Sustainable polymer solutions through biomass liquefaction processes

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Thanks be to God for everything I have in my life.

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Abstract:

In a context of better management of land resources and development of renewable biomass-based chemicals, lignin offers excellent alternative to replace certain fossil-based derivatives. Through the integration of green chemistry into biorefineries, and the use of low environmental impact technologies, we can establish future supply chains for genuinely green and sustainable chemical products. Indeed, lignin can be converted into polyols via several processes, mainly liquefaction. Liquefaction is considered an efficient method to generate polyols with high content of reactive hydroxyl groups. These final products can be used as raw materials for polymer synthesis, like in the production of polyurethanes and polyesters. In our study this alternative has been adopted; namely by using conventional heating system and microwave heating. The difference between the two is essentially based on energetic terms, given that liquefaction processes are usually carried out at high temperatures, using different types of liquefaction solvents and in the presence of acid catalysts. The use of microwave heating system has various advantages in terms of speed and consumed energy.

The objective of this study was to compare the liquefaction of sodium lignosulphonate lignin by conventional heating system and microwave system. The liquefaction was carried out using polyethylene glycol (Mw 400) and glycerol as solvents, and sulphuric acid as catalyst, and the conversion yield determined, aiming at achieve the best liquefaction conditions. In fact, several process conditions were tested namely the catalyst content (1, 2 and 3%, (w/w, solvent-basis) and liquefaction temperature (140, 160 and 180°C). The obtained polyols were characterized in terms of their most relevant technical properties: hydroxyl number (IOH), viscosity, and unreacted biomass. The chemical structure, which was evaluated by Fourier Transform Infrared analysis (FTIR) was also checked. Finally, the properties of the generated polyols were compared in order to evaluate the efficiency of both systems.

Keywords: Lignin, Liquefaction, Microwave, conventional reactor, biopolyols

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List of Abbreviations

CAT – Catalyst (H_2SO_4)

µ – Viscosity

µm – micrometer

An – acid number

FTIR – Fourier Transform Infrared Spectroscopy

GPC – Gel Permeation Chromatography

H – time in hours

H_2SO_4 – sulfuric acid

IOH – Hydroxyl number

KOH – potassium hydroxide

Min – minutes

Mw – Microwave

Ƞ – liquefaction yield

n.a – Not available

NMR – Nuclear Magnetic Resonance

n.u – not used

OH – hydroxyl group

Pa – Pascal

Pa.s – Pascal.seconde

PEG – Polyethylene Glycol

Pmax – Maximum pressure

T°C – Temperature in degrees Celsius

v/v – volume of solute/volume of solvent

w/w – weight of solute/weight of solvent

wt% – Weight percentage

1. Motivation and objectives

Polymers, commonly called "plastics", are indispensable to our practical life. Their widespread use, from the most banal objects (for example in packaging), to technical applications (building materials), or to cosmetics and food uses was due to the outstanding properties and extended lifetime, among other factors. However, their environmental harmful role on the greenhouse gases increasing, together with the drain of fossil reserves associated with their recalcitrant properties, are motivating the search for greener alternatives in the latest years. Herein, the development of biobased polymers derived from renewable resources is becoming a necessity for the future. Among the several available renewable resources, lignocellulosic biomass, composed mainly by cellulose, hemicelluloses and lignin, is one of the most abundant and cheaper options. In particular, those obtained as residues from agro-industrial processes are considered as one of the most interesting bioresources. Between the lignocellulosic components, lignin is after cellulose, the second most abundant biopolymer derived from biomass and represents about 30% of the organic matter in the biosphere. Today, the main applications of lignin relate to the use as a back-up fuel, and only 2% of the lignin produced is used as raw material for obtaining different products, like surfactants or vanillin. Yet, lignin is the only natural polymer with a phenolic skeleton representing a significant source of raw materials in organic chemistry that can be used to replace molecules derived from fossil sources. However, the complex chemical structure of lignin, together with molecular structure variation dependent on the used isolation processes, limits its valorization as a viable source in the synthesis of chemical, including polymer synthesis.

Lignin can be converted into polyols by two main processes: oxypropylation and liquefaction. Liquefaction is considered as an efficient method to generate polyols with high content of reactive hydroxyl groups. These final products are used as raw materials for polymer synthesis, like polyurethanes and polyesters. The liquefaction processes are usually carried out at high temperatures, using different types of liquefaction solvents and catalysts. In energetic terms, the requirements of this process when conventional heating systems are used is highly unfavorable, meaning that more efficient systems are needed. In this sense, the use of microwave systems can be advantageous, once the liquefaction is expected to be faster, resulting in lower energy consumption.

Based on the aforementioned, this work will be devoted to lignin liquefaction by using a microwave heating system, where polyhydric alcohols will be used as solvents to produce polyols. A systematic study will be performed, by testing different process conditions, in order to maximize liquefaction yield. Then, the generated polyols will be characterized in terms of their most relevant technical properties: hydroxyl number (IOH), viscosity, unreacted biomass, and chemical structure which (evaluated by Fourier Transform Infrared analysis, FTIR).

2. Introduction

Our society is facing new challenges, namely the rarefaction of fossil resources is forcing the search for new sources of energy and chemical raw materials. On the other hand, the increasing of greenhouse gases and pollution promotes the search for eco-responsible processes. Currently, the utilization of lignocellulosic biomass is being considered as one of the greatest challenges for the scientific community. Lignocellulosic biomass derived from wood and agricultural crops residues is considered one of the most abundant renewable raw materials in the world. These residues present unique intrinsic properties that can contribute for the development of a novel generation of high performance materials. All these factors, constitute, certainly, a driving force to promote and consolidate the utilization of renewable materials as raw materials for the production of new products, including polymeric materials.

Lignocellulosic biomass is rich in phenolic and aliphatic hydroxyl groups, as well as on carboxyl groups which have reactive hydrogen atoms, making it a very promising material for the production of polyurethane materials. Lignin is a crucial component of plant cell walls, which is produced in the amount of 5×10^7 tons annually (Gosz et al., 2018).

Currently, a vast amount of lignin is generated as a by-product of the pulp and paper industry. In general, lignin is used as fuel, and only a small amount (1–2%) is separated to be employed in industrial value-added applications (Bruijnincx et al., 2016). The obtained raw materials can be used in the production of polyurethanes, epoxy and phenolic resins (Yan et al.,2008, Gao et al.,2010, Hu S and Li Y, 2014), adhesives (Lee WJ and Lin MS., 2008), and foils (Kurimoto et al., 2000).

In this context, liquefaction of plant biomass is being studied due to the importance of its applications in the field of materials or energy. Based on the purpose and process, liquefaction can be classified into hydrothermal liquefaction and solvolytic liquefaction. Hydrothermal liquefaction, which is a traditional process, mainly operates under high temperatures and high pressure to obtain bio-oil (RunCang S, 2010). The technical edge of this process is the bio-crude that is obtained from this process and doesn’t require much treatment/upgrading procedures for their commercial utilization, However, the economy of the process is highly questionable due to the utilization of high pressure conditions (Gollakota A.R.K et al., 2018).

The solvolytic liquefaction, which operates under moderate and low temperatures or even under atmospheric pressure, has gained more and more importance. Besides the distinctly lower energy requirements, solvolytic liquefaction has several advantages compared with the other thermomechanical processes: The polymeric constituents of the biomass depolymerize only to a desired extent and react subsequently with a specific organic reagent to generate various valued-added polymer, chemical precursors or chemicals (Lim et al. 2004) and the presence of a solvent keeps the concentration of products low and prevents secondary reactions, cross-linking or re-polymerization (Pua et al.,2013).

2.1. Lignocellulosic biomass

Lignocellulosic biomass is composed mainly by cellulose (linear glucose polysaccharide), hemicelluloses (branched polysaccharides formed by sugars with 5 and 6 carbon atoms) and lignin (an aromatic polymeric complex). For example, considering wood or straw as lignocellulosic biomass, these contain, in average, 45% of cellulose, 25% hemicelluloses and 25% lignin (Wertz et al., 2015) (Figure 1).

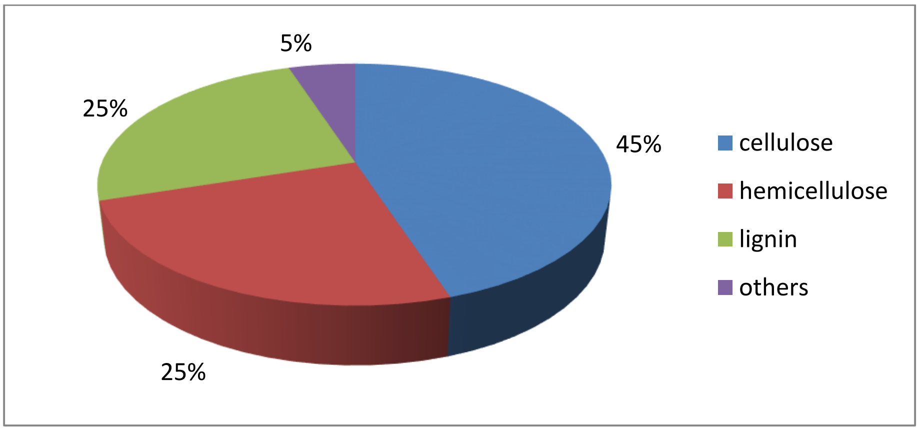
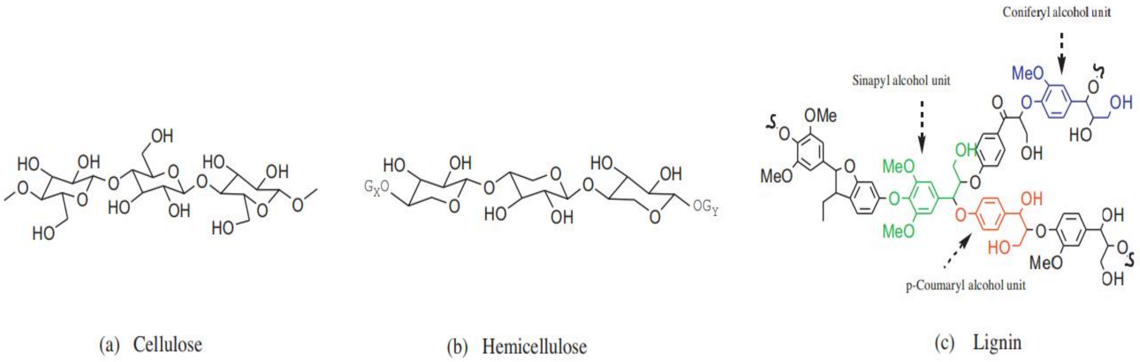


Figure 1.Typical composition of lignocellulosic biomass (Wertz JL et al., 2015).

Regarding the chemical structure, as shown in Figure 2, hemicellulose is a branched molecule, while cellulose is a long glucose-formed linear chain, and lignin is mainly composed by aromatic units (Yang et al., 2007).



(a) Cellulose (b) Hemicellulose (c) Lignin

Figure 2. Schematic representation: (A) cellulose, (B) hemicellulose, and (C) lignin (Gu et al., 2013)

Lignin is contained within the plant cells, filling the cellulose and hemicelluloses fibers, and acting as the structural component of the plants (Figure 3).

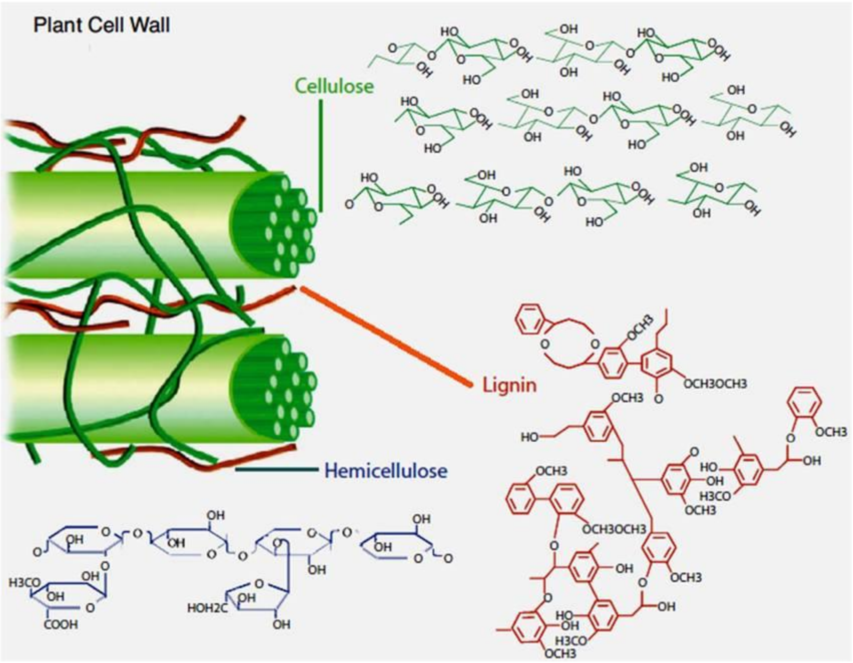


Figure 3 Overall structure of lignocellulosic biomass (Bamdad et al., 2017).

Lignin is a three-dimensional amorphous polymer and one of the most complex organic aromatic polymers present in nature (Zakzeski et al., 2010, Kibet et al., 2012). The exact structure of a native lignin network is still unknown. However, it is believed to be derived upon three aromatic alcohols: p-coumaryl, coniferyl, and sinapyl, as showed in Figure 4 (Zakzeski et al., 2010, de Wild et al., 2012, Kibet et al., 2012). From a chemical point of view, lignin consists of phenylpropane units (C6-C3 or C9).

The C9 units are linked together by ether bonds (C-O-C), representing approximately two-thirds of the inter-unit links, being the remaining units linked by carbon-carbon bonds (C-C) (Harkin JM, 1969).

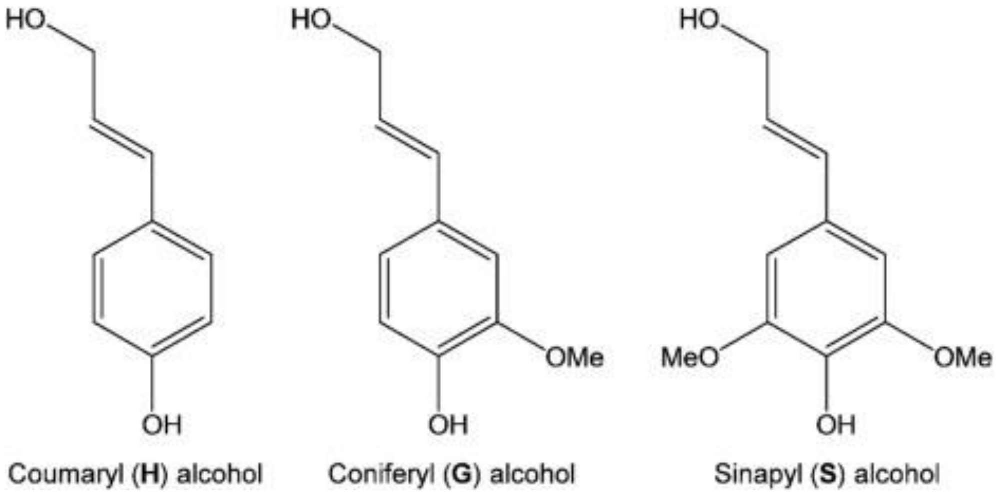


Figure 4. The three monolignols of a native lignin network: (A) coumaryl alcohol, (B) (William et al., 2011).

2.2. Lignin conversion into polyols

Due to lignin molecule complexity, together with the variations on its molecular structure derived from different isolation techniques, the conversion of lignin into high value compounds is a subject that mobilizes huge efforts from the scientific community in the last twenty years, and has been accelerating since 2006 (Sebhat et al., 2015).

Regarding the lignin valorization through the production of polyols, two main processes can be used: oxypropylation and liquefaction. The oxypropylation process can be summarized as a process where grafts of propylene oxide molecules are formed within the lignin molecule, forming covalent links with the previously activated lignin's OH groups. These groups are activated by a basic catalyst such as KOH. From this reaction, liquid polyols are produced. Usually, oxypropylation is made in an autoclave under moderated pressure and temperature conditions.

Liquefaction is a thermochemical treatment that converts solid biomass into liquid or solubilized products (Kržan et al., 2005). This process requires the application of temperatures (≈150°C) in presence of a solvent (phenol, glycols, water), and a catalyst (acid or base). A wide variety of protocols, reactor types and solvents can be used.

The comparison of the processes evidences the main differences between them: while oxypropylation requires moderated pressure and temperature conditions, liquefaction needs higher temperatures to be accomplished, being thus less efficient from the energetic perspective. However, oxypropylation requires the use of propylene oxide which is considered as a possibly toxic substance, while solvolytic liquefaction requires the application of mostly friendly solvents such as glycerol or polyhydric alcohols. A description of both processes typical conditions is presented in Table 1. To refer that one of the main advantages of using microwave energy sources is the fact of requiring low temperatures.

Table 1 Comparison of the parameters and the yield of the process of liquefaction and oxypropylation of the organosolv lignin

Process	Time (min)	T (°C)	P*max*/ (10^5 Pa)	Solvent (w/v)	Cat$^{(1)}$ (%,w/w)	$I_{OH}$$^{(2)}$ (mg KOH/g)	Reference
Oxypropylation	9	150-285	17.5	B/PO 10/40	KOH 5	300-800	Li and Ragauskas (2012b)
Microwave heating liquefaction	5	155		PEG400/ glycerol (80:20)	Sulfuric acid (1–3)	811.8	Sequeiros et al. (2013)

(1) Cat.-Catalyst; (2)I_{OH} -Hydroxyl index.

2.3. Lignin liquefaction under the biorefinery concept

Nowadays strong attention is being paid to the biomass-based biorefinery. A biorefinery can be defined as a multiplatform unit where lignocellulosic biomass is converted through different processes into intermediates and final products (Rodrigues et al., 2008).

This units operation is based on the biomass breakdown into its constituent components, cellulose, hemicelluloses and lignin by chemical or biological routes. Through hydrolysis, process sugars are obtained, which will be further processed in order to generate ethanol by fermentation. Converted lignin can be used for energy generation or may be upgraded to other products such as etherified gasoline (Crocker and Crofcheck, 2006). From this unit, liquid fuels, useful chemicals and environmentally friendly polymeric materials can be obtained via different liquefaction techniques such as pyrolysis and solvolysis (Hakkı Alma et al., 2013), as it is presented in Figure 5.

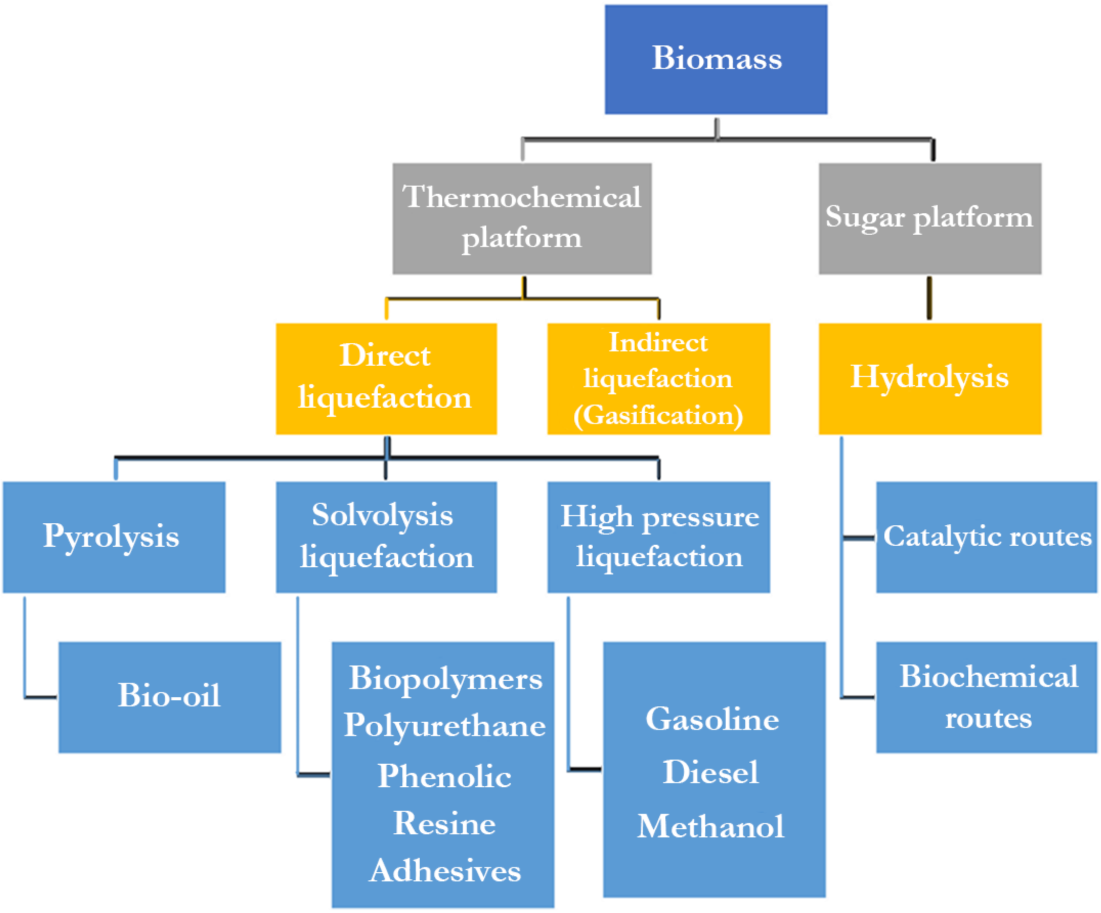


Figure 5 Strategies for biomass processing according to the biorefinery concept (Hakkı Alma et al., 2013).

Regarding the biomass liquefaction, this process is used to obtain liquefied products through complex physical and chemical reactions. Biomass is broken into small molecules in the presence of several factors such as heat, pressure, catalyst and solvents. Along the liquefaction different types of reactions such as solvolysis, depolymerization, decarboxylation, hydrogenolysis, and hydrogenation occur (Demirbas MF, 2009). Liquefaction can be divided in two categories, direct and indirect liquefaction. Direct liquefaction corresponds to pyrolysis, solvolysis liquefaction and high pressure hydrothermal/solvolytic liquefaction to produce liquid tars and oils and/or condensable organic vapors (Hakkı Alma et al., 2013). Indirect liquefaction involves the gasification of the biomass followed by, for exemple Fischer-Tropsch synthesis that brings the solid feed to a gaseous form prior to yielding a liquid product. Similarly, a pyrolysis without the presence of a liqid solvent is also an indirect liquefaction process (Beckham G T, 2018).

Liquefaction can be applied to the whole biomass or their individual components, like lignin. According to several studies, the liquefaction process is usually conducted at temperatures around 150°C under atmospheric pressure by using polyhydric alcohols, such as polyethylene glycol (PEG) and glycerol as liquefaction solvents and a catalyst (acid or base) (Balat M, 2008). The choice of the optimal solvent is relative to the technique; either it is a conventional heating system or emerging microwave heating sources (Li et al., 2015).

The main purpose of this process is to obtain polyols with low residue content. In this perspective, parameters with significant effect on lignin liquefaction efficiency are solvent type, catalyst type, and liquefaction temperature/time used (Sequeiros et al., 2013). For example, a study on the liquification of Organosolv (sugarcane bagasse) showed that the use of a conventionnel heating system implied a very high temperature that reaches 250°C, when using Ethanol:water (40:10) as solvent and 1-(4-sulfobutyl)-3-methyl imidazolium hydrosulfate as catalyst (Long et al., 2015). Beyond this, other conditions can be used, being summarized on Table 2.

Table 2 Examples of lignin liquefaction processes and used conditions.

Lignin	Process/Heat source	Solven mixture (w:w)	T (°C) t (min)	Cat. (%, w/w)	References
Alkaline (corncob)	G/M	PEG400:glycerol (80:20)	160 5–30	Sulfuric acid (1.5)	Xue et al. (2015)
Organosolv (olive tree pruning)	G/M	PEG400:glycerol (80:20)	130–180 5–15	Sulfuric acid (1–3)	Sequeiros et al. (2013)
Soda (non-wood biomass)	G/M	Glycerol: glycerin Polyglycidyl ether (2:10, 3:10, 4:10; 5:10, 5:15)	140 2	n.u.	Bernardini et al. (2015)
Bamboo	M	Glycerol (4/1)	120 7	Sulfuric acid (1.75)	Xie et al. (2016)

S-solvent ; T-temperature ; t-time ; G-glycolysis ; M-microwave Cat- catalyst , ; n.u.- not used

2.4. Liquefaction with alcohols

Different solvents are able to liquefy the lignocellulosic material. The most common are the polyhydric alcohols (ethylene glycol, polyethylene glycol 400, polypropylene, ethylene carbonate, glycerol), phenolic solvents (phenol, tetralin/creosote), water, and finally ionic liquids (Yuan et al., 2009), The mass ratio biomass/solvent is an important factor mostly varying in the consulted studies between 1/1 to 1/5, for the most common solvents (Hejna et al., 2016). Regarding the different energy sources, conventional heating and microwave systems can be used. Microwave irradiation offers the advantage of being extremely rapid throughout the volume of the reaction mixture because it penetrates and produces volumetrically distributed heat source. Parameters such as liquefaction temperature and reaction time on the liquefaction conversion yield have been extensively studied in several investigations. Despite the high conversion yield of microwave liquefaction, the energy consumption efficiency during this process and the quality of liquefied products with respect to various liquefaction parameters have not been investigated thoroughly (Huang et al., 2017).

Among the lignin liquefaction using microwave systems, Cinelli and coworkers (Cinelli et al., 2013) started by lignin drying at 80°C for 24h. Then the selected solvents, glycerol and polyethylene glycol (PEG 400), were putted together with lignin, according to a ratio of 0.5:0.5:2 (L0.5) and 1:0.5:2 (L1). The mixture was placed in a microwave oven using a power of 180W, and a temperature of 135ºC, during 3min. After, the produced polyols characterization give a hydroxyl index between 645 to 661 mgKOH/g, depending on the used ratio of substrates. In the case of the work developed by Xue and his group, (Xue et al., 2015), lignin was liquefied using a mixture of glycerol and PEG 400. Sulfuric acid was used as the catalyst for this reaction which was performed through microwave-assisted liquefaction at 140ºC. The achieved yield was 97.5% and the obtained polyol was characterized by a hydroxyl index of 863 mgKOH/g. In another study, the impact of the reaction time, as well as of chemical composition of the used chemical system, on the liquefaction process of lignin were evaluated (Gosz et al., 2018). Glycerol and PEG-400 were used as solvents in order to obtain a polyol with a high content of hydroxyl groups. Sulfuric acid was used as catalyst for this reaction. After 5min at 155ºC, under the presence of 3% of catalyst, the reaction yield reached 99%. The hydroxyl index of the obtained polyol was 263 mgKOH/g. Several studies have shown that glycerol can be successfully applied as a liquefying agent to produce polyols from different types of biomass. Furthermore, crude glycerol has got many advantages to offer, once it has a low economic value and it is generated as a by-product during biodiesel production (Gosz et al., 2018).

Regarding the of microwave heating, its use allow a fast and more efficient heating of the entire sample volume (de la Hoz et al., 2005). Microwave heating has many advantages, for example, low energy use, very high heating rate and low treatment time, resulting on the improvement of the final product physical and chemical properties. Moreover, it is simple and it presents lower risk for the environment, when compared with the alternative counterparts (Clark et al., 2000, Yadoji et al., 2003, Agrawal D, 2006, Menezes et al., 2007, Leonelli et al., 2008).

To assess their suitability for further applications, polyols obtained from liquefaction process are generally characterized in terms of hydroxyl index, acid number, viscosity, and molecular weight. Shengjun and coworkers (Shengjun et al.,2014) showed that at the early stages of the liquefaction process, a large amount of macromolecules are released, being then gradually degraded with the molecular weight of the polyols decreasing accordingly. However, the occurrence of re-condensation reactions during the last stage of the process results on the molecular weight increment. This will leads to a decrease of the polyol’s hydroxyl index, together with an increase of the polyol’s acid number, as the liquefaction proceeds. The decrease of polyol hydroxyl’s content is directly related with the presence of oxidation and dehydration reactions, where the hydroxyl moieties are consumed. These factors lead to the formation of organic acids from the decomposition of lignocellulosic biomass and/or the oxidation of polyhydric solvents, which usually results on a decrease of the polyol viscosity as the liquefaction process proceeds (Shengjun et al., 2014).

2.5. Characterization of the liquefaction-Derived Polyols

The liquefaction-derived polyols are typically characterized in terms of their major functional groups (hydroxyl index, acid number), solid residues and viscosity. Moreover, the chemical structure is also checked by Fourier Transform Infrared Spectroscopy (FTIR).

The solid content of polyols results from the unconverted biomass residues and is dependent on the liquefaction efficiency. The solids presence is directly related with the viscosity, once high solids content results in more viscous polyols, which are more difficult to process (Adkins and Chauk, 2007).

Considering the final application of the polyols, the hydroxyl index is of major importance, once it will dictate their utility. The hydroxyl index is generally determined by esterification, being the procedure adopted based on the ASTM D1638 standard, and is expressed in mg KOH per g of sample (Kafrani and Hossein, 2016, Cateto et al., 2009)

Regarding the FTIR analysis, through the polyol spectra analysis it is possible to identify the presence of the major functional groups, among other particularities. It is generally used to determine the structure of the bio-based polyol.

Based on the characterization results, these final products may be used as raw materials for polymer synthesis, like polyurethanes and polyesters.

3. Materials and methods

3.1. Reagent grade:

The reagents used for the liquefaction reaction and polyols characterization are listed in Table 3. All the reagents were of analytical grade.

Table 3 Used reagents for lignin liquefaction and characterization

Reagent	Brand	Average Molecular weight (g/mol)
Polyethylene glycol 400 (PEG400) $HO(C_2H_4O)nH$	PanReac	380-420
Glycerol $C_3H_8O_3$	Merck Millipore	92.1
Sulfuric acid H_2SO_4 95.0-97.0%	Sigma-Aldrich	98.08
1.4 Dioxane	Riedel- de Haën	88.106
Sodium hydroxide (NaOH) PA	Panreac	40
Pyridine (C5H5N) PA	Panreac	79.10
Phthalic anhydride (C8H403) PS 98%	Panreac	170.16
Potassium hydrogen phthalate (KHP)	Panreac	204,22
Imidazole	Sigma-Aldrich	68.08

3.2. Liquefaction process of lignin:

Lignin was provided by Borregaard LignoTech, Borresperse NA. It is sodium lignosulphonate, and is characterized by uses as dispersant for wettable powders, dry flowables and extruded water dispersible granules

Liquefaction was performed under two different methods; conventional reactor liquefaction and Microwave assisted liquefaction.

3.2.1. Conventional reactor liquefaction:

A mixture of PEG400 and glycerol in the proportion (90/10, w/w) was used as the solvent in the liquefaction process. The solvents are previously dried overnight in a vacuum oven at 45ºC. Different catalyst (H_2SO_4) contents were used (1, 2, 3 wt% of the solvent). The catalyst was added into a three neck flask reactor (250 mL) equipped with mechanical stirrer, temperature control and condenser (Figure 6). When the temperature of liquefying reactive mixture reached the setpoint value (140, 160 and 180°C), a specific quantity of lignin oven dried was gradually added. This quantity corresponds to a ratio lignin/solvent of 0.2. The mixture was continuously stirred during 1h. The liquefaction process is supposed to give rise to a homogeneously liquefied product. After reaching the established reaction time, the flask was cooled down to stop the reaction and the liquefied products collected for further use and analysis.

Figure 6 Conventional reactor assembly used in the present study.

3.2.2. Microwave assisted liquefaction:

Biotage® Initiator+ represents the latest in microwave synthesis performance (Figure 7). Reactions are performed in glass vials sealed with caps and heated in the microwave cavity. The reaction mixture is continuously mixed by magnetic stirring promoting homogenous heating throughout.

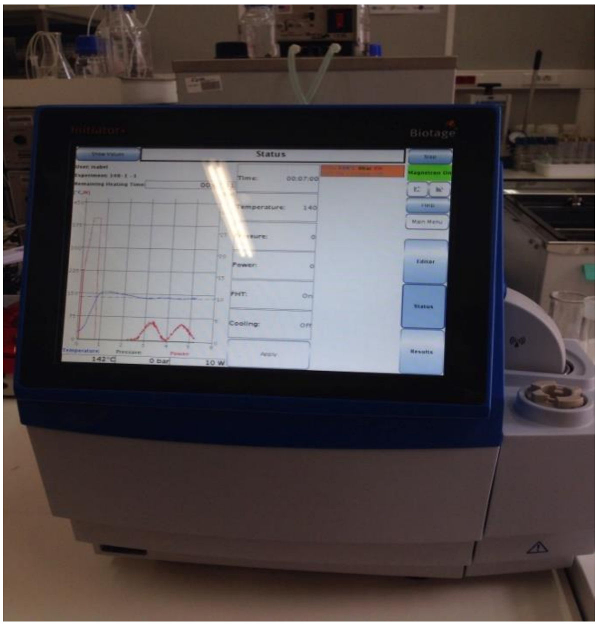


Figure 7 Biotage® Initiator+ Microwave Synthesizer

The experimental procedure comprised the mixture of solvent, lignin and catalyst added to the vessel (20 mL). The added quantities are equivalent to the ones used in the conventional reactor. Lignin-solvent ratio correspondent to 0.2 with PEG400 and glycerol at the proportion 90/10 (w/w) used as solvent. The catalyst ranged from 1 to 3%. After loading, the vessel is incorporated in the microwave equipment. The parameters are settled as follow; temperature (180, 160, 140°C), time (7 minutes) pre-stirring (2 minutes). At the end of the procedure, the vessel is automatically cooled down.

3.3. Characterization

3.3.1. Liquefaction yield:

After cooling, 1g of the liquefaction product was diluted in 20 ml of dioxane/water mixture (80/20 v/v), and the obtained mixture stirred for 4h. A vacuum-filtration was performed via a pre-dried fritted glass filtering crucible with a layer of glass fiber filter (1.6µm) to remove the remaining solids, which were thereafter dried to constant mass. The crucible was dried at 40°C overnight under vacuum. All the measurements were done in duplicate.

The used system is showed in Figure 8.

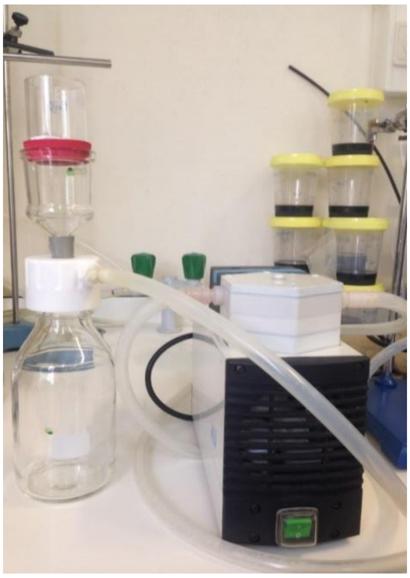


Figure 8 Vacuum filtration system

The liquefaction yield (η) and the residues content (%, w/w) were calculated as the weight percent based on the starting sample material according to Eq. 1 and 2.

$$\textbf{Residues (\%)} = \left(\frac{W1-W2}{W}\right) \times 100 \qquad \textbf{Equation 1}$$

$$\boldsymbol{\eta} = (100 - Residues) \qquad \textbf{Equation 2}$$

Where:

w_1 – weight of the crucible before drying in g

w_2 – weight of the crucible after drying in g

w – weigh of the polyol sample in g

3.3.2. Acid Values and Hydroxyl Number Determination

The acidity (An) which can interfere in the hydroxyl index (IOH) determination of the lignin-based polyol was determined by titration according to the American Society for Testing Materials (ASTM) D1638 standard.

If samples present acidity or alkalinity the hydroxyl number needs to be corrected. For that purpose, 0.4 g of polyol was dissolved in 50 mL of solvent (1.4-Dioxane/water, 4:1, v: v). After being totally dissolved, the mixture was titrated with 0.095 M KOH solution in ethanol. All measurements were carried out in duplicate. The amount of milligrams of KOH required to neutralize the acid present in one gram of sample was calculated following equation 3.

$$\mathbf{An} = \frac{(\boldsymbol{V_2}-\boldsymbol{V_1})*\boldsymbol{M}*\mathbf{56.1}}{\boldsymbol{W}} \qquad \textbf{Equation 3}$$

Where An = acid number (mg KOH. g−1);

V_1 = volume of the KOH solution in ethanol needed to titrated the blank (mL);

V_2= volume of the KOH solution in ethanol needed to titrated the sample (mL),

M= Concentration (M) of the KOH solution in ethanol;

W = amount of sample (g)

The value 56.1 correspond to the molecular weight of the KOH.

As for the hydroxyl index, the used reagent used needs to be prepared a day before. For that, 140g of phthalic anhydride is dissolved in 2L of pyridine and kept in dark overnight.

To determine the IOH number, 1g of the polyol is weighted and then mixed with 25mL of the phthalic reagent. The samples and the blanks are heated during 30min under 115°C. After that, the mixture is cooled at the room temperature and then added with 50ml of pyridine. The mixture is titrated with sodium hydroxide solution (0.5M). The IOH number is calculated based on the difference between the NaOH volume required for the titration of the blank and the volume required for the polyol sample. The titrations were carried out using an automatic titrator (TitroLine 6000, SI Analytics) equipped with a glass electrode (Figure 9).

The hydroxyl index (hydroxyl number) is defined as the amount of KOH in milligram equivalent to the OH content in 1 g of liquefied product (mg KOH.g−1). Corrected hydroxyl number was calculated using Equation 4.

$$\mathbf{IOH} = \frac{(\mathbf{V_1} - \mathbf{V_2}) * \mathbf{C} * \mathbf{56.1}}{\boldsymbol{W}} + \mathbf{An} \qquad \textbf{Equation 4}$$

Where:

IOH = hydroxyl number (mg KOH. g−1); the sample (mL);

V_1 = volume of the NaOH solution needed to titrate the blank (mL);

V_2 = volume of the NaOH solution needed to titrate the sample (mL);

C = is the NaOH concentration, in mol/L

W= amount of sample (g); and An = acid number (mg KOH. g−1).

56.1 corresponds to the molecular weight of KOH;

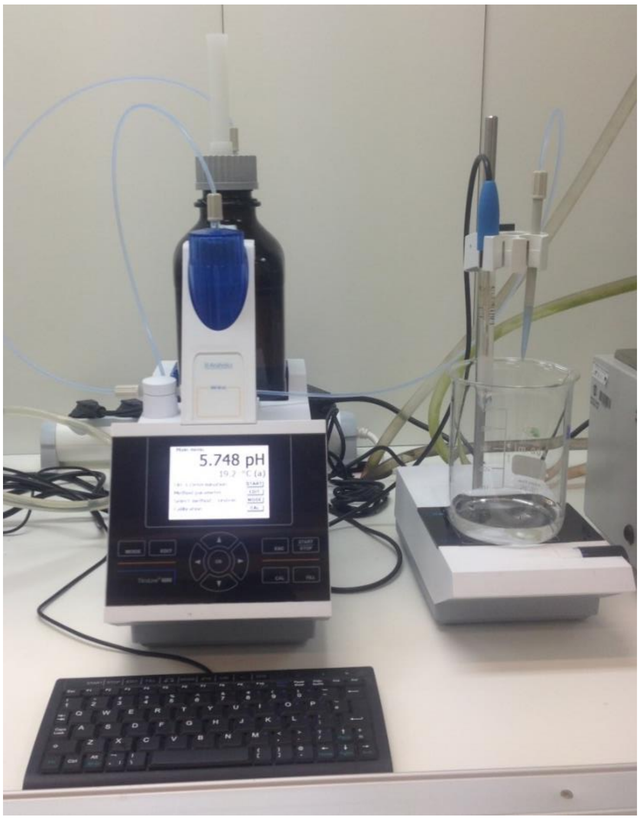


Figure 9 Automatic titrator Titroline 6000, SI Analytics.

3.3.3. Viscosity (μ):

This procedure was carried out using a viscometer Visco Star Fungilab, with concentric cylinders. It is equipped with a heating/cooling system that allows the control of the experimental temperature. The most suitable spindle for the measurements done in this work was the TL7. The used sample volume was 9.5mL.

At first the required sample volume is introduce in the cylinder, thereafter put back in the system and the spindle introduced in it. This procedure is performed under 25°C. It is important to start at the lowest cutting speeds to choose the one that allows to obtain values of %EOS (parameter of the measurement control of viscometer) near 90%.

The viscosity reading is kept until a constant viscosity value is reached, or, if this is not possible, the value that remains constant for 30 minutes is accepted.

This procedure is repeated twice for each polyol in a way that the difference between two measurements doesn’t surpass 3%.

3.3.4. Fourier Transform Infrared Spectroscopy:

A FTIR Bomem, Model MB 104, operating in the medium infrared range (500-4000 cm^{-1}) was used. The used software was Grams /32, being used to analyze and processing data in order to identify the main vibrations of the characteristic chemical groups.

4. Results and discussion

4.1. Effect of reactor type on liquefaction

To fully investigate the effect of the used liquefaction procedure (conventional or microwave heating) on lignin liquefaction, the reaction parameters were maintained identical for the two procedures (i.e., the conventional reactor or microwave reactor), As previously mentioned, the use of a microwave reactor provides numerous advantages, including rapid heat-up times, lower degradation of reagents and efficient energy absorption, to yield results similar to the ones achieved with conventional heating methods, The used experimental conditions in microwave reactor and conventional reactor modes are described in Table 4.

Table 4 the experimental conditions used for the microwave conventional reactor modes.

Reactor Type	Temperature (°C)	Time (minutes)
conventional reactor	140, 160, 180	60
Microwave reactor	140, 160, 180	7

Traditional heating depends on convection and thermal conductivity of materials, we have a certain loss of energy that leads to a lower temperature inside the vessel than required. (Krzan and Zagar 2009).

In contrast, microwave irradiation heats the bulk of the materials simultaneously by dipolar polarization and ionic conduction. The ability of a specific material or solvent to convert microwave energy into heat at a given frequency and temperature is determined by the tan δ of that material. In general, a reaction medium with a high tan δ has a good absorption of microwave energy and results in efficient heat. Ethylene glycol has a high tan δ value of 1.35, compared to that is 0.123 of water (Kappe., 2008). When PEG, the polymer form of ethylene glycol, was used as the liquefaction solvent and subjected to microwave heating, the temperature of the reaction system increased very quickly to the required temperature, and the liquefaction reaction likely reached an equilibrium stage within 3 min. The reaction could then be controlled by some other factors, such as the efficiency of the catalyst, rather than liquefaction temperature.

The advantages attributed to the microwave heating system makes it more and more interesting to adopt.

4.1.1. Effect of solvent type and catalyst on liquefaction

The liquefaction process is generally carried out at high temperatures, employing appropriate reagents and catalysts that have reactivity towards the lignin. In most of the literature works, the liquefaction reagents are alcohols such as phenols or glycols, e.g. glycerol and polyethylene glycol (PEG). The catalysts mostly used are strong acids like sulfuric acid. In this process the lignin is firstly degraded into fragments of lower molecular weight. The decrease of the molecular weight was also due to the incorporation of a large amount of PEG and glycerol. Then, the polyols are said to be formed by condensation reactions between the hydroxyl groups of glycerol and/or polyethylene glycol (PEG) and those of lignin, this leads to ether bonds in the liquefied products.

In the last step, fragments of residual lignin are produced due to self-polymerization reaction (Zhen et al., 2017) and the fragments re-condensed to form the residue.

Literature data confirm that glycerol can be successfully applied as a liquefying agent to the manufacturing of polyols from various types of biomass.

Advantages of glycerol in liquefaction process can be summarized as follows:

- Higher boiling/thermal degradation temperature;
- Polarity;
- Dehydration effect;
- By-product from biodiesel and soap productions.

The addition of glycerol to PEG400 plays a key role on the acceleration of the liquefaction rate and the retardation of the re-condensation reactions to enhance polyol formation yield. The ratio of PEG400 to glycerol for biopolyol synthesis was optimized in order to maximize the biomass conversion. This is the case of Yoon Ju.J and coworkers (Y.J. Jo et al.,2015) who used a PEG400 to glycerol ratio varying in the range of 5:5 to 10:0 (w/w). It was found that the biomass conversion increased as the ratio of PEG400 to glycerol was increased from 5:5 to 9:1 (w/w).

Conversely, the biomass conversion decreased as the ratio of PEG400 to glycerol ratio was increased from 9:1 to 10:0 (w/w). In terms of the viscosity of the biopolyol, it decreased as the ratio of PEG400 to glycerol increased from 5:5 to 9:1 (w/w), and then increased as the ratio was further increased.

Increasing the content of polyethylene glycol in the liquefaction solvent could accelerate the liquefaction, and thus increase the biomass conversion. However, when using pure PEG400 as the liquefaction solvent, the biomass conversion was lower when compared to the situation where a mixed solvent (PEG400/glycerol = 9/1) is used. This is due to the fact that glycerol greatly retarded the re-condensation and/or re-precipitation of the liquefied products.

According to some works published in the literature (Y. Jin et al., 2010, Yip. J et al 2009), it was found that the smaller the molecular weight PEG, the more beneficial it was for the liquefaction under the same processing conditions, and the liquefaction efficiency reached the highest rates.

The obtained results are roughly in accordance with the data published in literature when PEG400 was chosen as the main liquefied solvent for lignin (Appendix A, B). The hydroxyl number of liquefaction product, obtained by using PEG400 as the main liquefied solvent, reached 302 mg KOH/g using conventional reactor (conventional heating system) and 407 mg KOH/g (microwave reactor). Sulfuric acid promoted not only the degradation of lignin in the earlier stages but also the re-condensation of fragments in the later stage (Ge et al., 2003). Especially, lignin fragments are more apt to re-condense in acid medium (Chen and Lu, 2009).

In this work it was showed that the hydroxyl number decreased as the sulfuric acid to solvent ratio increased from 1% to 3%, whereas the residue content decreased as shown in Figure 10. These results pointed out that, increasing the catalyst loading reduces considerably the obtained residues. Also the type of reactor influences this parameter. It was found that microwave heating system gives rise to lower residues content, comparatively with conventional heating system when using the same experimental parameters.

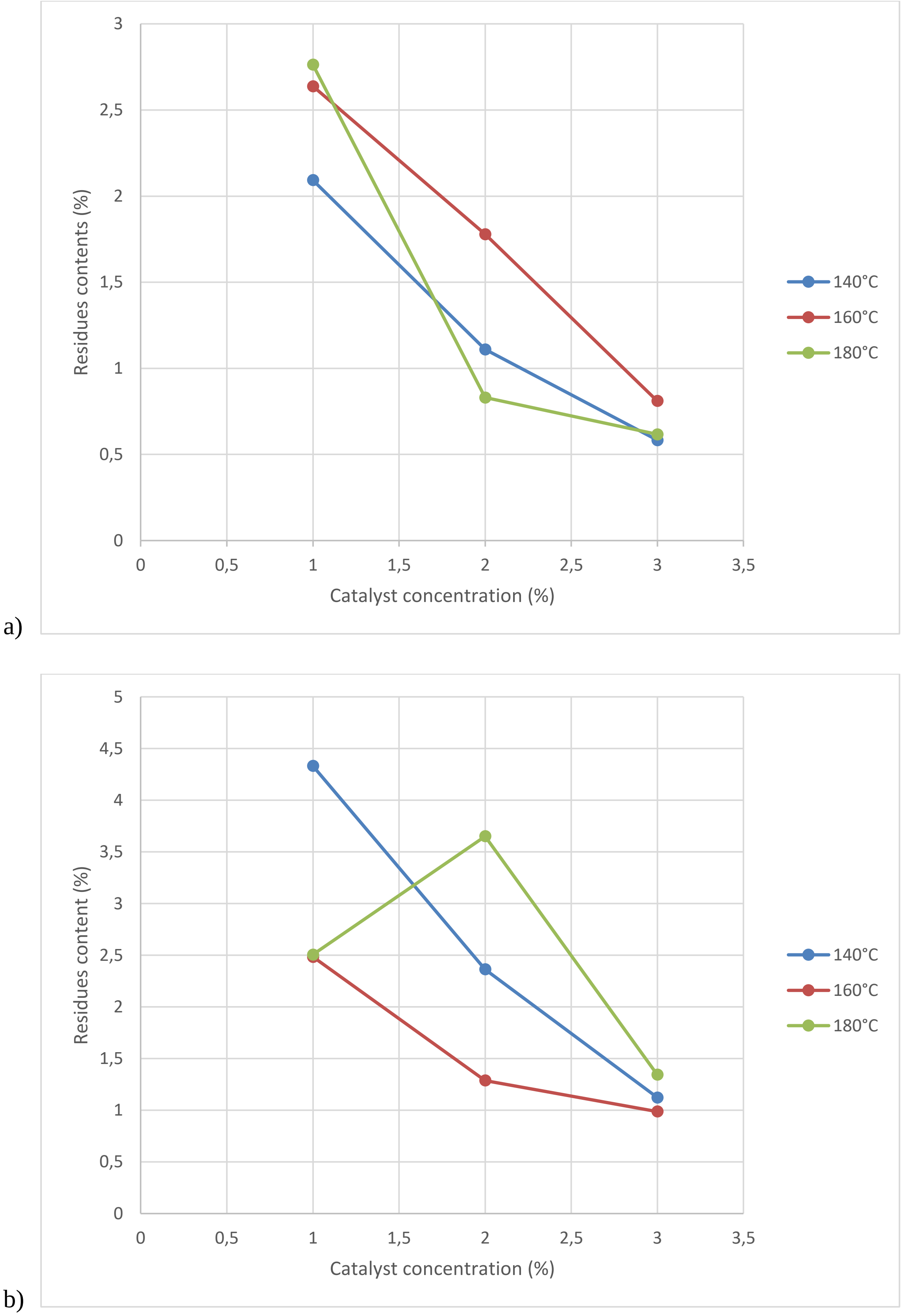


Figure 50 The effect of acid concentration for, (a) conventional reactor (b) microwave reactor, on residues content, Reaction conditions: temperature, 140°C; liquefaction solvent, PEG400/glycerol = 9/1

4.2. Effect of temperature on the liquefaction

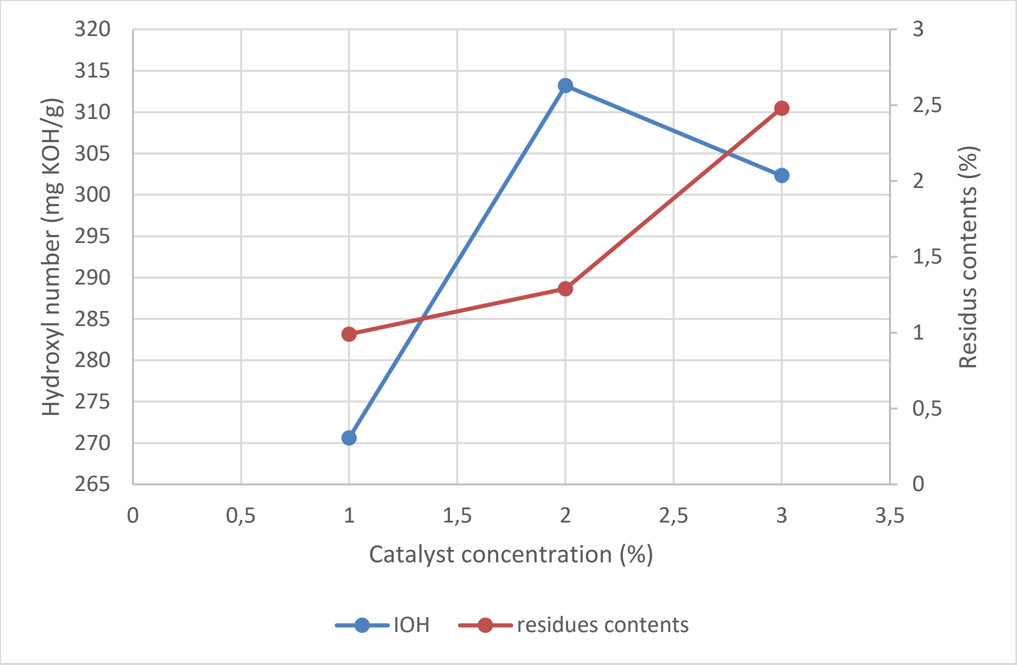
The liquefaction temperature is an important factor that impacts on the achieved residues content and energy saving. Raising the temperature would promote the decomposition of lignin and increase re-condensation reactions of the liquefaction intermediates (Chen and Lu, 2009).

Liquefaction yield increased rapidly with temperature increase. In this study, the temperature ranged from 140 to 180°C. It was found, as shown in table 5, that when the liquefaction temperature was 140°C, the hydroxyl number of the product reached the highest value (259.40 mg KOH/g), for the conventional reactor, and 407.40 mg KOH/g for microwave reactor. In terms of residues content, it was reached 4.33% and 2.09%, respectively for conventional and microwave reactor. This residues values are quite predictable since they are relative to the lowest catalyst concentration, and as previously mentioned, the hydroxyl number decreased as ratio of sulfuric acid to solvent increases. By increasing the temperature, it is noticed an increase in the hydroxyl number, and a decrease in the residue content. Figure 12 reflects this results, i.e. when the liquefaction temperature raised to 160°C, the hydroxyl number was 302 mg KOH/g, and the residue content 2.48% in the conventional reactor case. The opposite happens for the microwave reactor, where the hydroxyl number decrease to 213 mg KOH/g and the residues content goes to 2.64%

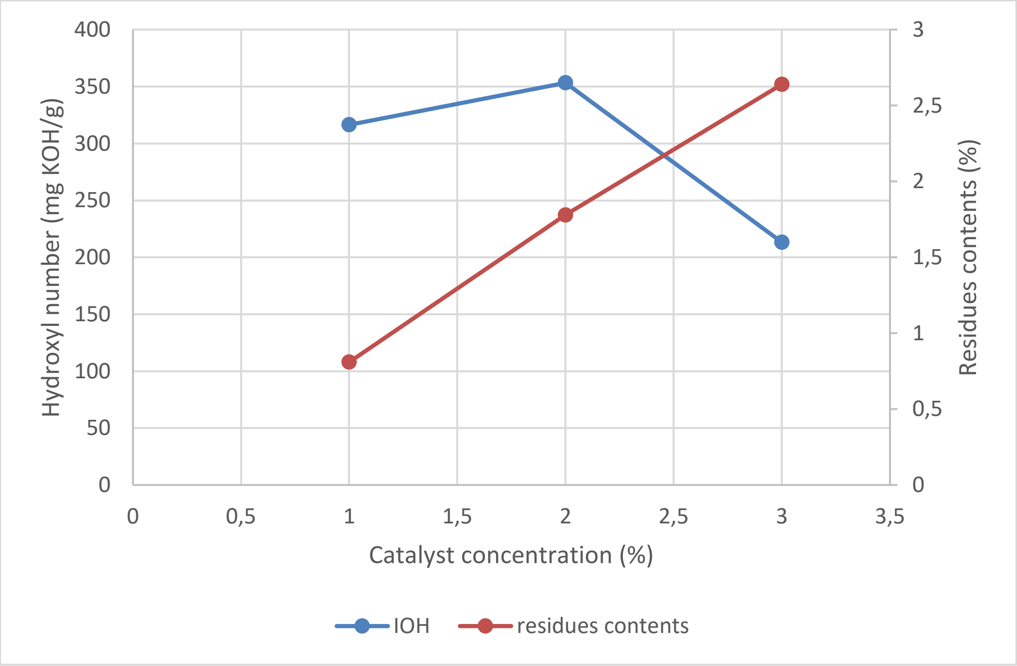
When the temperature is higher than 160°C, the hydroxyl number decreased and the residues reached higher values. This could be explained by the fact that the hydroxyl groups were decomposed and converted to products, such as organic acids, at high temperatures. Re-polymerization of liquefied products took then place and the residue percent slightly increases.

Table 5 Unreacted residues and hydroxyl number for polyols obtained at 140°C,160°C and 180°C using different catalyst to solvent ratios (1%, 2%, 3%) for conventional reactor and microwave reactor.

Temperature	Sulfuric acid ratio	Hydroxyl number		Residues content	
		conventional Reactor	Microwave reactor	conventional Reactor	Microwave reactor
140	3%	196.21±9.79	323.28±11.08	1.12±0.19	0.58±0.51
	2%	254.72±7.64	329.85±29.9	2.36±0.3	1.11±0.24
	1%	259.40±5.48	407.40±6.97	4.33±0.29	2.09±0.18
160	3%	282.30±1.8	329.22±3.03	0.99±0.01	0.81±0.12
	2%	313.20±7.63	357.19±11.06	1.29±0.4	1.78±0.012
	1%	302.33±17.89	213.36±12.07	2.48±0.29	2.64±0.24
180	3%	196.93±2.72	313.44±5.64	1.34±0.32	0.62±0.12
	2%	211.68±1.58	318.52±17.48	3.65±0.12	0.83±0.22
	1%	296.44±3.46	381.67±2.37	2.50±0.21	2.76±0.091



a)



b)

Figure 61 The effect of acid loading for, (a) conventional reactor (b) microwave reactor, on residues content and hydroxyl number. Reaction conditions: temperature, 160°C; liquefaction solvent, PEG400/glycerol = 9/1

4.3. Hydroxyl number

As shown in the Figures 12 and 13 the hydroxyl number decreases by increasing the catalyst concentration. For the conventional reactor, and for the lowest temperature, the value has dropped from 259.03 mg KOH/g to 187 mg KOH/g by increasing the catalyst concentration from 1% to 3%. However, for the microwave reactor, the hydroxyl number is much higher under the same conditions; a value of 407 mg KOH/g has been recorded for a concentration of 1% of H_2SO_4, which drops to 323 mg KOH/g for 3% of catalyst.

By raising the temperature to 160°C, different behaviors in both reactors were achieved. For the conventional reactor the hydroxyl number raises, when compared to the value at 140°C, yet it decreases for when using the microwave reactor. However, by conducting the reaction above 160°C, the hydroxyl number deceases dramatically, for both cases, to reach their lowest values; 297 mg KOH/g, 196 mg KOH/g respectively for microwave heating system and conventional heating system.

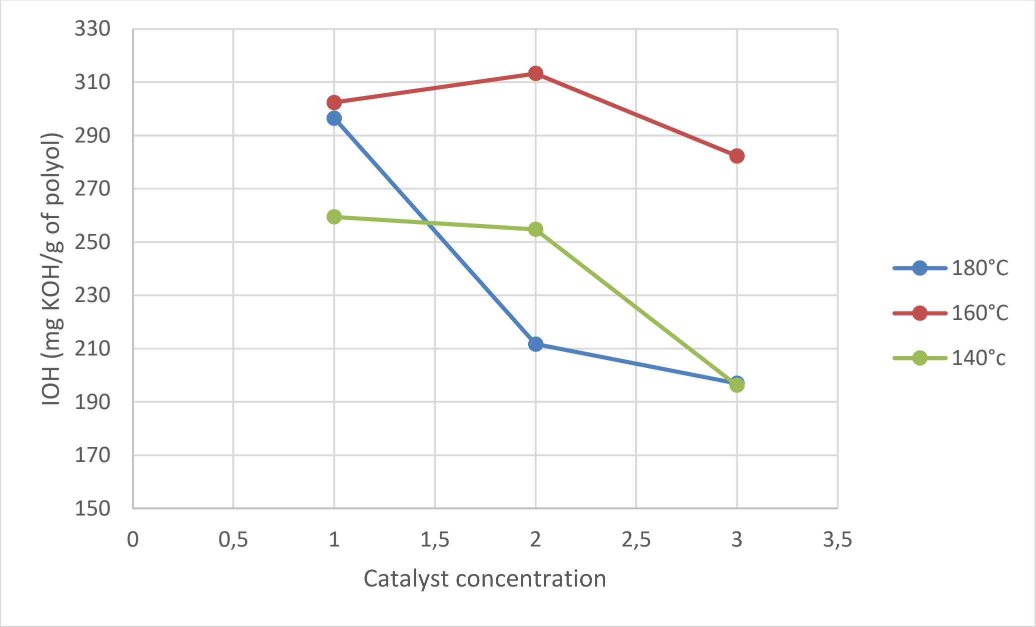


Figure 72 Evolution of hydroxyl number as a function of catalyst concentration for the series 140°C, 160°C and 180°C using conventional heating system.

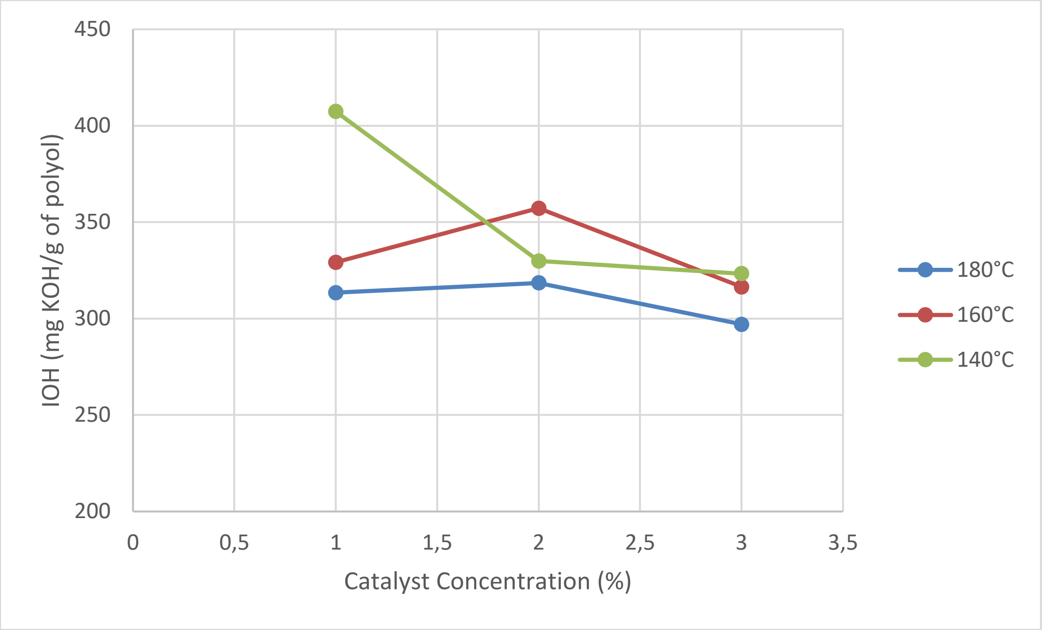


Figure 83 Evolution of hydroxyl number as a function of catalyst concentration for the series 140°C, 160°C and 180°C using microwave heating system.

4.4. Liquefaction Yield and Viscosity

The liquefaction yield increased by increasing the catalyst concentration, however, the liquefaction yield was slightly reduced when the temperature reaches 180°C. This could be attributed to the re-condensation polymerization of the lignin fragments during the liquefaction process. In contrast, according to recently published literature of Jin and coworkers (Jin et al., 2011) the optimal liquefaction yield under conventional heating condition was 98.4%, but the hydroxyl number of the liquefied products were relatively low. Moreover, the liquefaction time was long (60 min). Sequeiros et al (2013), showed that the optimal liquefaction yield under microwave heating could reach up to 99.07%; however, the reaction temperature was 155 °C (Se. Accordingly, 20 min was the optimal reaction time for microwave-assisted liquefaction of the lignin, with a maximum liquefaction yield of 98.75%. A fact should be considered, i.e. that the shorter times in the microwave-assisted liquefaction, comparatively with conventional reactions, can contribute to the flexibility of the process facilitating the development of a continuous process. Furthermore, the microwave heating time did not significantly influences the liquefaction yield; thus, 5 min could be selected as the alternative microwave heating time.

In this study, 7 min in a microwave reactor were enough to obtain ≈ 99% of conversion yield, and products with a hydroxyl number close to 300 mg KOH/g

The viscosity was found to be dependent on the composition of the liquefying agent. Thus, the viscosity evolution revealed that, within a series, it increased with the catalyst content increase, as shown in the figure 14. However, increasing the reaction temperature, viscosity of the ensuing polyols decreased. This is probably due to a higher reaction extent, as expected from higher reaction temperatures.

The data revealed that, for the microwave reactor, the viscosity oscillated in the same range, the lowest value was 0.626 Pa.s, whereas the highest was 0.926 Pa.s, for a conversion yield between 97% and 99%. As previously mentioned, condensation of solvent occurs during the liquefaction process, suggesting the generation of higher molecular weight products, hence contribute to the increase in viscosity.

The viscosity of the obtained polyols, when using conventional heating, was higher and a different behavior was showed. By raising the temperature from 140°C to 180°C, the viscosity goes from 0.77 Pa.s to 85 Pa.s. This can be explained by the fact that due to the increase of the pressure inside the reactor during heating, some of the solvent is lost by evaporation since the device was not welded. This phenomenon has led to a significant increase in the viscosity of the liquefied products produced under high temperatures.

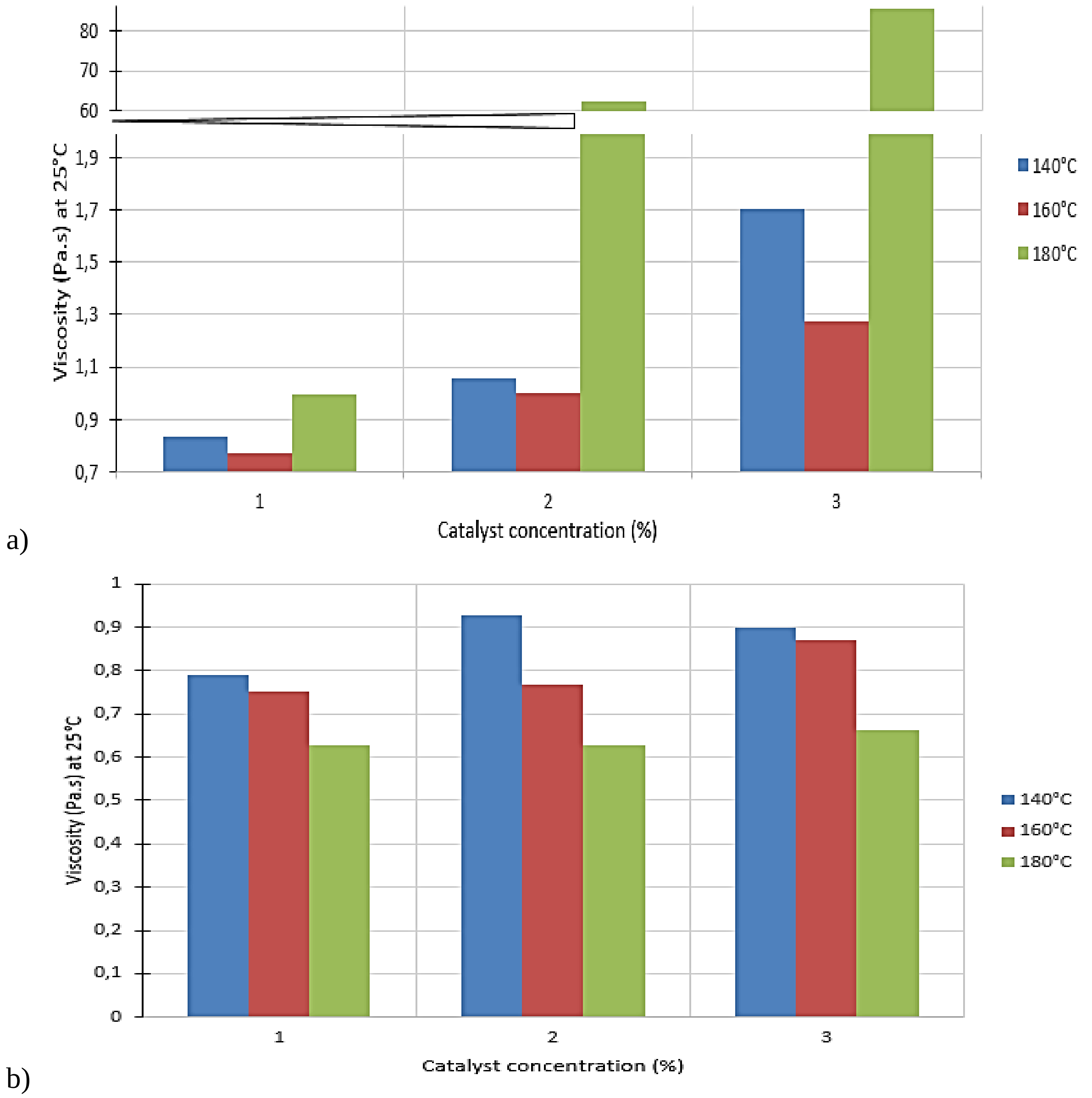


Figure 94 Evolution of viscosity at 25°C as a function of catalyst content for the series 140°C, 160°C and 180°C: a) conventional reactor and b) microwave reactor.

4.5. FTIR analysis of biopolyol

Figures 15 and 16 present the FTIR analysis of the produced biopolyols. The relatively large peak at 3300-3400 cm^{-1} corresponds to the stretching vibrations of hydroxyl groups, the signals in the 2940–2870 cm^{-1} region were attributed to the stretching of CH_3, CH_2 and CH aliphatic groups (Collier et al. 1997). On the other hand, the stretching vibrations associated with the C–O and C=O groups were assigned at 1220 cm^{-1} (Schwanninger et al. 2004). The bands characteristic of the C–O–C ether groups were found in the range of 1050–1000 cm^{-1}; their intensity suggests that the obtained polyol is polyether based polyol (Gottwald and Watcher 1997; Grube et al. 2006; Cai et al. 2007). The peak observed at 940 cm^{-1} resulted from the C=C or C–H out-of-plane vibrations of the aromatic rings of the lignin (Faix., 1991). The overall data is summarized in Table 6.

Table 6 Identification of the different chemical functional groups present in the produced polyols

Wavenumber (cm^{-1})	**Identification**	**Comment**
3401-3408	O-H	Large peak
2863-2870	CH_2	Small peak
1050–100	C–O–C	Sharp peak
1220	C–O	Small peak

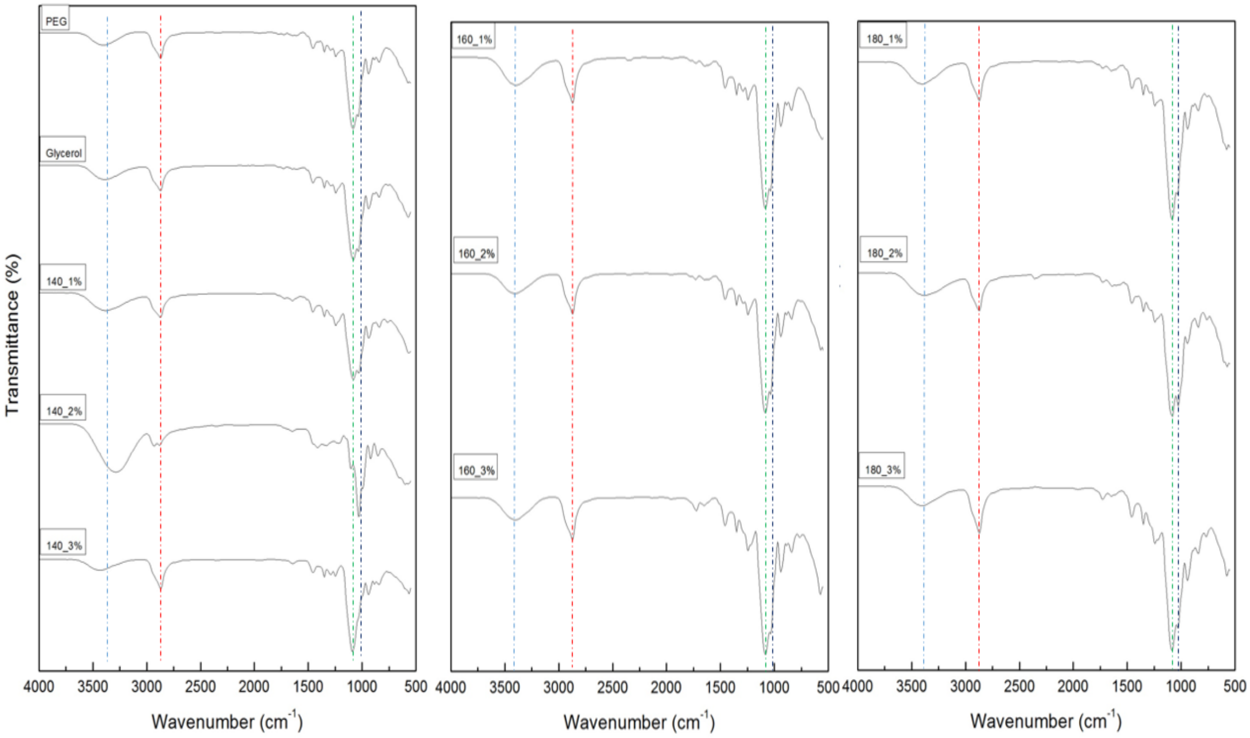


Figure 15 FTIR analysis of the polyols obtained with the conventional heating system at different temperatures (a: 140°C, b: 160°C, c: 180°C)

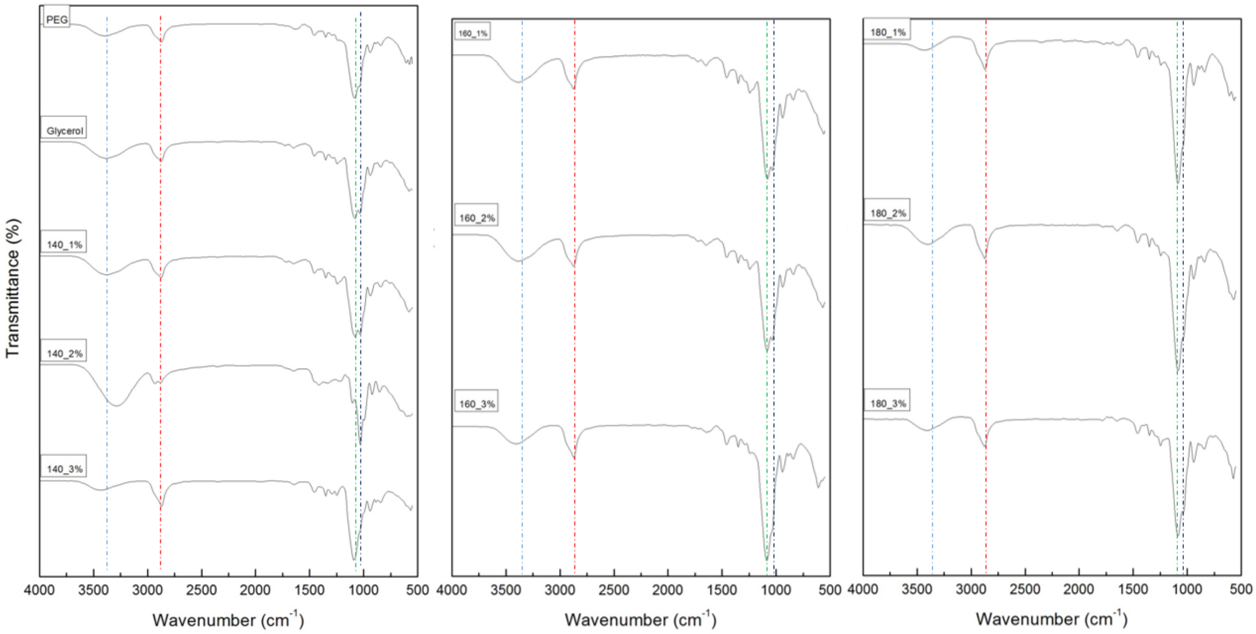


Figure 106 FTIR analysis of the polyols obtained with the microwave heating system at different temperatures (a: 140°C, b: 160°C, c: 180°C)

5. Conclusions and future work

As the most abundant aromatic polymer in earth, lignin has a great potential commercial value due to its properties. However, the complex and irregular structure of lignin poses large obstacles to its use. To disrupt the structure, heating is normally adopted and considered as an effective procedure. Among the current technologies for heating, microwave irradiation has been widely used and proven to be efficient for biomass conversion.

Although lignin has the potential to be converted into chemicals, there are only a few commercial scalable processes, such as vanillin production. The situation is mainly caused by the lack of competitive technology. In this study, it was showed thar lignin liquefaction into biopolyols is a promising strategy due to its feasibility.

Microwave and conventional conventional reactor were employed to liquefy lignin using crude glycerol and polyethylene glycerol as solvent. The liquefaction was achieved successfully in both reactors. The biopolyols were synthesized at three temperatures (140°C, 160°C and 180°C). The liquefaction was achieved successfully in both reactors and under the three setpoint temperatures. Lignin-based polyols were characterized in what concerns hydroxyl number, biomass conversion, viscosity, and structure. The results showed that the biopolyol obtained in the conventional reactor, and produced at a temperature of 160 °C with a catalyst concentration of 2%, has the following technical properties: IOH = 313.2 mg KOH/g, R = 1.29%, and μ = 1.003 Pa.s. For 3% catalysts the following polyol was achieved: IOH= 282.3 mg KOH/g; R = 0.99%; μ = 1.273 Pa s. These polyols might be suitable to be used in polymer synthesis. The biopolyols obtained with the microwave reactor have the following properties: IOH = 407.4 mg KOH/g; R = 2.09%; μ = 0.788 Pa s, and IOH = 329.85 mg KOH/g; R = 1.11%; μ = 0.926 Pa.s, for 140 ºC and 1% and 2% catalyst, respectively. In a general way, by increasing the catalyst concentration a decrease in the hydroxyl number was observed. Also for temperatures above 160°C the hydroxyl number decreases.

This study pointed out that liquefaction of lignin using glycerol and polyethylene glycerol is a promising alternative to petroleum-based materials, and the application of microwave heating significantly shortens the reaction time, which has a positive effect on the costs of the final product, namely when comparing with the conventional heating process.

The difference in the liquid products obtained from conventional and microwave reactors may be attributed to different reaction pathways. In general, increasing the reaction temperature from 140°C to 180 °C increased product yield. Proximate results were obtained in microwave system and conventional heating system, but with lower energy and catalyst use. The product from liquefied lignin polyols could potentially be developed and turn into a marketable product.

The work could be enriched by studding other parameters and by using other characterization techniques such GPC and NMR. Also the work can be enriched by performing thermogravimetric analysis.

The developed work will be presented in the Conference on Green Chemistry and Nanotechnologies in Polymeric Materials which will be help in Riga, Latvia (9-11 October 2019).

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Appendix A

Table A.1 Summary of characterization (Liquefaction yield, IOH, An and viscosity) of the resulting polyols using microwave heating system

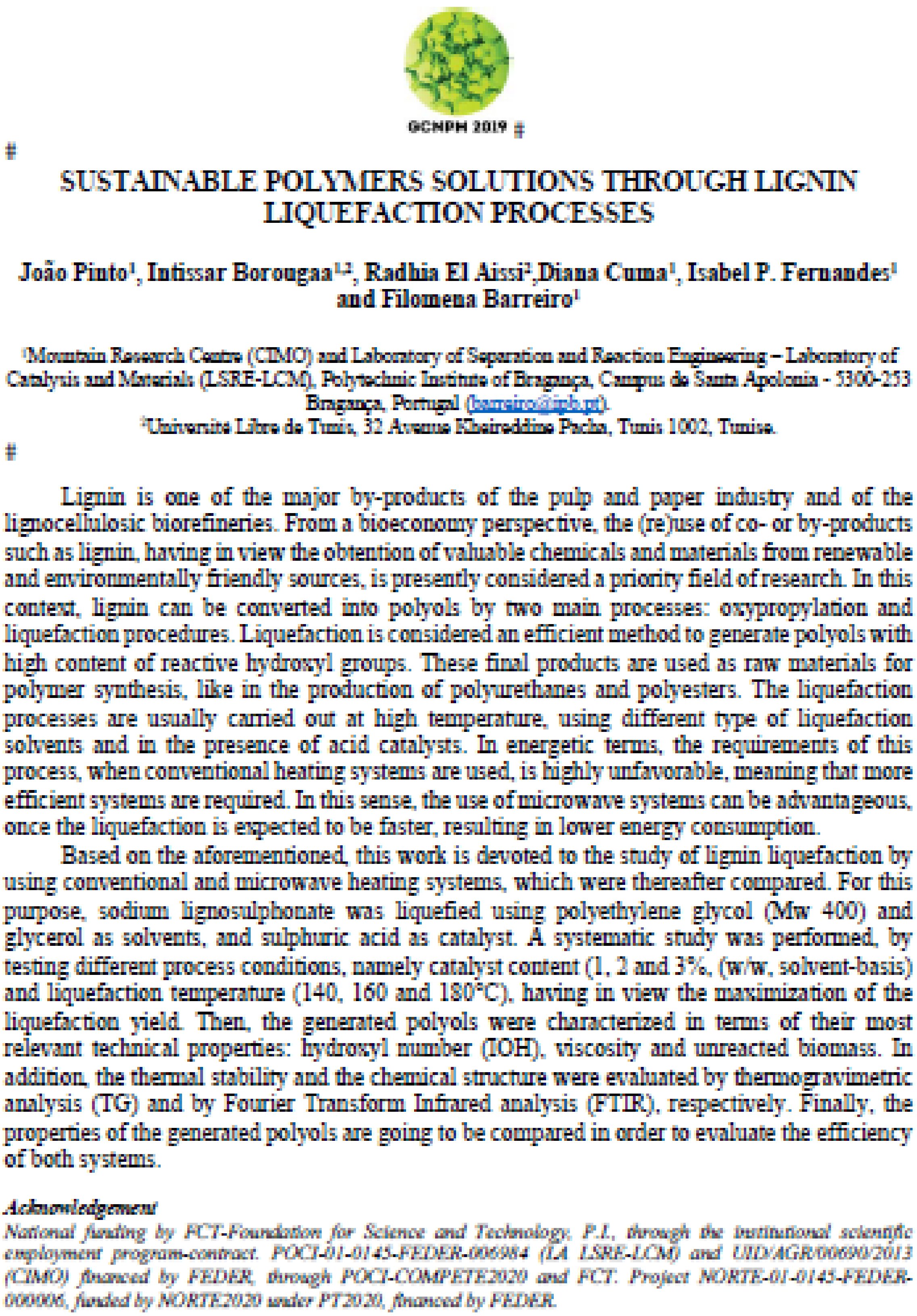
Temperature	Sulfuric acid ratio	Liquefaction Yield (%)		Viscosity (Pa·s) at 25°C		Hydroxyl number (mg KOH/g)		
		Replicas	**Mean value**	**Replicas**	**Mean value**	**Replicas**	**Mean value**	**Corrected IOH**
140°c	**3%**	99.05	99.41	0.778	0.897	304.57	312.41	323.27
		99.78		0.798		320.24		
	2%	99.22	99.05	0.929	0.926	305.30	326.49	329.85
		98.88		0.923		347.59		
	1%	97.77	97.90	0.778	0.788	402.23	407.16	407.40
		98.03		0.798		412.09		
160°C	**3%**	98.98	99.18	0.867	0.868	314.27	316.42	329.22
		93.39		0.869		318.56		
	2%	98.21	98.22	0.767	0.766	345.57	353.39	357.19
		98.23		0.765		361.22		
	1%	97.53	97.36	0.766	0.752	402.90	213.36	-
		97.18		0.738		385.82		
180°C	**3%**	99.29	99.38	0.661	0.662	293.02	297.01	313.44
		99.47		0.664		301.01		

	2%	99.32 99.01	99.16	0.630 0.623	0.626	324.70 299.97	312.33	318.52
	1%	97.30 97.17	97.23	0.630 0.622	0.626	379.98 383.34	381.66	-

Table A.2 Summary of characterization (Liquefaction yield, IOH, An and viscosity) of the resulting polyols using conventional heating system

Temperature	**Sulfuric acid ratio**	**Liquefaction Yield (%)**		**Viscosity (Pa·s) at 25°C**		**Hydroxyl number (mg KOH/g)**		
		Replicas	**Mean value**	**Replicas**	**Mean value**	**Replicas**	**Mean value**	**Corrected IOH**
140°c	**3%**	99.01 98.74	98.88	1.703 1.703	1.703	210.06 165.54	187.80	196.21
	2%	97.42 97.85	97.64	1.055 1.055	1.055	259.83 249,02	254.43	254.72
	1%	94.51 96.81	95.67	0.829 0.832	0.83	262.91 255.15	259.03	259.40
160°C	**3%**	99.00 99.02	99.01	1.276 1.270	1.273	271.89 269.34	270.61	282.30
	2%	98.42 98.99	98.71	0.997 1.009	1.003	307.79 318.59	313.20	-
	1%	97.72 97.30	97.52	0.773 0.767	0.77	289.67 314.98	302.33	-
180°C	**3%**	98.42 98.88	98.66	83.759 87.479	85.619	193.93 190.09	192.01	196.93
	2%	96.26 96.43	96.35	61.869 62.377	62.123	210.55 212.79	211.68	-
	1%	97.34 97.64	97.49	0.994 0.990	0.992	293.99 298.88	296.44	-

Appendix B



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SUSTAINABLE POLYMERS SOLUTIONS THROUGH LIGNIN LIQUEFACTION PROCESSES

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Lignin is one of the major by-products of the pulp and paper industry and of the lignocellulosic biorefineries. From a bioeconomy perspective, the (re)use of co- or by-products such as lignin, having in view the obtention of valuable chemicals and materials from renewable and environmentally friendly sources, is presently considered a priority field of research. In this context, lignin can be converted into polyols by two main processes: oxypropylation and liquefaction procedures. Liquefaction is considered an efficient method to generate polyols with high content of reactive hydroxyl groups. These final products are used as raw materials for polymer synthesis, like in the production of polyurethanes and polyesters. The liquefaction processes are usually carried out at high temperature, using different type of liquefaction solvents and in the presence of acid catalysts. In energetic terms, the requirements of this process, when conventional heating systems are used, is highly unfavorable, meaning that more efficient systems are required. In this sense, the use of microwave systems can be advantageous, once the liquefaction is expected to be faster, resulting in lower energy consumption.

Based on the aforementioned, this work is devoted to the study of lignin liquefaction by using conventional and microwave heating systems, which were thereafter compared. For this purpose, sodium lignosulphonate was liquefied using polyethylene glycol (Mw 400) and glycerol as solvents, and sulphuric acid as catalyst. A systematic study was performed, by testing different process conditions, namely catalyst content (1, 2 and 3%, (w/w, solvent-basis) and liquefaction temperature (140, 160 and 180°C), having in view the maximization of the liquefaction yield. Then, the generated polyols were characterized in terms of their most relevant technical properties: hydroxyl number (IOH), viscosity and unreacted biomass. In addition, the thermal stability and the chemical structure were evaluated by thermogravimetric analysis (TG) and by Fourier Transform Infrared analysis (FTIR), respectively. Finally, the properties of the generated polyols are going to be compared in order to evaluate the efficiency of both systems.

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