degree. If it flattened, froth outflow had occurred and a value under 5 was given, depending on its degree. Both of these properties were independent of one another and could or not at the same time. If froth didn't shrink nor flattened, a value of 5 was given.



Figure 21 - Froth shrinkage (left) and froth outflow (right).

It was very important to measure these properties in one minute after spraying, because after that it was very probable that post expansion, the reaction of free NCO groups with humidity producing CO_2 , had begun.

2.4.1.4 Crumbling

This property was related to the friability of cells in the foam. After dispensing a small bead after the main spray sample in the paper, it was checked by pressing it after 1, 2 and 24 hour at 5 and 23°C. If the foam shows crumbling, it should crack under the finger with a notorious sound. If it cracks easily, it should get a rate of -5 but if it does not crack a rate of 5 should be given. It was normal to observe some crumbling at lower temperature because of the low humidity in the air and the crystallization of NCO groups, which both retards the curing reaction and consequently increase the foam friability. Two types of crumbling could occur: a permanent crumbling of foam sprayed at ambient temperature, and a temporary crumbling of a foam sprayed at 5°C which then disappears after the foam was placed at ambient temperature for some time. The crumbling could be lowered by raising the quantity of plasticizers or by lowering the NCO:OH ratio of the formulation.

2.4.1.5 Glass bubbles

When the froth was curing, gas bubbles can aggregate at the surface of the sprayed froth, forming a shiny vitreous like layer. This phenomenon was called “Glass bubbles” and it was due to a bad combination of the gases mixed with the liquid inside the can. The gases were a mix of low and high boiling point gases, and after shaking and spraying the liquid, the gases propel the froth and try to escape it. The ones with a low boiling point escaped the froth easily, but the ones with a high boiling point will take more time to do it. Sometimes the bubbles can take some time to reach the surface, becoming trapped under it if it already solidified, resulting in the coalescence of the bubbles and the formation of a shiny vitreous coating. The rating score was inversely proportional to the bubbles size. This phenomenon was more pronounced at lower temperatures, due to the slower evaporation of the gases. When the foam was applied using the straw adapter, the glass bubbles size was lower, maybe because some of them had already coalesced in the straw and then could escape faster.



Figure 22 - Foams with glass bubbles score 5 (left) and score 3 (right).

2.4.1.6 Curing shrinkage/warping and shrinkage mould

When the pressure inside the foam was low during the curing process, the foam shrunk in mould and it warped in paper. The mould shrinkage was measured while removing the foam from the mould. A better rating was given depending on how fully the mould was filled by it after one day of being sprayed. When the foam was sprayed in paper, instead of shrinking, it warped in a concave or convex shape. The rating is attributed by how much it warped. If the foam presented a very low score of shrinkage, it could be raised by using more

functionalized polyols, decreasing the quantity of plasticizer and surfactant, and/or raising the NCO:OH ratio of the foam.^{37,38}

2.4.1.7 Cell structure

Cell structure was classified according to the size (average diameter) and distribution of foam cells. Ideal foam should have an evenly distributed small sized cell network. An higher NCO:OH ratio, more plasticizer, more blowing agent, less surfactant can all increase the average cell size and worsen the cell structure. At lower temperatures the cell size increased but the structure was more regular due to the better miscibility.^{38,39}

2.4.1.8 Voids & pinholes

Voids and pinholes were gas pockets that remain in the foam after it fully cured. These voids were a direct consequence of a bad miscibility between blowing agent and the prepolymer due to low solubility of gases or to not enough shaking of the can. Higher polyol functionality could lessen this phenomenon. Spraying technique was also important. The foam should not be applied above another foam bead in order to let the gas escape more easily.^{38,39}

2.4.1.9 Base holes

Base holes, as the name suggests, were cavities that present at the base of the cured foam bead. They were formed by the high volatile blowing agents entrapped in the cavities of the surface during the froth expansion, which dissolved all of the froth that they come in contact forming the referred holes. This effect could be mitigated increasing the viscosity of the pre-polymer, which could be achieved by using polyols with an higher functionality, decreasing the quantity of plasticizer, decreasing the NCO:OH ratio and decreasing the blowing agent quantity in the formulation. The higher the viscosity of the froth, less base holes were observed because less gas was mixed in it. If the foam was sprayed on a smooth surface the gas escaped quickly and no base holes were observed. Foam where fewer base holes were formed will have a better adhesion, making this property very important to monitor in order to obtain good quality foam.³⁹



Figure 23 - Foams with base holes score 5 (left) and score -3 (right).

2.4.1.10 Curing streaks and cell collapse

When the curing process was slow due to low humidity level, low temperature or high hydrophobicity in the prepolymer, which reduces the stabilization of the of the silicon surfactant, the cells will begin to coalesce forming zones of coarser cells with low flexibility. These zones were normally in the form of a straight streak, but it could be also curved. They were more common in the centre of the foam where the humidity takes longer to penetrate.

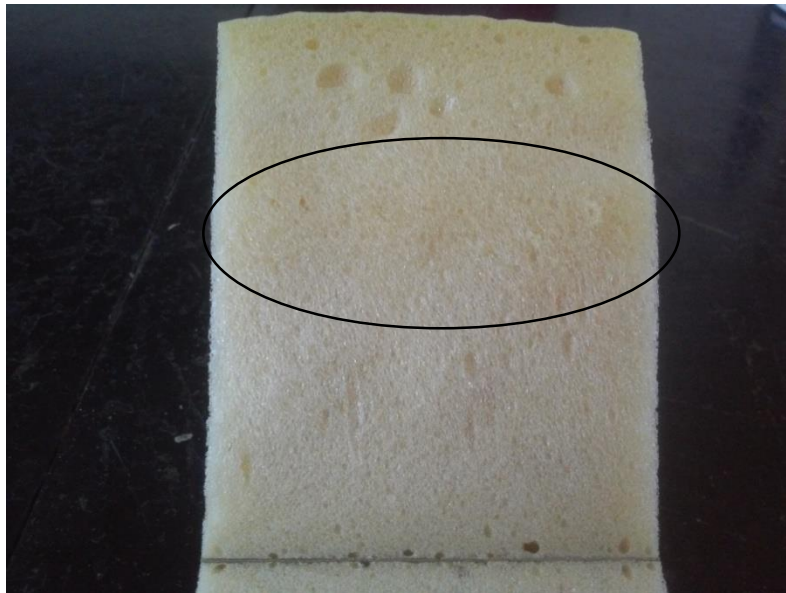


Figure 24 - Foam with curing streak score 4.

If the referred parameters were particularly low, the weak zone could collapse, forming huge gaps in the foam. These were different from the voids and pinholes due to the fact that they have an irregular shape and open cells.

In order to avoid this phenomenon it's very important to use an adequate quantity of catalyst in the formulation. If a higher quantity was used, a curing velocity gradient will form, where the foam cures more quickly in its extremity due to the higher humidity present, hardening its surface early and impeding the further penetration of the humidity to its interior, promoting the formation of curing streaks and cell collapse. A high quantity of the plasticizer present in the formulation will weaken the cells and further promote this two phenomenon, so this parameter must be carefully checked too.³⁷⁻³⁹

2.5 Ignitibility test

The ignitibility of lignopolyol based foams was tested according to the norm DIN-4102, part 1 of 1998.

The samples were prepared by spraying the foam into a mould composed of two 78 cm long and 10 cm height, placed 5.5 cm apart and parallel from each other, as shown in figure 25. The mould width is assured by two wooden wedges secured by clamps at the extremities. Current laboratory paper shall be used for the base of the mould. After the mould was prepared, it was sprayed by water, and it was filled until half with a uniform layer of foam. After 2 or 3 min, it was sprayed again with water and another layer of foam was applied, filling it completely. After spraying it a third time with water, it was left to rest at ambient temperature for 14 days.



Figure 25 - Ignitibility test samples.

After the resting time was finished, the mould was cut with an electric saw into 6 samples 19 cm long and 5 cm large, drawing a gauge mark at 15 cm above the bottom edge. The sample were burned in the chamber presented in figure 25 at 20°C with an air flow between 0,6 and 0,8 cm/s. After setting a 2 cm flame in the burner, the sample was placed into the holder/frame and the flame was pushed closer to the edge of the sample for 15 seconds, while recording it on camera. Then the video was examined in slow motion and if the flame

had not passed the 15 cm gauge mark, the foam was classified as a B2 (flammable) material. If not, it was classified as a B3 (easily flammable) material.⁴⁰



Figure 26 - Ignitability test chamber.

2.6 Determination of the isocyanate group (NCO) content

The method for the determination of the isocyanate group (NCO) content is based on ASTM D 2572, which consists of reacting dibutylamine with the free NCO groups of the compound in question. The excess dibutylamine is then titrated and NCO content is then determined by an equation.

The first step of the method is to weight 1 to 2 g of the sample in a 200 ml cup. Then, 80 ml of acetone is added to the cup and mixed until the liquid is homogenous. After that, 10 ml of 1N dibutylamine solution is added to the cup and mixed for 10 min using the magnetic stirrer. In this step the dibutylamine is reacting with the free NCO groups according to the following reaction:

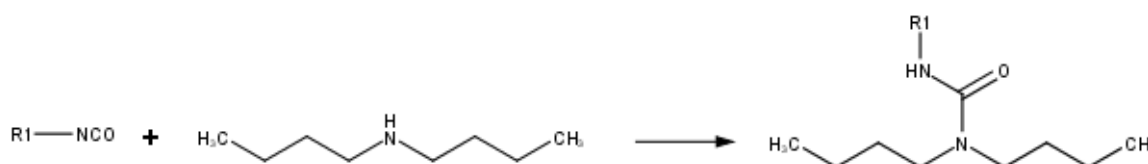


Figure 27 - Reaction of free NCO groups with dibutylamine.

Finally, some bromophenol blue indicator and the unreacted dibutylamine is titrated with 1N hydrochloric acid solution, until the colour turns yellow. Then the following formula is used to obtain the percentage in weight of the free NCO groups:

$$\% NCO = \frac{(V_b - V_a) \times 4,2}{m}$$

V_b – volume of acid consumed in the titration of the blank solution (which is 10,1 ml);

V_a – volume of acid consumed in the titration of the sample (ml);

m – mass of the sample (g);

2.7 Prepolymer preparation

The method developed by the company for the production of isocyanate prepolymers consisted of an addition of two different polyols, a diol and a monol, to an isocyanate in two different stages of the reactions. First, the polyol and isocyanate quantities are automatically defined using an excel worksheet by inserting the final total mass. Then, two predefined NCO contents are given, one that sets when the monol shall be added to the reaction vessel, and another that sets the final point of the reaction is to be. After heating an oil bath until 80°C, a flask with the isocyanate is inserted in it. A magnetic stirrer is set in order to provide mixing. Then, the diol is added in full and the NCO content is measured in 10 minutes intervals. When, the reaction reach the first NCO content value, the monol should be added and the NCO content should be monitored until the final value. When the new prepolymer is needed, it should be previously placed inside a bath at 80°C for 1h.

3 Results and discussion

3.1 Liquefaction

3.1.1 Biomass liquefaction results

Three types of plant biomass were liquefied using the previously mentioned process. The next table summarizes some relevant results of each liquefaction:

Table 2 - Biomass liquefaction results.

Reaction name	Type of biomass	Quantity of biomass used (g)	Reaction time	Conversion (%)
Cork 1	Cork powder	70	20min*	71
Cork 2	Cork powder	70	2h	67
Cork 3	Cork powder	70	2h	79
Eucalyptus 1	Blue gum bark	20	1h30min	60
Eucalyptus 2	Blue gum bark	50	1h	58
Eucalyptus 3	Blue gum bark	50	2h	66
Poplar 1	Poplar wood chips (Arrezima s)	85	1h30min	88
Poplar 2	Poplar wood chips (Arrezima)	85	1h15min	91
Poplar 3	Poplar wood chips (Balsas)	85	1h	83

*the reaction was stopped at 20 minutes because it was realized that the termopar regulator was not working properly and the temperature had been too high (>160 °C) throughout all the reaction. Nevertheless, the polyols were used and the conversion was calculated.

Theoretically any kind of plant biomass can be to produce polyols using the solvolysis method. In this work four kinds of wood were chosen according to the sources presented in the introduction chapter.

Cork powder or dust is a low value sub product from the cork processing and transformation industry. It is composed of very small particles with dimensions lower than 0,25 mm and its mainly used as combustion fuel. Every plank of cork bark produces an average of 25-30% of cork powder in weight in the cork-stopper production industry.⁴¹ At present, it was already liquefied for the production of lignopolyols and used successfully for the production of polyurethane foams.²²

The residual blue gum bark (*eucalyptus globulus*) used in this work, comes from the first step of the paper pulp production process: the debarking. This process is present in both Kraft and sulphite pulping processes, and consists of removing the bark with the rubbing of the logs against each other – drum debarking. It can be made directly in the field after cutting the tree or in the wood pulp factory. This process produces a residue that consists of long and thin wood strings with wood chips attached. In the beginning it was used to produce energy in the factory boiler, but as the time goes, it's beginning to be discarded away because sometimes it contains sand and debris, which produce negative effects in the boiler machinery even in low quantities. Since the liquefaction is unaffected by sand and common solid debris, this sub product can prove to be a viable and sustainable source of plant biomass.

In many countries of northern Europe the concept of energetic plantations became very popular in recent years. Mainly, it consists of planting rapid growth and low resource consuming trees for the exclusive production of energy via plant biomass. In Portugal, some research about the potential role of poplar wood as a carbon source for bioenergy and chemicals was already been made.⁴² Three types of poplar clones from the same plantation, noted as *arrezima s*, *arrezima* and *balsas*, were used in order to evaluate if the conversion ratio would be affected by different chemical composition of the same wood.

Maritime pine wood (*pinus pinaster*) is the most used tree in the woodworking industry. In the wood cutting process, small wood chips are produced and are considered a waste. Normally they are used as fuel in combustion energy generators, because they don't have a great monetary value. One component foam based on lignopolyols derived from this kind of wood was already developed in several works^{15,43} and the ones used for this work were already synthetized, requiring only a water removal.

All the plant biomasses were liquefied successfully using the method described in chapter 2.1. However every biomass had a maximum amount that could fit the reactor, mainly because of its physical characteristics. Cork powder was composed of fine particles, blue gum

bark was fine bark threads enveloped in each other with some bark chips and poplar was composed of chips of various sizes:



Figure 28 - Cork powder (top left), blue gum bark (top right) and poplar wood chips (bottom).

The following table has the chemical composition of the biomass used in this work:

Table 3 - Chemical compositions of different types of biomass.

Type of biomass	Maritime pine wood ²⁴	Cork powder ²⁵	Blue gum bark ⁴⁴	Poplar wood ⁴⁵
lignin	28%	22%	34 %	26%
cellulose	40%	18%	62%	42%
hemicellulose	28%			17%
suberin	-	40%	1%	-

All the liquefied woods had sensibly the same chemical composition, but some differences were noted. Blue gum bark had a little bit more lignin due to the fact that was an outer bark. The major compound of cork powder was the suberin, which is the compound responsible for the many improved properties of cork.

As already said in the introduction, it's expected that different wood chemical compositions will differently affect the reaction times of the liquefactions. Poplar

liquefactions were the fastest and the ones with higher conversion ratio. This data can be explained by the fact that the used poplar chips are derived from the inner wood of the tree where the lignin and suberin contents are low. Suberin proved to be hard to decompose in previous cork liquefactions using sulphuric acid.²³

3.1.2 Lignopolyol characterization

In order to characterize the obtained lignopolyols, the following techniques were applied: acid and OH value determination titrations, Karl Fischer titration and Fourier transform infrared spectroscopy (FTIR).

3.1.2.1 Acid and OH value

Using the procedure mentioned in the previous chapter, the following results were obtained:

Table 4 - Lignopolyols acid and OH values.

<i>Lignopolyol</i>	Acid value (mg KOH/g)	OH value (mg KOH/g)
<i>Cork</i>	1	272
<i>Eucalyptus</i>	1	280
<i>Pine</i>	7	303
<i>Poplar</i>	2	193

The polyols produced in previous works^{12-16,18} had hydroxyl values as high as 1285 mg KOH/g and acid numbers as high as 28 mg KOH/g, which are substantially higher than the ones of the lignopolyols used in this work. This is due to the fact that the sugars were extracted from the produced lignopolyols previous to the measures. If these sugars, which are primary alcohols, are presented in great quantities in the formulation, the resultant foam will be very frail due to low crosslinking in the blowing reaction after the spray.

These values are needed to calculate the molecular mass (in g/mol) of the lignopolyols according to the following formula:

$$M_w = \frac{f \times 56100}{OH_v}$$

The functionality was assumed to be 2,5 as a mean value between linear (f=2) and branched polyols (f=3).

3.1.2.2 Water content

The determination of the water content in the samples was done using the Karl-Fischer titration method in an 831 KF Coulometer from Metrohm. It uses methanolic solution of iodine, sulphur dioxide and a base as a buffer. The results are in the following table.

Table 5 - Lignopolyol water content.

<i>Lignopolyol</i>	Water content (%)
<i>Cork</i>	0,35
<i>Eucalyptus</i>	0,51
<i>Pine</i>	1,07
<i>Poplar</i>	0,41

In OCF formulations water content is a crucial parameter and will greatly influence the overall performance of the foam in short term. The value should be as low as possible in order to try to avoid a blowing reaction inside the can, which can lead to the production of CO₂ inside the can and an eventual explosion.

3.1.2.3 FTIR spectra

MIR (Mid InfraRed) spectra of the liquefied product and respective fractions were analyzed resorting to an FT-MIR spectrometer from BOMEM FTLA2000-100, ABB CANADA equipped with a light source of SiC and a DTGS detector (Deuterated Tryglycine Sulfate). The used accessory was an ATR with single horizontal reflection (HATR) containing a ZnSe crystal of 2mm of diameter from PIKE Technologies. The specters in the range of 600-4000 cm⁻¹ were collected with the BOMEM Grams/32 software.

The obtained infrared spectra of all the used lignopolyols is presented in the figure below:

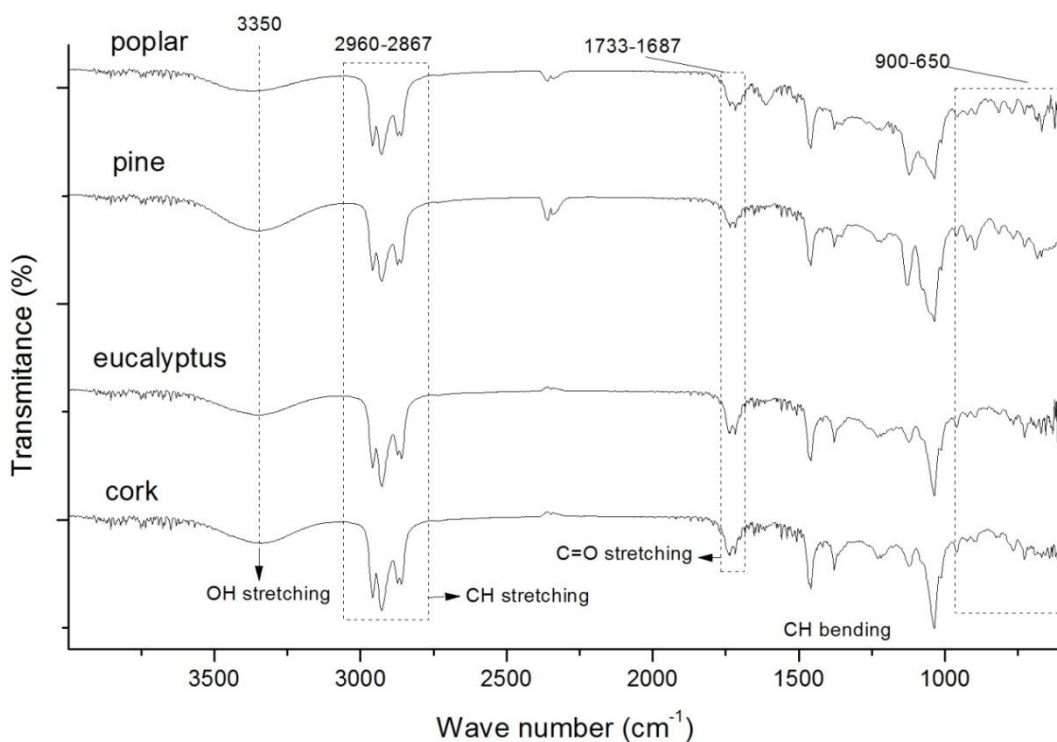


Figure 29 - FTIR spectra of the used lignopolyols.

As can be seen in the previous figure, the obtained spectra of the lignopolyols were very similar to each other, except in the 1630 cm^{-1} region. The broad strong band at 3350 cm^{-1} is the characteristic OH stretch of alcohol groups. The bands at the 2960-1867 cm^{-1} are characteristics of aromatic groups, which there should be plenty since the polyols are derived of the aromatic lignocellulosic compounds. The 1733-1687 cm^{-1} bands are characteristic of the carbonyl C=O stretching. The bands between the 900-650 cm^{-1} regions are characteristic of aromatics and carboxylic acids.

3.2 Foam formulation development

In order to organize the developed formulations a unique numbering system was created. First, all of the formulations that had lignopolyols in it were given a prefix “L” in order to distinguish them from the other formulations that were created in the company. Then, the first digit signified a major change done to a base formulation, summarized in the following table:

Table 6 - First digit definitions.

L1x	5% replacement in parts of the base polyols from 456 formulation by the lignopolyol x
L2x	50% replacement in parts of the base polyols from 456 formulation by the lignopolyol x
L3x	100% replacement in parts of the base polyols from 456 formulation by the lignopolyol x
L4x	100% replacement in parts of the base polyols from 533 formulation by the lignopolyol x
L5x	100% replacement in parts of the base polyols from 946 formulation by the lignopolyol x

The second digit was attributed to a type of lignopolyol, in the following order:

Table 7 - Second digit definitions.

Lx1	eucalyptus
Lx2	cork
Lx3	pine
Lx4	poplar
Lx5	cardolite

Finally, the last digit after the dot signified small changes or improvements done to the previous formulation.

The starting point was the gradual introduction and eventual replacement of the base formulation 456 polyols by all the lignopolyols individually. The reason that this formulation was chosen was because it had the better overall quality and output value results in 0, 3, 6 and 12 months. In order to observe if the introduction of these new lignopolyols would lower the foam quality, a gradual approach was made. In the first experimentation, classified as “L1”, 5% in parts of the base polyols were replaced by lignopolyols according to the procedure referred in the previous chapter. Five different formulations were made and can be seen in appendix 1. The quick test and foam evaluation results of the L1 foams are presented in the following table along the results of the base formulation for easy comparison. Ideally, a good quality foam is defined as not to have any parameter score below 3, in any temperature, and an output value more than 3,5, but in reality maybe be very hard. An error of ± 1 is assumed in every given score.

Table 8 - Overall quality of the L1 foams.

Formulation		456		L11.0		L12.0		L13.0		L14.0		L15.0	
Output (g/s)		7,9		12,5		13,8		2,3		8,0		7,4	
Temperature (°C)		23	5	23	5	23	5	23	5	23	5	23	5
Paper	Shaking rate	5	4	5	5	5	5	5	1	5	5	5	4
	Froth shrinkage	5	5	5	5	5	5	5	5	5	5	5	5
	Froth outflow	5	4	5	4	5	5	5	5	5	4	5	4
	Crumbling 1h	5	5	5	5	5	5	5	5	5	5	5	5
	Crumbling 2h	5	5	5	5	5	5	5	5	5	5	5	5
	Crumbling 24h	5	5	5	5	5	5	5	5	5	5	5	5
	Glass bubbles	5	4	5	4	5	4	4	4	5	4	5	4
	Curing shrinkage/warping	5	5	-3	5	4	5	5	5	-2	5	0	5
	Cell structure	5	4	5	5	5	5	4	2	5	5	5	5
	Voids & pinholes	3	3	3	4	3	4	3	4	4	3	3	2
	Base holes	-1	2	-3	-3	-3	-2	-1	3	-2	-2	-3	-2
	Cell collapse	5	5	5	5	5	5	5	5	5	5	5	5
Curing streaks	5	5	5	5	5	4	5	5	5	5	5	5	
Mould	Shrinkage mould	3	4	3	5	2	4	5	5	4	5	5	4
	Glass bubbles	4	3	4	4	4	4	4	4	4	4	4	4
	Cell structure	4	4	4	4	4	5	4	3	4	5	5	5
	Voids & pinholes	4	3	3	3	3	2	3	4	4	3	3	1
	Base holes	0	1	-3	-3	-1	-2	4	-2	-1	0	0	0
	Cell collapse	4	5	5	5	5	5	5	5	5	5	5	5
	Curing streaks	4	4	4	4	4	4	4	3	4	4	4	4

While examining the previous table, the worse parameter common in every foam is the base holes. In the beginning there was no explanation for this fact, but after spraying water in the paper and mould in the L3 foams experience, the base holes score improved so at this point will be discarded in the discussion. With this in mind, the L11.0, L12.0 and L15.0 foams had two parameters below 3, L13.0 had two plus a bad output value, making it the worst quality foam, and L14.0 had only one, making it the better quality foam of this experimentation. Besides L13.0 and L15.0, all the outputs were greater than the base formulation. Photos from all these foams are in appendix 1.

Following the previous experimentation, a second experimentation, codenamed “L2” was realized replacing 50% in parts of the 456 polyols by the lignopolyols. As above, the quick test and foam evaluation results are displayed in the following table:

Table 9 - Overall quality of the L2 foams.

Formulation		456		L21.0		L22.0		L23.0		L24.0		L25.0	
Output (g/s)		7,9		15,1		17,6		7,6		8,2		5,4	
Temperature (°C)		23	5	23	5	23	5	23	5	23	5	23	5
Paper	Shaking rate	5	4	5	5	5	5	5	5	n/a	5	5	5
	Froth shrinkage	5	5	5	5	5	5	5	5	n/a	5	5	5
	Froth outflow	5	4	5	5	5	5	5	5	n/a	5	5	5
	Crumbling 1h	5	5	5	5	5	5	5	5	n/a	5	5	5
	Crumbling 2h	5	5	5	5	5	5	5	5	n/a	5	5	5
	Crumbling 24h	5	5	5	5	5	5	5	5	n/a	5	5	5
	Glass bubbles	5	4	5	4	5	4	5	3	n/a	4	5	5
	Curing shrinkage/warping	5	5	5	5	5	5	5	5	n/a	5	5	5
	Cell structure	5	4	5	4	5	4	5	3	n/a	4	5	4
	Voids & pinholes	3	3	2	2	3	3	4	3	n/a	3	2	2
	Base holes	-1	2	-2	-1	0	-4	-4	-4	n/a	-1	-2	-3
	Cell collapse	5	5	5	5	5	5	5	5	n/a	5	5	5
	Curing streaks	5	5	5	5	5	5	5	5	n/a	5	5	5
Mould	Shrinkage mould	3	4	2	3	3	4	4	5	n/a	4	3	5
	Glass bubbles	4	3	5	4	5	4	5	3	n/a	4	5	1
	Cell structure	4	4	4	4	4	4	4	3	n/a	4	3	3
	Voids & pinholes	4	3	2	2	3	4	3	3	n/a	4	2	3
	Base holes	0	1	0	-3	-1	-1	0	0	n/a	1	0	0
	Cell collapse	4	5	5	5	5	5	5	5	n/a	5	5	5
	Curing streaks	4	4	4	4	3	4	4	4	n/a	4	4	4

Excluding the base holes again, the foams yielded relatively good results. The L22.0 foam had the best quality and the L21.0 the worst, comparing to the base foam. Relative to the control foam L25.0, L23.0 and L22.0 were better and L21.0 was worst in terms of number of scores below 3. The results and output value yielded by the L24.0 formulation were very good

at 5°C, but when the spray in 23°C was being made, some viscous dark brownish liquid began to come out. This could mean that a poor mixing was applied after the can was filled with the gases, not resulting in homogenous liquid and consequently a poor reaction inside the can. Meanwhile, the foams L21.0, L22.0 and L23.0 began to get a light brownish colour, whereas the L24.0 got dark brownish. The control foam L25.0 began to get orange coloured. In order to solve the base holes problem, the paper and mould began to be sprayed with water prior to spraying the foam. In the previous experiment, the paper and mould were priority wetted by in the 23°C spray of formulation L22.0. A relative improvement has been observed relative to the other foams so this method was applied from now forth.

Finally, a 100% polyol replacement was made onto 456 base formulation. Codenamed “L3”, the quick test and foam evaluation results are shown in the following table:

Table 10 - Overall quality of the L3 foams.

Formulation		456		L31.0		L32.0		L33.0		L34.0		L35.0	
Output (g/s)		7,9		12,3		18,0		24,5		16,3		24,6	
Temperature (°C)		23	5	23	5	23	5	23	5	23	5	23	5
Paper	Shaking rate	5	4	5	5	5	5	5	5	5	5	5	5
	Froth shrinkage	5	5	5	5	5	5	5	5	5	5	5	5
	Froth outflow	5	4	5	5	5	5	5	5	5	5	5	3
	Crumbling 1h	5	5	5	5	5	5	5	5	5	5	5	5
	Crumbling 2h	5	5	5	5	5	5	5	5	5	5	5	5
	Crumbling 24h	5	5	5	4*	5	5*	5	4	5	5*	5	5*
	Glass bubbles	5	4	5	3	5	4	4	3	5	5	5	5
	Curing shrinkage/warping	5	5	5	5	5	5	5	5	5	4	3	5
	Cell structure	5	4	5	3	5	4	4	5	5	2	5	4
	Voids & pinholes	3	3	3	2	3	2	3	2	3	3	4	2
	Base holes	-1	2	3	0	4	3	3	3	-1	5	0	1
	Cell collapse	5	5	5	5	5	5	5	5	5	5	5	4
	Curing streaks	5	5	5	5	5	5	5	5	5	5	5	5
Mould	Shrinkage mould	3	4	2	3	3	4	3	5	1	5	1	5
	Glass bubbles	4	3	5	3	5	4	4	3	4	4	4	4
	Cell structure	4	4	4	3	4	4	4	5	3	3	4	5
	Voids & pinholes	4	3	3	2	3	2	3	3	4	3	4	3
	Base holes	0	1	5	5	3	5	5	4	4	5	3	4
	Cell collapse	4	5	5	5	5	5	5	5	5	5	5	5
	Curing streaks	4	4	4	4	3	4	5	5	5	5	5	4

*Crumbling score after one day at ambient temperature.

The solution discussed above of wetting the paper and mould before spraying the froth, seemed to have worked because the overall base holes scores were better relative to the previous experimentations. Still base holes existed in some formulations. The foam that presented the best quality was L33.0, or the one which was based in the pine lignopolyol, with

only one low score in the 5°C paper spray. The worst quality foam was L35.0, the control cardolite based foam, with four scores below 3. One important fact was that L31.0, L32.0, L33.0 and L35.0 foams presented some crumbling after the 24 hours at 5°C, contrary on what's in the table. The presented score was given when the foams were left at ambient temperature another 24 hours and the friability ceased to exist. This phenomenon is concordant to what's reported in the company "Global Report" document.³⁹

3.2.1 Shelf life

One of the requirements for the development of a new OCF formulation is that the quality of the foam is maintained after one year of being synthesized. This parameter is called one year shelf life and it's evaluated by realizing the previous quality tests to formulations submitted to accelerated aging. In this process, the cans are placed in a stove at 45°C for a determined time, where one day inside corresponded to one week at 23°C. For this evaluation to take place, four cans were made per formulation by quadrupling the reactants quantities. Three of them were for the 0, 6 and 12 month and one was for the ignitibility test. The 0 month can was sprayed and the foam evaluated one day after it was made, but the 6 and 12 month cans were evaluated after staying 26 and 52 days, respectively, in the stove. In addition, 5g of zinc borate flame retardant was added to every can in order to check if it would influence the foam quality in the aging process. Since only one the results of these formulations, codenamed "L3x.1", are shown in the following tables:

Table 11 - Overall quality of L31.1 foam.

Formulation		456		L31.1		L31.1		L31.1	
Month		0		0		6		12	
Output (g/s)		7,9		15,9		19,3		14,8	
Temperature (°C)		23	5	23	5	23	5	23	5
Paper	Shaking rate	5	4	5	4	2	3	4	4
	Froth shrinkage	5	5	5	5	5	5	5	5
	Froth outflow	5	4	5	5	4	5	5	5
	Crumbling 1h	5	5	5	5	5	5	5	5
	Crumbling 2h	5	5	5	5	5	5	5	5
	Crumbling 24h	5	5	5	5	5	5	4	4
	Glass bubbles	5	4	5	4	5	4	5	4
	Curing shrinkage/warping	5	5	4	5	4	5	5	5
	Cell structure	5	4	5	3	5	4	5	3
	Voids & pinholes	3	3	3	3	3	3	3	2
	Base holes	-1	2	4	5	3	5	3	5
	Cell collapse	5	5	5	5	5	5	5	5
	Curing streaks	5	5	5	5	5	5	5	5
Mould	Shrinkage mould	3	4	2	4	1	3	3	4
	Glass bubbles	4	3	5	4	5	4	5	4
	Cell structure	4	4	4	3	4	4	4	3
	Voids & pinholes	4	3	3	3	2	3	2	2
	Base holes	0	1	3	4	5	5	5	4
	Cell collapse	4	5	5	5	5	5	5	5
	Curing streaks	4	4	4	5	4	4	4	5

After analysing table 10, it is possible to see that the overall quality of the foam didn't degrade too much after 12 months. The foams had a very good overall quality and high output values relative to the base formulation. The shaking rate decreased in the 6 month while the mould shrinkage improved a little bit at 23°C. The voids and pinholes score decreased below the acceptable value. After 12 months, the shaking rate was good again and the voids and pinholes score in mould and in paper decreased a little bit at 5°C.

The aging test results from the cork based lignopolyol formulation are presented in the following table:

Table 12 - Overall quality of L32.1 foam.

Formulation		456		L32.1		L32.1		L32.1	
Month		0		0		6		12	
Output (g/s)		7,9		15,7		21,9		26,7	
Temperature (°C)		23	5	23	5	23	5	23	5
Paper	Shaking rate	5	4	4	4	4	3	5	5
	Froth shrinkage	5	5	4	5	5	5	5	5
	Froth outflow	5	4	4	4	4	5	5	3
	Crumbling 1h	5	5	5	5	5	5	5	5
	Crumbling 2h	5	5	5	5	5	5	5	5
	Crumbling 24h	5	5	5	5	5	5	4	4
	Glass bubbles	5	4	5	4	5	4	5	4
	Curing shrinkage/warping	5	5	3	5	3	5	5	5
	Cell structure	5	4	5	4	5	4	4	3
	Voids & pinholes	3	3	4	3	3	3	3	3
	Base holes	-1	2	4	5	4	4	5	5
	Cell collapse	5	5	5	5	5	5	5	5
	Curing streaks	5	5	5	5	5	5	5	5
Mould	Shrinkage mould	3	4	2	4	3	5	5	5
	Glass bubbles	4	3	5	4	5	4	5	4
	Cell structure	4	4	4	4	5	4	4	3
	Voids & pinholes	4	3	3	3	3	2	3	3
	Base holes	0	1	5	5	4	5	5	5
	Cell collapse	4	5	5	5	5	5	5	5
	Curing streaks	4	4	4	5	4	4	4	5

Looking at the results, the foam had a very good overall quality and high output values relative to the base formulation. The mould shrinkage scores improved from 0 to 12 months and a little decrease was observed at 5°C, 6 months foam sprayed at mould, but it may be associated to the error of the evaluation.

The following table presents the aging test results for the pine based lignopolyol foam:

Table 13 - Overall quality of L33.1 foam.

Formulation		456		L33.1		L33.1		L33.1	
Month		0		0		6		12	
Output (g/s)		7,9		27,0		20,0		23,0	
Temperature (°C)		23	5	23	5	23	5	23	5
Paper	Shaking rate	5	4	4	4	4	4	5	3
	Froth shrinkage	5	5	5	5	5	5	5	5
	Froth outflow	5	4	5	5	4	4	4	4
	Crumbling 1h	5	5	5	5	5	5	5	5
	Crumbling 2h	5	5	5	5	5	5	5	5
	Crumbling 24h	5	5	5	5	5	5	5	4
	Glass bubbles	5	4	5	4	4	3	5	4
	Curing shrinkage/warping	5	5	4	5	5	5	4	5
	Cell structure	5	4	5	4	5	4	4	4
	Voids & pinholes	3	3	3	3	3	2	3	3
	Base holes	-1	2	5	2	4	3	4	3
	Cell collapse	5	5	5	5	5	5	5	5
	Curing streaks	5	5	4	5	4	5	5	5
Mould	Shrinkage mould	3	4	4	5	4	5	4	5
	Glass bubbles	4	3	5	4	4	3	5	4
	Cell structure	4	4	4	4	4	4	3	4
	Voids & pinholes	4	3	3	3	2	3	3	3
	Base holes	0	1	3	5	5	5	-1	4
	Cell collapse	4	5	5	5	5	5	5	5
	Curing streaks	4	4	4	5	4	5	4	5

Comparing to the base formulation, the pine lignopolyol foam did not fall too much behind in terms of quality. First of all, the output values were higher in every stage. The voids and pinholes score was almost constant in mould and paper, excluding the low scores in the 5°C, 6 month paper spray and the 23°C, 6 month mould spray. The base holes at 5°C, in the

paper sprayed foams, improved a little bit from 0 to 12 month, while they worsened in the mould sprays.

Table 14 - Overall quality of L34.1 foam.

Formulation		456		L34.1		L34.1		L34.1	
Month		0		0		6		12	
Output (g/s)		7,9		13,6		11,8		24,2	
Temperature (°C)		23	5	23	5	23	5	23	5
Paper	Shaking rate	5	4	5	5	2	2	5	1
	Froth shrinkage	5	5	5	5	5	5	5	5
	Froth outflow	5	4	5	5	5	5	4	5
	Crumbling 1h	5	5	5	5	5	5	5	5
	Crumbling 2h	5	5	5	5	5	5	5	5
	Crumbling 24h	5	5	5	2	5	0	5	4
	Glass bubbles	5	4	5	4	5	4	5	5
	Curing shrinkage/warping	5	5	5	5	2	5	5	5
	Cell structure	5	4	5	3	5	4	5	3
	Voids & pinholes	3	3	3	3	3	3	3	3
	Base holes	-1	2	-3	-3	3	5	4	5
	Cell collapse	5	5	5	5	5	5	5	5
	Curing streaks	5	5	5	5	5	5	5	5
	Mould	Shrinkage mould	3	4	2	4	3	4	3
Glass bubbles		4	3	5	4	5	4	5	4
Cell structure		4	4	4	3	5	4	4	3
Voids & pinholes		4	3	4	3	3	3	3	3
Base holes		0	1	2	4	5	4	2	4
Cell collapse		4	5	5	5	5	5	3	5
Curing streaks		4	4	5	4	4	5	5	5

In the case of the poplar based lignopolyol foam, the quality results were mixed and diverse. As all the formulations until now, the output values were well above the 3,5 mark and higher than the base formulation. The shaking rate scores decreased at the final stages, some crumbling at 5°C have occurred in the 0 and 6 month foams, which then disappeared after

letting the foam at ambient temperature for some time. Finally, base holes were an occurring problem at 0 and 12 month foams, having a particularly low score at the 0 month paper spray.

In order to be possible to compare all the previous lignopolyol base formulations to commercial biomass derived polyol based foam, the same aging test was applied to 100% cardolite based foam with 5g of flame retardant, obtaining the following results:

Table 15 - Overall quality of L35.1 foam

Formulation		456		L35.1		L35.1		L35.1	
Month		0		0		6		12	
Output (g/s)		7,9		9,5		24,8		16,2	
Temperature (°C)		23	5	23	5	23	5	23	5
Paper	Shaking rate	5	4	4	4	4	3	5	3
	Froth shrinkage	5	5	5	5	5	5	5	5
	Froth outflow	5	4	4	4	4	5	4	3
	Crumbling 1h	5	5	5	5	5	5	5	5
	Crumbling 2h	5	5	5	5	5	5	5	5
	Crumbling 24h	5	5	5	5	5	5	5	5
	Glass bubbles	5	4	5	5	5	5	5	5
	Curing shrinkage/warping	5	5	5	5	5	5	5	5
	Cell structure	5	4	4	4	5	5	5	3
	Voids & pinholes	3	3	3	3	3	3	3	3
	Base holes	-1	2	3	5	3	5	5	4
	Cell collapse	5	5	5	5	5	5	5	5
	Curing streaks	5	5	5	5	5	5	5	5
Mould	Shrinkage mould	3	4	3	5	4	4	5	5
	Glass bubbles	4	3	5	4	4	3	5	4
	Cell structure	4	4	4	4	4	4	4	4
	Voids & pinholes	4	3	3	3	2	3	2	3
	Base holes	0	1	4	5	5	5	4	5
	Cell collapse	4	5	5	5	5	5	5	5
	Curing streaks	4	4	4	5	4	4	4	5

In general the foams had very good quality compared to the base formulation. All the output values were very good and the only flaw was a little decrease below 3 in the voids and pinholes score at 6 and 12 month.

3.2.2 Distillate free formulation

As it's already known, all the previous lignopolyol based formulations were based in 456 formulation, which used GA13 as the source of isocyanate groups. This compound is not available in the market, so it's normally produced *in situ* from the distillation of Ongronat 2500. In order to obtain it, the company relied on external personnel and equipment to make GA13 which presented a constant expense. This year, a new formulation, named 946, was made following a previous work³⁷ in which a formulation was developed by replacing GA13 with Ongronat 2500. This achievement was only possible by making some adjustments to the components of the base formulation and introducing a new prepolymer. That said, a new L52.0 formulation was developed by introducing cork lignopolyol into 946 formulation by replacing 100% in parts of the base polyols. The obtained results are presented in the following table:

Table 16 - Overall quality of L52 foams.

Formulation		946		L52.0		L52.1	
Output (g/s)		21,7		-		-	
Temperature (°C)		23	5	23	5	23	5
Paper	Shaking rate	3	2	4	4	4	3
	Froth shrinkage	5	5	5	5	5	5
	Froth outflow	4	5	4	5	5	4
	Crumbling 1h	5	5	5	5	5	5
	Crumbling 2h	5	5	5	4	5	5
	Crumbling 24h	5	5	5	5	5	0
	Glass bubbles	5	5	5	4	5	4
	Curing shrinkage/warping	2	5	5	5	5	5
	Cell structure	5	4	5	4	5	4
	Voids & pinholes	4	3	2	2	3	3
	Base holes	2	4	5	3	4	2
	Cell collapse	5	5	5	5	5	5

	Curing streaks	5	5	5	5	5	5
Mould	Shrinkage mould	5	4	-1	1	2	4
	Glass bubbles	5	5	4	4	4	4
	Cell structure	4	4	4	4	4	3
	Voids & pinholes	3	3	-4	-4	3	2
	Base holes	5	4	5	4	3	4
	Cell collapse	5	5	5	5	5	5
	Curing streaks	5	5	5	5	4	4

The 946 formulation only presented three scores below 3: low shaking rate at 5°C, warping and large base holes at the 23°C. These low scores were solved after the cork lignopolyol was directly introduced into the formulation. However, large voids and pinholes in the paper spray appeared, the foam shrank in the mould at both working temperatures and huge voids and pinholes appeared, resulting in relative lower quality foam. In an attempt to solve the previous problems and to completely exclude petroleum derived polyols in the formulation development, a new formulation codenamed “L52.1” was developed from L52.0 by introducing new cork prepolymer synthesized using the method explained in chapter 2.7. Contrary to what was observed in the synthesis of the prepolymer used in 946, the reaction was very fast and violent, maybe due to a higher functionality of the cork lignopolyol. Because of this, the desired 1,2% free NCO groups was very difficult to achieve and a very low value, 0,1%, was obtained. Nevertheless, its introduction was made and the resulting foam had much smaller voids and pinholes and shrank lesser in the mould. However, large base holes and some crumbling were observed at the 5°C paper spray. Because of the novelty of this experiment, only 30% of the can was filled with the formulation and the output was not measured.

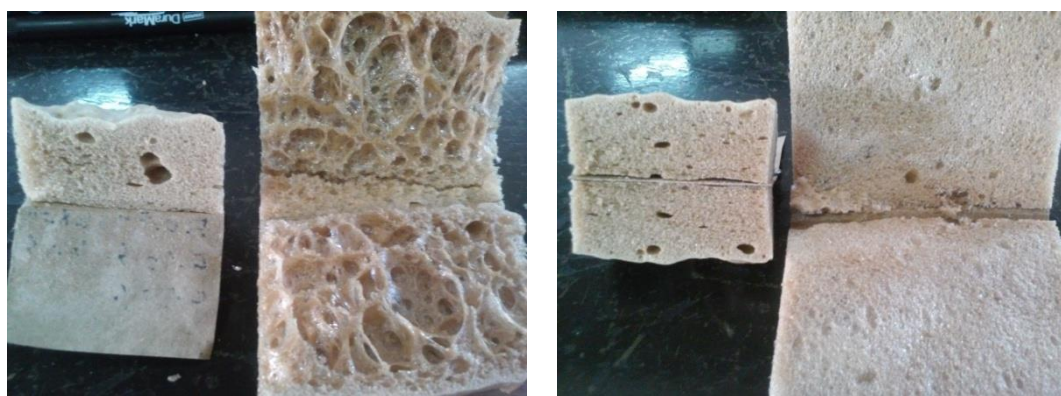


Figure 30 - L52.0 at 23°C (left) and L52.1 at 23°C (right).

3.3 Ignitility test

After preparing the samples and proceeding with the ignitibility test of all the foams using the method described in the chapter 2.5, the following mean flame heights were obtained:

Table 17 - Ignitibility test results.

Formulation	Flame height (cm)
456	17,2
L31.1	22,0
L32.1	25,0
L33.1	23,0
L34.1	18,0
L35.1	23,0

As it's clearly to see, all the foams, even the base formulation and the control L35.1, passed the 15 cm gauge mark and failed the test, being classified as B3 (very flammable). These proved that the added quantity of zinc borate was not enough or that another type of flame retardant should have been used. Besides, the addition of lingopolyols and cardolite to the base formulation increased the flame height. Interestingly, the L34.1 and L31.1 had lower flame heights relative to the control L35.1.

4 Conclusions

In this work, several types of biomass were successfully liquefied using a method which has some differences from the ones presented in the literature. Some biomass types, like blue gum bark and poplar wood, were liquefied for the first time. Poplar wood was liquefied relatively fast (1h to 1h30min) with the best conversion ratios (83-91%). Blue gum bark was liquefied after 1 to 2 hours of liquefaction with conversion ratios between 60% and 66%, which are not very high. This may be due to particular fact that the lignin concentration was higher than the other plant biomasses. Finally, cork powder or dust was liquefied after 2 hours of reaction with conversion ratios between 67% and 79%. The hydroxyl and acid value were relatively high (between 193 and 272 mg KOH/g) and low (between 1 and 7 mg KOH/g), which made the polyols suitable for producing foams. The infrared spectra analysis concluded that they were an aromatic compound, with carbonyl and OH groups, which led to the conclusion that they must be derived only from lignin and suberin, since these are the only aromatic compounds in plant biomass and the sugars derived from cellulose and hemicellulose were extracted.

The gradual replacements of 5%, 50% and 100% in parts per weight of the base formulation polyols by the new lignopolyols were done successfully. A control formulation of cardolite, a commercially available polyol derived from the cashew fruit, was done in every replacement. Excluding the base holes for the fact that water spray was not applied in all of these replacements, the quality of the foam didn't degrade too much, so the 100% replacement can safely be done at the 456 formulation. Also, the quality didn't degrade after 12 months in every formulation, even with the flame retardant included in the formulation. In terms of quality, the best lignopolyol was the one based on cork lignopolyols, which was like the control. However, neither of the formulations were better than the base formulation.

All the foams were B3 in the ignitibility test, including the control and the base formulation. This was due to insufficient quantity of flame retardant or it was not suitable for this kind foams. Further investigation in this topic shall be made in future works.

Finally, the introduction of the cork lignopolyol was attempted at the distillate free formulation 946, in order to produce cheaper formulations. The quality of the resultant foam was very bad compared to the 946 base formulation, having large voids and pinholes. In order to remove every compound that was derived from petroleum based polyol, a new cork

lignopolyol based prepolymer was developed by using the standard company method. After it was introduced in the formulation, the resulting foam quality improved drastically and the large voids and pinholes disappeared.

5 Future work

In order to make them a commercially viable product, the foams had to have any property from the evaluation tests equal or greater than 3, an output value greater or equal than 3,5 g/s, 12 months shelf life, be B2 and had a free monomeric NCO value below 1%. The only criteria met in this work were the output value and 12 month shelf life, so further work shall be done.

In the distillate free formulation, a new method shall be developed in order to better control the NCO content of the final prepolymer because of the violent reaction. One suggestion is to add the lignopolyol to the isocyanate slowly and monitor the NCO content until the desired value is met.

6 Ambient, security, and monetary costs

6.1 Biomass liquefaction process

Because the lignopolyols are a relatively new product and still not available in the market, the ambient and security was not available at the moment. Because of this, it should be treated with all the care using full body protection when handling them.

The liquefaction has the following security considerations:

- Dust protection mask shall be used when handling with cork powder.
- Because of the high temperatures involved in the process, dangerous vapours will be released so it shall ALWAYS be made in a ventilated place like a fume hood.
- Body, hands and eye protection shall be used at all times.
- If the reactor shall be moved for some reason while it is hot, heat resistant gloves shall be used.
- When cleaning the lab material, a residue container for the liquefaction residues shall be used.

Next, a table with the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) data of the all the chemicals and another with the monetary costs of this part of project are presented below:

Table 18 - Total monetary costs of the liquefaction².

Product	Price per weight (€/Kg)	Used quantity (g)	Cost (€)	Total (€)
cork powder	0,4	50	0,020	0,345
Solvent B	1,71	150	0,257	
Solvent A	1,3	50	0,065	
Catalyst	1,9	1,5	0,003	

Table 19 - Total monetary costs of the lignopolyol extraction².

Product	price per volume (€/l)	Used quantity (ml)	Cost (€)	Total (€)
Acetone	35,2	100	3,52	7,58
Methanol	40,6	100	4,06	

² Water and electricity costs were excluded.

Table 20 - Formulation compounds list and GHS hazard and precaution statements.

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6.2 One component foams

Fully cured polyurethane rigid foams are not dangerous to the environment. They are insoluble in water and most organic solvents. However, some important security aspects have to be taken in various stages of the manufacturing and handling of the OCF cans:

- Some chemicals used in the production of the OCF formulations, like isocyanates and tertiary amine catalyst, present some risk to the health and environment and especial precautions should be taken. However, other chemicals, like surfactants, have low toxicity. The lignopolyols toxicity is unknown so full body protection and ventilation should be used when working with them.
- Before the cans get filled with gases, they should be checked if they are tightly sealed in order to avoid any gas leak.
- Because of the exothermic characteristic of the gelation reaction, the pressured can will heat up, so it should be placed inside a secure room or container for a day in order to ensure maximum protection if it blows. Moreover, water content of all the compounds should be low.
- When the foam is to be sprayed the body, eyes and hands shall be protected.
- The prepolymer preparation should be done in a well ventilated place and full body protection, including gas mask, shall be used.

Next, a table with the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) data of the all the chemicals is presented below:

Table 21 - Formulation compounds list and GHS hazard and precaution statements.

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Appendix 1

Formulations







Appendix 2

Foam ratings






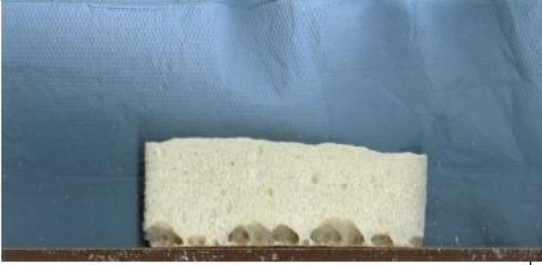





Cell Structure

5		- 1	
4		- 2	
3		- 3	
2		- 4	
1		- 5	
0			

Voids & Pin Holes

5				
4				
3				
2				
1				
0				


Base Holes

5		- 1	
4		- 2	
3		- 3	
2		- 4	
1		- 5	
0			








Cell collapse

5		- 1	
4		- 2	
3		- 3	
2		- 4	
1			
0			

CURING STREAKS

5 NONE	
4 MINOR	
3	
2.5 MODERATE	
1	
0 EXTENSIVE	

GLASS BUBBLES

5		0	
4		- 1	
3		- 2	
2			
1	