



Universidad de Valladolid



PROGRAMA DE DOCTORADO EN INGENIERÍA
QUÍMICA Y AMBIENTAL

TESIS DOCTORAL:

Lignin depolymerization by
supercritical water ultrafast reactions.

Presentada por Nerea Abad Fernández para
optar al grado de
Doctora por la Universidad de Valladolid

Dirigida por:
Dr. María José Cocero Alonso
Dr. Eduardo Pérez Velilla

Anyone who never made a mistake never tried anything new.

Albert Einstein.

ABSTRACT	9
INTRODUCTION	13
AIMS AND CONTENTS	25
CHAPTER I: Depolymerization of kraft lignin using sub- and supercritical water.	29
CHAPTER II: Obtention of aromatic monomers from lignin through ultrafast reactions in water using sodium hydroxide as catalyst.....	53
CHAPTER III: Base-catalyzed depolymerization of lignins: influence of lignin nature and valorization of pulping and biorefinery residues.....	79
CHAPTER IV: Simulation of a continuous recovery of low-molecular-weight lignin depolymerization products.	113
CONCLUSIONS	133
ANNEX I: PATENT- Ultra-fast lignin depolymerization.....	139
RESUMEN: Despolimerización de lignina mediante hidrólisis ultra-rápida en agua supercrítica.....	179
ABOUT THE AUTHOR.....	191
ACKNOWLEDGEMENTS	197

ABSTRACT

LIGNIN DEPOLYMERIZATION BY
SUPERCRITICAL WATER
ULTRAFAST REACTIONS.

Surviving on a planet provided with limited resources to support our increasing population is the greatest challenge humanity has faced so far. The main problem is based on that our economy is driven by many technologies that are not sustainable at all. This necessity of developing sustainable technologies capable of addressing such challenges, together with the increasing concern over environmental protection and questions about future availability of petrochemical feedstock have spurred research and development toward new materials from renewable resources environmentally friendly and sustainable. Within this context, lignin, a complex natural polymer obtained as by-product in large quantities in paper industries and biorefineries, arises as a promising candidate for these purposes.

The aim of this thesis is to valorise lignin obtaining low molecular weight aromatic products of high value through an ultra-rapid and environmentally friendly technology employing sub and supercritical water as solvent and reaction medium, in order to achieve high yields and selectivity, which has been a challenge to this day.

Three main products were obtained from the reaction mixture after separation and extraction: a light oil, containing low molecular weight compounds, a heavy oil, containing oligomers, and char.

The research started with studying the effect of the parameters that control the depolymerization of lignin: temperature and reaction time. For this study, Kraft lignin as an example of pulp and paper industry by-product was chosen as raw material. Different temperatures between 300 and 400°C and reaction times as short as 60 ms were studied, with a lignin concentration in the reactor of 0.1% w/w. Increasing temperature and reaction time promoted secondary reactions of repolymerization. At 386°C and 170 ms, the highest yield in light oil (44.6%), as well as the highest selectivity in aromatic monomers (9.9%) were achieved, with a formation of char of only 3.5%.

The second step of this research consisted in increasing both the light oil yield and the monomeric selectivity by adding NaOH at the optimal temperature of

386±2°C, and increasing the lignin concentration 5-times (i.e. 0.5% w/w of lignin in the reactor). Different reaction times below 0.5 s were studied. Using this base-catalysed supercritical water depolymerisation, the reaction reached an optimum point at 300 ms with a light oil yield of 60% and a selectivity in key compounds such as guaiacol, creosol, vanillin and acetovanillone of around 20 wt%. The char formation in this point was surprisingly low (4 wt%).

In the third part of this thesis, the depolymerization process in alkaline supercritical water was extrapolated to real pulp and biorefinery residues, such as as kraft black liquors with low lignin content and to other lignins. The optimal conditions (386°C and 300 ms) were applied to all raw materials for comparison purposes, considering that they were obtained from different biomasses (woody and non-woody) and by different processes (kraft, organosolv, biomass hydrolysis, enzymatic hydrolysis). In addition, it was proven that the proposed technology is equally effective to treat directly industrial black liquors than when using the corresponding technical lignin, obtaining yield higher than 50 wt% to light oil, containing as main monomers guaiacol (2.7 wt%), syringol (3.0 wt%) and syringaldehyde (7.3 wt%).

Finally, as we were focused on the development of a complete continuous process for its future industrialization, in the fourth chapter, the downstream process for recovering the low molecular weight products from the reaction mixture has been simulated using Aspen HYSYS V10. The best separation strategy to obtain an economically and energetically feasible and continuous method was studied. This separation strategy combined flash separators, liquid-liquid extraction and vacuum distillation. Process simulation confirmed that, up to 93.1 wt% of monomers, dimers and trimers could be recovered from the light oil obtained from lignin depolymerization product mixture. The calculated total plant capital investment was about 2.9 M€ for a plant capacity of 15 Tonnes feedstock/day. The estimated minimum light oil price was 3.8 €/kg, which could be a competitive price in the market in the future if interesting applications were found for the light oil.

INTRODUCTION

LIGNIN DEPOLYMERIZATION BY
SUPERCRITICAL WATER
ULTRAFAST REACTIONS.

Lignin is a major component of terrestrial lignocellulosic biomass. The effective utilization of lignin is critical for the accelerated development and deployment of the advanced cellulosic biorefinery. However, we acknowledge that, despite some markets and uses of lignin which stretch back decades, it has been long said in the pulp industry that “one can make anything from lignin except money.” [1]

1. Biomass and biorefinery concepts.

The biorefinery concept embraces a wide range of technologies able to separate biomass (i.e. agricultural, forestry and industrial residues) into their components (i.e. cellulose, hemicellulose and lignin) for their later conversion to value added products, biofuels and chemicals. Cellulose has a strong molecular structure made by long chains of glucose molecules (C6 sugar) and constitutes 30-50% of total lignocellulosic dry matter. Its crystalline structure has high tensile strength and is difficult to break. Hemicellulose is a relatively amorphous component containing a mix of C6 and C5 sugars, which is easier to break down through chemical or thermal processes than cellulose. Hemicellulose constitutes 20–40% of total feedstock dry matter. Lignin, made of phenolic polymers, is essentially the glue that provides rigidity to the structure of plants and trees and it constitutes 15–35% of total feedstock dry matter [2]. Figure 1 shows the lignocellulosic biomass composition and structure.

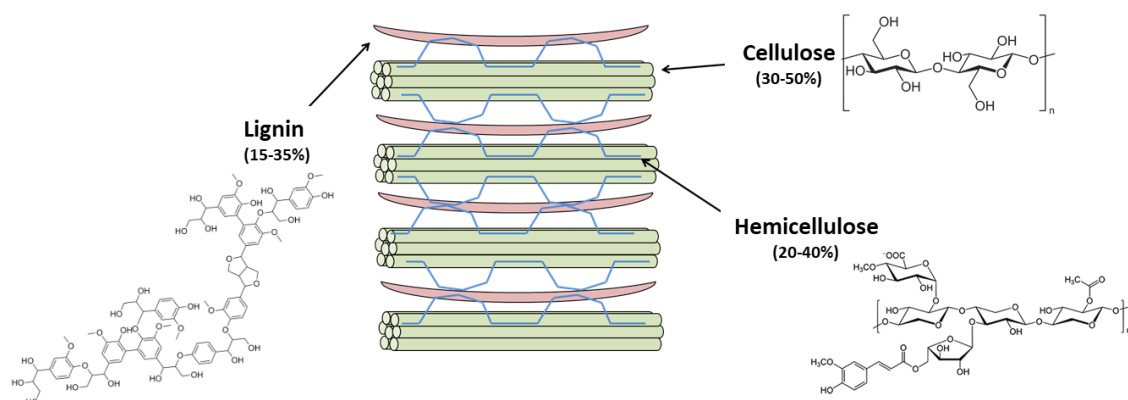


Figure 1. Lignocellulosic biomass composition.

While cellulose and hemicellulose have been used for many years in high-value industrial applications (i.e. paper, textile, plastic, pharmaceutical or fuel), lignin is considered a by-product from paper industry and the modern biorefineries, being mostly consumed as low-grade fuel (Figure 2) [3].

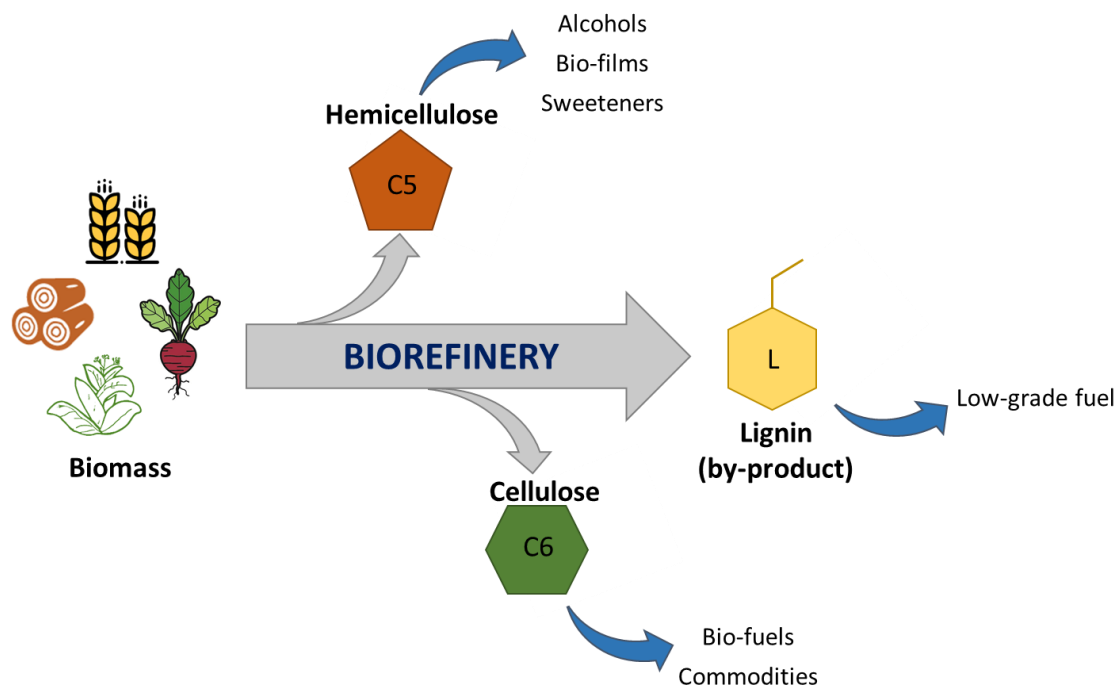


Figure 2. Simplified scheme of a biorefinery process.

However, lignin, as the only large-scale source of renewable aromatic moieties, has a great potential by itself or as a source of chemicals. Thus, its utilization from both an economic standpoint and from a sustainability perspective, is an important consideration for our future [4]. For this reason, research is recently focused on lignin valorisation, trying to find high-value applications of this biopolymer, as well as to produce high-value materials from it, in order to push biorefineries towards a sustainable and cost-effective reality.

2. Lignin.

Lignin, after cellulose, is the second most abundant renewable raw material of organics [5]. It is an amorphous aromatic biopolymer with a highly branched structure. It is widely accepted that lignin comes from the polymerization of three

phenylpropane monomeric units (monolignols), namely coniferyl, sinapyl, and p-coumaryl alcohols. These monolignols produce guaiacyl, syringyl and p-hydroxyphenyl propanoic units into the lignin polymer, where are linked together mainly by ether linkages (e.g. α -O-4, 5-O-4 and β -O-4) and also by C-C bonds (e.g. 5-5, β - β , β -5 and β -1) [6]. It is present in secondary cell walls and confers structural support, impermeability and resistance against microbial attack to the plant [7]. The lignin content differs for hardwood and softwood species and herbaceous plants. In hardwood trees, it is 27–33%, softwood trees 18–25%, and for herbaceous plants it is 17–24% [4]. On the other hand, the number of functional groups and type of linkages in the lignin molecule vary from species to species, tree to tree, and even in woods from different parts of the same tree. Hence, lignin from softwood is composed mainly of moieties derived from coniferyl alcohol (type-G), hardwood lignin contains residues derived from both coniferyl and sinapyl alcohols (type-G and S) [8], whereas lignins derived from grasses and herbaceous crops contain the three basic phenol units (types-H,G and S). In addition, the monolignols in wood are basically linked by carbon-carbon and ether-type bonds [4]. Figure 3 presents a simple and general lignin structure model, as well as a table with the possible linkages in the molecule.

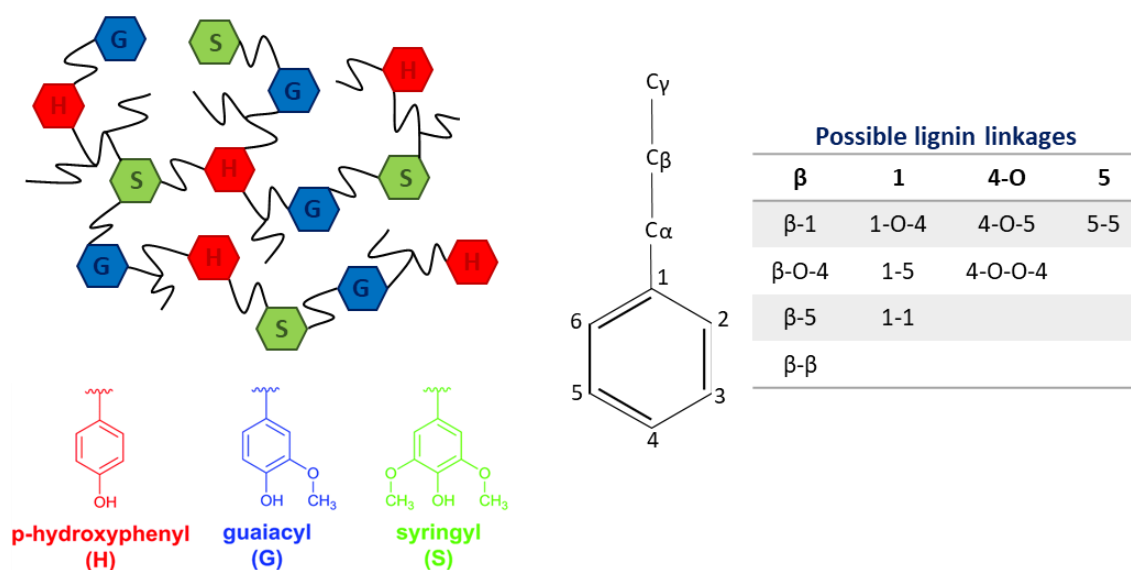


Figure 3. General idea of lignin structure and possible lignin linkages.

3. Extraction of lignin.

Lignin can be obtained through different delignification processes of lignocellulosic biomasses. The lignin extraction process is an essential technique to provide a robust and reproducible process for biomass valorization because it overcomes some physical and chemical barriers that make lignin resistant to later bioprocesses to be converted in high-value products. The lignin extraction technologies are divided in four categories: physical treatment (e.g., ball milling), solvent fractionation (including the organosolv process, together with phosphoric acid fractionation and the use of ionic liquids), chemical treatment (acidic, alkaline, and oxidative), and biological treatment (using mainly fungi).

Some of these delignification methods are soda and organosolv processes. In the soda delignification process, biomass is digested by the treatment with an aqueous solution of NaOH at temperatures of about 160 °C. Lignin depolymerization occurs principally by the cleavage of α - and β -aryl ether bonds and saponification of intermolecular ester bonds cross-linking hemicelluloses and lignin. However, the organosolv process consists on the delignification of wood using organic solvents in order to produce high-quality lignins. In this process, lignin is cooked at temperatures of 100-200°C for 1 h.

On the other hand, lignin can be also recovered from black liquor obtained as residue in pulp and paper industries via precipitation of lignin or using membranes, for example. The acid sulphite pulping process dissolves lignin by applying SO_3^{2-} at acidic environment and 130–160 °C. This sulphite lignin, known as *lignosulfonate*, is produced at a rate of 8–10 million tons per year. The other pulping process, *Kraft* pulping, cleaves the β -O-4 linkages between the phenylpropane units in lignin by sodium sulphide at alkaline environment and up to 170 °C. Since the chemicals in Kraft process can be mostly recovered after use while the sulphite process cannot, the Kraft pulping has gained a dominating role in paper industries covering greater than 80% pulping capacity. The Kraft lignin is produced nowadays at a rate of 40 million tons per year. While lignosulfonate lignin, present in soluble form, is used in market for a huge

number of applications (i.e. dispersants, adsorbents, antioxidant or polymer additives), Kraft lignin, present in insoluble form, is mostly burned onsite to recover energy for process use [8].

A simplified scheme of the lignin recovery processes from biomass and black liquor is shown in Figure 4.

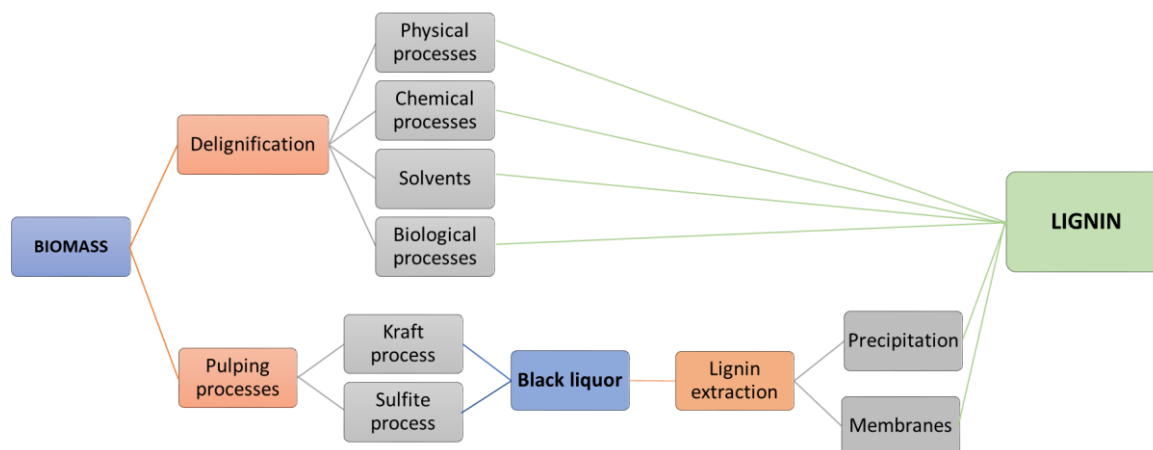


Figure 4. Extraction methods of lignin from biomass and black liquors.

Although many methods are available nowadays for the extraction and purification of lignin from biomass or black liquors, none of them indeed provides a 100% yield and structural authenticity. One of the reasons for the lack of perfect extraction is the aggressive treatment often performed during the process. The extraction method employed directly influences the structure and properties of lignin. Thus, the lignin behaviour, as well as the type of lignin products will depend on not only the biomass source, but also on the extraction and purification strategy previously employed.

4. Valuable products from lignin.

Nowadays, the existing applications of lignin are limited to low value-added products, leading to growing attention being poured into the development of high value-added materials made from lignin [9]. Several routes have been proposed over several years of research to obtain products of interest from this biopolymer. Theoretically, a depolymerization process may break the molecule into a family of phenolic structures, such as vanillin, which is a high-value

INTRODUCTION

chemical because of its properties, pharmacological applications, and use as chemical intermediate for the synthesis of other products. However, the selective transformation of lignin into high value products still remains elusive [4]. Different strategies, including thermolysis, hydrogenolysis, hydrothermal hydrolysis, chemical depolymerisation and reductive or oxidative transformation are being extensively investigated for lignin conversion [10].

Thermolysis is referred to the pyrolytic decomposition of organic matter at elevated temperatures by a rapid heating in the absence of oxygen, in order to avoid combustion of lower molecular weight fragments obtained from biomass. In case of lignin, it is a quite complex mechanism where many parallel radical coupling and rearrangement reactions take place simultaneously. Using catalyst such as zeolite HZSM-5 and high temperatures, interesting products such as BTX can be obtained. However, this technology presents an important handicap: laboratory-scale results found with milligram-scale experiments cannot be extrapolated to large-scale experiments [4].

Hydrogenolysis is referred to the pyrolytic transformation of lignin under reducing conditions in the presence of a catalyst and a reducing agent such as H_2 . Because of the presence of a reducing agent, the oxygen content of the fragments and simpler molecules is lower than that of starting lignin. Phenol-rich mixtures can be obtained from this process, but the procedure requires relatively high pressures and specific expensive catalysts [4].

On the other hand, lignin can be depolymerized and converted into a liquid mixture of hydrolytically transformed products by treatment with water, and even supercritical water, at high temperatures and pressures. Hydrothermal hydrolysis, compared to other lignin-degradation methods, shows three main advantages: 1) It is not necessary to carry out a pre-drying procedure, directly transforming papermaking wastewater lignins; 2) nitrogen and sulfur oxides formed in other degradation processes can be dissolved directly in water, and further treatment is not needed; 3) the required hydrothermal temperature is

usually lower than other biomass thermochemical methods, including pyrolysis and steam gasification [4].

Chemical depolymerization is probably the most direct method to produce high-value chemicals from lignin, but it is also probably the most challenging. In most cases, there is little selectivity and yields are modest. An additional problem is the difficulty of isolation of the products from the degradation of the polymer. Some of common methods for chemically induced depolymerization of lignin are base-catalysed and supercritical fluids-assisted depolymerization. Treating lignin with aqueous NaOH solution at high temperatures leads to phenols and derivatives. The process is relatively simple, but its selectivity remains still unsatisfactory, probably due to the reaction conditions employed in most studies. High reaction times favour the formation of by-products and complex mixtures. For this reason, controlling this reaction parameter is extremely important in this process. On the other hand, lignin has shown good solubility in supercritical fluids and the depolymerization process proceeds with high selectivity. In some cases, a base such as NaOH is added to the solvent, while in others no additional reactant other than solvent is added. The use of supercritical fluids for lignin depolymerization presents a problem related to the high cost or to the equipment employed to perform the reaction. Thus, the design of adequate reactors is required to do this process cost-effective [4].

Another approach to lignin depolymerization consists of oxidative treatment, which is achieved as a method for chemical preparation from side-product lignin in paper chemistry or as part of an integrated biorefinery process [11]. However, certain selectivity and yields are needed to produce chemicals, especially aromatic compounds, for a process to be considered economically viable. Table 1 shows the different lignin conversion strategies and the lignin products obtained from them [4].

INTRODUCTION

Table 1. Thermochemical and chemical lignin transformation processes.

PROCESS	CONDITIONS	PRODUCTS
Thermolysis	Catalyst; 150-900°C	Ethylbenzene, BTX, phenols, cresols, xylenols, light alkenes
Hydrogenolysis	Catalyst+reducing agent; 30-200 bar, 370-850°C	Phenol-rich mixtures, p-ethylphenol, p-propylphenol, m-cresol, cyclohexanes, naphthalenes, phenanthrenes
Hydrothermal hydrolysis	150-430°C, 30-260 bar	Phenols, guaiacol, syringol, catechol.
Chemical depolymerization	Catalyst (NaOH), supercritical fluids; 270-420°C, 35-300 bar	Phenols, guaiacol, catechol, vanillin, syringol
Oxidative transformations	Chlorinated reagents, ozone, H ₂ O ₂ ...	Quinones, ring-opening products, carboxylic acids, MeOH, CO ₂

Despite the constant effort to valorise this biopolymer through different processes, Tuck et al. [12] concluded that the pathway for lignin to aromatics is “deceptive” since extensive researches over years cannot identify economically feasible route to yield selectively aromatics from lignin. The reasons could be two: 1) As it was mentioned above, lignin structure and physicochemical properties changes with the biomass source and the extraction/purification method. Thus, to produce high-value compounds (i.e. vanillin) with high yields from lignin it is necessary to start from a suitable raw material; 2) Repolymerization reactions are always in competition with lignin depolymerization. These reactions among the highly reactive lignin degradation products/intermediates form dimers, trimers, oligomers and char. This repolymerization is traduced in a loss of lignin reactivity and solubility after harsh conditions [13]. However, it is well known that the amounts of higher molecular weight residue can be minimized by simultaneous optimization of the

reaction temperature and the residence time [5]. Controlled depolymerization of lignin is one of the most challenging and promising technologies to produce small aromatic chemicals that now are obtained only from petrochemical industry.

5. Lignin depolymerization using sub and supercritical water.

As it was seen in the previous sections, due to the complex structure and presence of various linkages between monomers in the lignin structure, the conversion of this phenolic heteropolymer to value-added compounds is substantially more difficult than that of polymeric carbohydrates (such cellulose or starch). In recent years, the use of supercritical technique is believed to have positive effect on the depolymerization of lignin material to small molecules [6].

A supercritical state is defined as a fluid at a temperature and pressure above its critical temperature, T_c , and critical pressure, P_c . In the gas-liquid transition regime, supercritical fluids technique presents thermodynamic properties intermediate between gases and liquids, which makes them very suitable for the development of new processes that cannot be carried out with conventional liquid or gaseous fluids. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing the solvent properties of a supercritical fluid to be "fine-tuned". In addition, due to the creation of a homogeneous reaction environment, supercritical fluids possess a number of unique advantages as enhanced mixing kinetics, heat and mass transfer, fast reactions and good scalability, suitable for the development of continuous processes [6]. Supercritical water (SCW: $T_c=374\text{ }^{\circ}\text{C}$ and $P_c=22\text{ MPa}$), is an alternative environmentally benign solvent for rapid depolymerization of lignin. In SCW, lignin reacts to form a complex phenolic mixture of polyhydroxylated and alkylated phenol compounds as well as char and volatile components. Even below the critical point of water, lignin can undergo rapid depolymerization and subsequent product conversion [6]. However, there are some significant differences between the reaction media in sub and supercritical

water, most notably the difference in ionic product of water, presenting the subcritical water medium a higher concentration of ions thus favouring ionic reactions vs the radical reactions that are prevalent under SCW conditions [14].

References.

1. Ragauskas, A.J., et al., *Lignin Valorization: Improving Lignin Processing in the Biorefinery*. Science, 2014. **344**(6185): p. 1246843.
2. Cherubini, F., *The biorefinery concept: Using biomass instead of oil for producing energy and chemicals*. Energy Conversion and Management, 2010. **51**(7): p. 1412-1421.
3. Pińkowska, H., P. Wolak, and A. Złocińska, *Hydrothermal decomposition of alkali lignin in sub- and supercritical water*. Chemical Engineering Journal, 2012. **187**: p. 410-414.
4. G. Calvo-Flores, F., et al., *Lignin and Lignans as Renewable Raw Materials: Chemistry, Technology and Applications*. 2015.
5. Gosselink, R.J.A., et al., *Co-ordination network for lignin—standardisation, production and applications adapted to market requirements (EUROLIGNIN)*. Industrial Crops and Products, 2004. **20**(2): p. 121-129.
6. Wang, X., et al., *Depolymerization of Lignin with Supercritical Fluids: A Review*. Vol. 821-822. 2013. 1126-1134.
7. Hendriks, A.T.W.M. and G. Zeeman, *Pretreatments to enhance the digestibility of lignocellulosic biomass*. Bioresource Technology, 2009. **100**(1): p. 10-18.
8. Hu, J., Q. Zhang, and D.-J. Lee, *Kraft lignin biorefinery: A perspective*. Bioresource Technology, 2018. **247**: p. 1181-1183.
9. Zhang, F., J. Lin, and G. Zhao, *Preparation and Characterization of Modified Soda Lignin with Polyethylene Glycol*. Materials (Basel, Switzerland), 2016. **9**(10): p. 822.
10. Wang, H., et al., *From lignin to valuable products—strategies, challenges, and prospects*. Bioresource Technology, 2019. **271**: p. 449-461.
11. Pérez, E., C.O. Tuck, and M. Poliakoff, *Valorisation of lignin by depolymerisation and fractionation using supercritical fluids and conventional solvents*. The Journal of Supercritical Fluids, 2018. **133**: p. 690-695.
12. Tuck, C.O., et al., *Valorization of Biomass: Deriving More Value from Waste*. Science, 2012. **337**(6095): p. 695-699.
13. Li, J., G. Henriksson, and G. Gellerstedt, *Lignin depolymerization/repolymerization and its critical role for delignification of aspen wood by steam explosion*. Bioresource Technology, 2007. **98**(16): p. 3061-3068.
14. Cocero, M.J., et al., *Understanding biomass fractionation in subcritical & supercritical water*. The Journal of Supercritical Fluids, 2018. **133**: p. 550-565.

AIMS AND CONTENTS

Lignin, a complex natural polymer obtained as by-product in large quantities in paper industries and biorefineries, is a promising candidate for obtaining aromatic high value products from a renewable resource. The main problem present in most studies is the difficulty to depolymerize this biopolymer in low molecular weight compounds with high yield and selectivity, avoiding repolymerization reactions of the fragments previously formed.

The main hypothesis of this thesis is that:

‘Undesired repolymerization reactions of lignin products can be controlled with two reaction parameters: temperature and reaction time. Working with reaction times as short as milliseconds, an unexplored region until nowadays, and an adequate temperature, the repolymerization of lignin could be avoided.’

Thus, the main purpose of this research work was to depolymerize lignin using an environmentally friendly process able to work with reaction times short enough to avoid or control repolymerization, obtaining in this way high yield and selectivity in aromatic monomers of interest such as vanillin. For that purpose, a continuous technology employing sudden-expansion micro-reactors, as well as hot and pressurized water as solvent was employed.

In order to achieve the aim of this thesis, the following partial objectives were defined and described in the four chapters constituting the thesis:

1. Search for optimal operating conditions for lignin depolymerization using sub and supercritical water.

- Depolymerization of Kraft lignin using continuous sudden-expansion microreactors at different temperatures (300-400 °C) and different reaction times (60 ms – 4.6 s).
- Determination of the optimal operating conditions for obtaining the maximum monomeric yield.

2. Improvement of the lignin depolymerization process using supercritical water by addition of NaOH as catalyst.

- Depolymerization of Kraft lignin at the optimal temperature and different reaction times below 0.5 s using base-catalysed supercritical water in order to increase the monomeric yield.
- Determination of the optimal reaction time for obtaining the maximum monomeric yield.
- Study of reaction mechanisms of lignin depolymerization in alkaline supercritical water.

3. Application of the ultra-fast base-catalysed supercritical water technology to real pulping and biorefinery residues for its valorisation.

- Depolymerization of different lignins obtained from diverse biomasses and isolation methods using alkaline supercritical water at the optimal operating conditions determined for Kraft lignin in basic medium.
- Direct treatment of Kraft black liquors using supercritical water at the optimal operating conditions determined for Kraft lignin.
- Study of the influence of lignin nature in the alkaline supercritical water depolymerization process and in the type of lignin products.

4. Development of a strategy to recover low-molecular-weight products from the lignin product mixture in a continuous process.

- Simulation of a continuous downstream process for separating low-molecular-weight products from the lignin product mixture using Aspen HYSYS.
- Optimization of the downstream process in order to minimize the monomeric losses.
- Study of the economic profitability of the process.

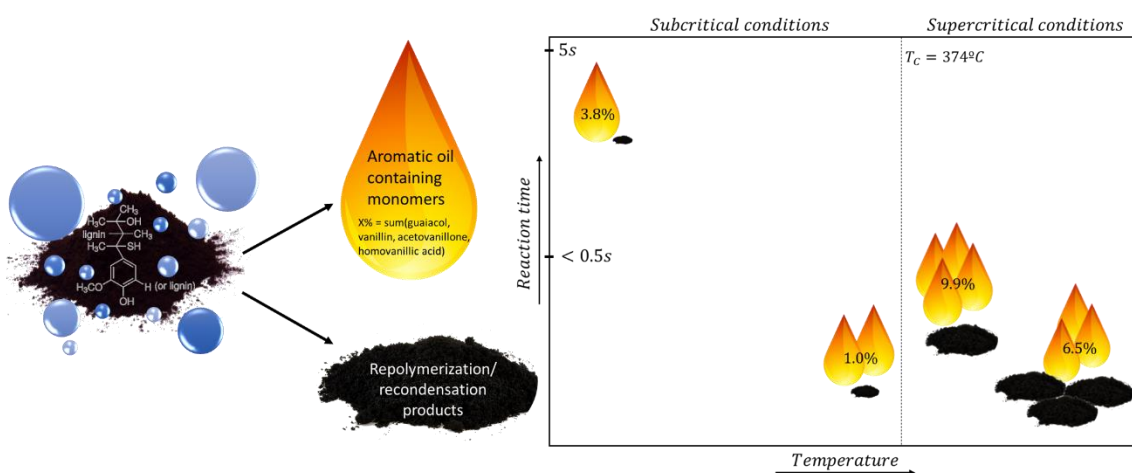
CHAPTER I

DEPOLYMERIZATION OF KRAFT
LIGNIN USING SUB- AND
SUPERCRITICAL WATER.

DEPOLYMERIZATION OF KRAFT LIGNIN USING SUB- AND SUPERCRITICAL WATER.

Abstract.

Kraft lignin, as an example of pulp and paper industry by-product, was rapidly depolymerized in a continuous reactor using sub- and supercritical water. The reaction yielded an aromatic oil rich in high value aromatic monomers such as guaiacol, vanillin, acetovanillone and homovanillic acid. Different temperatures between 300 and 400°C and reaction times from 60 ms were studied. An increment in reaction time at every temperature studied promoted secondary reactions of repolymerization of the lignin products. Those undesired reactions were more relevant as temperature increased. An optimal temperature of 386°C at a reaction time of 170 ms was found, with a maximum yield in phenolic compounds obtained. At those conditions, a bio-oil containing low-molecular-weight compounds was obtained with a yield of 44.6%. A selectivity in the four cited monomers of 9.9% was achieved, with little formation of solid residue (3.5%). The concentration of monomers in the aromatic oil was determined by gas chromatography–mass spectrometry, whereas the solid residue was analysed by FT-IR spectroscopy.



1. Introduction.

Lignin is one of the most important components of lignocellulosic biomass. It is mainly formed by hydroxyl-phenylpropane units (p-hydroxyphenyl, guaiacyl and syringyl units) derived from three monomers (monolignols), p-coumaryl, coniferyl and sinapyl alcohols (Figure 1), differently distributed depending on the vegetal material: softwood, hardwood or grass [1]. Hardwood lignins are primarily composed by guaiacyl and syringyl units with traces of p-hydroxyphenyl propanoid units, whereas softwood lignins are composed mainly of guaiacyl units with small amount of p-hydroxyphenyl propanoid units. On the other hand, grass lignins are also classified as guaiacyl-syringyl lignin containing a low level of structural elements derived from p-coumaryl alcohol [2].

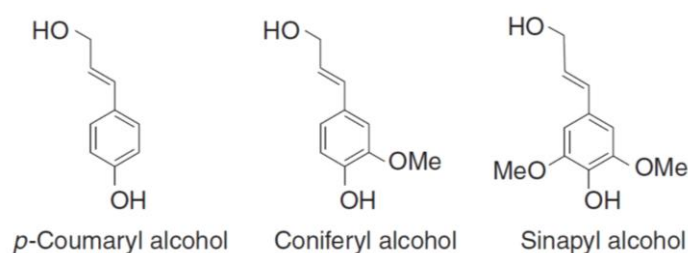


Figure 1. Structure of monolignols forming lignin.

Lignin is produced mainly as a by-product in pulp and paper processes and more recently in biorefineries, where is treated as waste material being mostly consumed as low-grade fuel [3].

Recently, many studies have been focused on the hydrothermal decomposition of lignin [3-9]. In those studies, high temperature pressurized water has proven to be effective on the degradation of lignin to high value-added products (i.e. phenolic compounds). At conditions close to the critical point (22.1 MPa, 374°C), water has very interesting properties, such as a low dielectric constant, which makes it a good solvent for organic substances, and a low viscosity, which makes water an excellent medium for fast, homogeneous and efficient reactions [10]. On the other hand, the adjustable properties of supercritical water allow controlling the performance of the reaction. Optimization of the temperature and reaction

time can be done to maximize the reaction selectivity, as well as to avoid the generation of undesired products formed by repolymerization reactions. The density, dielectric constant and ionic product of water (pK_w) from 300°C to 400°C at a pressure of 25 MPa are plotted in Figure 2.

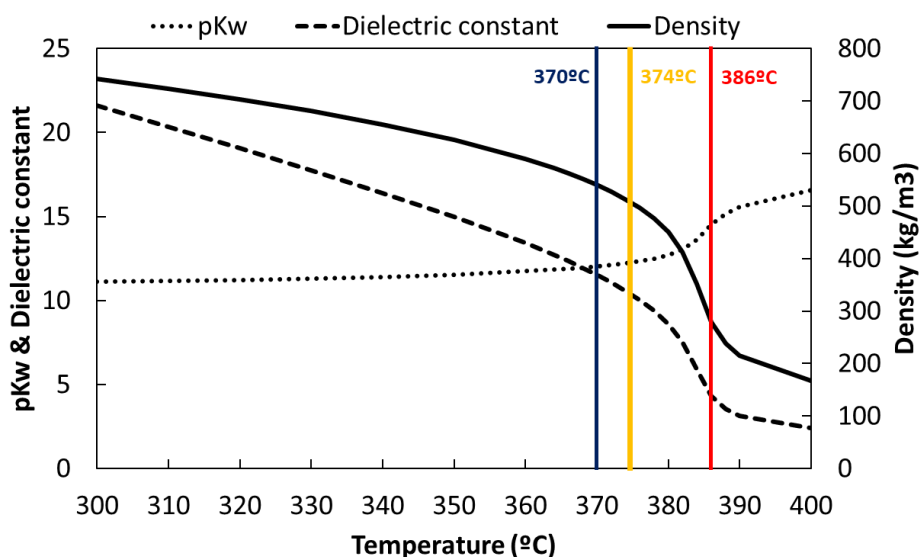


Figure 2. Properties of pressurized water below and above the critical temperature of water (374°C) calculated according to the equations developed in literature [11].

As explained in previous works, reactions in sub- and supercritical water (SCW) are dominated mainly by ionic or radical mechanisms respectively [8, 12]. Ionic reactions are more favoured in the subcritical than in the supercritical region because of the higher dielectric constant. Also, higher concentration of H⁺ and OH⁻ ions from the water dissociation promote acid or basic-catalyzed reactions. On the other hand, radical reactions favourably occur under supercritical conditions.

Most studies focused in the hydrothermal depolymerization of lignin use catalysts and batch type reactors and operate with reaction times from minutes to hours. Only Yong and Matsumura [8, 9] have investigated shorter reaction times down to 0.5 s. However, even at those short reaction times, the depolymerization of lignin has not been so effective as could be expected, since repolymerization reactions took place rapidly.

The purpose of this study was to examine the trend of decomposition of Kraft lignin in sub- and supercritical water as a fast-continuous process for times below 0.5 s and to determine the effect of the reaction parameters (temperature and time) on the degree of lignin decomposition to form phenolic compounds. Four temperatures were selected for this study: two at subcritical conditions (300 and 370°C) and two at supercritical conditions (386 and 400°C). These are temperatures with different water properties close to and far from the critical point of water (Figure 2). The lignin used in the experiments was a commercial lignin of relatively high molecular weight ($M_w \sim 10,000$). The major low-molecular-weight phenolic compounds contained in the liquid product fractions were quantified by GC-MS, while solid residues were examined by FT-IR.

2. Materials and methods.

2.1. Materials.

All the chemicals were purchased from Sigma-Aldrich. Kraft lignin with low sulfur content (4%) was used as starting material. Properties of this lignin can be seen in Table S1. Distilled water was used as the reaction medium to run the experiments. Ethyl acetate (>99%) was employed to extract the lower-molecular-weight aromatic compounds from the liquid products. The calibration standards used in the GC-MS analysis were: guaiacol ($\geq 99\%$), vanillin (99%), acetovanillone ($\geq 98\%$), homovanillic acid ($\geq 97\%$), as well as the internal standard 2-phenyl ethanol ($\geq 99\%$).

2.2. Methods.

2.2.1. Calculation of the reaction time.

The reaction time was calculated as the equivalent to the residence time in the reactor as shown in equation 1, where V is the volume of the reactor, ρ is the density of water at working temperature and pressure, calculated as Wagner et al. [13], and M is the total mass flow. Density was considered as that of water because of the low concentration of lignin.

$$t_R = \frac{V \cdot \rho}{M} \quad (1)$$

The reactor volume was calculated as the sum of the volume of the different parts composing the reactor (See Figure 5): 1/3 of a T-union (point of mixing) + tube before thermocouple + 2/3 of T (thermocouple) + tube after thermocouple + valve connector + valve adapter. Valve connector and adapter volumes, not appreciable in Figure 5, were $4.1 \cdot 10^{-2}$ and $1.8 \cdot 10^{-1} \text{ cm}^3$, respectively. Tubes and pieces of 1/8" and 1/4" were used, depending on the reaction time required.

2.2.2. Recovery of the lower-molecular-weight phenolic compounds.

Once the reaction finished, 140 mL of the reaction mixture were treated in order to recover the phenolic monomers in a concentrated oil and calculate the oil yield. Firstly, the solid was separated from the liquid by centrifugation (10 min, 7000 rpm). The liquid was recovered by carefully pipetting it without shaking the decanted solid. Then, the wet solid was washed with milli-Q water and dried in an oven at 45°C, obtaining the *solid fraction*. The liquid fraction was subjected to a liquid-liquid extraction process with ethyl acetate (1:2 vol/vol). The solvent was evaporated from the aqueous extract using a rotary evaporator and the extract was then dried in a vacuum oven at 40°C yielding a fraction, weighed and labeled as *aromatic oil*. Finally, the water was removed from the aqueous residue in a freeze-dryer and it was weighed and labeled as *aqueous residue*.

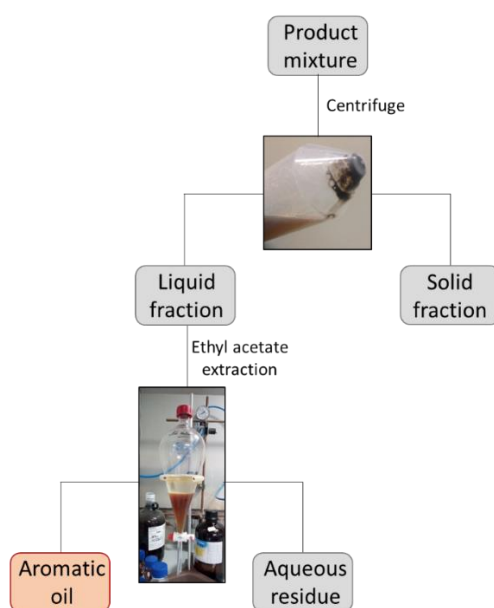


Figure 3. Scheme of the product fractionation process in order to recovery the phenolic monomers in an aromatic oil.

2.2.3. Characterization of the depolymerization products.

Phenolic monomers contained in the *aromatic oil* were detected and quantified by a gas chromatograph equipped with a capillary column HP-5ms, 30 m x 0.25 mm x 0.25 μm (Agilent Technologies, USA). Data of the chromatographic separations were acquired using a quadrupole mass spectrometer detector (5977A-Agilent Technologies, USA). The equipment was used in split-less mode and Helium was used as carrier gas. The oven temperature was programmed as follows: initial temperature was set at 32 °C and kept for 10 min, then temperature was raised to 52 °C at 2°C/min, and kept for 2 min; to 65°C at 2°C/min, and kept for 2 min; to 93°C at 4°C/min, and kept for 2 min; to 230°C at 2°C/min and kept for 3 min; and finally, to 300°C at 15°C/min, and kept for 3 min. To eliminate the acquisition of the solvent (acetone) by the MS, a solvent delay was programmed at 3.70 minutes after confirming that no compounds were removed with the solvent. For compound identification, the data obtained in the GC-MS analysis were compared with m/z values compiled in the spectrum library Wiley. Data analysis was performed using the Agilent MassHunter software (Agilent Technologies, USA). Validation of compound identification was carried out by comparison of their MS spectra and their retention times with standards. Quantification of the major monomers identified in the oily products was done following the internal standard method [14].

The *solid fraction* and the *aqueous residue* were analyzed by FT-IR (ATR with diamond crystal) at ambient temperature with a Bruker Tensor 27 equipment.

2.2.4. Calculation of fractionation yields and selectivity of monomers.

For calculating the yield of the fractionation product 'i', % Y_i , equation 2 was used:

$$\%Y_i = \frac{C_i}{C_{Lg}} \times 100 \quad (2)$$

Where C_i is the concentration of the fraction 'i' in the product mixture, expressed in $\text{g} \cdot \text{L}^{-1}$ and C_{Lg} the concentration of lignin in the reactor just before the reaction, expressed in $\text{g} \cdot \text{L}^{-1}$.

Analogously, the yield in the monomer 'x', %Y_x, present in the product mixture, is referred to the total amount of lignin and calculated as equation 3:

$$\%Y_x = \frac{C_x}{C_{Lg}} \times 100 = \frac{X_x^{oil} C_{oil}}{C_{Lg}} \times 100 = X_x^{oil} \cdot Y_{oil} \quad (3)$$

Where C_x is the concentration of the monomer 'x' in the product mixture, X_x^{oil} (g · g⁻¹) is the mass fraction (or selectivity) of the monomer 'x' in the aromatic oil and C_{oil} is the concentration of the aromatic oil in the product mixture (g · L⁻¹).

2.3. Experimental setup.

The fast-continuous process employed to depolymerize lignin using sub- and supercritical water was similar to the one designed in a previous work by our group to hydrolyze cellulose [15]. A simplified scheme of the pilot plant is shown in Figure 4. Sudden-expansion micro-reactors (SEMR) were employed. Inconel 600 tubes were used to build the reactors in order to reduce corrosion. The reaction section was thermally isolated. An illustration of a SEMR can be seen in Figure 5. Heating was achieved by mixing the compressed room temperature lignin solution with a stream of hot pressurized water in a "T" junction, in order to quickly reach the target temperature (300-400°C) between 0.1 and 3 ms. A thermocouple located in the middle point of the reactor monitored the reaction temperature. Instantaneous cooling to 150-180°C was achieved by sudden decompression using a high-temperature valve, model Autoclave 30VRMM4812-HT, stopping rapidly the reaction. This cooling method is more effective than the conventional heat transfer methods because the temperature change is instantaneous (0.01-1 ms), allowing an accurate control of the reaction time. After the decompression, a jacket cooler was set up in order to get the sample to room temperature.

The reactions were carried out at four different temperatures, two of them at subcritical conditions (300 and 370 ±2°C), while other two at supercritical conditions (386 and 400 ±2°C). The pressure in the reactor was fixed at 260 ±8 bar for all the experiments. Reactions in SCW and in subcritical conditions but close to the critical point (370°C) were performed at reaction times between 60 and 360

± 5 ms (below 0.5 s). However, reactions at subcritical conditions away from the critical point of water (300°C) were carried out in a broader range of reaction times, from ms to 4.6 s, since at lower temperatures, longer reaction times would be required for an effective decomposition of lignin. The reaction time was controlled by changing the inlet flow to the reactor and the reactor volume. At 300°C, the minimum reaction time reached using the smallest reactor and the maximum flow rate was 170 ms, because of the high density of water. The lignin concentration at the inlet of the reactor was 1000 ppm (0.1%w/w) in all experiments. This low initial concentration was fixed due to clogging problems in the inlet of the decompression valve because of solid particles formed. The lignin solution was fed to the reactor by a Lewa EK1 pump at a flow rates within 1.6-2.5 L h⁻¹, and water was pumped by a Milton Roy pump at flow rate within 3.5-5.1 L h⁻¹. Micro-reactors were built with reaction volumes between 0.5 and 12.3 cm³, depending on the reaction times required. The short time needed to start and stop the reaction, along with the small reactor volume, allowed the micro-reactor to be considered as isothermal, having a constant and homogenous reaction rate through the whole reactor.

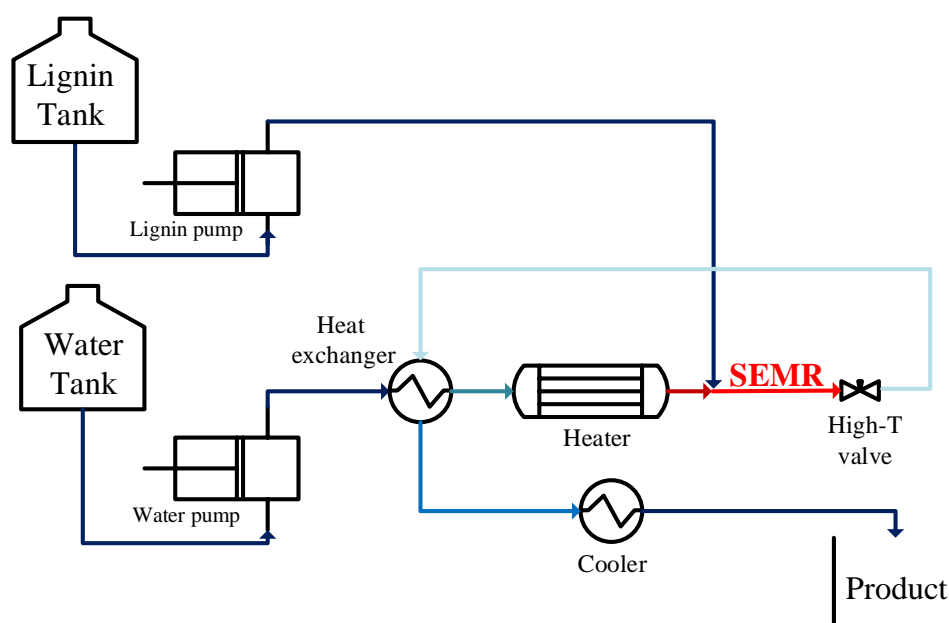


Figure 4. Simplified schema of the pilot plant used for depolymerizing lignin using sub- and supercritical water.

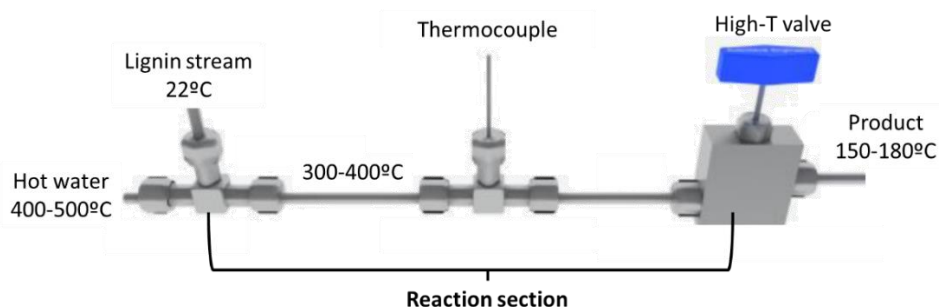


Figure 5. Sudden-expansion micro-reactor (SEMR). Instantaneous heating of lignin solution is achieved by mixing it with hot water. Instantaneous cooling is achieved by sudden decompression using a high-temperature valve.

3. Results and discussion.

A total of 19 experiments were performed in order to examine the trend of hydrothermal decomposition of Kraft lignin in sub- and supercritical water and to determine the effect of the reaction parameters (temperature and time) on the degree of lignin conversion to low-molecular-weight phenolic compounds. A summary of the experiments is shown in Table S2.

3.1. Solid and aqueous residue fractions characterization.

Fourier Transform Infrared Spectroscopy (FT-IR) provides information about chemical functionalities present in the lignin structure. Figure 6 shows the FT-IR spectrum of Kraft lignin, three solid fractions and two aqueous residues (AqR) obtained at different operating conditions taken as examples for comparison purposes. Table S3 shows some typical bands.

As can be observed, the FT-IR spectra of lignin and aqueous residues were very similar, which indicated that they have a similar structure and functional group types. Small differences could only be observed in the 3000-2800 cm^{-1} region corresponding to the stretching of C-H bonds typical of aromatic and aliphatic hydrocarbons. With this similarity in the chemical functions of AqR and lignin, it is possible to confirm that AqR fraction is practically unconverted or partially depolymerized soluble lignin.

On the other hand, solid fractions spectra look also like lignin spectrum with some differences in bands $1710\text{-}1665\text{ cm}^{-1}$, typical of unsaturated aldehydes and ketones, $1400\text{-}1300\text{ cm}^{-1}$ and $900\text{-}700\text{ cm}^{-1}$ corresponding to the C-H bending typical of saturated and unsaturated hydrocarbons, respectively, and the band corresponding to C-O stretching in the region $1300\text{-}1000\text{ cm}^{-1}$, which indicates that the structure of lignin has been altered mainly in C-O bonds. Thus, the solid fractions obtained after both sub- and supercritical conditions have been proposed to be lignin fragments that have suffered repolymerization, as it was also reported in literature [16]. The FTIR spectra agree with this as more unsaturated structures are observed.

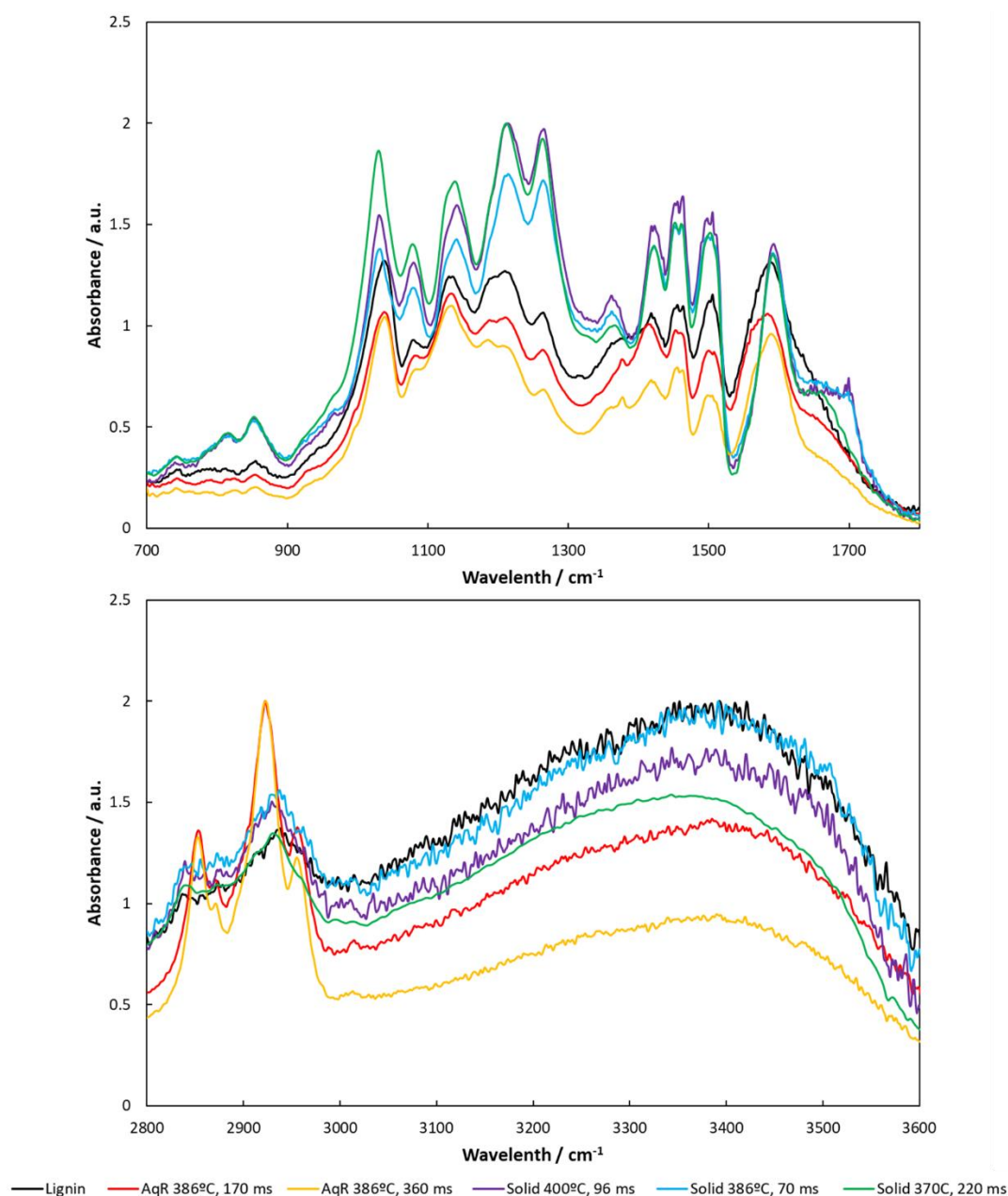


Figure 6. Comparison of the lignin structure with solids and aqueous residues (AqR) obtained at different operating conditions analysed by FT-IR. Only five fractions were shown here as examples in order to confirm AqR is practically unconverted or partially depolymerized soluble lignin and solid fraction is lignin with some chemical modifications, probably due to repolymerization reactions.

3.2. Effect of temperature and reaction time in the depolymerization and repolymerization products.

Hydrothermal treatments of lignin under sub- and supercritical water conditions have been investigated by many authors in the last years, where the reactions

lead to gas (mainly CO₂), an organic phase, an aqueous phase and sometimes solid chars [1]. Here, the yield of the main products (aromatic oil and solid fraction) obtained at different temperatures and reaction times is presented in Figure 7.

Higher conversion of lignin to an aromatic oil containing low-molecular-weight phenolic compounds was observed under supercritical conditions (400 and 386°C) or under subcritical conditions close to the critical point of water (370°C). As observed in Figure 7A-7C, depolymerization of lignin occurred rapidly, in 90 ms at 400°C, 170 ms at 386°C and 140 ms at 370°C, reaching a maximum in the aromatic oil yield of 40.4, 44.6 and 32.4% respectively. On the other hand, under subcritical conditions at a temperature far from the critical point (300°C, Figure 7D), lignin depolymerized slowly, reaching a maximum oil yield of only 11.8% at much higher reaction times (2.2 s). Thus, at higher temperatures, lower reaction times are required for reaching higher yields in aromatic low-molecular-weight fragments, as expected from the kinetic point of view. This also suggests that decomposition of lignin is accelerated by radical reactions, as reflected by its increased rate under supercritical conditions, where the ionic product and dielectric constant are much lower. The rapid depolymerization of lignin under supercritical conditions occurred mainly because of the cleavage of ether bonds from the abundant β -aryl ether (β -O-4) linkages in softwood lignin [17, 18]. Faravelli et al. [19] discovered that the weakest bond inside the lignin structure favoured radical formation and initiated the radical reaction.

Additionally to the decomposition of lignin into soluble products, it was also observed that insoluble products were formed at all temperatures, increasing its yield when the reaction time increased. The solid formation was more significant at higher temperatures. At 400°C (Figure 7A) the solid yield increased drastically with the reaction time. However, at 300°C (Figure 7D), higher reaction times of seconds were required to observe a minor formation of non-soluble products since radical reactions are less favoured under subcritical conditions. Although supercritical conditions enhanced the decomposition of lignin into monomers, rapid interaction of these highly reactive radicals to form higher molecular

weight fragments instead of further depolymerization into basic phenolic compounds occur. Moreover, in SCW, the dielectric constant of water decreases with increasing temperature, promoting the dissolution of lignin and the reaction of soluble lignin fragments with low-molecular-weight soluble compounds to form polymers and cross-linked phenolic fragments [20]. Thus, the repolymerization reactions via radical coupling and/or via ionic reactions (condensation) were promoted by increasing temperature, as it was affirmed by Wahyudiono et al. [4]. This was also noticed in other study, where heavier products were formed during hydrothermal reactions leading to condensed compounds and, when high temperatures and/or long residence times were reached, to cross-linked phenolic fragments [21].

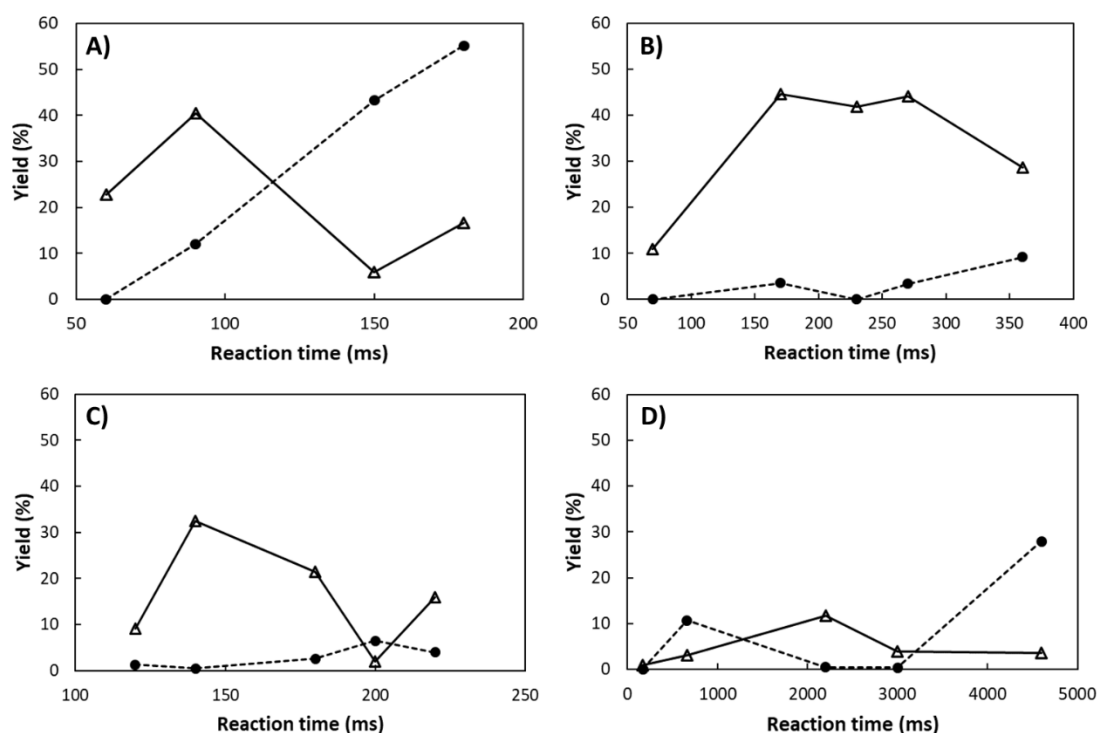


Figure 7. Yield of aromatic oil (continuous line) and solid fractions (dotted line) vs reaction time at A) 400 °C, B) 386°C, C) 370°C and D) 300°C. Fractionation yields calculated as in equation 2.

One hypothesis proposed here is that depolymerization and repolymerization of lignin occurs cyclically: In a first step, lignin depolymerizes giving a maximum oil yield (i.e. high formation of low-molecular-weight fragments); in a second step, lignin fragments trend to repolymerize, decreasing the aromatic oil yield

and being formed repolymerization products (i.e. solid fraction); in a third step, lignin seems to depolymerized again, increasing the amount of phenolic compounds. It is probable that the repolymerized products depolymerize again, giving a lower aromatic oil yield in this second depolymerization, since repolymerized lignin has probably a more compact and complex structure than the unreacted lignin. A simplified scheme of this hypothesis is shown in Figure 8. This hypothesis could explain why other studies at longer reaction times gave lower aromatic oil yields. A long experimental work would be necessary to corroborate this hypothesis.

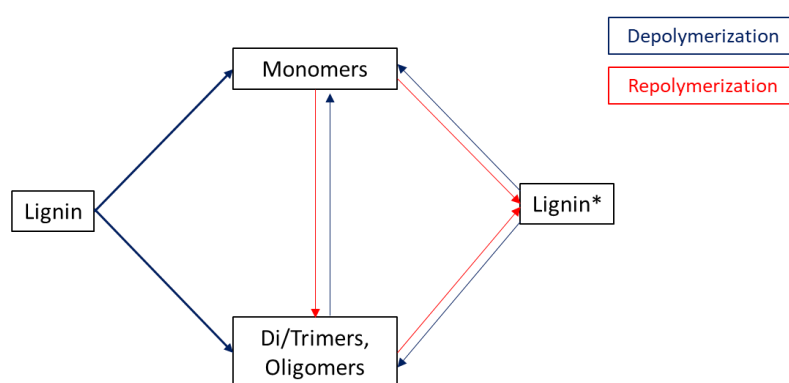


Figure 8. Possible reaction pathway of lignin in hydrothermal processes using sub and supercritical water. The main depolymerization occurs from unreacted lignin (bold lines). Repolymerization reactions are promoted by increasing temperature and reaction time.

This study showed the rapid decomposition of lignin in sub- and supercritical water. Higher aromatic oil yields were achieved under supercritical conditions and extremely low reaction times, being 386°C the optimal temperature with an aromatic oil yield of 44.6% at only 170 ms, and with a minimum formation of undesired solid products (3.5%). The repolymerization reactions, which were more favoured at higher temperatures, could be controlled with the reaction time.

3.3. Selectivity and yield of aromatic monomers with temperature and reaction time.

During hydrothermal degradation, various aromatic monomers were formed. Table S4 shows the results of the qualitative examination of the aromatic oils using GC-MS, while Figure S1 shows a model chromatogram. The major compounds identified in the aromatic oils were guaiacol, vanillin, acetovanillone and homovanillic acid; all of them are derived from coniferyl alcohol, which is the main monomer of softwood lignins. Other analytes were also detected in small amounts (Table S4). Indeed, a total of 17 compounds have been identified, showing the complexity of the degradation pathway. The selectivity of the major monomers in the aromatic oil vs time, as well as the yield of those compounds referred to lignin for the different temperatures studied are shown in Figure 9.

At 400°C, the curve of the selectivity of monomers in the oil (Figure 9-A1) followed the same increasing trend than in the case of solid fraction yield, as it was seen in the previous section (Figure 7A). This similar trend between the monomers and solid formation could be explained as in the previous section: reaction of soluble lignin fragments to form polymers and cross-linked phenolic components was promoted at higher temperatures. At 400°C the soluble lignin fragments seem to repolymerize preferentially than monomers. Acetovanillone was the first compound formed at 60 ms. Then, this compound disappeared and vanillin and homovanillic acid were formed. Homovanillic acid continued increasing with the reaction time up to 6.6% in the aromatic oil at 170 ms. At 150 ms, when vanillin started to decrease, acetovanillone increased again, up to 2.8% in the oil at 170 ms.

However, it was important for determining the optimal reaction time for each temperature to consider not only the selectivity in the oil, but also the yield of this fraction after the hydrothermal process. Taking account of both selectivity in the oil and oil yield, yield of monomers referred to lignin can be calculated as presented in equation 3. Thus, as can be seen in Figure 9-A2, the optimal time in terms of monomeric yield in the whole liquid product was 90 ms, with a total

yield of 2.6%: 1.6% homovanillic acid, 0.5% vanillin, 0.3% acetovanillone and 0.2% guaiacol. It was reported in previous works that guaiacol and other methoxy phenols are formed partly by hydrolysis of ether-bonds [1].

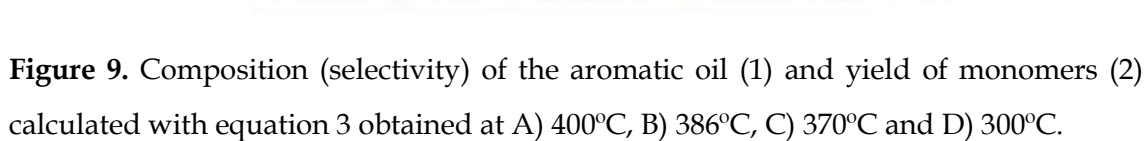
At 386°C (Figure 9-B1), the trend of monomers selectivity (total curve) was similar to that of the oil yield (Figure 7B). Thus, the optimal reaction time in terms of monomeric yield corresponded to that of the highest aromatic oil yield (170 ms), with 4.4% of phenolic monomers, corresponding 2.2% to guaiacol, 1.1% to vanillin, 0.7% to homovanillic acid and 0.7% to acetovanillone. At this temperature, the aromatic oil fraction was very selective, with a total composition in high value monomers of 10% (4.5% guaiacol, 2.6% vanillin, 1.6% homovanillic acid and 1.3% acetovanillone). Homovanillic acid and acetovanillone were formed firstly, and then, when those disappeared, the formation of guaiacol and vanillin took place. These trends were similar to those at 400°C, where vanillin and acetovanillone were formed and decomposed conversely.

At 370°C the trend of the monomer formation (Figure 9-C2) was different to that of the aromatic oil formation (Figure 7C). The maximum in the monomeric yield (170 ms) occurred at a reaction time longer than the maximum in aromatic oil yield. This indicates that di-trimers were formed first and they further cleave to form the monomers, being the former those which control the trend of the oil curve. The highest selectivity in the oil appeared at 200 ms (Figure 9-C1) with 8.0%, being 4.4% homovanillic acid, 1.8% vanillin, 1.0% acetovanillone and 0.8% guaiacol. However, the highest yield was obtained at 170 ms (Figure 9-C2), but with a low value of 0.5%, since the oil yield at this reaction time was only 21.4% (Figure 7C). This indicates that di-trimers seem to be involved mostly in the repolymerization reactions because they disappeared much faster than monomers to form solid residue. At 370°C, vanillin and acetovanillone were firstly formed, and subsequently, they seem to degrade. Both homovanillic acid and guaiacol were formed reaching a maximum at 170 ms.

At 300°C (Figure 9-D), the highest peak of yield was reached at a longer reaction time (2.2 s) with a low value of 0.4%. The main compounds in the oil at that time

were vanillin (3.2%) and acetovanillone (1.8%). In here, acetovanillone and guaiacol were firstly formed, and then homovanillic acid increased up to 2.3% at 2.2s. After this time, the latter was decomposed and vanillin and acetovanillone increased until reaching the maximum yield at 3.0 s, for finally decreasing (and homovanillic acid increased again).

From these observations, it was apparent that changing the reaction conditions from sub- to supercritical, as well as the reaction time, strongly influenced the lignin degradation behaviour. A more comprehensive study would be required for understanding the mechanism of those reactions.



4. Conclusions.

The hydrothermal decomposition of lignin was performed in sub- and supercritical water. Kraft lignin as an example of a residue from pulp and paper industry was chosen for this study. This lignin was successfully degraded into low-molecular-weight components such as guaiacol, vanillin, acetovanillone and homovanillic acid, being the optimal operating conditions 386°C and 170 ms. At this temperature and reaction time, a yield of aromatic oil yield of 44.6% was obtained, with a total of the four selected monomers of 9.9%, suppressing almost totally the solid formation. The solid fraction consisted of repolymerized products, reaction more favoured at higher temperatures and reaction times.

It was also concluded that changing the reaction conditions from sub- to supercritical, as well as the reaction time, strongly influenced the lignin degradation reactions into phenolic monomers. A more comprehensive study would be required for understanding the mechanism of those reactions.

Hydrothermal decomposition of kraft lignin in sub- and supercritical water could become an environmentally friendly technology to produce effectively aromatic monomers of high value-added.

Supplementary information.

Table S1. Properties of Kraft lignin.

pH	6.5 (25 °C, 5%, aqueous solution)
Solubility	H ₂ O: Mostly soluble NaOH: 0.05% (warm 5% aqueous) MEK, methanol: partially soluble Benzene, hexane: insoluble Dioxane, ethylene glycol: soluble
Density	1.3 g/mL at 25 °C

Table S2. Summary table of the experiments performed in sub- and supercritical water conditions at different reaction times. A total of 6 different reactors were made.

Experiment	Temperature	Reaction time	Reactor volume (cm ³)
1	300°C	170 ms	0.5
2	300°C	660 ms	1.2
3	300°C	2.2 s	5.3
4	300°C	3.0 s	5.3
5	300°C	4.6 s	12.3
6	370°C	120 ms	0.5
7	370°C	140 ms	0.5
8	370°C	180 ms	0.6
9	370°C	200 ms	0.6
10	370°C	220 ms	0.6
11	386°C	70 ms	0.5
12	386°C	170 ms	0.6
13	386°C	230 ms	1.5
14	386°C	270 ms	1.2
15	386°C	360 ms	1.5
16	400°C	60 ms	0.5
17	400°C	90 ms	0.6
18	400°C	150 ms	1.2
19	400°C	180 ms	1.2

Table S3. Characteristic IR absorptions

Frequency, cm ⁻¹	Bond	Functional group
3600–3200	O-H stretch	phenols, aliphatics
3000–2800	C-H stretch	aromatic and aliphatic hydrocarbons
1710–1665	C=O stretch	α, β-unsaturated aldehydes, ketones
1600–1585	C-C stretch (in ring)	aromatics
1500–1400	C-C stretch (in ring)	aromatics
1400–1300	C-H bend	saturated aromatic hydrocarbons
1300–1000	C-O stretch	alcohols, carboxylic acids, esters, ethers
900–700	C-H bend	saturated aromatic hydrocarbons

Table S4. GC-MS compounds list present in the aromatic oils. Only the major compounds (guaiacol, vanillin, acetovanillone and homovanillic acid) were quantified. Dodecylbenzene was also identified in Kraft lignin, being probably an impurity.

Retention time (min)	Compound
29.99	Guaiacol
34.46	5-methyl guaiacol
35.30	4-methyl guaiacol (creosol)
40.12	4-Ethylguaiacol
42.18	4-Vinylguaiacol
44.42	Syringol
44.76	Eugenol
47.20	Vanillin
50.08	Isoeugenol
52.35	Acetovanillone
54.76	Homovanillyl alcohol
57.61	Propiovanillone
61.29	Homovanillic acid
65.50	4-hydroxy-3-methoxycinnamaldehyde
65.79	Acetosyringone
69.73	Dehydrozingerone
74.59	Dodecylbenzene

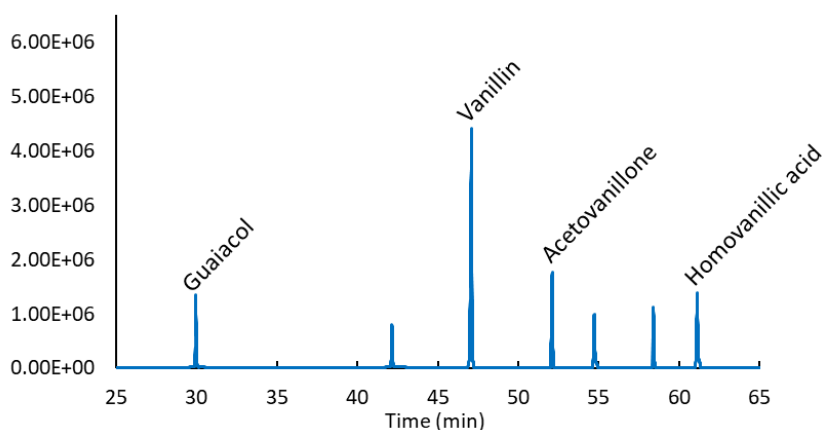


Figure S1. Example of a chromatogram obtained by GC-MS for an aromatic oil obtained at 170 ms and 386°C.

References.

1. Joffres, B., et al., *Thermochemical Conversion of Lignin for Fuels and Chemicals: A Review*. Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles, 2013. **68**(4): p. 753-763.
2. Liu, W.-J., H. Jiang, and H.-Q. Yu, *Thermochemical conversion of lignin to functional materials: a review and future directions*. Green Chemistry, 2015. **17**(11): p. 4888-4907.

3. Pińkowska, H., P. Wolak, and A. Złocińska, *Hydrothermal decomposition of alkali lignin in sub- and supercritical water*. Chemical Engineering Journal, 2012. **187**: p. 410-414.
4. Wahyudiono, M. Sasaki, and M. Goto, *Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water*. Chemical Engineering and Processing: Process Intensification, 2008. **47**(9): p. 1609-1619.
5. Saisu, M., et al., *Conversion of Lignin with Supercritical Water–Phenol Mixtures*. Energy & Fuels, 2003. **17**(4): p. 922-928.
6. Fang, Z., et al., *Reaction chemistry and phase behavior of lignin in high-temperature and supercritical water*. Bioresource Technology, 2008. **99**(9): p. 3424-3430.
7. Okuda, K., et al., *Disassembly of lignin and chemical recovery—rapid depolymerization of lignin without char formation in water–phenol mixtures*. Fuel Processing Technology, 2004. **85**(8): p. 803-813.
8. Yong, T.L.-K. and Y. Matsumura, *Reaction Kinetics of the Lignin Conversion in Supercritical Water*. Industrial & Engineering Chemistry Research, 2012. **51**(37): p. 11975-11988.
9. Yong, T.L.-K. and Y. Matsumura, *Kinetic Analysis of Lignin Hydrothermal Conversion in Sub- and Supercritical Water*. Industrial & Engineering Chemistry Research, 2013. **52**(16): p. 5626-5639.
10. Toor, S.S., L. Rosendahl, and A. Rudolf, *Hydrothermal liquefaction of biomass: A review of subcritical water technologies*. Energy, 2011. **36**(5): p. 2328-2342.
11. Brunner, G., *Chapter 2 - Properties of Pure Water, in Supercritical Fluid Science and Technology*, G. Brunner, Editor. 2014, Elsevier. p. 9-93.
12. Antal, M.J., et al., *Heterolysis and Homolysis in Supercritical Water, in Supercritical Fluids*. 1987, American Chemical Society. p. 77-86.
13. Wagner, W., et al., *The IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam*. Journal of Engineering for Gas Turbines and Power, 2000. **122**(1): p. 150-184.
14. Baumard, P.a.B., H., *Internal standard quantification method and Gas Chromatograph-Mass Spectrometer (GC-MS): A reliable tool for Polycyclic Aromatic Hydrocarbon (PAH) quantification in natural matrices*. Analysis, 1997. **25**(7): p. 246-252.
15. Cantero, D.A., M. Dolores Bermejo, and M. José Cocero, *High glucose selectivity in pressurized water hydrolysis of cellulose using ultra-fast reactors*. Bioresource Technology, 2013. **135**: p. 697-703.
16. Pérez, E. and C.O. Tuck, *Quantitative analysis of products from lignin depolymerisation in high-temperature water*. European Polymer Journal, 2018. **99**: p. 38-48.
17. Li, J., G. Henriksson, and G. Gellerstedt, *Lignin depolymerization/repolymerization and its critical role for delignification of aspen wood by steam explosion*. Bioresource Technology, 2007. **98**(16): p. 3061-3068.
18. Kang, S., et al., *Classified Separation of Lignin Hydrothermal Liquefied Products*. Industrial & Engineering Chemistry Research, 2011. **50**(19): p. 11288-11296.
19. Faravelli, T., et al., *Detailed kinetic modeling of the thermal degradation of lignins*. Biomass and Bioenergy, 2010. **34**(3): p. 290-301.
20. Wahyudiono, et al., *Decomposition of a Lignin Model Compound under Hydrothermal Conditions*. Chemical Engineering & Technology, 2007. **30**(8): p. 1113-1122.
21. Barbier, J., et al., *Hydrothermal conversion of lignin compounds. A detailed study of fragmentation and condensation reaction pathways*. Biomass and Bioenergy, 2012. **46**: p. 479-491.

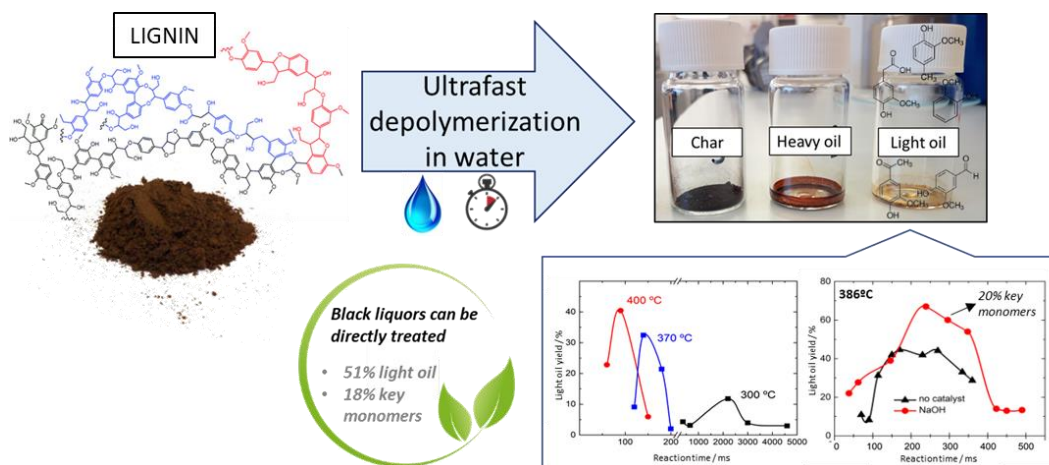
CHAPTER II

OBTENTION OF AROMATIC
MONOMERS FROM LIGNIN
THROUGH ULTRAFAST SCW
REACTIONS USING SODIUM
HYDROXYDE AS CATALYST.

OBTENTION OF AROMATIC MONOMERS FROM LIGNIN THROUGH ULTRAFAST REACTIONS IN WATER USING SODIUM HYDROXYDE AS CATALYST.

Abstract.

Nowadays, valorization of lignin, the largest natural source of aromatics on earth, is being a challenge for the scientific community. In this study, kraft lignin is effectively converted into aromatic monomers by ultrafast depolymerization in hot and pressurized water. At reaction times below 500 ms, it is possible to avoid char formation originated from undesirable repolymerization reactions by controlling accurately the reaction time. Under alkaline medium, the reaction reaches an optimum point at 386°C and 300 ms with a light oil yield of 60% with a selectivity in key compounds such as guaiacol, creosol, vanillin and acetovanillone of around 20 wt%. The char formation in this point was surprisingly low (4 wt%). Analysis and quantification of the products allows to identify the evolution of the different reaction steps and propose plausible mechanisms for the depolymerization and repolymerization stages. Furthermore, it is proven that the proposed technology is equally effective to treat directly industrial black liquors with a yield higher than 50 wt% to light oil, containing as main monomers guaiacol (2.7 wt%), syringol (3.0 wt%) and syringaldehyde (7.3 wt%).



1. Introduction.

Bio-based polymers' growth rates are at same level as synthetic polymers: Worldwide production capacity is forecasted to increase from 6.6 million tons in 2016 to 8.5 million in 2021. In the absence of renewables aromatic building blocks, polymers are currently produced from a petrochemical aromatic molecule and a bio-based aliphatic molecule [1]. Lignin is an aromatic biopolymer that constitutes a major component of lignocellulosic biomass. It is composed by combination of three phenylpropanoid units (p-coumaryl, coniferyl and synapyl alcohols) randomly connected in different proportions depending on the biomass of origin. Despite its abundance and promising molecular structure for obtaining high value monoaromatic compounds, lignin is still underutilized compared to other feedstocks [2]. Currently, lignin is produced in large quantities in the pulp and paper industry as the main component of black liquor, a low-value residual stream that is further processed to be burned and obtain energy in the same plant. Moreover, with the increasing role of biorefineries in a bio-based economy, even more generation of lignin is expected. Depolymerization is an obvious strategy to valorize lignin as it provides single aromatic chemicals. However, this route has been deceptive because of the low selectivity of the compounds targeted and the tendency of lignin fragments to recombine to form char-type by-products [2]. However, this has not discouraged the scientific community who has redoubled its efforts to obtain a solution and as consequence, important advances have been achieved. Some of the most successful approaches explored were catalyst improvement [3], or pretreatment stages with oxidants [4] or formaldehyde [5, 6]. Nevertheless, this kind of meticulous processes are very far of being translated into commercial practice due to the several non-continuous steps that must be carried out and the long time required. Ragauskas et al. [7] have presented this paradigm, posing the reality: *"although fundamental research has historically focused on converting lignin to chemicals materials, very little of this effort has been translated into commercial practice"*. So, what has changed to address this deadlock? An answer to it could be the continuous hydrothermal depolymerization approaches [8] possess certain advantages such as the cost and safety of the solvent or, since

the black liquor containing lignin is already in aqueous phase, it can be directly treated. The depolymerization products can then be fractionated to be utilized as a mixture while added-value components are isolated [2, 9]. The most common versions of hydrothermal lignin depolymerization include hydrothermal pyrolysis/hydrolysis [10, 11], base catalyzed depolymerization (BCD) [12, 13], hydrogenolysis [14] and oxidative cleavage [2, 9] in sub- and supercritical water. These techniques require high temperatures and therefore they imply an additional energetic cost. However, reaction kinetics are enhanced reducing the reaction times, which allows a feasible scale-up of the process since small reactor volumes are required. Some studies have demonstrated that residence times of the order of seconds are enough to convert most of the lignin to a mixture of products [2]. However, as temperature is raised, a phenolic char is preferentially formed through crosslinking of phenolic units and formation of recalcitrant C-C aromatic to aromatic bonds [15]. These undesirable repolymerization reactions seem to occur rapidly, at rates comparable to those the depolymerization reaction so that it is not possible to control them by conventional batch reactors. Yong and Matsmura [10] have achieved high lignin conversion of organosolv lignin at reaction times as low as 0.5 second in a continuous apparatus in SCW conditions, but still obtaining a high amount of char due to repolymerization reactions. Thus, it is necessary to work at reaction times short enough to determine the reaction time in which the repolymerization of lignin starts, avoiding the problem present until today and obtaining high yields and selectivity towards mono-aromatics, with a low char formation. Achievement of accurately time-controlled reactions in supercritical water at the range of milliseconds can be achieved using the Sudden Expansion Micro-Reactor (SEMR) developed in our laboratory [16]. The keys of this design are very small continuous reactors and an instantaneous cooling step achieved by sudden decompression thanks to the Joule-Thompson effect. This way, residence times down to 40 ms can be reached with an uncertainty of ± 1 ms. Despite of being a bench-scale plant, it can reach a treatment capacity of 3 kg/h of solution. To increase the concentration of lignin, NaOH must be added to favour the solubility of the reaction products and to

avoid blockages, with the additional advantage that it acts as catalyst [2]. To facilitate understanding and analysis of the reaction products, it has been common to fractionate the samples according to their solubility in water and organic solvents [2, 10, 13]. As polar solvents would dissolve similar solutes, lignin fragments from lignin breakdown would distribute within the solvents according to their chemical characteristics. Ethyl acetate seems to be a good candidate as extracting solvent as it is non-costly and environmentally benign. Experimentally, it was demonstrated that EtAc could easily extract monomers but also higher molecular weight compounds soluble in water [17]. Thus, a light fraction can be extracted from the water-soluble compounds, namely *light oil*, mainly composed by aromatic fragments from depolymerization. The water-insoluble compounds can likewise be fractionated into a *heavy oil* and a solid residue that has been commonly designated as *char*.

2. Materials and methods.

2.1. Materials.

Lignin used in this work was kraft lignin with low sulfide content (4% sulfur) from Sigma-Aldrich. Distilled water was used as the reaction medium to run the experiments. Sodium hydroxide used as catalyst was purchased from Sigma-Aldrich. The calibration standards used in the GC-MS analysis were all purchased from Sigma-Aldrich (USA): syringol ($\geq 98\%$), acetosyringone (97%), homovanillic acid ($\geq 97\%$), guaiacol ($\geq 99\%$), creosol ($\geq 98\%$), acetovanillone ($\geq 98.0\%$), vanillin (99%), syringaldehyde ($\geq 97\%$) and the internal standard 2-phenyl ethanol ($\geq 99\%$). Ethyl acetate ($>99\%$) employed for carrying out the extractions was purchased from Sigma Aldrich. Kraft lignin named as HKL and the corresponding black liquor (HKBL) were supplied by a Spanish paper industry.

2.2. Supercritical water process.

Details for the continuous process used to depolymerize lignin in SCW were reported elsewhere [18]. A simplified scheme of the process is shown in Figure 1.

Sudden Expansion Micro-Reactors (SEMR) consisting in short inconel steel tubes with small internal diameters (1.4-4.8 mm) were used in order to achieve reaction times as short as 60 milliseconds. The lignin solution is continuously compressed and pumped up to the operation pressure, remaining at room temperature until the inlet of the reactor. NaOH, used as catalyst, is premixed with the lignin stream. Heating is achieved by mixing the compressed room temperature lignin solution with a stream of hot pressurized water in the T junction. The product is depressurized through a high temperature needle valve (high-T valve), instantaneously cooling down the effluent down to ca. 150 °C and therefore stopping the reaction. To further reduce the temperature down to ambient, a cooler was set after the preheater used to preheat the SCW.

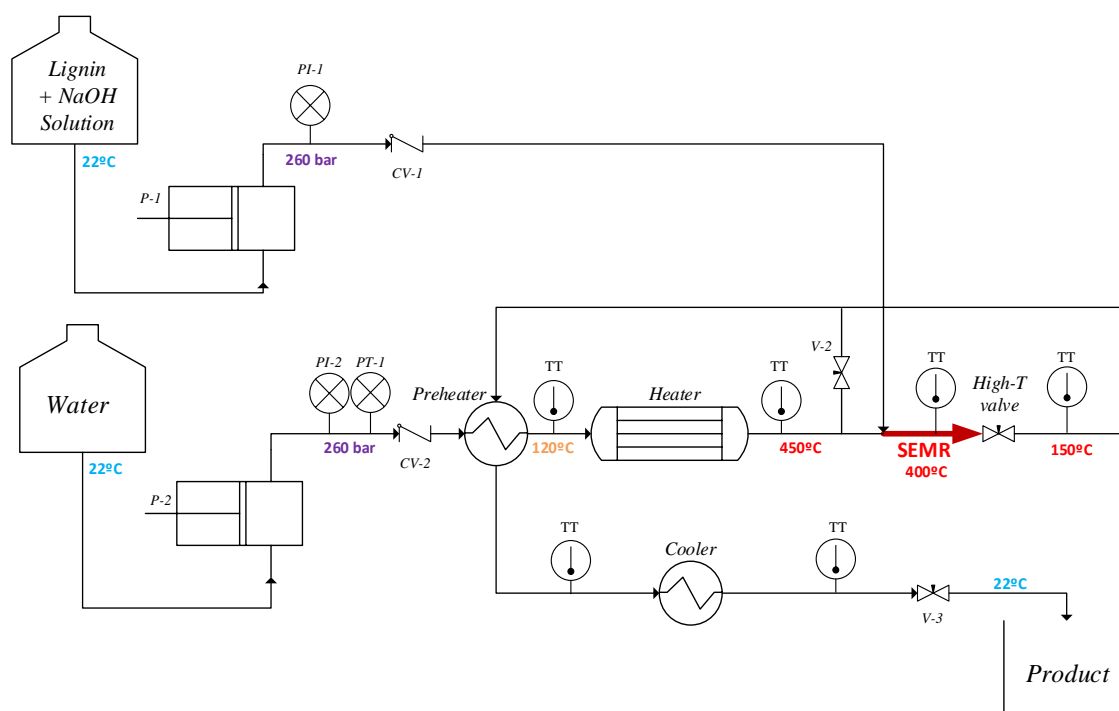


Figure 1. Scheme of the SCW plant.

In this study, base-catalyzed reactions were carried out at $386 \pm 2.6^\circ\text{C}$ and 260 ± 5 bar with low reaction times between 40 and 500 ms. The reaction time was controlled by changing the inlet flow to the reactor and the reactor volume. The flows were varied between 1.4 and 2.6 L h⁻¹ of the basic lignin solution and 3.4-4.4 L h⁻¹ of SCW. Two reactors were made with volumes of 0.6 and 1.1 cm³ for this set of experiments. The lignin concentration at the inlet of the reactor was 0.5% w/w (5-times greater than in non-catalyzed reactions of Chapter I) in a basic

solution of NaOH 0.2 M (pH 13). All the experiments were made by triplicate referring results as the arithmetic average value. Carbon losses (TOC+IC) because of gasification (CO₂) and/or volatilization of monomers between 0.4 and 15.2 wt% were determined for experiments performed at 386°C.

2.3. Fractionation of depolymerization products.

Once the reaction finished, the reaction product was treated to recover the aromatic monomers of interest following a similar procedure that in previous chapter. Figure 2 presents a simplified scheme of the procedure used to separate the mixture into four fractions. Product mixture (P) was acidified by adding concentrated H₂SO₄ dropwise until the solution reached pH=2. The water-insoluble solids precipitated and a brown suspension was formed. After centrifugation, the supernatant was carefully recovered by a pipette and the wet solid was washed with acidified water at pH=2. After washing, the solid fraction (S) was extracted with ethyl acetate and centrifuged, obtaining solution of a solid extract and a solid residue. The solvent was evaporated using a rotary evaporator and the remaining material was dried, weighted and labeled as *heavy oil*. The solid residue was dried, weighed and labeled as *char*. The aqueous fraction (L) was extracted with ethyl acetate to give an aqueous extract and the aqueous residue. The solvent was evaporated from the aqueous extract using a rotary evaporator, this fraction was dried, weighed and labeled as *light oil*. Finally, the water was removed from the aqueous residue by freeze-drying, weighed and labeled as *aqueous residue*.

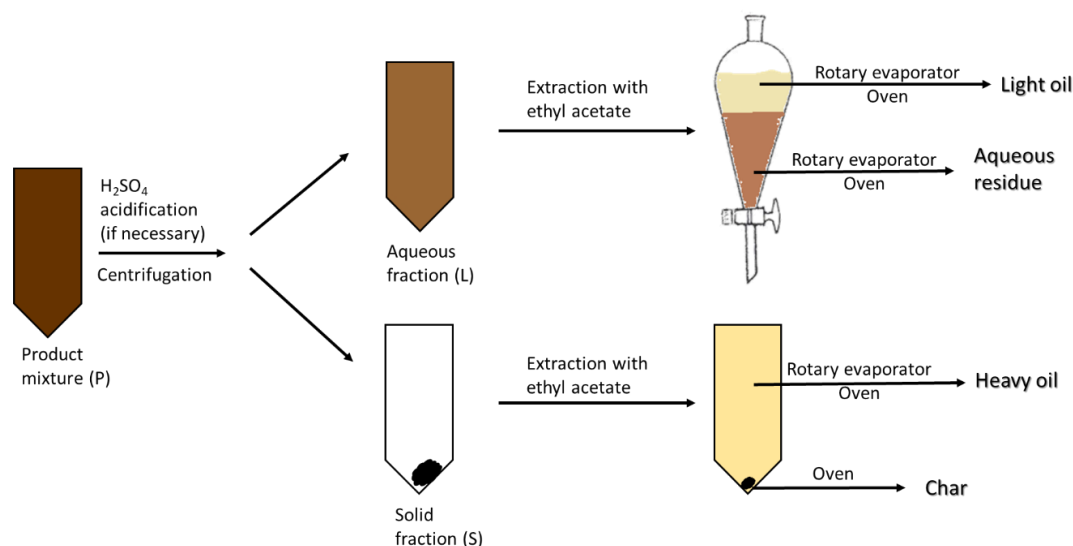


Figure 2. Separation sequence for product fractionation after lignin depolymerization.

The product of interest in this study was *light oil* containing the low-molecular-weight phenolic compounds. The aqueous residue fraction contained salts formed (Na_2SO_4) during neutralization and it was not considered in this study.

2.4. Characterization procedures.

2.4.1. GC-MS analysis of the oily fractions.

Compounds were detected and quantified by a gas chromatograph equipped with a quadrupole mass spectrometer detector (5977A-Agilent Technologies, USA). The separation was done with a capillary column HP-5ms, 30 m \times 0.250 mm \times 0.25 μm (Agilent Technologies, USA). The equipment was in splitless mode. Helium was used as carrier gas. The oven temperature was programmed as follows: initial temperature was set at 32 $^{\circ}\text{C}$ and kept for 10 min, then temperature was raised to 52 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{min}$, and kept for 2 min; to 65 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{min}$, and kept for 2 min; to 93 $^{\circ}\text{C}$ at 4 $^{\circ}\text{C}/\text{min}$, and kept for 2 min; to 230 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{min}$ and kept for 3 min; and finally, to 300 $^{\circ}\text{C}$ at 15 $^{\circ}\text{C}/\text{min}$, and kept for 3 min. This oven ramp was chosen after several runs as the best option to obtain clear chromatograms with a good separation between peaks. To eliminate the acquisition of the solvent (acetone) by the MS, a solvent delay was programmed at 3.70 minutes after confirming that no compounds were removed with the solvent. For compound identification, the data obtained in the GC-MS analysis

were compared with m/z values compiled in the spectrum library Wiley. Data analysis was performed using the Agilent Mass Hunter software (Agilent Technologies, USA). Validation of compound identification was carried out by comparison of their MS spectra and their retention times with standards. Quantification was carried out employing the internal standard method. With this calibration method, the peak area of each compound was normalized to the peak area of the internal standard. Some calibration curves are represented in Figure 3.

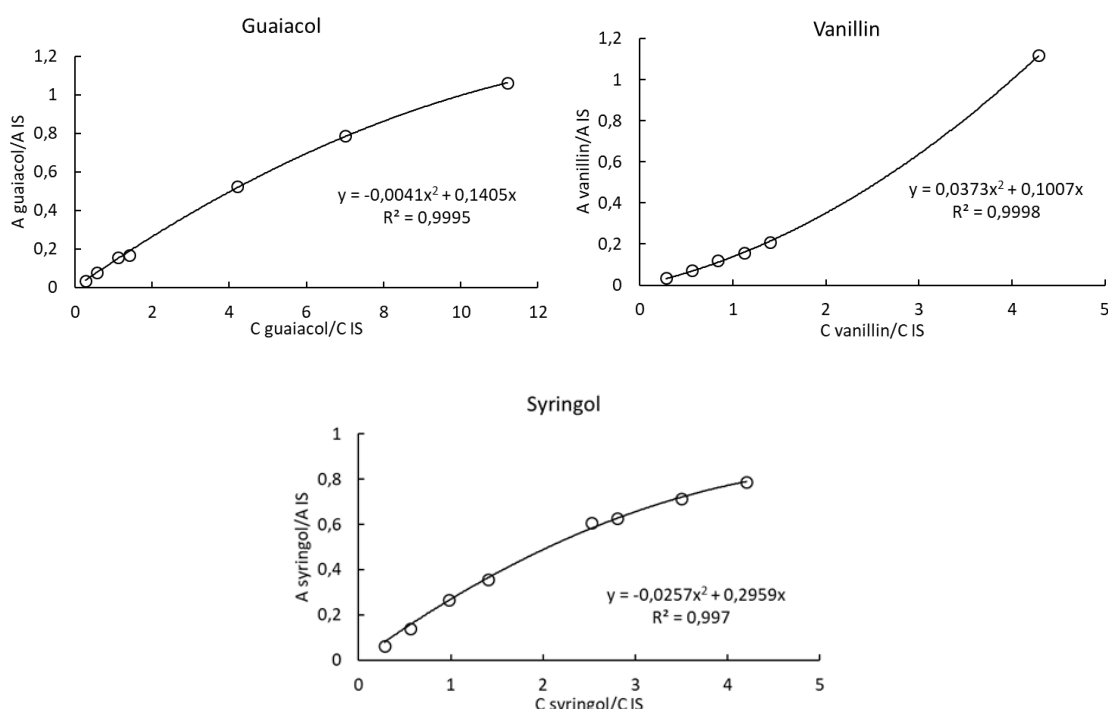


Figure 3. Calibration curves for guaiacol, vanillin and syringol using the internal standard method for GC-MS.

2.4.2. Gel Permeation Chromatography (GPC).

The molecular weight distribution of the different samples was determined by gel permeation chromatography (GPC) with a Jordi Gel Sulphonated Plus 10000 Å 250 x 10 mm column and using a Waters IR detector 2414 (210 nm) and a Waters dual λ absorbance detector 2487 (254 nm). The column was operated at 35 °C. The mobile phase was a solution water:methanol 90:10 vol, adjusted to pH = 12 at a flow rate of 1 mL/min. Samples were dissolved directly in the eluent with

concentration between 2 and 6 mg/mL. The injection volume was 25 μ L. Further details can be found in reference 2. Calibration standards were not used since the objective of this work was to study the molecular weight distribution qualitatively. Base line was corrected manually and chromatograms were normalized to the highest peak (Y-axis) for comparison purposes.

2.4.3. Micro-elemental analysis CHNS.

LECO CHNS-932 and VTF-900 analyzer equipped with an automatic sampler with capacity for 50 samples and an ultra-microbalance SARTORIUS M2P (precision ± 0.001 mg) were used.

Proportion of each element was corrected to exclude the moisture according to the following equations:

$$\%_C = \frac{\%_C^0}{100 - \%_{\text{moist.}}} \times 100$$

$$\%_H = \frac{\%_H^0 - \frac{2}{18} \%_{\text{moist.}}}{100 - \%_{\text{moist.}}} \times 100$$

$$\%_S = \frac{\%_S^0}{100 - \%_{\text{moist.}}} \times 100$$

$\%_C$, $\%_H$, $\%_S$ are the corrected percentages for C, H and S respectively; $\%_C^0$, $\%_H^0$, $\%_S^0$ are the nominal percentages. $\%_{\text{moist.}}$ is the percentage of moisture.

2.4.4. Fourier Transform Infrared Spectroscopy (FTIR-ATR).

The equipment used for FT-IR analysis of lignin and char was a Bruker Tensor 27 with a diamond crystal. The analysis were performed at room temperature. The spectra are recorded in mode Attenuated Total Reflection (ATR). The base line was corrected, and the peaks were normalized to the area between 1393 and 1816 cm^{-1} (aromatic skeletal vibration).

2.4.5. Thermo Gravimetric Analysis (TGA).

TGA analysis were carried out in a TGA/SDTA RSI analyzer of Mettler Toledo. Samples of approximately 5 mg were heated at a rate of 20 $^{\circ}\text{C}/\text{min}$ under N_2

atmosphere (60 mL/min flow) from a temperature of 50 °C up to temperatures around 850 °C. Keeping a constant temperature of 850°C, air was flowing during 5 min with a flow of 60 ml · min⁻¹.

Content of moisture was determined from TGA traces as the mass loss within temperature up to 120 °C.

2.4.6. Nuclear Magnetic Resonance (NMR).

NMR spectra were collected using an Agilent DD2 500 instrument equipped with cryoprobe, operating at 499.81 MHz for ¹H and at 125.69 MHz for ¹³C. Pyridine was used as solvent, and the experiments were performed at room temperature.

2.5. Calculation of fractionation yields and selectivity of monomers.

For calculating the yield of the fractionation product 'i', %Y_i, equation 1 was used:

$$\%Y_i = \frac{C_i}{C_{Lg}} \times 100 \quad (1)$$

Where C_i is the concentration of the fraction 'i' in the product mixture, expressed in g · L⁻¹ and C_{Lg} the concentration of lignin in the reactor, expressed in g · L⁻¹.

Analogously, the yield in the monomer 'x', %Y_x, present in the product mixture, is referred to the total amount of lignin and calculated as equation 2:

$$\%Y_x = \frac{C_x}{C_{Lg}} \times 100 = \frac{X_x^{oil} C_{oil}}{C_{Lg}} \times 100 = X_x^{oil} \cdot Y_{oil} \quad (2)$$

Where C_x is the concentration of the monomer 'x' in the product mixture, X_x^{oil} (g · g⁻¹) is the mass fraction (or selectivity) of the monomer 'x' in the aromatic oil and C_{oil} is the concentration of the aromatic oil in the product mixture (g · L⁻¹).

3. Results and discussion.

3.1. Effect of reaction parameters on the kraft lignin depolymerization/repolymerization: Mechanisms.

The light oil fraction mainly consisted on a mixture of dimers and trimers, but it also concentrated the monomeric products, with a good selectivity, as it was determined by GC-MS. Thus, it can be envisaged as a desired crude

depolymerization product since monomers can be more easily isolated from the remaining mixture of di-trimers and the latter be used as precursor of materials [9]. Optimization of this fraction depends on time and temperature (Figure 4) as maxima were found at longer reaction times for lower temperatures, as it was seen in Chapter I. However, it seems that reaction time has a more detrimental effect than temperature as the highest yield of light oil was obtained at 400 °C and short times. These results are in agreement with other studies where it is shown that increasing the reaction time (i.e. increasing the reaction severity), decreases the concentration of phenolic compounds (monomeric oil production) as the importance of repolymerization reactions increases [15].

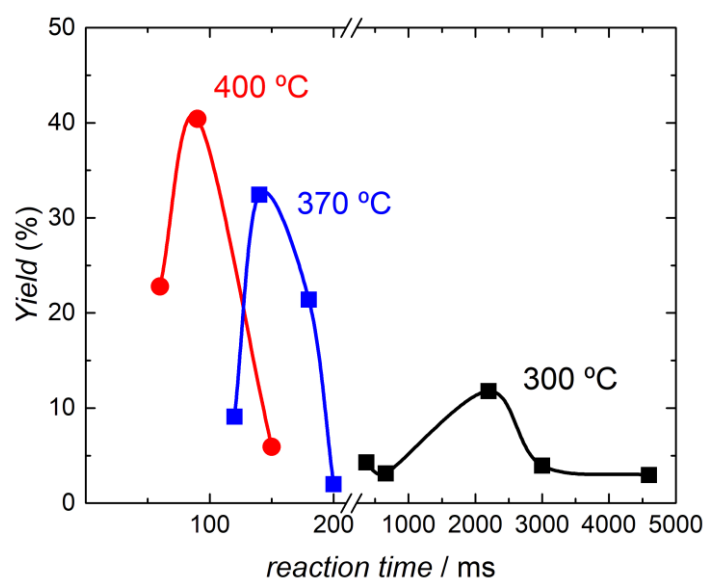


Figure 4. Non-catalyzed depolymerization of lignin in sub- and supercritical water (results from Chapter I). Light oil yield vs reaction time at different temperatures.

Hydrolysis of lignin can be enhanced using bases as catalyst [2, 12, 13] which are proposed to help cleavage of the β -O-4 ether bond via nucleophilic attack of an adjacent methoxy group [19], or heterolytically via a six-membered transition state [13]. Most of these studies have been done at water well below the critical point; one of the reasons may be that due to the ionic nature on the catalysts, conditions of high ionic product are required. However, at reaction times of seconds, NaOH can also be an efficient catalyst at supercritical temperatures [2]. Figure 5a shows that this is true even at timescales of two orders of magnitude

lower and temperatures where ionic pathways are supposed to be less important. NaOH increased the light oil yield to almost double, even reacting a lignin concentration 5-times greater than in the case of non-catalytic reaction.

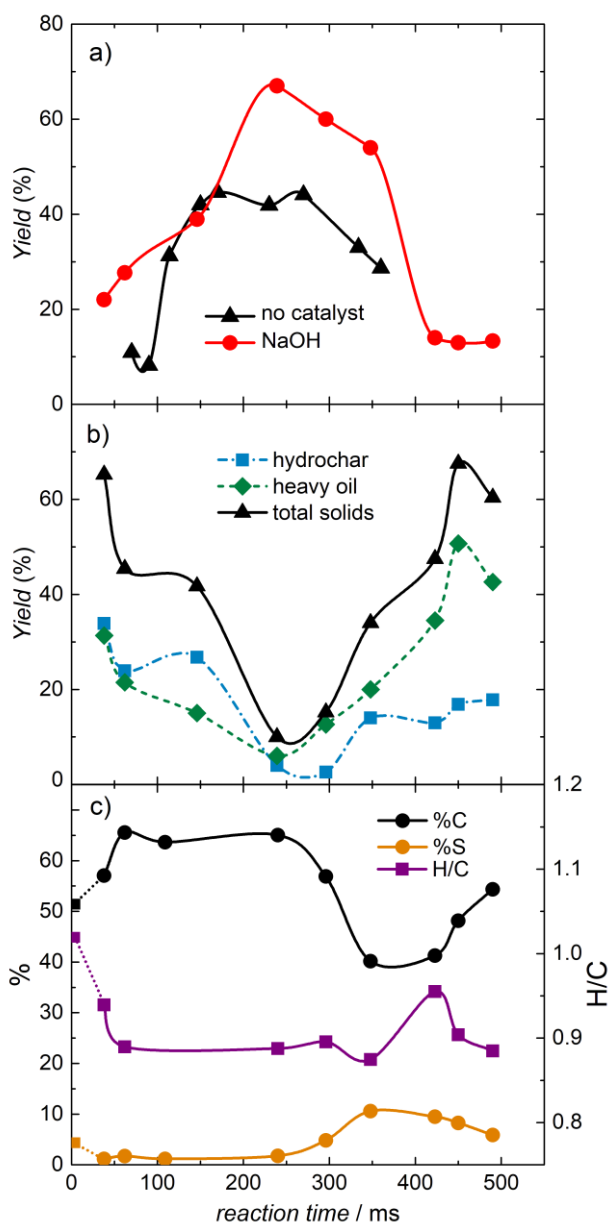


Figure 5. Evolution of the depolymerization reaction of kraft lignin vs time at 386 °C. a) Light oil yield with and without NaOH catalyst addition. b) Yield of heavy oil and char obtained in the base-catalyzed reaction. c) Elemental composition for char. A triplicate extraction of one experiment was performed in order to determine the standard deviation for each fraction: char 4.6 wt%, heavy oil 5.0 wt% and light oil 1.3 wt%.

However, an anomalously high yield of the solid fractions at times below 240 ms was really surprising, reaching a minimum at the point of maximum light oil

yield. This behavior was also observed at other temperatures in Chapter I. It was thought that water insoluble fractions obtained at reaction times below or over 240 ms must be different in composition than each other and therefore, originated by different kind of reactions. Indeed, TGA done to these samples reveal that the latter are more stable than the former as a peak in the derivative at $T = 770\text{ }^{\circ}\text{C}$ is appreciated in Figure 6a, which is coherent with the presence of resilient repolymerization products. Nevertheless, whatever transformations are occurring they do not alter significantly the aromatic structure as little difference was observed in the FT-IR spectrum at wavenumbers within 1400 and 1650 cm^{-1} (Figure 6b). This is not the case of the C-O bonds whose signals appeared within 1000 and 1300 cm^{-1} as spectra of lignin, and solid at short and long residence times were different.

Elemental analysis also shows a significant change in %C, %H and %O respect the starting lignin (Figure 5c). The values of H/C quickly decreased within the first 64 ms while those for %C increased. These changes point to a first very fast reaction step of dehydration of the aliphatic backbone as proposed in Figure 7. This hypothesis can be further supported by Heteronuclear Single-Quantum Correlation (HSQC), which is a 2D NMR technique that detects ^{13}C - ^1H coupling separated by three or four bonds. The -OH groups located in the aliphatic backbone of lignin disappeared upon SCW treatment (see *Section 3.3. Additional results*, Figure 13).

Dehydration reactions have been observed in water at both sub- and supercritical conditions [20, 21]. However, the dominating mechanisms are significantly different. Below the critical point, water has an ionic product several orders of magnitude higher, so dehydration can proceed via ionic pathways. On the other hand, at higher temperatures ($>400\text{ }^{\circ}\text{C}$), radicalary mechanisms are preferential. At the intermediate temperatures studied in this paper, a combination of both mechanisms is a plausible assumption that can be assumed [19, 22]. In any case, SCW treatment implies a loss of -OH groups, which can be a plausible explanation for lignin decreasing solubility in water.

Once the equilibrium is established, the β -O-4 ether linkages will be progressively cleaved. According to McDonough [19], dehydration will be followed by a hydrolysis that generates an enolate that will immediately proceed to form the corresponding ketone via keto-enol tautomerization. However, Roberts et al. [12] proposed a basic-catalyzed reaction through resonance-stabilized benzyl carbocations. These mechanisms are proposed for temperatures not higher than 300 °C, where ionic pathways are dominant. As discussed above, reaction temperatures in this work are higher so additional pathways must be considered [22]. Apart from breaking ether linkages, depolymerization can proceed via different homolytic cleavages to produce the main monomers including the homovanillic acid, which has never been reported in significant amounts from lignin depolymerization.

As depolymerization proceeds, smaller oligomers and monomers will be incorporated to the aromatic oil fraction increasing its yield while the amount of solid fraction decreases down to an optimum point at 240 ms.

At reaction times higher than 240 ms, the tendency changes and the amount of solids increases again following mechanisms of repolymerization of lignin low-molecular-weight fragments (i.e. monomers, dimers and trimers) to higher molecular weight compounds, as proposed in literature [10, 12]. However, no information about their chemical composition has been reported, so the kinetics and mechanisms of the reaction remain speculative. Elemental analysis of char (over 240 ms) provided additional clues about the evolution of the reaction as two distinct stages can be clearly distinguished: initially (between 300 and 420 ms), progressive decreasing of %C accompanied by an increment in H/C ratio to values more typical of the aromatic oil is observed, that is indicative of a repolymerization by coupling from the components of monomers and oligomers [12, 15, 18]. At the later steps of the reaction (>400 ms), this tendency is again reversed probably due to further reactions of carbonization, loss of -OH [10], or demethylation [2].

An interesting observation is the figure for %S (Figure 5c). Its concentration in char is kept low and steady until the repolymerization process starts. Then sulfur, presumably from the starting lignin, is progressively incorporated to this fraction up to values of 10.6 % (approximately 35% of the total sulfur originally contained in kraft lignin). One can hypothesize the formation of analogous thioaldehydes and thioketones from -SH substituted units of kraft lignin that will readily incorporate to the repolymerized structure as they are not stable and are known to aggregate. More detailed studies are necessary to determine the fate of sulfur in sulfur lignins, as the mechanisms involved seem to be strongly dependent on the type of the sulfur moiety. For example, it has been observed that, unlike sulfide moieties, sulfonate groups present in liginosulphonates, do not incorporate to char or other fractions but they tend to remain in the aqueous residue as partially reacted lignin or free sulfate [2].

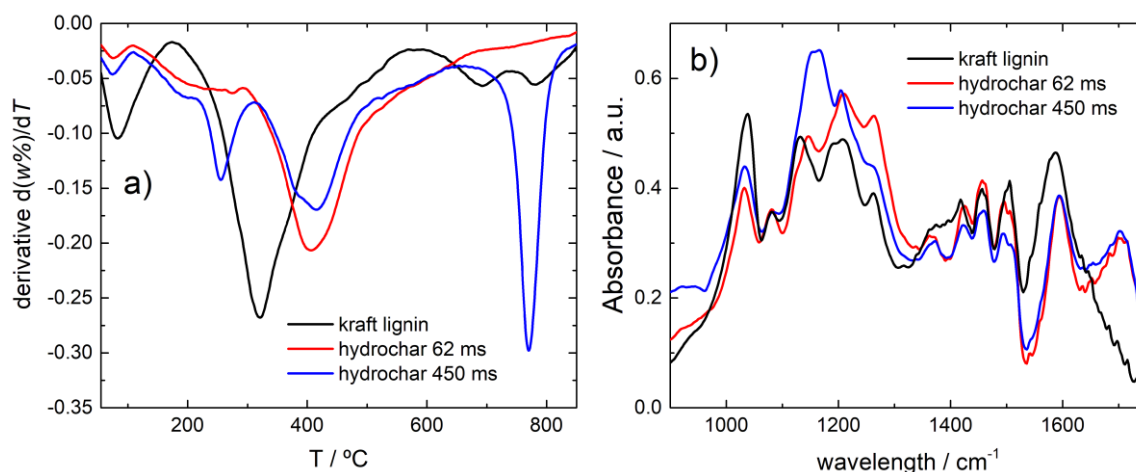


Figure 6. Comparison between chars obtained at 62 ms and 450 ms reaction time and starting lignin. a) Thermo Gravimetrical Analysis (derivative). b) FT-IR spectra.

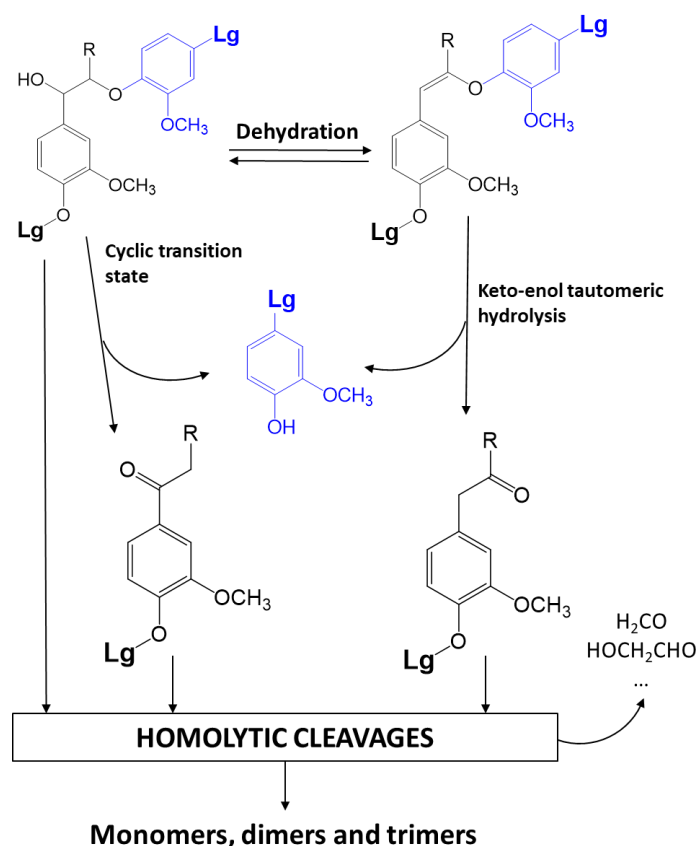


Figure 7. Proposed reaction scheme for the aromatic products from kraft lignin in SCW.

On the other hand, Figure 8 presents the yield of monomers with reaction time. Any clear tendency was observed, which indicates that monomers were formed and destroyed randomly, without any preference. However, comparing the total monomeric yield curve with the light oil yield (Figure 9), it can be seen that light oil fraction, containing monomers, dimers and trimers, was formed milliseconds before the monomers, reaching a maximum at 240 ms. Then, monomers were formed, reaching its maximum 60 ms later, at 300 ms. This suggests that dimers and trimers started to degrade forming monomers, at the same time the former started to repolymerize.

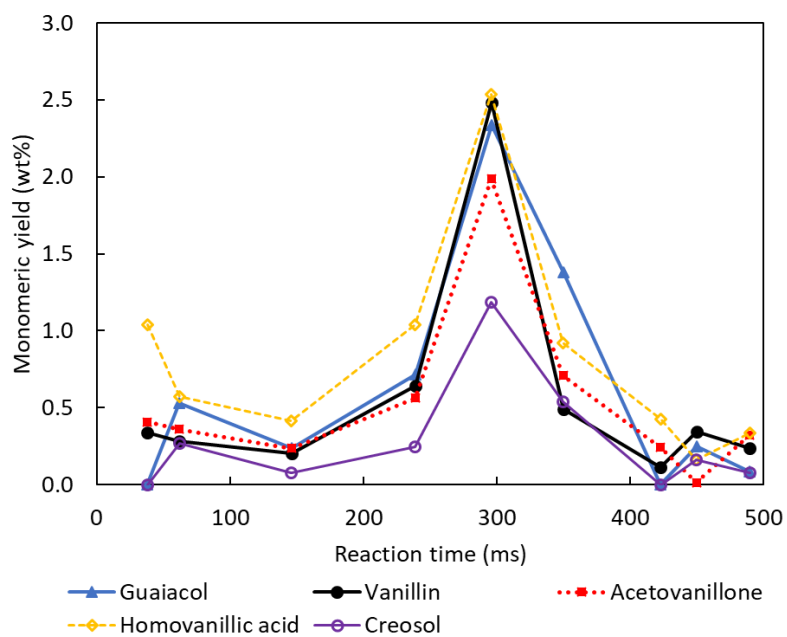


Figure 8. Monomers yield as function of the reaction time, referred to the total amount of lignin (calculated as equation 2).

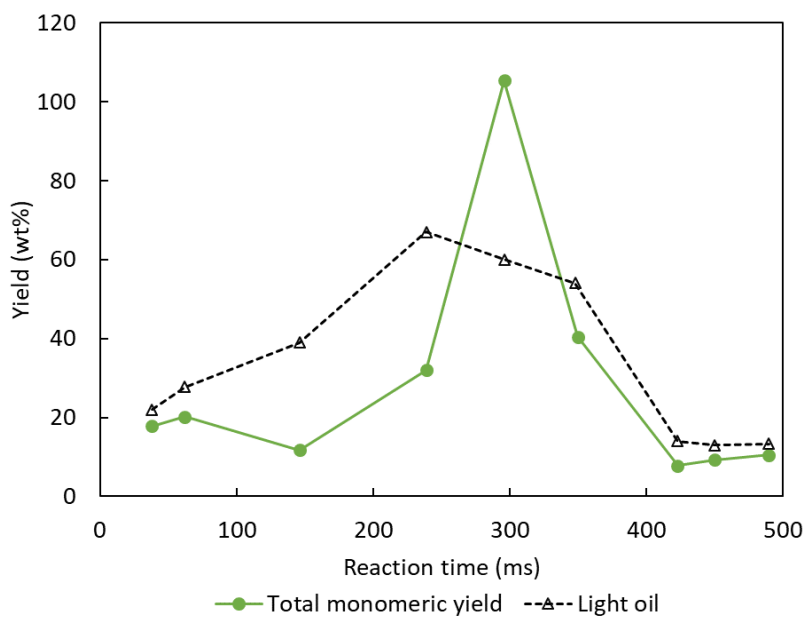


Figure 9. Light oil and total monomeric yield with time. Total monomeric yield is the sum of all monomers of Figure 8 multiplied by 10, for comparison purposes in this figure.

3.2. Supercritical water hydrolysis of a black liquor with low content of lignin.

Nowadays, lignin residual streams like black or brown liquors, which are obtained as residues in some industries (e.g. pulp and paper industries), impose significant technical challenges to be used in high value applications. Kraft black liquors are further processed in the same plant to recover the inorganic reactants. Very often, lignin production exceeds the necessities of the plant, so the remaining material is burned to generate electric energy. Thus, black liquor can be considered a low-value by-product and direct valorization of it would be very desirable. In this work, we demonstrate that ultrafast depolymerization in SCW is also applicable to these industrial streams, which would be a more advantageous process because the steps of lignin isolation are no longer necessary. Moreover, the black liquor stream from Kraft process itself is already in alkaline medium (pH 12-13), being no necessary the base-catalyst addition.

A black liquor supplied by a paper industry with low content of lignin was depolymerized through the base-catalyzed SCW process, as well as the corresponding Kraft lignin isolated from it (namely HKL) for comparison purposes. A reaction time of 300 ms was chosen for performing these experiences since it was the optimal reaction time in terms of monomeric selectivity determined in the previous section for the commercial Kraft lignin (named in this section as SKL lignin). The results obtained are shown in Table 1 and they indicate that the base-catalyzed depolymerization using SCW is feasible, even if lignin is contained in a complex mixture as it is black liquors. The light oil yield obtained for the black liquor (51.3%) is similar to that obtained for the commercial SKL lignin and significantly higher than the corresponding HKL lignin. The monomeric selectivity for both, BL and its lignin, as well as the results of SKL lignin for comparison purposes, is also presented in Table 1. A high selectivity in monomers of up to 17.9% was achieved in the BL depolymerization, being the major compounds syringol and syringaldehyde, with selectivities of 3.0% and 7.3%, respectively. Figure 10 presents the GC-MS traces of light oils obtained from both lignins and the black liquor, showing that the monomeric compounds are obtained with a high selectivity, which is unusual in hydrothermal reactions

at such high temperatures. It seems that the short reaction times are not only useful to control the char production but also the monomeric selectivity.

The main differences observed between light oil compositions are related to the starting lignin. Units derived from coniferyl alcohol were mostly detected from commercial lignin from Sigma, concluding that this must have been originated from softwood. Black liquor and lignin from the paper industry, on the contrary, present significant proportions of sinapyl alcohol derived units revealing its hardwood origin. However, depolymerization of HKL yielded much less amounts of coniferyl alcohol-derived units than the corresponding black liquor. This difference can be due to the modified structure of the HKL lignin after being extracted from the black liquor. This new structure could be more complex and compact, making it more difficult to depolymerize. In any case, the direct treatment of the black liquor results again beneficial compared to that of the isolated lignin as coniferyl alcohol derived units are commercially more valuable.

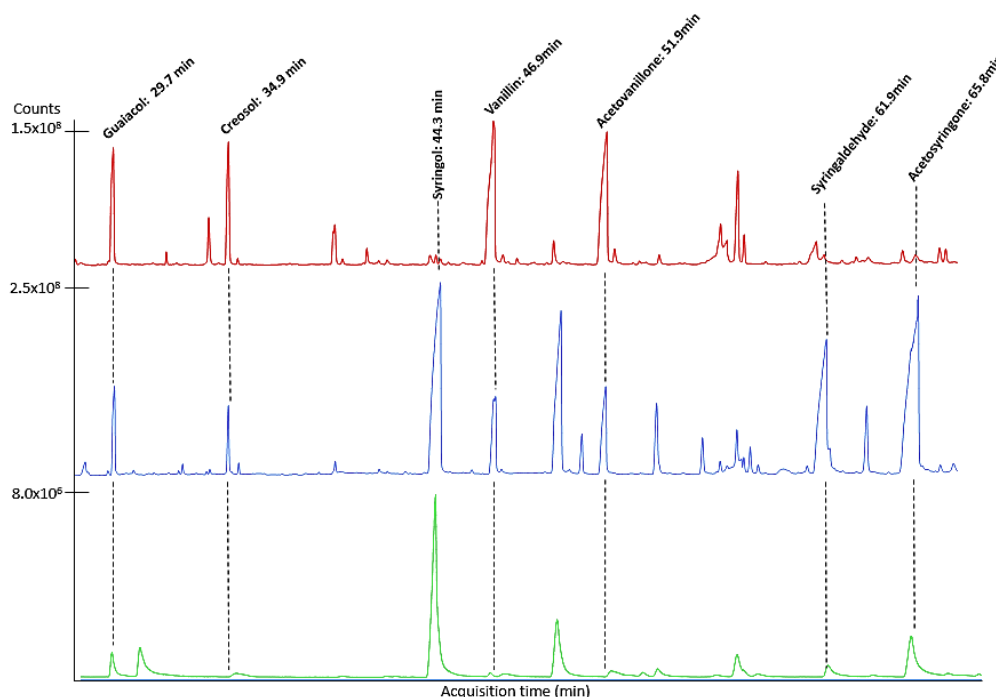


Figure 10. GC-MS chromatograms of light oils obtained in the depolymerization process at 300 ms and 386°C in alkaline medium from: SKL (red); HKBL (blue); HKL (green).

Table 1. Ultrafast depolymerization of lignins and black liquor using supercritical water in alkaline medium (386°C, 300 ms). Light oil yield and selectivity of the major monomers. All values expressed as wt%. Heavy oil contained negligible concentrations of monomers.

	SKL	HKBL	HKL
<i>Light oil yield</i>	60.0	51.3	23.5
Guaiacol	3.9	2.7	0.8
Vanillin	4.1	0.6	0.3
Acetovanillone	3.3	1.6	0.3
Homovanillic acid	4.2	0.0	0.0
Creosol	2.0	0.8	0.0
Syringol	0.1	3.0	4.1
Syringaldehyde	0.7	7.3	4.0
Acetosyringone	1.5	1.9	3.8
TOTAL	19.8	17.9	13.3

3.3. Additional results.

In order to support the previous results, as well as the hypothesis and reaction mechanisms proposed, additional analysis were performed.

3.3.1. Molecular weight distribution of char with time.

Figure 11 (left) shows the normalized GPC chromatogram for SKL and some chars obtained at different times. Retention time of the maxima increases (i.e. the molecular weight decreases) with reaction time up to 240 ms, being those chars similar in size than the original lignin. At 300 ms, the tendency changes, indicating that the repolymerization starts in this point. Above 300 ms, the retention time of the maxima decreases with time (i.e. molecular weight of char increases), indicating that the repolymerization continues. In figure 11 (right) the same information than in figure 11 (left) can be observed, where the retention time of the maxima of chars at different reaction times is represented with the respective reaction time. In this figure, the affirmations done above can be seen clearly.

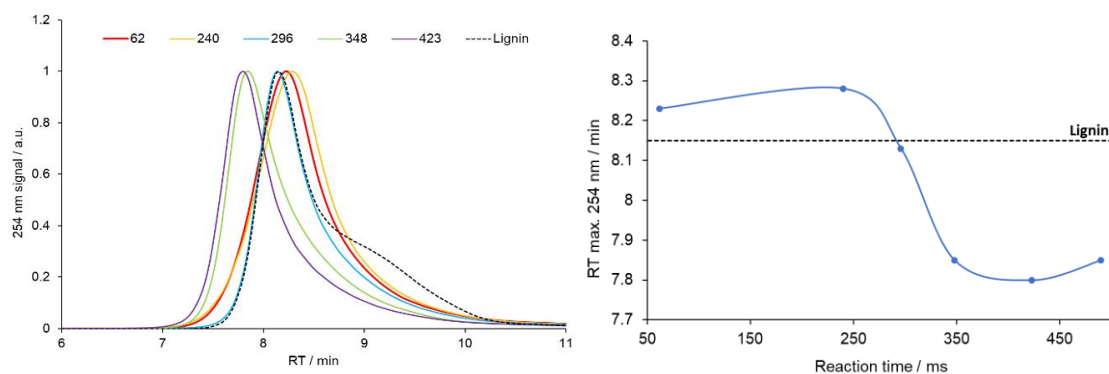


Figure 11. Left: GPC traces for hydrochars obtained at different reaction times from kraft lignin depolymerization in alkaline SCW (386 °C); Right: Curve of the retention times at which the 254 nm signal is maximum for the hydrochars at different reaction times vs the respective reaction time. The dotted line represents the retention time of maximum UV signal for kraft lignin.

3.3.2. Characterization of the structure of char.

3.3.2.1. FT-IR and TGA.

Figure 12 presents TGA and FT-IR analysis done to char obtained at 386°C and different reaction times. A clear change of tendency is observed at times higher than 296 ms. TGA derivative traces indicate that for higher reaction times the material is more stable because decomposition peaks at higher temperatures are appearing. FT-IR also indicates a change in the C-O bond vibrations.

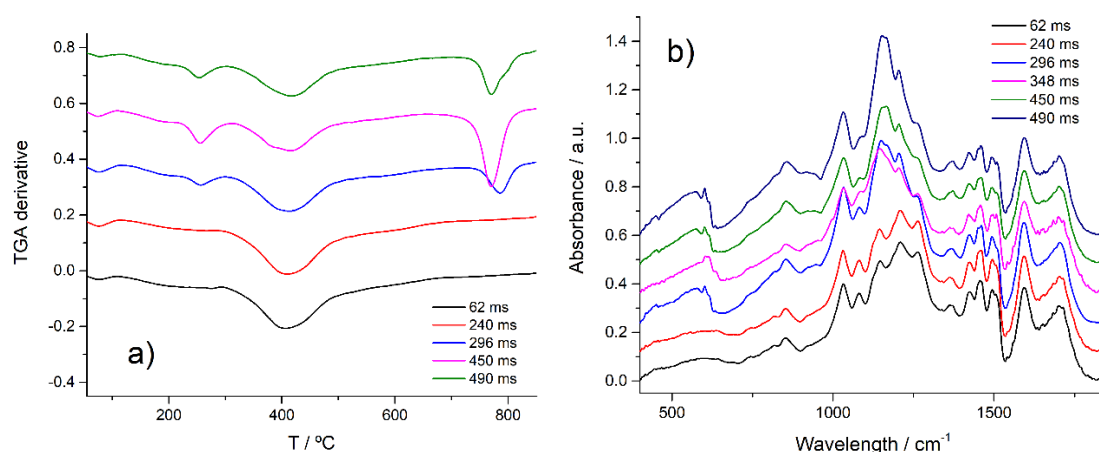


Figure 12. Analysis of char fraction obtained at 386 °C in alkaline conditions, at different reaction times. a) TGA; b) FT-IR.

3.3.2.2. 2D HMBC NMR.

2D NMR Heteronuclear Multiple Bond Correlation (HMBC) technique detects ^{13}C - ^1H coupling through three or four covalent bonds. It was used to provide additional evidence of loss of aliphatic hydroxyl groups. Figure 15 shows the HMBC spectra for the region of $\text{R}_1\text{R}_2\text{CH-O}$ protons for kraft lignin and the hydrochar obtained at 62 ms. A large signal can be appreciated at ca. $\text{H}=3.6\text{--}3.9$ ppm; $\text{C}=145\text{--}150$ ppm for both spectra, characteristic of the methoxy groups of the aromatic units. In the spectra of lignin, however, additional smaller signals appear, which are likely to correspond to protons attached to C_α , C_β and/or C_γ of the aliphatic backbone. These signals disappear upon SCW treatment.

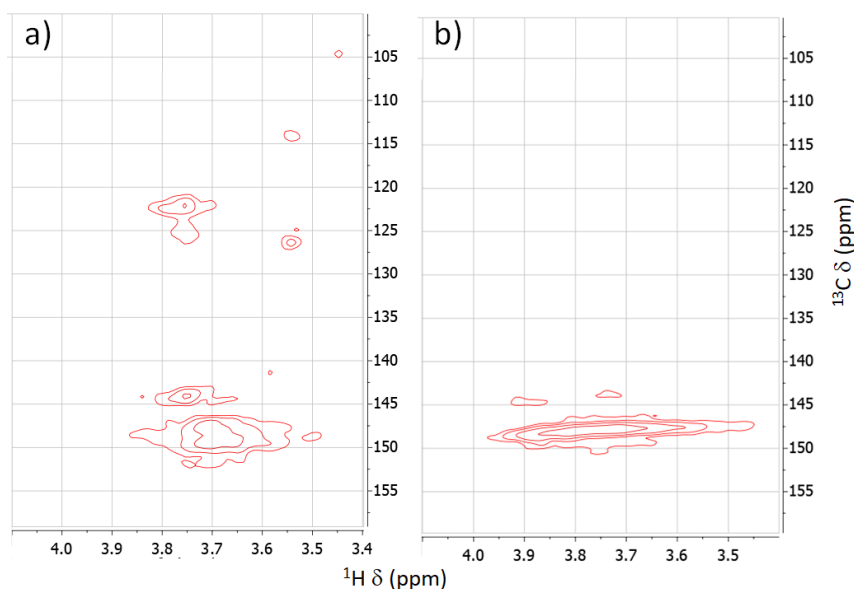


Figure 13. HMBC spectra for the region of $\text{R}_1\text{R}_2\text{CH-O}$ protons for a) SKL and b) char obtained at 62 ms.

4. Conclusions.

Commercial kraft lignin can be effectively depolymerized with hot and pressurized water at times below 500 ms using a Sudden Expansion Micro-Reactor. By controlling reaction time, it is possible to avoid char formation due to repolymerization of the lignin molecule while maximizing the yield of light oil containing phenolics with high selectivity. At 300 ms, 386 °C and using NaOH as

catalyst, the light oil yield was 60.0 wt% with a concentration of key monomers close to 20%. Analysis and quantification of the reaction products allowed distinguishing the different stages of the reaction: Depolymerization starts with a very rapid dehydration step followed by cleavage of C-O and C-C bonds up to the optimum point. Low-molecular-weight fragments start to repolymerize at longer reaction times to yield char. Organic sulfur is incorporated to the latter at the last stages of the reaction. The ultrafast base-catalyzed SCW technology was used to directly treat a black liquor and it was found to be equally effective than when using commercial kraft lignin and even better than the lignin isolated from the black liquor. Those results represent a significant advance because black liquors can be directly treated without need of further treatment by our fast and intensified process, which presents important advantages (i.e. small reactors resulting in a feasible scale-up, cost and safety of the solvent and accurately time control to avoid undesirable repolymerization reactions).

This novel technology for converting lignin into high value-added products has been patented under the Title 'ULTRA-FAST LIGNIN DEPOLYMERIZATION PROCESS' (European Patent Office, Application number 17382892.2 - 1109).

References.

1. Aeschelmann, F. and M. Carus, *Bio-based Building Blocks and Polymers in the World – Capacities, Production and Applications: Status Quo and Trends toward 2020*, n.-l. GmbH, Editor., Michael Carus (V.i.S.d.P.): Hürth, Germany.
2. Pérez, E. and C.O. Tuck, *Quantitative analysis of products from lignin depolymerisation in high-temperature water*. European Polymer Journal, 2018. **99**: p. 38-48.
3. Rinaldi, R., et al., *Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis*. Angewandte Chemie International Edition, 2016. **55**(29): p. 8164-8215.
4. Rahimi, A., et al., *Chemoselective Metal-Free Aerobic Alcohol Oxidation in Lignin*. Journal of the American Chemical Society, 2013. **135**(17): p. 6415-6418.
5. Rahimi, A., et al., *Formic-acid-induced depolymerization of oxidized lignin to aromatics*. Nature, 2014. **515**: p. 249.
6. Shuai, L., et al., *Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization*. Science, 2016. **354**(6310): p. 329-333.
7. Ragauskas, A.J., et al., *Lignin Valorization: Improving Lignin Processing in the Biorefinery*. Science, 2014. **344**(6185): p. 1246-1249.
8. Pandey, M.P. and C.S. Kim, *Lignin Depolymerization and Conversion: A Review of Thermochemical Methods*. Chemical Engineering & Technology, 2011. **34**(1): p. 29-41.

9. Pérez, E., C.O. Tuck, and M. Poliakoff, *Valorisation of lignin by depolymerisation and fractionation using supercritical fluids and conventional solvents*. The Journal of Supercritical Fluids, 2018. **133**: p. 690-695.
10. Wahyudiono, M. Sasaki, and M. Goto, *Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water*. Chemical Engineering and Processing: Process Intensification, 2008. **47**(9): p. 1609-1619.
11. Yong, T.L.-K. and Y. Matsumura, *Reaction Kinetics of the Lignin Conversion in Supercritical Water*. Industrial & Engineering Chemistry Research, 2012. **51**(37): p. 11975-11988.
12. Roberts, V.M., et al., *Towards Quantitative Catalytic Lignin Depolymerization*. Chemistry – A European Journal, 2011. **17**(21): p. 5939-5948.
13. Miller, J.E., et al., *Batch microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents*. Fuel, 1999. **78**(11): p. 1363-1366.
14. Oasmaa, A. and A. Johansson, *Catalytic hydrotreating of lignin with water-soluble molybdenum catalyst*. Energy & Fuels, 1993. **7**(3): p. 426-429.
15. Shuai, L. and B. Saha, *Towards high-yield lignin monomer production*. Green Chemistry, 2017. **19**(16): p. 3752-3758.
16. Cocero, M.J., et al., *Understanding biomass fractionation in subcritical & supercritical water*. The Journal of Supercritical Fluids, 2018. **133**: p. 550-565.
17. Vigneault, A., D.K. Johnson, and E. Chornet, *Base-Catalyzed Depolymerization of Lignin: Separation of Monomers*. The Canadian Journal of Chemical Engineering, 2007. **85**(6): p. 906-916.
18. Cantero, D.A., et al., *Simultaneous and selective recovery of cellulose and hemicellulose fractions from wheat bran by supercritical water hydrolysis*. Green Chemistry, 2015. **17**(1): p. 610-618.
19. McDonough, T.J., *The chemistry of organosolv delignification*. TAPPI Journal, 1993. **76**(8): p. 186.
20. Bühler, W., et al., *Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water*. The Journal of Supercritical Fluids, 2002. **22**(1): p. 37-53.
21. Cantero, D.A., M.D. Bermejo, and M.J. Cocero, *Governing Chemistry of Cellulose Hydrolysis in Supercritical Water*. ChemSusChem, 2015. **8**(6): p. 1026-1033.
22. Erdocia, X., et al., *Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature*. Biomass and Bioenergy, 2014. **66**: p. 379-386.

CHAPTER III

BASE-CATALYZED

DEPOLYMERIZATION OF

LIGNINS: INFLUENCE OF LIGNIN

NATURE AND VALORIZATION

OF PULPING AND BIOREFINERY

RESIDUES.

BASE-CATALYZED DEPOLYMERIZATION OF LIGNINS: INFLUENCE OF LIGNIN NATURE AND VALORIZATION OF PULPING AND BIOREFINERY RESIDUES.

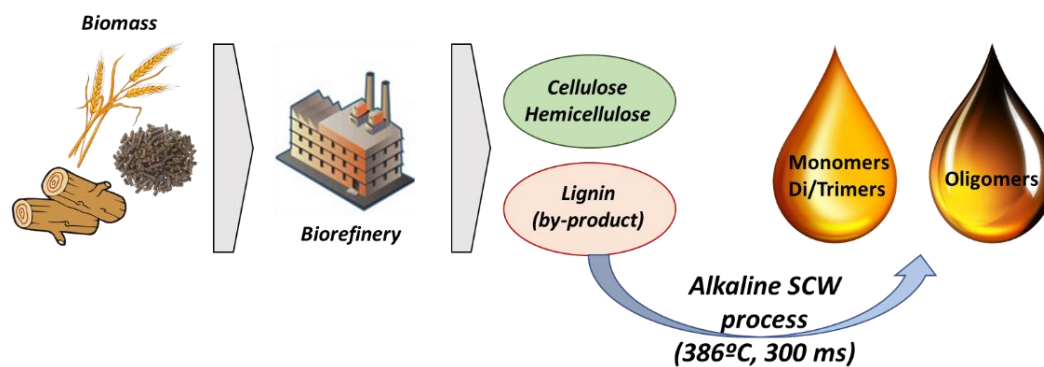
Abstract.

Different lignins obtained from different sources (hardwoods, softwoods and crop residues) and isolated by different processes (kraft, organosolv, enzymatic and sub- and supercritical water hydrolysis) were depolymerized in alkaline supercritical water (SCW: 386°C and 260 bar) in a continuous process to produce high value-added compounds with low-molecular-weight in only 300 milliseconds of reaction time. The products obtained (light oil, heavy oil and char) were analysed determining their yield, monomeric selectivity, linkages, structure and functional groups, molecular weight distribution and thermal stability in order to study the effect of the lignin nature in this depolymerization process.

The highest phenolic yield was obtained from the depolymerization of a commercial Kraft lignin from softwood, with 9.4 wt%, followed by hardwood lignins. Non-wood lignins containing biomass obtained from the fractionation of crop residues via biomass hydrolysis were not as suitable for obtaining phenolic monomers as extracted technical wood lignins, with monomeric yields lower than 1.0 wt%.

A great advantage of this technology is that it can be used to directly treat black liquors with low lignin content obtained as residues from pulp and paper industries. It was found to be equally effective than when using technical lignins and even better that the corresponding lignin isolated from the black liquor. A phenolic yield of 9.2 wt% was obtained. These results represent a significant advance to the strategy of rapid base-catalysed SCW depolymerization of lignin because black liquors can be treated with no need of previous lignin isolation step while obtaining a high conversion into phenolic monomers and controlling the undesired repolymerization reactions with a low reaction time. The char fraction yield was lower than 8.0 wt% in most cases, and it presented a similar

nature whatever the lignin nature was since dehydration reactions occurred in all the lignins studied.



1. Introduction.

Lignocellulose is the most abundant, cheapest and easiest grown form of biomass composed mainly of cellulose (30–50%), hemicellulose (20–40%) and lignin (15–35%) [1]. These fractions represent potential feedstocks for bio-sourced commodity chemicals, but due to their differing chemical functionalities (lignin is made up of linked aromatic units, hemicellulose of C5 and C6 sugars and cellulose of C6 sugars) separation steps are necessary to isolate the appropriate fraction and break it into its individual building blocks (e.g. sugars for cellulose/hemicellulose and aromatic units for lignin). The base of the lignocellulosic biorefinery consists in fractionating biomass into its individual building blocks for their valorisation [2]. Various strategies have already been developed to obtain high value-added compounds from cellulose and hemicellulose. However, lignin is traditionally viewed as waste material or low value by-product which is in most cases burned to produce energy. Nowadays, research is focused on the effective depolymerization of this biopolymer. Unfortunately, most of studies resulted to be deceptive. The main reason is the complex structure of lignin and the uncontrolled repolymerization reactions that produce high amounts of char [3].

The biomass fractionation process is an essential key for the subsequent lignin valorisation. Different lignin extraction methods use different operating conditions including temperatures, pressures, solvents, and pH ranges that alter the chemical structure and linkages of the native lignin.

On the other hand, different feedstocks can be employed such as lignocellulosic biomass and wastes, cereals or corn, grasses or sugar. It is well known that 3-propylphenols that form the molecule of lignin (monolignols) can be linked in a wide variety of ways leading to many types of functional groups and structures, which vary from species to species, tree to tree, and even in woods from different parts of the same tree [3]. Hence, hardwood lignins are primarily composed by guaiacyl and syringyl units with traces of p-hydroxyphenyl propanoid units, whereas softwood lignins are composed mainly of guaiacyl units (around 90% of

the total) with low levels of p-hydroxyphenyl propanoid units. The theoretical structure of lignin presenting the different possible chemical structures is shown in Figure 1. Grass lignins are also classified as guaiacyl-syringyl lignin. However, unlike hardwood lignins, grass lignins additionally contain small but significant amounts of structural elements derived from p-coumaryl alcohol.

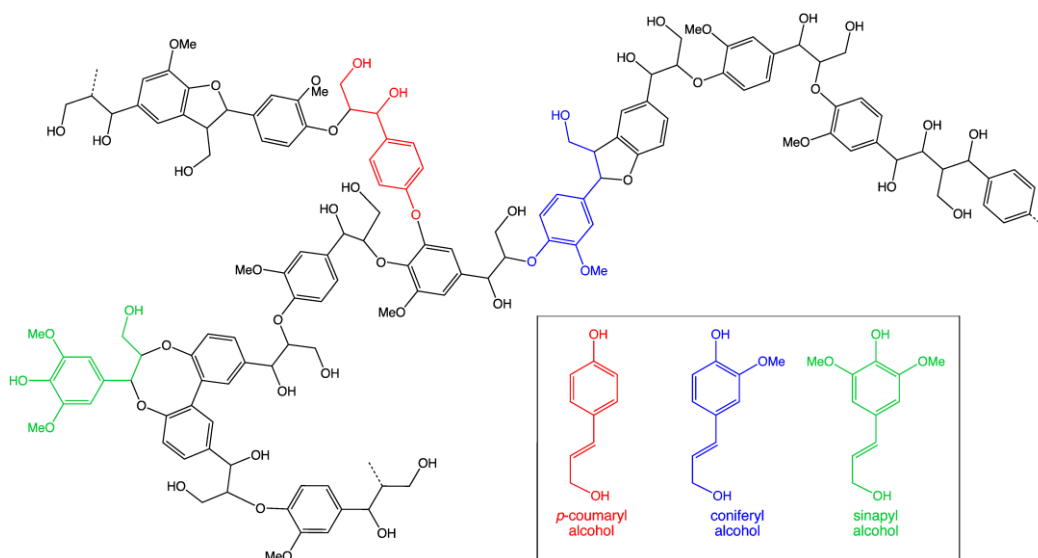


Figure 1. Chemical structures for varieties of lignin: p-coumaryl/hydroxyphenyl, coniferyl/guaiacyl and sinapyl/syringyl alcohol [4].

Hence, the physicochemical behaviour of lignin, which depends on the amount, position and relative ratio of the different functional groups present in the lignin molecule, will be strongly affected by the biomass source but also by the isolation method used.

The final aim of this work is to valorise different lignins obtained as by-products in pulp and paper industries and in biorefinery processes, as well as to study the effect of the lignin nature in the alkaline SCW process at 386°C, 260 bar and 300 ms of reaction time (parameters optimized in the previous chapter for SKL. The main products (bio-oils and char) were measured and analysed by different techniques in order to determine their yield, monomeric selectivity, linkages, structure and functional groups, molecular weight distribution and elemental composition. For this purpose, different analytical methods were used: gas chromatography/mass spectroscopy (GC-MS), gel permeation chromatography

(GPC), nuclear magnetic resonance (^{31}P NMR), Fourier-transform infrared spectroscopy (FT-IR) and micro-elemental analysis CHNS.

2. Materials and methods.

2.1. Materials.

Different technical lignins and biorefinery residues with high lignin content, as well as black liquors containing low amounts of lignin were studied in the present work. Kraft lignin with low sulfur content (4%) was purchased from Sigma-Aldrich and named as SKL; organosolv lignin was obtained from Fraunhofer Center for Chemical-Biotechnological Processes CBP (Germany), and it was named as HOL; kraft lignin named as HKL corresponds to the lignin isolated from the black liquor HKBL; lignins obtained after the fractionation of tobacco vein and beet pulp were extracted in our laboratory (High Pressure Processes Group, University of Valladolid), and they were named as THL and BHL, respectively; lignin from wheat straw was given by the Institute of Thermal Separation Processes, Hamburg University of Technology, and named as WHL. Black liquor was supplied by a Spanish paper industry, and The Bio-resources Thermo-conversion laboratory (Grenoble, France), and they were named as HKBL and HBL, respectively. Table S2 shows a summary of the extraction method and biomass source for the different lignins and liquors.

Distilled water was used as the reaction medium to run the experiments. Sodium hydroxide used as catalyst was purchased from Sigma-Aldrich. Sulfuric acid (96%) and ethyl acetate (>99%) employed for carrying out the fractionation of the products were also purchased from Sigma-Aldrich.

The calibration standards used in the GC-MS analysis were all purchased from Sigma-Aldrich (USA): syringol ($\geq 98\%$), acetosyringone (97%), guaiacol ($\geq 99\%$), creosol ($\geq 98\%$), acetovanillone ($\geq 98\%$), vanillin (99%), syringaldehyde ($\geq 97\%$), as well as the internal standard, 2-phenyl ethanol ($\geq 99\%$).

All compounds used for ^{31}P NMR were also purchased from Sigma-Aldrich: 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%), n-hydroxy-5-norbornene-2,3-dicarboximide (98%), chromium (III) acetylacetonate (>99%), deuterated pyridine (>99%), deuterated chloroform (>99%).

2.2. Experimental procedure and analytical methods.

2.2.1. Base-catalysed depolymerization.

The continuous process used to depolymerize lignins and black liquors in SCW was described in the previous chapter. In this study, the reactions were performed for all lignins at the optimal operating conditions determined in the previous chapter for SKL (i.e. 386 °C, 260 bar and 300 ms). A reactor of 1.6 ml of volume was used for all the experiments with a total flow of around 7 kg h⁻¹. The lignin concentration at the inlet of the reactor was in all cases 5000 ppm (0.5 wt%) in a basic solution of NaOH (0.2 M). In the case of the black liquors, they were diluted until reaching 5000 ppm of lignin at the inlet of the reactor as well for comparison purposes.

2.2.2. Fractionation of depolymerization products.

Product mixture was fractionated into four fractions (light oil, heavy oil, aqueous residue and char) as described in the previous chapter.

2.2.3. Calculation of fractionation yields and selectivity of monomers.

Fractionation yields and selectivity of monomers were calculated as in Chapter II (see section 2.5).

2.2.4. Characterization procedures.

All analytical techniques (GC-MS, GPC, Micro-Elemental Analysis CHNS, FT-IR, and TGA) were performed as in the previous chapter. NMR was carried out in a different equipment located in Aalto University (Espoo, Finland) during a 3 months short stay. A Bruker AVANCE 400 MHz 5 mm (BBFO) equipment was used and ^{31}P NMR was performed in order to quantitate lignin hydroxyl groups. The number of scans applied was 128 and a delay of 5 s. The data was processed using TopSpin 3.0 software.

2.2.4.1. Sample preparation for ^{31}P NMR lignin analysis.

We have used the most common standard protocols for the ^{31}P NMR lignin analysis [5, 6], particularly in terms of reagents and internal standards. The solvent to prepare the sample and all auxiliary solutions was a mixture of pyridine and deuterated chloroform (1.6:1, v/v). About 20 mg of sample was completely dissolved in 0.4 mL of freshly prepared solvent 50 μL of relaxant solution (11.4 mg chromium (III) acetylacetonate in 1 mL of solvent) and 100 μL of an internal standard solution (0.12 M of endo-n-hydroxy-5-norbornene-2,3-dicarboximide in solvent) were added. Thus, the ratio of the internal standard to lignin was about 0.3 $\mu\text{mol}/\text{mg}$, in agreement with the standard protocols [5, 6]. Finally, 100 μL of phosphorylation reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) was added to the mixture, the vial content was vortexed, transferred into an NMR tube, and submitted for NMR acquisition.

2.2.4.2. ^{31}P NMR calculations.

Concentration of $-\text{OH}$ functionalities, C_{OH} obtained from ^{31}P NMR spectra were expressed as mmol of OH per gram of sample. For converting the area of the peaks to mmol_{OH} , the internal standard (IS) was taken as reference (equation 3, where C_{IS} is the IS concentration, V_{IS} is the volume of IS in the sample, and M_{IS} is the molar mass of the IS). Equation 4 shows the calculation of the amount of $-\text{OH}$ functional groups in mol, n_{OH} , where area of IS (A_{IS}) was equal to 1. Equation 5 shows the calculation for obtaining the results as mmol_{OH} per mass of sample, m_{sample} , where lignin content was assumed to be 1 (purity of 100%). Table 1 shows the chemical shift in ppm for each hydroxyl group, which was adapted from literature [7].

$$n_{\text{IS}} = \frac{C_{\text{IS}} * V_{\text{IS}} * \text{Purity IS}}{M_{\text{IS}}} \quad (3)$$

$$n_{\text{OH}} = \frac{n_{\text{IS}} * A_{\text{OH}}}{A_{\text{IS}}} \quad (4)$$

$$C_{\text{OH}} = n_{\text{OH}} * \frac{1000}{m_{\text{sample}} * \text{lignin content}} \quad (5)$$

Table 1. Chemical shifts for the different hydroxyl groups determined by ^{31}P NMR.

	Chemical shift (ppm)
IS	152.1-151.7
Aliphatic	151.7-145.0
5-subst	145.0-141.1
Gnc	141.1-138.6
H	138.6-136.0
COOH	136.0-133.1

2.2.4.3. Composition of raw materials.

The total amount of lignin, sugars and ashes in the raw materials was determined according to the standard methods published by the National Renewable Energy Laboratory (NREL) [8]. The procedure consists in quantifying the structural carbohydrates and lignin in the raw materials as follows: A) The raw material was dried in an oven at 105 °C for 24 hours. B) 300 mg of dried solid were hydrolyzed in 3 ml of 72 wt% sulfuric acid solution at 30 °C for 30 min, in order to break the bonds between biopolymers and the main solid structure. C) The mixture of oligomers obtained in the previous step was diluted using 84 ml of deionized water and heated at 120 °C for 60 min with the aim of hydrolyzing hemicellulose and cellulose in order to obtain their corresponding monomers. D) The solid was separated from the solution by vacuum filtration. E) The total mass of solubilized sugars was quantified as the difference in weight between the original solid and the exhausted solid after oven drying. F) The exhausted solid was placed in a muffle at 550 °C for 24 h and the remaining residue was weighted before and after this step to calculate the insoluble lignin and the ash content of the sample. G) A liquid aliquot was analyzed with UV-Vis spectrophotometer to calculate the amount of soluble lignin. Different wavelengths and extinction coefficients were used for each lignin, which are presented in Table S1. H). Another liquid aliquot was neutralized to pH range 6 to 7, then it was filtered using a 0.2 μm membrane and analyzed by HPLC determining the carbohydrates composition. This procedure was performed using a column SUGAR SH-1011 (Shodex) with a 0.01 N of sulfuric acid solution as a mobile phase. To identify the

soluble products, two detectors were used: Waters IR detector 2414 (210 nm) and Waters dual λ absorbance detector 2487 (254 nm).

3. Results and discussion.

3.1. Characterization of lignins.

The lignins studied here are technical lignins and biorefinery residues extracted with different extraction methods. The conditions used for the different extraction methods employed is present in Table S2. Some conditions are unknown. In order to understand the behaviour of these starting materials in the base-catalysed SCW depolymerization process, some analysis were performed. The content of lignin, ashes and sugars, as well as the elemental composition of the different starting materials in this work is present in Tables 2 and 3, respectively, for future discussion. Technical lignins SKL, HKL and HOL contained mainly lignin (>85 wt%), with low ash and sugars content. However, WHL, BHL and THL lignins contained high amounts of sugars (up to 45 wt%) and ashes (up to 11 wt%). On the other hand, black liquors are complex mixtures formed by high amounts of salts and a minor amount of lignin.

Table 2. Composition of lignins and black liquors: Lignin content (Klason+ASL), ash, sugars and others (extractives, proteins...). All data are expressed in wt% and calculated on dry basis.

	Lignin %	Ash %	Total sugars	
			%	Others %
SKL	96.0	0.0	0.0	4.0
HKL	86.4	0.3	3.3	10.0
HOL	96.5	0.0	0.4	3.1
WHL	78.2	11.0	10.8	0.0
BHL	50.8	4.4	44.8	0.0
THL	79.7	0.0	23.8	0.0
HKBL	-	-	-	-
HBL	5.9	0.1	6.0	88.0

Elemental composition of the raw materials can be seen in Table 3. Data for black liquors are not totally informative since both HKBL and HBL are complex

mixtures, as it was mentioned above. Only Kraft lignins contained sulfur. BHL, THL and WHL contained nitrogen, which can be attributed to impurities. All lignins presented a similar hydrogen content (4.6-5.7 wt%), while they differed more in the carbon content (40.8-63.3 wt%).

Table 3. Elemental composition of lignins and black liquors.

	wt %				
Lignin	C	H	N	S	O*
SKL	49.1	4.6	0.1	4.1	42.1
HKL	57.0	5.1	0.0	2.2	35.7
HOL	63.3	5.7	0.0	0.0	31.0
WHL	50.8	5.5	1.1	0.0	42.5
BHL	40.8	5.3	0.6	0.0	53.4
THL	41.5	5.6	1.3	0.0	51.5
HKBL	-	-	-	-	-
HBL	6.0	2.4	0.0	0.0	91.7

*Estimated data

FT-IR spectra, thermograms and molecular weight distributions curves for the starting materials, which can be useful for understanding the results obtained in this work, are shown in Figures 2-4. HKL and OS, both hardwood lignins, present similar chemical functionalities, structure and thermal stability (Figure 2 and 3), as well as a similar molecular weight distribution (Figure 4). Lignins from the same biomass source were similar, even if the extraction method was different (i.e. kraft and organosolv).

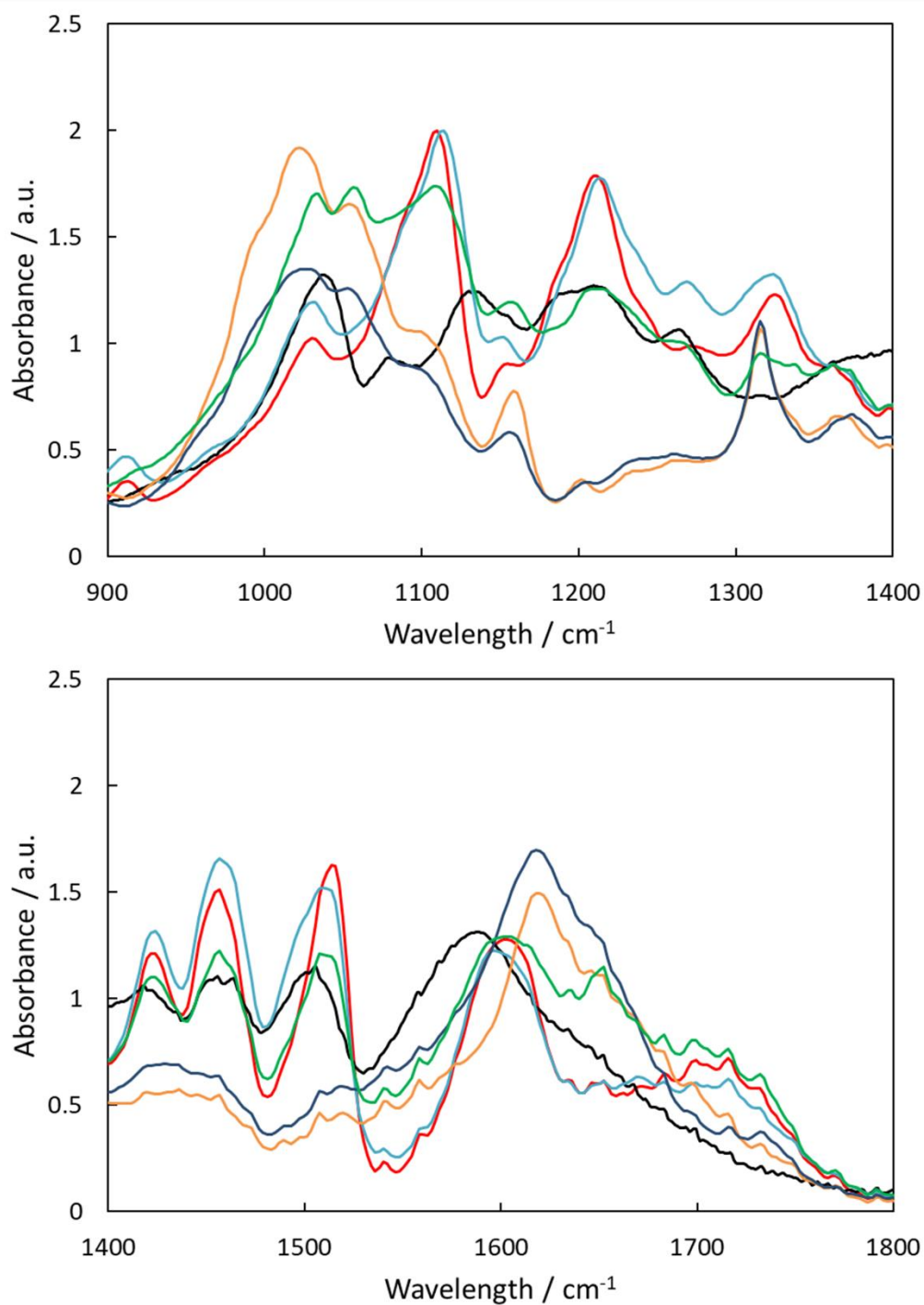


Figure 2. FT-IR of original lignins: BHL (yellow), WHL (green), THL (dark blue), SKL (black), HKL (red), HOL (light blue).

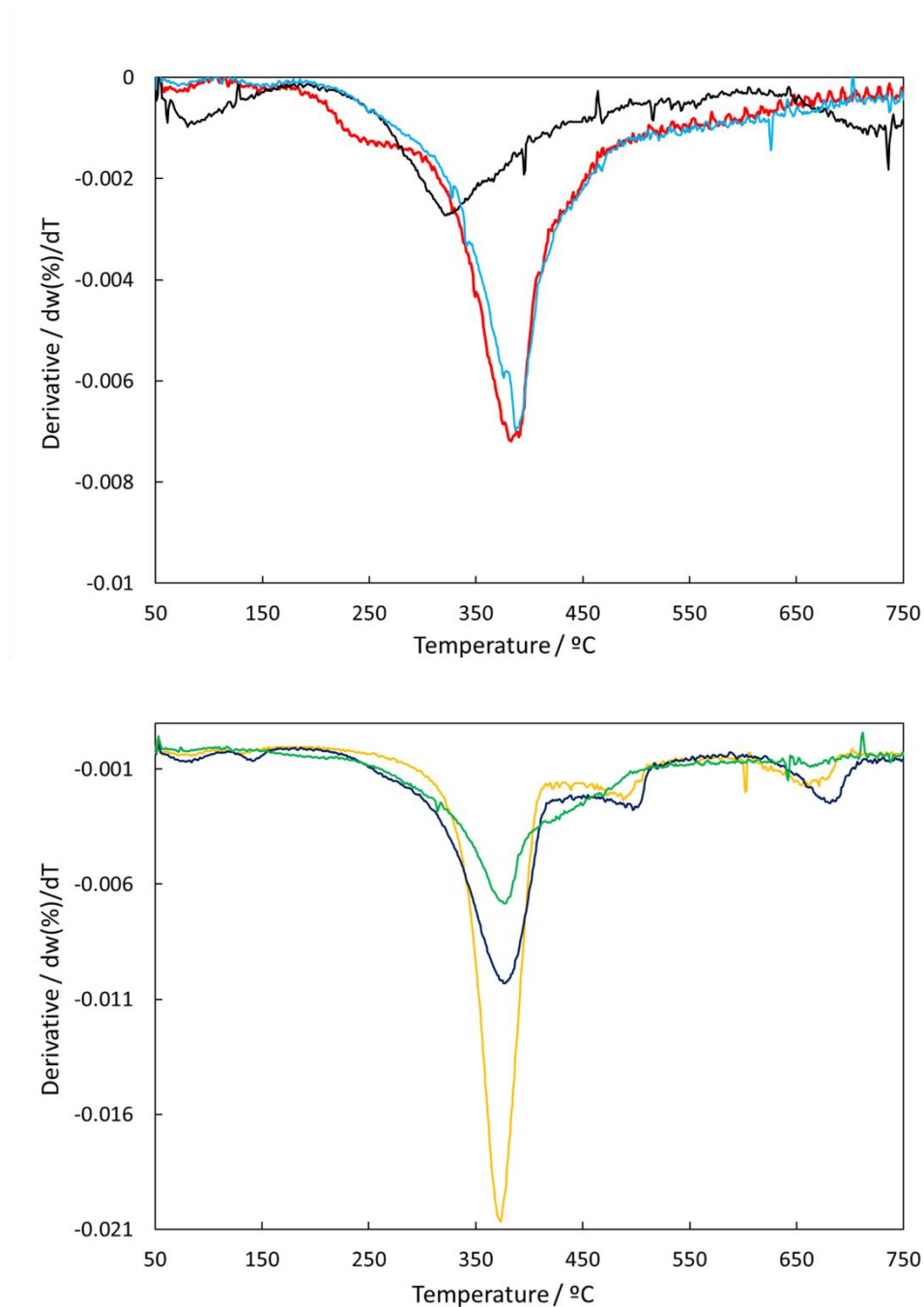


Figure 3. DTG of original lignins. UP: SKL (black), HKL (red), HOL (light blue); DOWN: BHL (yellow), WHL (green), THL (dark blue).

In regard with the molecular weight distribution, it can be seen in Figure 4 that WHL, THL and BHL contain the highest-molecular-weight fragments since they present shoulders at the lowest retention time (7-8 min), but also the lowest-molecular-weight fragments (shoulders at 10-11 min), which could be attributed to sugar monomers. HOL and HKL, as well as BHL and THL present similar

molecular weight distribution and similar retention time in which the maximum appears.

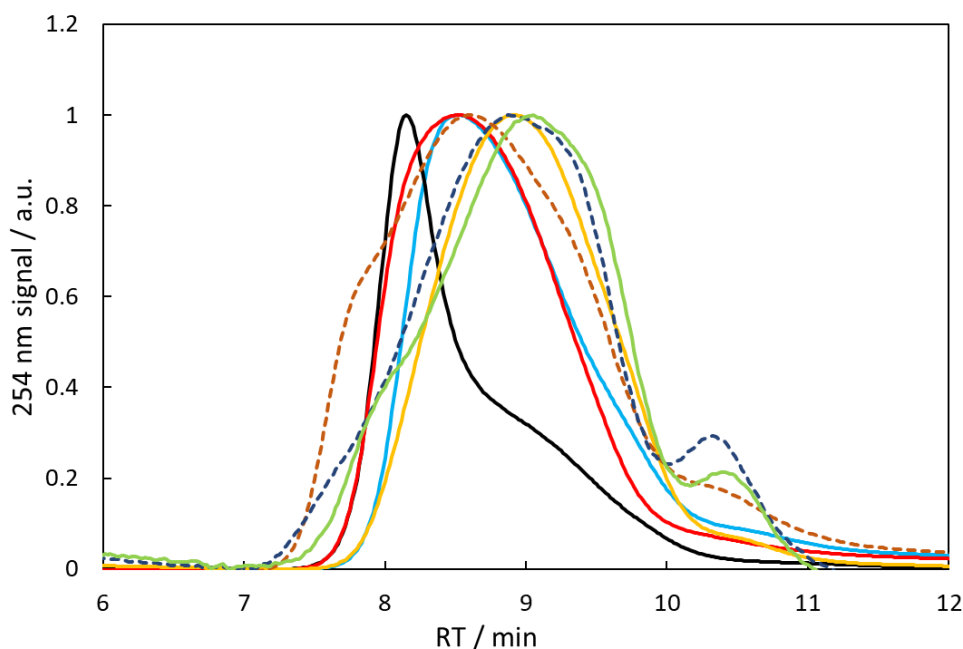


Figure 4. GPC of original lignins: SKL (black), HKL (red), HOL (blue), WHL (brown dotted), THL (blue dotted), BHL (green) and HKBL (yellow).

Since all lignins presented different compositions, properties and structure, it is expected that their behaviour in the depolymerization process will be different in terms of optimal reaction time, fractionation yields and tendency with time. The unique exception was HKL and HOL lignins, which presented similar DTG, FT-IR and GPC curves, being possible to obtain similar depolymerization yields.

3.2. Lignin depolymerization in base-catalysed SCW: Effect of lignin nature.

A total of 8 experiments with 6 different lignins and 2 black liquors were done in this chapter. Four fractions were obtained from each experiment: light oil containing monomers and di-trimers, heavy oil containing oligomers, char including the repolymerization products and aqueous residue. The latter was formed mainly by inorganic salts produced during the fractionation process of the depolymerization products, and by non-reacted lignin, as it was seen in Chapter I. Light and heavy oils were analysed by GC-MS, GPC and ^{31}P NMR.

Chars and starting lignins were analysed by FT-IR, GPC, ^{31}P NMR and CHNS analysis.

3.2.1. Alkaline depolymerization of lignins.

Lignin conversion to phenolic monomers reported in literature is performed in most cases from extracted technical lignins [9, 10]. The use of technical lignin has the important advantage that non-lignin components, like carbohydrates, have been removed to a large extent, as can be seen in Table 2.

Usually, kraft lignin obtained as by-product in pulping processes is used for energy generation that it is normally employed for fulfilling the requirements of the same industry [11]. However, it is known that lignin from the kraft process can be transformed in aqueous solutions at temperatures and pressure close to the critical point of water [12-18]. However, lignin has not yet been effectively converted with high yields into high-value compounds.

A commercial lignin from softwood (SKL) and a lignin extracted from the black liquor HKBL (HKL) obtained as by-product from a hardwood biorefinery process were depolymerized at 386°C and 300 ms to study the effect of the wood type in the de-/repolymerization of kraft lignins. The results obtained were very different in terms of oil yields. A light oil yield of 60.0% was obtained for the case of SKL (softwood), in contrast to a yield of 23.5% in the case of HKL (hardwood). Regarding the heavy oil, which is mostly oligomers containing a small quantity of monomers (<1.0%), a yield of only 12.6% was obtained for SKL, while 68.0% was obtained for HKL. Those differences in the fractionation yields were expected since both lignins were very different, as it was seen in the previous section (DTG, FT-IR, GPC). Thus, the optimal reaction time, as well as the production of monomers also differed. Moreover, the fractionation yield tendency with time could be also different.

Table 5 shows the monomeric selectivity of lignins. It is possible to see that the main monomers obtained after the SCW depolymerization of SKL (softwood) were guaiacol (3.9%), creosol (2.0%), vanillin (4.1%) and acetovanillone (3.3%). However, the main compounds from the depolymerization of HKL (hardwood)

were syringol (4.1%), syringaldehyde (4.0%) and acetosyringone (3.8%), as it was seen in Chapter II. These results agree with the structure of the starting lignin, as softwood contains mainly guaiacyl monomers and hardwood a higher proportion of syringyl monomers. Our results were better than those obtained in other hydrothermal studies. The best work found was carried out at 350 °C and 1 h giving yields of bio-oils lower than 45%, and low selectivity (< 6.5%) [16]. In the case of char, the yield of this fraction after the depolymerization reaction of both lignins was very low: 2.6% for the case of SKL and 3.8% for the case of HKL. The low amount of char formed is one of the advantages of the ultra-rapid SCW depolymerization process, due to the extremely low reaction time applied of 300 ms.

An organosolv hardwood lignin (HOL) was also depolymerized in alkaline SCW in order to compare the effectiveness of this process for hardwood lignins obtained from different process: kraft and organosolv. For this purpose, HOL was compared with HKL. Similar results were obtained: HOL gave 28.5% of light oil, 62.8% of heavy oil and 5.6% of char, and in terms of selectivity (Table 5), the major aromatic monomers for both lignins were those syringyl-based, which is in accordance with the type of wood. Total monomeric yields of 3.1 and 2.3 wt% HKL and HOL, respectively, were obtained. The yields of the depolymerization products were expected to be similar since both lignins, coming from the same type of biomass, had similar characteristics. Moreover, the yields of these lignins could be lower than those obtained for SKL because of the more complex structure (i.e. broader thermal degradation range, as can be seen in Figure 3).

The results obtained in this study for HOL lignin were promising. A study about HOL lignin depolymerization in supercritical conditions using solvents as acetone and batch reactors was found, in which the total oil yield (heavy oil + light oil) was lower than 39.0% [19], in contrast to 91.3% obtained in our case. In addition, the selectivity in 13 low-molecular-weight compounds in that study was only of 3.0%, while in our study was 8.1% in 7 phenolic monomers of high added-value. In another study [20], an acetosolv lignin was depolymerized by alkaline hydrolysis in a batch reactor obtaining as the highest oil yield 18.5%.

Gosselink et al. [21] showed that organosolv hardwood lignin was converted in a supercritical fluid consisting of carbon dioxide/acetone/water (300-370°C, 100 bar) to a phenolic oil consisting on oligomeric fragments and monomeric aromatic compounds with a total yield of only 10%. Thus, not only the solvent used affects the yields, but also the reaction time.

Finally, lignins isolated from non-wood biomasses via hydrolysis were also investigated. The results obtained here were interesting and completely different among crop lignins. The highest light oil yield was achieved by BHL with 75.0%, followed by THL with 53.8% and finally by WHL with 21.3%. The opposite trend was observed for heavy oil and char yields, being greater for the case of WHL, followed by BHL and finally THL (Table 4). However, no lignin gave high selectivity in aromatic monomers. Only 0.1% and 0.2% of guaiacol and vanillin, respectively, were quantified in the light oil of THL lignin. Thus, it is possible that due to the high content of sugars in these lignins (44.8% in BHL and 23.8% in THL), light oil was mainly formed by sugar di-trimers or derived compounds instead of aromatic monomers from lignin. Another factor that could influence in the non-wood lignins yields could be the impurities contained in these lignins (i.e. %N, Table 3). In addition, it is important to consider that grass lignins contain p-hydroxyphenyl units, which are less stable than guaiacyl and syringyl units, and thus, they tend to degrade (in fact, these units were not detected by GC-MS), contributing to the lower monomeric yields. Although WHL gave the lowest light oil yield, the selectivity was not so poor in comparison with BHL and THL, being the main monomers guaiacol (0.7%), vanillin (0.4%) and syringaldehyde (3.4%).

Table 4. Fractionation yields (wt%) of lignins after alkaline SCW depolymerization process at 386°C and 300 ms. All data are referred to the initial lignin.

	Light oil	Heavy oil	Char
SKL	60.0	12.6	2.6
HKL	23.5	68.0	3.8
HOL	28.5	62.8	5.6
THL	53.8	7.0	0.4
BHL	75.0	13.4	6.1
WHL	21.3	36.3	15.0

Table 5. Selectivity for the major monomers contained in the light oil from the depolymerisation of different lignins. The corresponding chromatograms can be seen in Figure S1. All data are given in wt% and they are referred to the light oil. 'Total selectivity' is referred to the light oil, and 'total yield' to lignin.

	SKL	HKL	HOL	THL	BHL	WHL
Guaiacol	3.9	0.8	0.2	0.1	0.0	0.7
Creosol	2.0	0.0	0.0	0.0	0.0	0.0
Vanillin	4.1	0.3	0.8	0.2	0.0	0.4
Acetovanillone	3.3	0.3	0.3	0.0	0.0	0.1
Syringol	0.1	4.1	1.0	0.0	0.0	0.1
Syringaldehyde	0.7	4.0	4.3	0.0	0.0	3.4
Acetosyringone	1.5	3.8	1.5	0.0	0.0	0.0
Total selectivity	15.7	13.3	8.1	0.3	0.0	4.8
Total yield	9.4	3.1	2.3	0.2	0.0	1.0

The results obtained for the three crop lignins studied in the present section were much poorer than in the case of wood lignins, indicating that non-wood lignins isolated via hydrolysis are less convenient than wood lignins, both Kraft and Organosolv, for the obtention of aromatic monomers.

After studying the chemical functionalities in lignins and chars obtained after the lignin depolymerization process, the same conclusion than in the previous chapter can be done: whatever transformations are occurring in the SCW reactions they do not alter significantly the aromatic structure as little difference was observed in the FT-IR spectrum at wavenumbers within 1400 and 1650 cm⁻¹ (Figure 5). The complete FT-IR spectra for chars can be seen in Figure S1 in the 'Supplementay Information'.

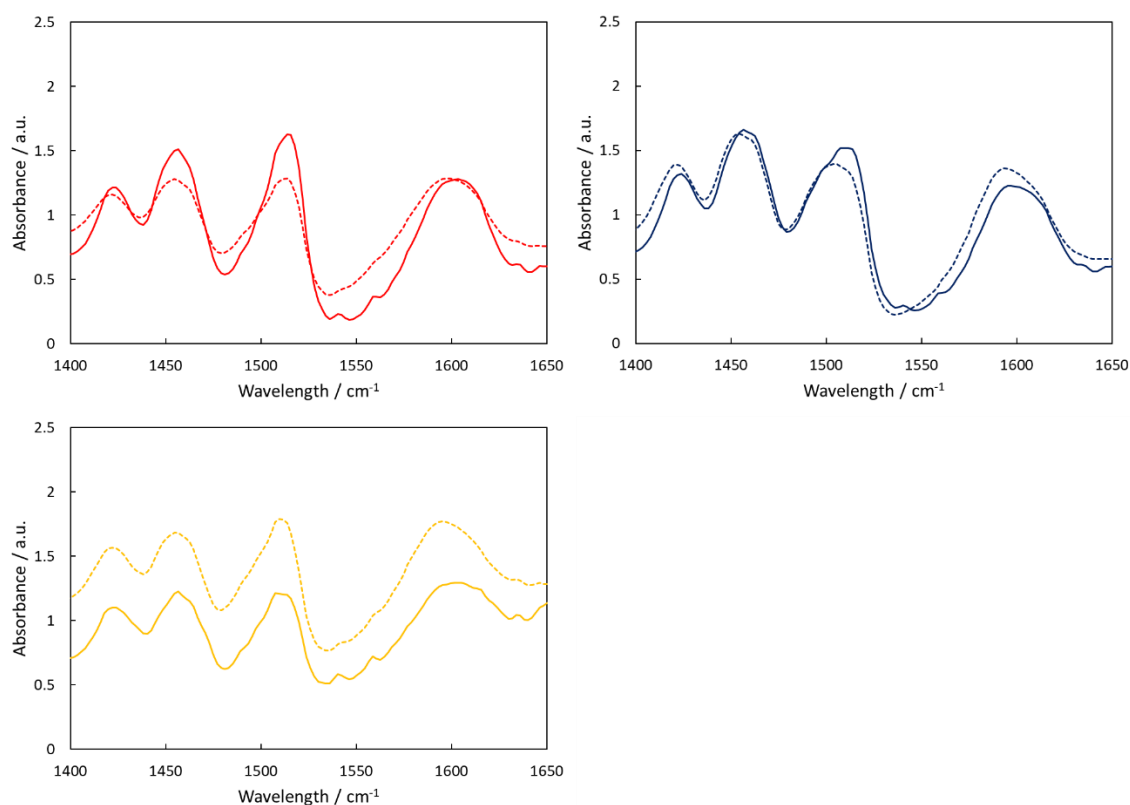


Figure 5. FT-IR spectra at wavenumbers corresponding to aromatic structure for HKL lignin (red) and its char (red dotted); HOL lignin (blue) and its char (blue dotted); WHL (yellow) and its char (yellow dotted).

^{31}P NMR spectroscopy of lignin enables the quantification of different types of hydroxyl groups, such as aliphatic groups. These functional groups are among the major lignin functionalities and therefore their quantification is important in lignin structural analysis. In the ‘supplementary information’ section, Tables S4-S6, the quantification of the different hydroxyl groups for HKL, HOL and WHL lignins and their depolymerization products is present. Table 6 presents the concentration of the aliphatic hydroxyl groups in some lignins and in their chars determined by ^{31}P NMR. As it can be observed, aliphatic hydroxyl groups were reduced after the SCW process in all cases. This decrease in the aliphatic groups is in accordance with the dehydration reactions proposed in the previous chapter for SKL depolymerization. Thus, reaction mechanisms could be not affected by lignin nature.

Table 6. Quantification of aliphatic hydroxyl groups by ^{31}P NMR for HKL, HOL and WHL and the corresponding chars. Data expressed as $\text{mmol OH} \cdot \text{g}^{-1}$

	Lignin	Char
HKL	1.3	0.7
HOL	2.2	1.6
WHL	1.6	1.0

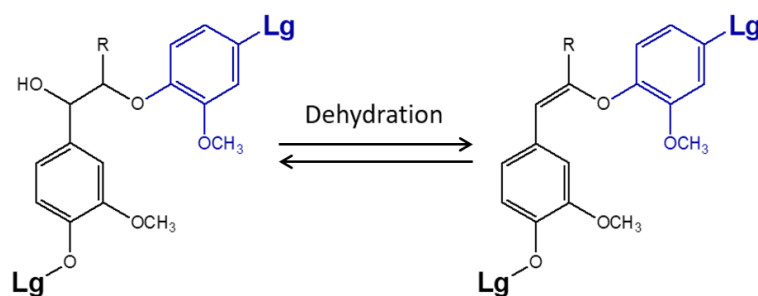


Figure 6. Dehydration reaction of lignin.

Molecular weight distribution of lignins and its fractionation products are present in Figure 7. In every case, light oil was lighter than heavy oil and char, corroborating that the former was the lower-molecular-weight products. For SKL, lignin and char gave the maximum UV signal at the same retention time, around 8.2 min, indicating that the MW was similar. In the case of the other lignins, char molecules were heavier than lignin molecules showing clearly that the former are repolymerisation products. Notice that retention time for all the chars was similar (except for WHL which was slightly lower) regardless of the original size of lignin. This homogenizing role of SCW treatment in molecular weight distribution has been previously observed for lignosulfonates [22] and it seems that it is reproduced for other lignins. As it was discussed before, lignins studied in this chapter were different to SKL. Thus, the repolymerization times will be different for each case.

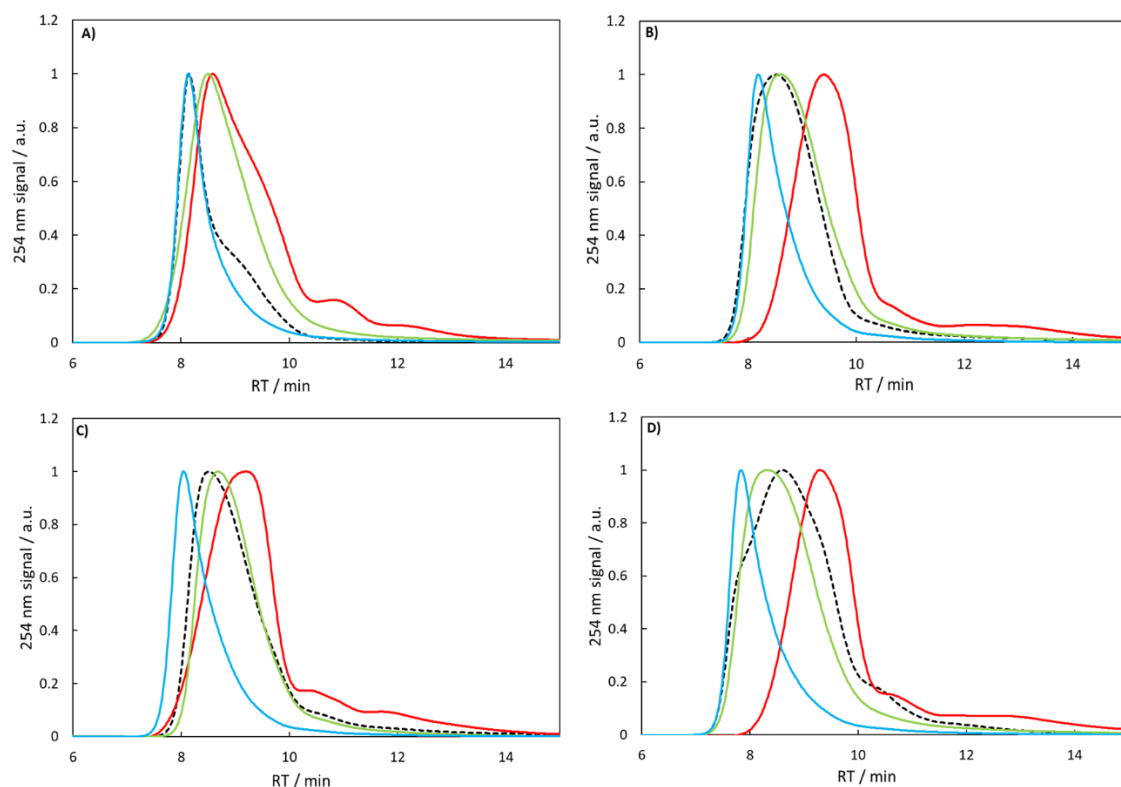


Figure 7. GPC for A) SKL; B) HKL; C) HOL; D) WHL. Original lignin (black dotted line), char (blue line), light oil (red line) and heavy oil (green line).

3.2.2. Black liquors with low lignin content.

BL is a suitable waste stream for upgrading to valorized products. Approximately 7 tonnes of black liquor are produced in the manufacture of one tonne of pulp [23]. To increase pulp production, techniques to extract the lignin part of BL have been developed [24-26], in order to convert such lignin to high value products. However, a more interesting pathway would be to process directly dilute black liquors. The main goal of this section is to convert lignin contained in BL to a light oil comprising monomeric phenolic compounds with high yields. Two dilute black liquors were directly treated with SCW. The black liquor named as HBL contained 5.8% of lignin. The composition of HBL can be seen in Table 2. No information about composition was supplied for HBL due to confidentiality reasons. The elemental composition CHNS for both liquors is given in Table 9.

After the alkaline SCW process, different results were obtained. The highest light oil yield was achieved by HKBL, with 51.3%, in contrast to 30.0% in the case of

HBL. Light oil monomeric selectivity can be seen in Table 8. The major monomers identified in both HKBL were guaiacol (2.7% in HKBL and 0.7% in HBL), syringol (3.0% in HKBL and 4.6% in HBL), syringaldehyde (7.3% in HKBL and 11.9% in HBL) and acetosyringone (1.9% in HKBL and 5.8% in HBL). Even with different light oil yields, the monomeric selectivity in both oils was similar, with a high proportion of syringol. The formation of char was low in the case of HKBL (5.0%) and relatively high for the case of HBL (17.7%). The high amount of char after HBL depolymerization could be due to the carbonization of additional unknown components contained in the HKBL.

Table 7. Fractionation yields (w/w%) of black liquors after alkaline SCW depolymerization process at 386°C and 300 ms. All data are referred to the initial lignin.

	Light oil	Heavy oil	Char
HKBL	51.3	45.0	5.0
HBL	30.0	39.7	17.7

Table 8. Major monomers contained in the light oils, identified and quantified by GC-MS. All data are given in wt% and they are referred to the light oil, except 'total yield', which is referred to lignin.

	HKBL	HBL
Guaiacol	2.7	0.7
Creosol	0.8	0.0
Vanillin	0.6	0.0
Acetovanillone	1.6	0.0
Syringol	3.0	4.6
Syringaldehyde	7.3	11.9
Acetosyringone	1.9	5.8
Total selectivity	17.9	23.0
Total yield	9.2	6.9

Comparing with literature, our results look great in terms of monomeric selectivity, since it was reported in the best case in the hydrothermal processing of black liquors with 5 wt % of lignin, a light oil containing 5 wt % of monomers at 380 °C and 1 hour of reaction time [27]. Thus, ultrafast SCW treatment of BL is

a promising methodology to incorporate into a kraft process, giving the possibility to obtain a bio-oil suitable for fuel and material purposes.

The FT-IR of BLs could not be analysed by technical reasons, so the chemical functionalities of these starting materials are unknown. However, the aromatic structure of chars from both BLs was very similar, differing in the C-O bonds (Figure 8). Thus, it is possible that also in the case of BLs, repolymerization reactions do not alter significantly the aromatic structure of lignin. Comparing Tables 3 and 9, it can be observed that the oxygen content was extremely reduced in char (2.6 times) with respect to the original BL, as it is well known in hydrothermal processes a large proportion of the oxygen is removed as carbon dioxide [14]. This decrease in the oxygen content is also in agreement with the hypothesis of dehydration reactions are occurring also in lignins contained in black liquors.

Table 9. Elemental composition of chars.

	wt %				
	C	H	N	S	O*
HKBL	60.1	4.7	0.6	2.3	32.3
HBL	58.2	4.7	0.2	1.0	35.8

*Estimated data

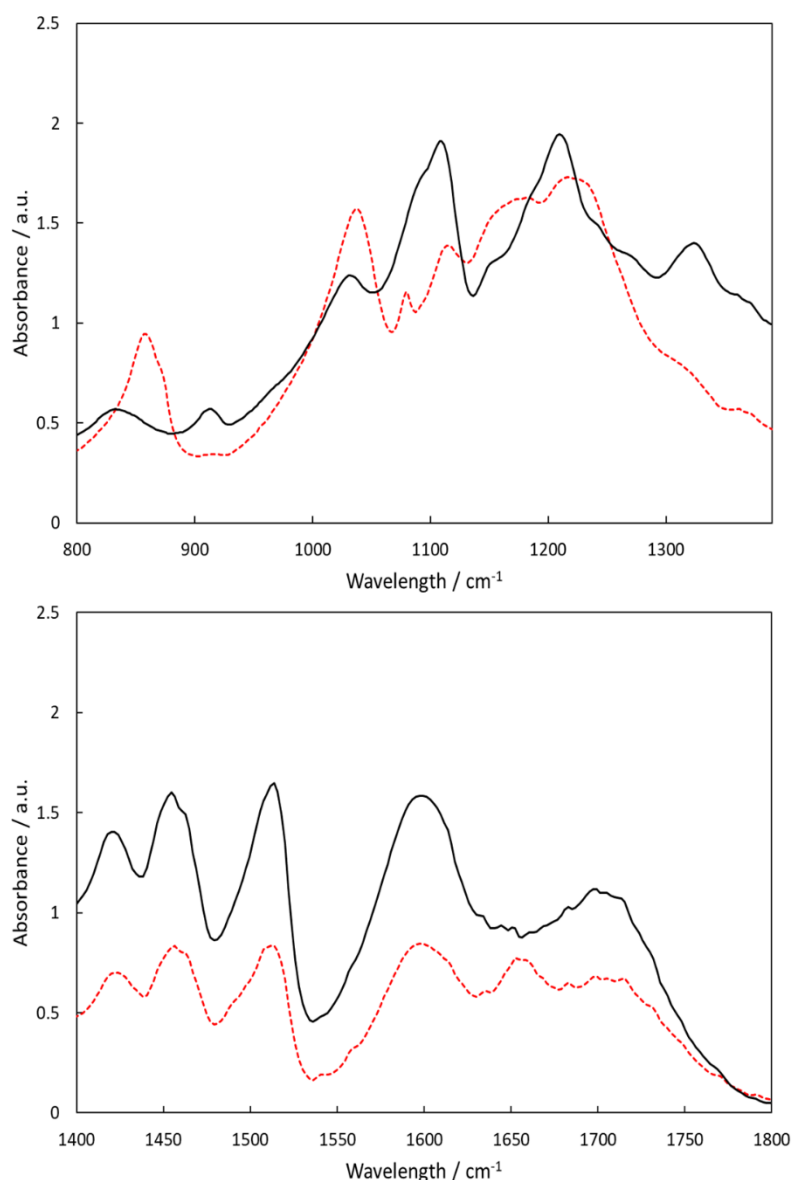


Figure 8. FT-IR of chars obtained after depolymerization of HKBL (black line) and HBL (red dotted line).

4. Conclusions.

In this study, different lignins were depolymerized using base-catalysed SCW at a reaction time of 300 ms. Since they were isolated from different biomasses using different methods, their behaviour in the depolymerization reaction differed, obtaining different yields at the same conditions of temperature and reaction time. The unique exception was the similar depolymerization of two hardwood lignins obtained through Kraft and Organosolv processes (named as HKL and

HOL lignins, respectively), since those lignins had similar properties and structure. The high yields and selectivity obtained for Kraft lignins in our study are really promising in comparison with other works, with yields of bio-oils (light oil + heavy oil) of up to 92 wt% and a selectivity in aromatic monomers of up to 16 wt%. On the other hand, HOL lignin depolymerization via alkaline SCW also seemed to be a promising route for obtaining high yields in bio-oils (i.e. 28.5 %wt light oil and 62.8 %wt heavy oil) containing a high proportion in phenolic monomers (i.e. 8.1 wt% in light oil). However, non-wood lignins seemed to be less convenient for the obtention of aromatic low-molecular-weight compounds. Despite those differences in yields and selectivity, all lignins suffered dehydration during the base-catalysed SCW process, and the lignin aromatic structure after repolymerization was not altered. Repolymerization could be controlled thanks to the low reaction time applied, and as result, the amount of char formed was low in all cases. However, the reaction time would be optimized for each lignin in order to obtain the highest recovery of monomers and the minimum formation of char.

Finally, the ultra-rapid SCW treatment of diluted black liquors is a promising methodology to incorporate into a kraft process, giving the possibility to obtain bio-oils suitable for fuel and chemical production with no need of catalyst addition.

Supplementary Information.

The following tables show additional data about parameters used in UV-Vis spectrophotometry and extraction methods employed for the different lignins and their biomass source.

Table S1. Wavelengths and extinction coefficients used for determining the soluble lignin by UV-Vis spectrophotometry.

Raw material	Wavelength (nm)	Extinction coefficient ($\text{Lg}^{-1}\text{cm}^{-1}$)	Reference
Hardwood	205	105.0	[28]
Softwood	205	105.0	[28]
Beet Pulp	280	17.1	[29]
Tobacco	280	20.1	[30]
Wheat Straw	280	18.7	[29]

Table S2. Summary table of lignins and black liquors: Extraction method and source.

Lignin/BL	Extraction method	Source
SKL	Kraft process	Softwood
HKL	Kraft process	Hardwood
HOL	Organosolv process	Hardwood
WHL	SBCH (200°C, 30 min)+EH	Wheat straw
BHL	SBCH (160°C, 80 min)+SCWH(393°C, 60 ms)	Beet pulp
THL	SCWH (370-382 °C; 0.15-0.31s)	Tobacco
HKBL	Kraft pulping process	Hardwood
HBL	Unknown	Hardwood

Where; EH: enzymatic hydrolysis; SBCH: Subcritical water hydrolysis; SCWH: Supercritical water hydrolysis.

Functional hydroxyl groups contained in lignins and depolymerization products, quantified by ^{31}P NMR are shown in Tables S3-S5, for HKL, HOL and WHL respectively.

Table S3. Hydroxyl groups determined by ^{31}P NMR for HKL and its fractionation products. Where; 5-susbt: C5-substituted phenolic-OH (Syringyl+5-condensed guaiacyl); Gnc: non-condensed G-phenolic-OH; H: p-hydroxyphenyl- OH. Total aromatic-OH was calculated as the sum of 5-subst, Gnc and H.

	$\text{mmol}_{\text{OH}} \cdot \text{g}^{-1}$			
	Lignin	Char	Heavy oil	Light oil
Aliphatic	1.3	0.7	0.4	0.7
5-subst	3.0	2.0	2.4	3.0
Gnc	0.9	0.8	0.8	1.0
H	0.1	0.2	0.1	0.2
COOH	0.6	1.1	0.8	1.2
Total aromatic-OH	4.0	3.0	3.3	4.2
Total -OH	6.0	4.8	4.4	6.1

Table S4. Hydroxyl groups determined by ^{31}P NMR for HOL and its fractionation products. Where; 5-susbt: C5-substituted phenolic-OH (Syringyl+5-condensed guaiacyl); Gnc: non-condensed G-phenolic-OH; H: p-hydroxyphenyl- OH. Total aromatic-OH was calculated as the sum of 5-susbt, Gnc and H.

	$\text{mmol}_{\text{OH}} \cdot \text{g}^{-1}$			
	Lignin	Char	Heavy oil	Light oil
Aliphatic	2.2	1.6	0.4	0.4
5-susbt	2.6	2.3	2.4	1.4
Gnc	1.2	1.0	1.2	0.6
H	0.4	0.1	0.2	0.1
COOH	0.4	0.6	0.6	0.8
Total aromatic -OH	3.8	3.4	3.8	2.2
Total -OH	5.9	5.6	4.9	3.4

Table S5. Hydroxyl groups determined by ^{31}P NMR for WHL and its fractionation products. Where; 5-susbt: C5-substituted phenolic-OH (Syringyl+5-condensed guaiacyl); Gnc: non-condensed G-phenolic-OH; H: p-hydroxyphenyl- OH. Total aromatic-OH was calculated as the sum of 5-susbt, Gnc and H.

	$\text{mmol}_{\text{OH}} \cdot \text{g}^{-1}$			
	Lignin	Char	Heavy oil	Light oil
Aliphatic	1.6	1.0	0.9	0.5
5-susbt	1.0	1.1	1.9	0.9
Gnc	0.9	1.1	1.4	0.6
H	0.3	0.3	0.4	0.3
COOH	0.7	0.9	0.8	0.5
Total aromatic-OH	2.3	2.6	3.8	1.8
Total -OH	4.7	4.4	5.4	2.9

The elemental composition CHNS-O for chars obtained from the depolymerization of different lignins is presented in Table S6. Elemental composition was similar between chars, even though the starting lignins composition was different (Table 3).

Table S6. Elemental composition of chars.

	wt %				
	C	H	N	S	O*
SKL	55.7	4.4	0.3	4.7	34.9
HKL	56.0	4.8	0.5	4.2	34.6
HOL	61.6	5.4	0.2	0.0	32.8
WHL	62.9	5.3	1.8	0.2	29.8
THL	57.3	4.4	3.7	1.6	33.0

FT-IR spectra for chars in the wavelength 800-1800 cm^{-1} are shown in Figure S1. The aromatic structure (1400-1650 cm^{-1}) was similar in all chars, differing in the C-O bonds, whose signals appeared within 1000 and 1300 cm^{-1} .

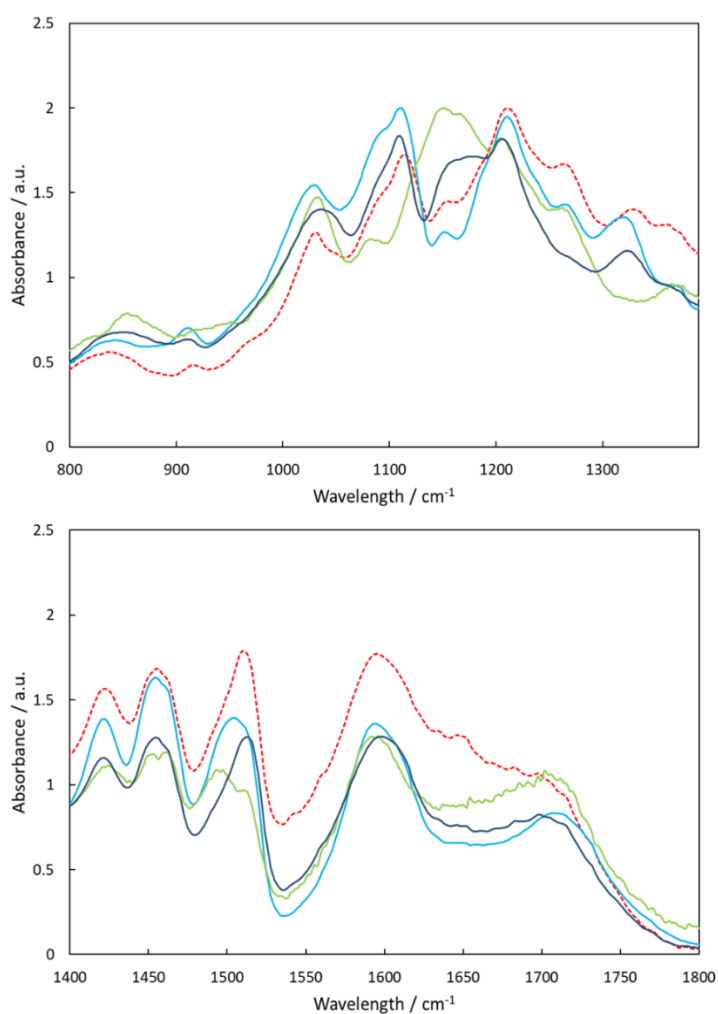


Figure S1. FT-IR of chars obtained after depolymerization of HOL (blue), SKL (green), HKL (purple), and WHL (red dotted).

^{31}P NMR spectra obtained for HKL lignin and its depolymerization fractions are shown in Figure S2. Similar spectra were obtained for the rest of lignins, which are not presented here. What is possible to determine from this figure is the monomeric/di-trimeric nature of the light oils (narrow peaks), in comparison with the oligomeric nature of the rest of fractions and original lignin (broad peaks). Thus, it is possible to corroborate qualitatively the effective depolymerization of lignins in only 300 ms of reaction time, giving monomeric light oils. In addition, chars and heavy oils gave similar spectra to lignins, corroborating its polymerized nature.

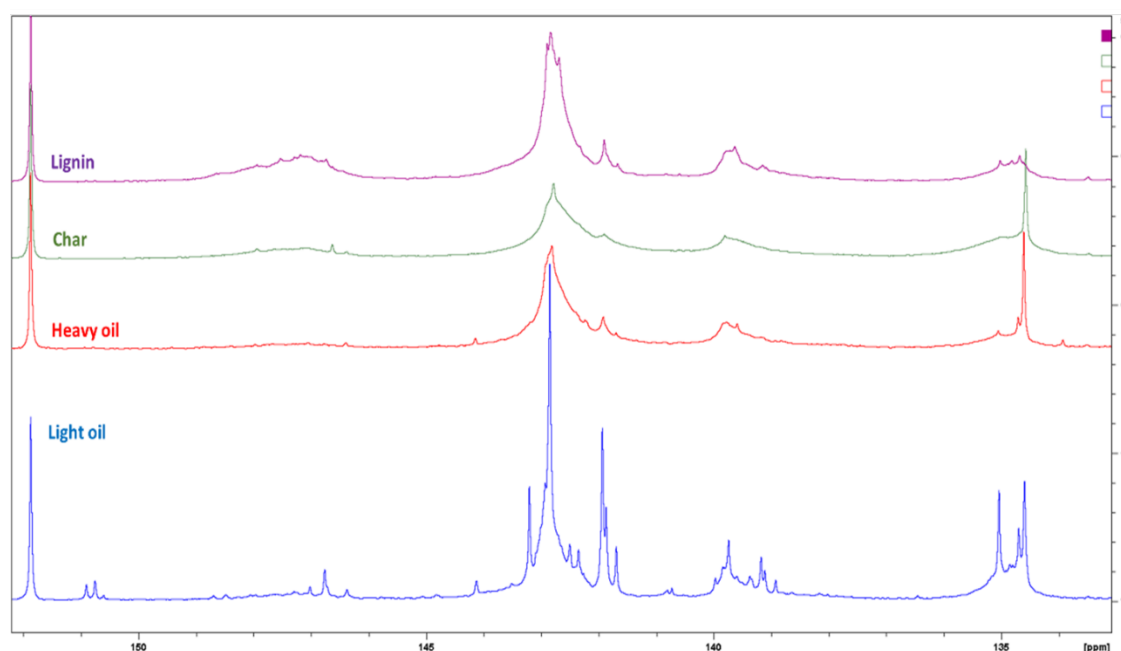


Figure S2. ^{31}P NMR spectra obtained for HKL.

Figure S3 presents the spectra obtained using ^{31}P NMR for light oils of WHL, HKL, SKL and HOL lignins, where peaks corresponding to p-hydroxyphenyl, guaiacyl and syringyl+guaiacyl condensed hydroxyl groups can be distinguished depending on the type of starting lignin: non-wood, softwood or hardwood, respectively. Thus, in the case of WHL lignin, a peak corresponding to p-hydroxyphenyl group can be detected, as well as HKL and HOL (both hardwood) has as main peak that corresponding to syringyl+guaiacyl condensed. On the other hand, the highest peak in the light oil of SKL (softwood) corresponds to guaiacyl groups.

C

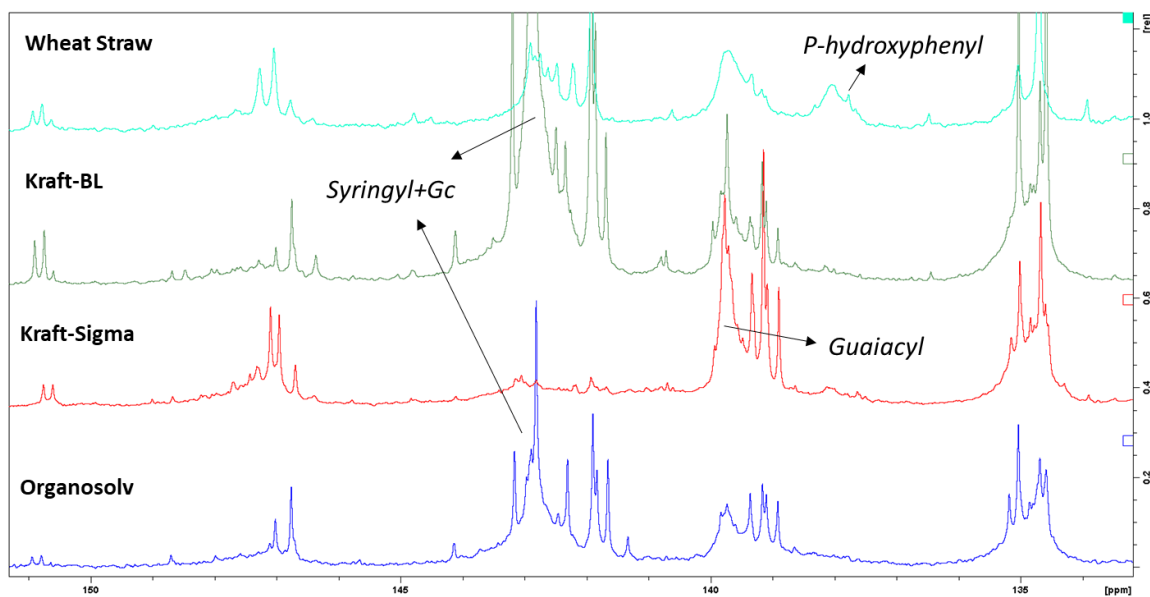


Figure S3. Spectra obtained from the analysis by ^{31}P NMR of different light oils as products from the depolymerization of WHL, HKL, SKL and HOL lignins.

Figure S4 shows the GC-MS chromatograms of light oils obtained from different lignins.

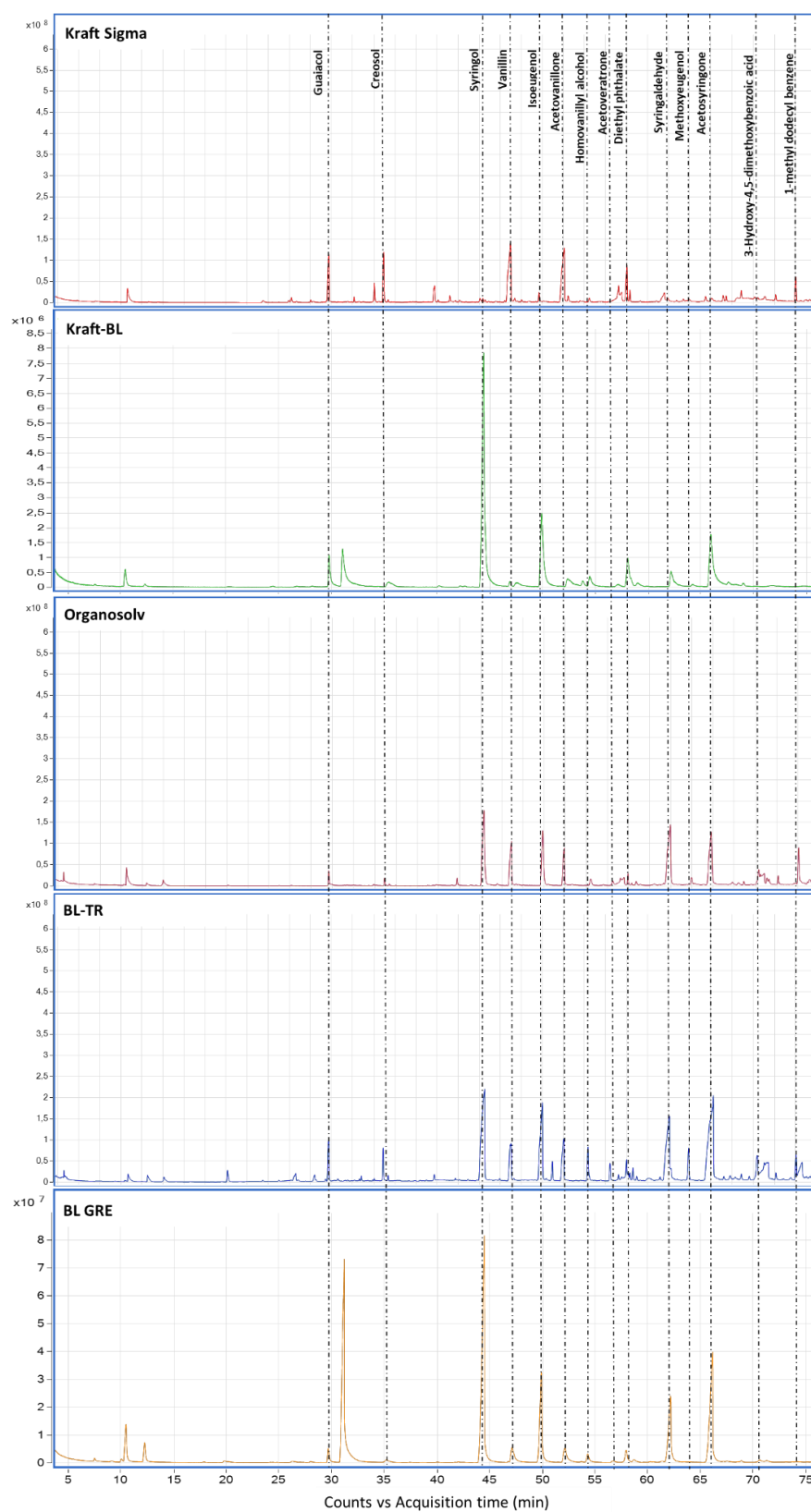


Figure S4. GC-MS chromatograms of light oils obtained from SKL, HKL, HOL, HKBL and HBL.

References.

1. Cherubini, F., *The biorefinery concept: Using biomass instead of oil for producing energy and chemicals*. Energy Conversion and Management, 2010. **51**(7): p. 1412-1421.
2. Huber, G.W., S. Iborra, and A. Corma, *Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering*. Chemical Reviews, 2006. **106**(9): p. 4044-4098.
3. Pandey, M.P. and C.S. Kim, *Lignin Depolymerization and Conversion: A Review of Thermochemical Methods*. Chemical Engineering & Technology, 2011. **34**(1): p. 29-41.
4. <https://en.wikipedia.org/wiki/Lignin>.
5. Granata, A. and D.S. Argyropoulos, *2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins*. Journal of Agricultural and Food Chemistry, 1995. **43**(6): p. 1538-1544.
6. Guerra, A., et al., *Comparative Evaluation of Three Lignin Isolation Protocols for Various Wood Species*. Journal of Agricultural and Food Chemistry, 2006. **54**(26): p. 9696-9705.
7. Balakshin, M. and E. Capanema, *On the quantification of lignin hydroxyl groups with ³¹P and ¹³C NMR spectroscopy*. Journal of Wood Chemistry and Technology, 2015. **35**(3): p. 220-237.
8. Government, U.S., *Determination of Structural Carbohydrates and Lignin in Biomass: Laboratory Analytical Procedure (LAP)*. 2012: General Books LLC.
9. Amen-Chen, C., H. Pakdel, and C. Roy, *Production of monomeric phenols by thermochemical conversion of biomass: a review*. Bioresource Technology, 2001. **79**(3): p. 277-299.
10. Zakzeski, J., et al., *The Catalytic Valorization of Lignin for the Production of Renewable Chemicals*. Chemical Reviews, 2010. **110**(6): p. 3552-3599.
11. Sahoo, S., et al., *Characterization of industrial lignins for their utilization in future value added applications*. Biomass and Bioenergy, 2011. **35**(10): p. 4230-4237.
12. Ma, R., et al., *Catalytic Ethanolysis of Kraft Lignin into High-Value Small-Molecular Chemicals over a Nanostructured α -Molybdenum Carbide Catalyst*. Angewandte Chemie International Edition, 2014. **53**(28): p. 7310-7315.
13. Yuan, Z., M. Tymchyshyn, and C. Xu, *Reductive Depolymerization of Kraft and Organosolv Lignin in Supercritical Acetone for Chemicals and Materials*. ChemCatChem, 2016. **8**(11): p. 1968-1976.
14. Goudriaan, F. and D.G.R. Peferoen, *Liquid fuels from biomass via a hydrothermal process*. Chemical Engineering Science, 1990. **45**(8): p. 2729-2734.
15. Johansson, A., *A new chemical recovery system for the Kraft process. Results from continuous bench-scale operations*. Biomass, 1984. **4**(2): p. 155-160.
16. Islam, M.N., et al., *Yield of Phenolic Monomers from Lignin Hydrothermolysis in Subcritical Water System*. Industrial & Engineering Chemistry Research, 2018. **57**(14): p. 4779-4784.
17. Miller, J.E., et al., *Batch microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents*. Fuel, 1999. **78**(11): p. 1363-1366.
18. Nguyen, T.D.H., et al., *Catalytic depolymerisation and conversion of Kraft lignin into liquid products using near-critical water*. The Journal of Supercritical Fluids, 2014. **86**: p. 67-75.
19. Erdocia, X., et al., *Depolymerization of Different Organosolv Lignins in Supercritical Methanol, Ethanol, and Acetone To Produce Phenolic Monomers*. ACS Sustainable Chemistry & Engineering, 2016. **4**(3): p. 1373-1380.
20. Erdocia, X., et al., *Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature*. Biomass and Bioenergy, 2014. **66**: p. 379-386.

21. Gosselink, R.J.A., et al., *Lignin depolymerisation in supercritical carbon dioxide/acetone/water fluid for the production of aromatic chemicals*. Bioresource Technology, 2012. **106**: p. 173-177.
22. Pérez, E. and C.O. Tuck, *Quantitative analysis of products from lignin depolymerisation in high-temperature water*. European Polymer Journal, 2018. **99**: p. 38-48.
23. Biermann, C.J., *Essentials of pulping and papermaking*. 1993: Academic Press.
24. Öhman, F., H. Wallmo, and H. Theliander, *Precipitation and filtration of lignin from black liquor of different origin*. Nordic Pulp and Paper Research Journal, 2007. **22**(2): p. 188-193.
25. Wilson, K.P., M.L. Laver, and W.J. Frederick Jr. *ULTRAFILTRATION OF KRAFT BLACK LIQUOR: MEMBRANE PERFORMANCE AND LIQUOR CHARACTERISTICS*. in *American Institute of Chemical Engineers, National Meeting*. 1986.
26. Lake, M.A.a.B., J. C., *Process for Recovering Lignin*. U.S. Patent US20110294991A1.2011.
27. Orebom, A., J.J. Verendel, and J.S.M. Samec, *High Yields of Bio Oils from Hydrothermal Processing of Thin Black Liquor without the Use of Catalysts or Capping Agents*. ACS Omega, 2018. **3**(6): p. 6757-6763.
28. Ferraz, A., et al., *Estimating the chemical composition of biodegraded pine and eucalyptus wood by DRIFT spectroscopy and multivariate analysis*. Bioresource Technology, 2000. **74**(3): p. 201-212.
29. Fukushima, R.S. and R.D. Hatfield, *Comparison of the acetyl bromide spectrophotometric method with other analytical lignin methods for determining lignin concentration in forage samples*. Journal of Agricultural and Food Chemistry, 2004. **52**(12): p. 3713-3720.
30. Blee, K., et al., *Antisense and sense expression of cDNA coding for CYP73A15, a class II cinnamate 4-hydroxylase, leads to a delayed and reduced production of lignin in tobacco*. Phytochemistry, 2001. **57**(7): p. 1159-1166.

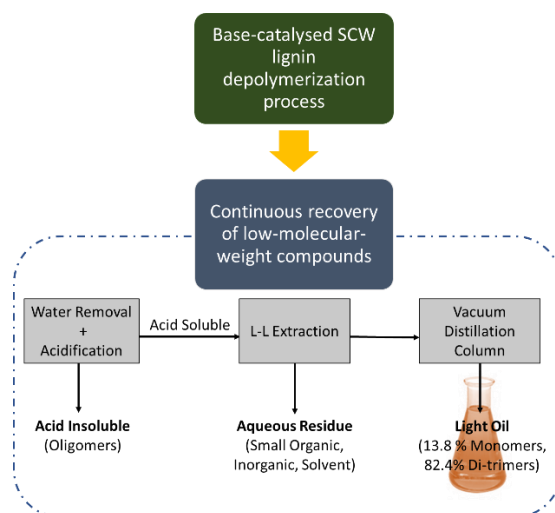
CHAPTER IV

SIMULATION OF A
CONTINUOUS RECOVERY OF
LOW-MOLECULAR-WEIGHT
LIGNIN DEPOLYMERIZATION
PRODUCTS.

SIMULATION OF A CONTINUOUS RECOVERY OF LOWER-MOLECULAR-WEIGHT LIGNIN DEPOLYMERIZATION PRODUCTS.

Abstract.

Focused on the development of a continuous downstream process for the recovery of low-molecular-weight lignin products generated during the hydrothermal base-catalysed depolymerization of lignin, a feasible method has been proposed and simulated with Aspen HYSYS V10. The separation strategy combines flash separators, liquid-liquid extraction and vacuum distillation. Process simulation confirmed that up to 93.1 wt% of low-molecular-weight compounds could be recovered from the lignin depolymerization product mixture with our strategy. The calculated total plant capital investment was about 2.9 M€ for a plant capacity of 15 Tonnes feedstock/day. The estimated minimum light oil price was 3.8 €/kg, which could be a competitive price in the future market if interesting applications were found for this bio-oil.



1. Introduction.

Recently, research is strongly focused on the usage of lignin obtained as by-product in different biomass treatments, as raw material for high value-added products production. The use of this component for the production of fuel additives and bio-based chemicals is crucial for the success of the integral development of lignocellulosic biorefinery processes. In the previous chapters, a base-catalysed process using supercritical water (386°C, 260 bar) with an extremely low reaction time (300 ms) was proposed to depolymerize lignin with high yields and high selectivity in aromatic monomers avoiding char formation. The quantity of monomers generated during the base-catalysed supercritical water process (BC-SCW) was optimized for Kraft lignin, obtaining a yield of 11.9 wt%. These monomers, together with dimers and trimers, were separated from oligomers and char and concentrated in a light oil through a conventional laboratory process which implies three main steps: 1) Lignin oligomers precipitation by acidification of the product mixture; 2) Liquid-liquid extraction (LLE) of the low-molecular-weight compounds contained in the acid soluble fraction; 3) Elimination of the solvent from the extract. Many studies found in literature recover phenolic low-molecular-weight compounds using similar processes [1-3]. However, these steps are so far carried out in batch mode which is very far of being translated into commercial practice. This kind of methods is feasible when small amounts of product mixture are treated for analytical purposes. However, it is a tedious and slow method unacceptable for large-scale plants and which may imply important losses during steps such as filtration or LLE. Our work proposed a strategy to obtain the light oil containing low-molecular-weight compounds through a continuous process and for a pilot scale plant with a capacity of 15 Tonnes feedstock/day, combining four main steps: 1) Water evaporation + Acidification; 2) Liquid-liquid extraction; 3) Vacuum distillation; and 4) Solvent Recycling. All these steps were simulated using Aspen HYSYS V10. In this way, the global process, which implies BC-SCW lignin depolymerization and low-molecular-weight lignin products recovery, will be continuous, and thus, it will be closer to the industrial application. The general

objective of the simulation was to develop basic data for a pilot size process flow diagram, evaluate monomer losses during the separation and study the economic feasibility of the process.

2. Materials and methods.

2.1. Aspen HYSYS V10 Simulation.

Aspen HYSYS V10 simulations were performed. The thermodynamic package used was NRTL and the binary coefficients were estimated by UNIFAC. Electrolyte NRTL was not employed since the amount of acid and base in our process is small and it does not affect the equilibrium. Moreover, with Electrolyte NRTL the system is calculated as ideal, since no binary coefficients were available. The system included water, guaiacol, vanillin, acetovanillone, bisphenol and ethyl acetate. Since only guaiacol, vanillin and acetovanillone were present in the HYSYS compound databank, the rest of monomers were included in those components as it is explained in Section 3.2 guidelines. Bisphenol was chosen to represent dimers and trimers. Acidification combined with the removal of water in a flash tank, liquid-liquid extraction and vacuum distillation were simulated. The simulations were performed assuming a yield of 11.9 wt% monomers and 48.1% dimers and trimers from a lignin feed of 100 kg/day (yields based on our previous work of SKL lignin depolymerization at 386°C and 300 ms).

2.2. Recovery of low-molecular-weight products.

Acidification of the depolymerization mixture after SCW reaction was performed in order to precipitate the repolymerization products and lignin oligomers. 1mL of sulfuric acid (96%) was added for 150 mL of product mixture. After acidification, the acid insoluble fraction was separated from the acid soluble fraction containing the lower-molecular-weight compounds of interest. The former was conducted to solid-liquid extraction to recover the lignin oligomers as heavy oil, as it was seen in the previous chapters. On the other hand, the acid soluble fraction was conducted to liquid-liquid extraction. Ethyl acetate was used

for the extraction of monomers, since it was reported this solvent totally extracts the lower-molecular-weight compounds [4]. Three extractions with ethyl acetate using a volume of one third of the acid soluble fraction volume were done. The extract from the LLE was named light oil, as in the previous chapters. The aqueous raffinate contained unconverted soluble lignin, salts and solvent (losses). The solvent was removed using a single stage rotary evaporator at 40°C under vacuum. Exhaustive evaporation to completely remove the solvent would likely have resulted in the loss of important monomers such as phenol. In the light oil, less than 20% of the fraction could be identified as monomers. The rest of the fraction was probably residual dimers and trimers, which were not separated from monomers by LLE [4]. Ethyl acetate demonstrated very good performance for the extraction, but it has an important drawback: It is soluble in water up to 8.3 wt% [5]. Thus, to minimize losses and costs, future extractions should be performed with solvents that will extract a maximum of monomers, dimers and trimers from water and have a lower water solubility. A good choice could be vinyl acetate, n-butyl acetate or methyl isobutyl ketone.

3. Experimental results and discussion.

3.1. Strategy.

As it was seen in Chapter II, the lignin depolymerization base-catalysed SCW process leads to a complex mixture of monomers, dimers, trimers, oligomers and char. Acidification is required to precipitate the higher-molecular-weight products (i.e. lignin oligomers and char). As it was performed in the laboratory, a ratio of 1:150 v/v sulfuric acid:BCD products will be used in this simulation. Then, the solids must be eliminated from the process via filtration, cyclonic separation or decantation, depending on the particle size. Acidification and filtration leave an aqueous phase containing basically monomers, dimers and trimers. The following step involves LLE. The cost of this operation will be relatively low, since previously to the acidification step the amount of water in the BCD products stream will be enormously reduced using a flash tank

separator after the decompression valve using to decrease suddenly the reaction temperature from 386°C to 150°C, stopping the lignin de-/repolymerization reactions. Thus, the monomers, dimers and trimers will be extracted from the acid soluble fraction using ethyl acetate in a liquid-liquid separator. As it was carried out in our laboratory, the extraction will be performed using a ratio of 1:3 v/v ethyl acetate:acid soluble fraction at ambient conditions. After LLE, the recovery of the solvent is required. For that purpose, a distillation column operating under vacuum will be used, producing the light oil containing the monomers, dimers and trimers with a minimum amount of ethyl acetate.

Solid-liquid extraction of the acid insoluble fraction containing lignin oligomers and char was performed in the laboratory, but it will not be simulated in this work since the main objective is to recovery the lower-molecular-weight compounds.

The aqueous residue obtained after the LLE unit containing mainly salts and solvent (losses), should be treated in an adsorption unit for solvent recovery, but this operation will not be simulated in this work.

Figure 1 presents the overall strategy proposed to recover the lower-molecular-weight compounds from the base-catalysed depolymerization (BCD) products after the SCW reaction through a continuous process.

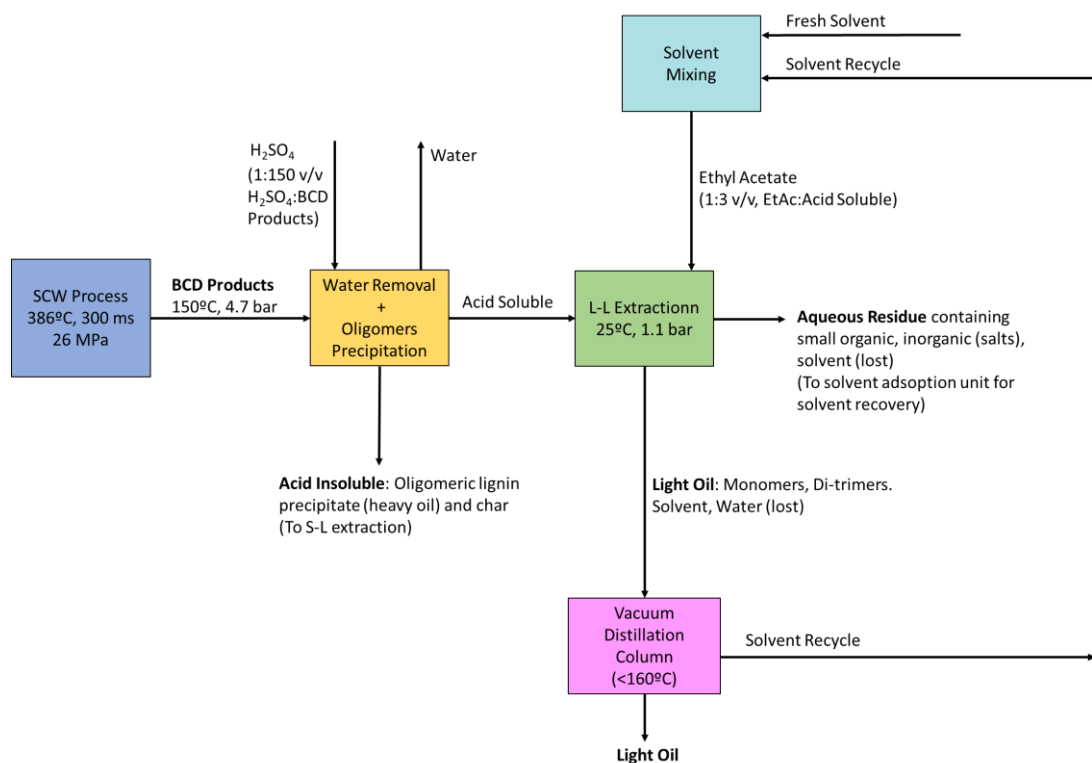


Figure 1. Block diagram of the proposed continuous recovery of low-molecular-weight compounds (light oil fraction).

Guidelines.

Some assumptions were made for this simulation, and some process limitations were considered. The following guidelines were followed in this work:

- 1) A lignin feed of 100 kg/d was assumed, maintaining the lignin concentration in the reactor (0.5%) and the NaOH concentration (0.2 M) as in the previous works. The monomeric yields determined in Chapter II for SKL at the optimal operating conditions (386°C, 300 ms) were used for this simulation (see Table 1).

Table 1. Light oil yield and composition of the major monomers obtained after the base-catalysed SCW depolymerization process of SKL. All values of the monomers (% w/w) are referred to the aromatic oil production. Calculations for light oils were performed in base of the lignin concentration at the inlet of the reactor.

<i>Light oil yield</i>	60.0
Guaiacol	3.9
Vanillin	4.1
Acetovanillone	3.3
Homovanillic acid	4.2
Creosol	2.0
Syringol	0.1
Syringaldehyde	0.7
Acetosyringone	1.5

2) Since in the HYSYS compound databank most of monomers formed during the SCW lignin depolymerization process are not available, syringol and creosol will be included in guaiacol, while acetosyringone, syringaldehyde and homovanillic acid will be included in vanillin. Thus, the monomers used in this simulation will be guaiacol, vanillin and acetovanillone. This approach has been chosen taking into account the similarity of the molecular structures of the compounds (C=O linkages).

3) Bisphenol, a dimer present in the HYSYS compound databank, was chosen to represent dimers and trimers. Since those compounds were not quantified, it was assumed that the fraction of the light oil that is not monomers is dimers and trimers.

4) Oligomers were assumed to be non-volatile and their effect negligible on the removal of water. Oligomers were therefore not included in the simulation. They were assumed to be removed from the system after acidification and filtration.

5) Sodium hydroxyde and sulfuric acid were not included since electrolytes did not affect the simulation. The heat generated during acidification was considered

since it vaporized a water fraction of the mixture. This reaction heat was calculated on HYSYS as $4.6 \cdot 10^4$ kcal/kmol, which considering sodium hydroxide as limiting reactant is 5827 kcal/h.

6) Since distribution coefficients for the water-ethyl acetate-guaiacol/vanillin/acetovanillone system were not determined in the LLE, this operation was simulated as a 3-phase separator unit (with $V = 0$). It was considered as one-stage extraction.

7) The distillation column was optimized to have minimum heat duties in both the reboiler (HDR) and the condenser (HDC); a temperature in the overhead product not too low since refrigerants are expensive; and a temperature in the bottom product (light oil) not too high ($< 160^\circ\text{C}$) in order to avoid the degradation of dimers and trimers and consequently, the formation of char.

3.2. Simulation on Aspen HYSYS V10.

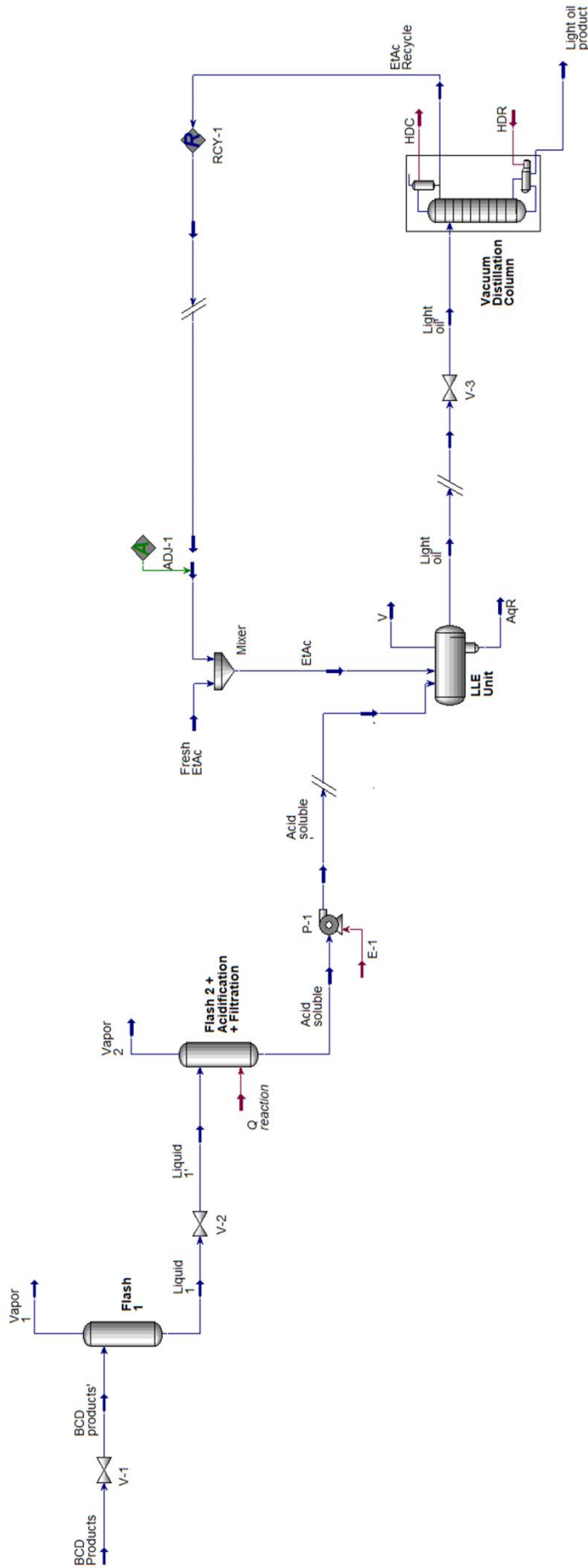
Figure 2 presents the flowsheet used to simulate the lower-molecular-weight compounds recovery continuous process. The blue streams represent material streams, while the red streams represent energy streams. The process was optimized to reduce the monomer losses and to save as much energy as possible. Tables incorporated in the Figure 2 show the properties of the material streams and energy streams.

Valve V-1 simulated the high-temperature valve employed experimentally in the base-catalysed SCW process, stopping suddenly the de-/repolymerization reactions of lignin. The sudden decompression brought the BCD products from 386°C and 260 bar to 149.7°C and 4.7 bar (BCD products). Since a calculation base of 100 kg/d lignin was assumed, the total flow of this product stream was 635.8 kg/h, with mass fractions of $9.96 \cdot 10^{-1}$ in water, $2.4 \cdot 10^{-4}$ in guaiacol (including syringol and creosol), $4.1 \cdot 10^{-4}$ in vanillin (including acetosyringone, syringaldehyde and homovanillic acid), $1.3 \cdot 10^{-4}$ in acetovanillone and $3.2 \cdot 10^{-3}$ in dimers and trimers (represented by bisphenol). BCD products stream was driven to Flash 1 in order to remove most of water. A total of 592.3 kg/h water were eliminated as vapor from the system, losing in this step 78.5% of guaiacol, 12.8%

of vanillin, 9.8% of acetovanillone and only 0.5% of dimers and trimers. These monomers could be recovered condensing the vapor stream (for example, using this vapor to pre-heat the supercritical water up to around 140°C in the SCW depolymerization process), and extracting those monomers using ethyl acetate as described below. A total flow of 43.3 kg/h was recovered in Liquid 1, containing 94.6% water and the rest of monomers and di-trimers. The monomeric losses in Flash 1 were considerable, even if those losses were overestimated. It is important to consider that in the real process, the monomer losses will be lower, since in the simulation we have considered syringol as guaiacol and acetosyringone, syringaldehyde and homovanillic acid as vanillin, compounds that have different physical properties to guaiacol and vanillin. Specifically, the boiling point of syringol is higher than that of guaiacol, and the boiling points of acetosyringone, syringaldehyde and homovanillic acid are higher than that of vanillin. The monomer losses could be reduced in several decompressions, but as it was seen in the previous chapters, an exhaustive control of the reaction time in the SCW process is crucial for a selective lignin depolymerization. For this reason, the temperature must be reduced at temperatures below 160°C in the first decompression to avoid repolymerization reactions and the degradation of dimers and trimers. Nevertheless, monomers in Vapor 1 could be recovered from this stream via adsorption. Other option could be to condensate water contained in Vapor 1 to separate water from monomers, but due to their low proportion, most of monomers will be swept along the water phase. Liquid 1, containing still a considerable amount of water, was driven to Flash 2 for acidification and additional water removal with help of vacuum (3 kPa). The heat generated during acidification (5827 kcal/h) vaporized a fraction of mixture, specifically 10 kg/h water. Thanks to vacuum, a total flow of 19.1 kg/h was vaporized in Flash 2 with negligible monomer losses (only 1.1% of guaiacol and less than 0.01% of vanillin and acetovanillone of the 'BCD products' input). The precipitated lignin oligomers were assumed to be eliminated from the system via filtration with a filter installed in the flash. The acid soluble fraction, with a total flow of 24.2 kg/h was driven to the LLE unit. Ethyl acetate was chosen as solvent for LLE.

Experimentally, it was demonstrated that ethyl acetate could easily extract monomers but also higher molecular weight compounds soluble in water. In this operation, monomers, dimers and trimers were extracted with ethyl acetate at ambient conditions in one-stage unit. The aqueous residue obtained as raffinate from this operation contained mainly water (96.7%). The monomer losses were negligible in the AqR stream: only 0.4% guaiacol and 0.9% acetovanillone of the 'BCD products' inlet. However, the solvent losses were considerable of 9.3% of the EtAc stream, since ethyl acetate has the drawback of being soluble in water up to 8.1 wt%[5]. Thus, a solvent recovery from the aqueous residue fraction would be necessary, but this operation was not simulated in this work. The final step is the solvent separation from low-molecular-weight compounds via vacuum distillation. For that purpose, the light oil fraction with a total flow of 9.8 kg/h, corresponding 74.7% to ethyl acetate, 1.6% water, 20.3% dimers and trimers and 3.4% monomers. A distillation column of three stages (considering the reboiler) with inlet in the second stage was required to separate the low-molecular-weight compounds from the solvent with a minimum energy consumption in the condenser and in the reboiler of 1351 and 694.5 kcal/h, respectively. The optimal reflux ratio was 0.7 and the distillate rate 0.09 kmol/h. The distillation column is shown in detail in Figure 3 with the corresponding streams data table. A mass flow of 2.4 kg/h of light oil concentrated low-molecular-weight lignin compounds could be recovered in the bottom product at a temperature of 124.1°C containing 82.3% dimers and trimers and 13.8% monomers, with only 0.02% of water and 3.8% of ethyl acetate. Laboratory experiments are needed to corroborate the distillation operation yield. The solvent was totally recycled to the LLE unit with a purity of 97.8%. A low amount of 0.8 kg/h of fresh solvent was only required.

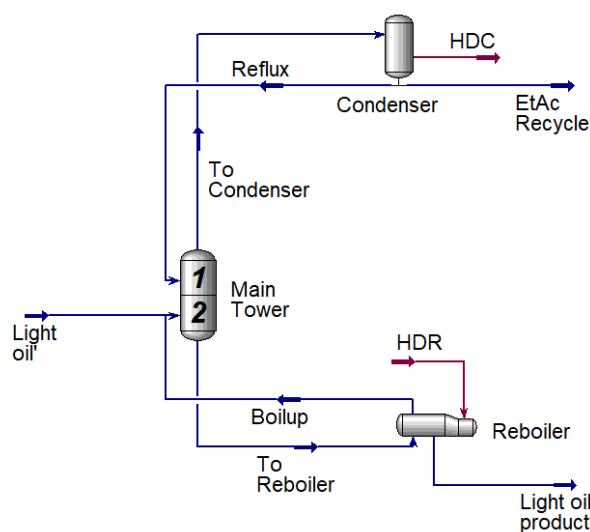
Figure 2. Flow diagram of the continuous fractionation process of the base-catalysed lignin depolymerization products (BCD) in order to recovery the lower-molecular-weight compounds and tables of properties of the material streams (blue streams) and energy streams (red streams). - Next page.



	BCD Products	BCD products'	Vapor 1	Liquid 1	Liquid 1'	Vapor 2	Acid soluble	Acid soluble'	EtAc	AqR	V	Light oil	Light oil'	Light oil product	EtAc Recycle	Fresh EtAc
Vapour Fraction	0.00	0.93	1.00	0.00	0.22	1.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Temperature (°C)	386.00	149.70	149.70	149.70	24.11	24.11	24.11	24.12	24.71	23.24	23.24	23.24	23.24	124.14	18.94	25.00
Pressure (bar)	260.00	4.70	4.70	4.70	0.03	0.03	0.03	1.10	1.00	1.00	1.00	1.00	0.11	0.11	0.10	1.00
Mass Flow (kg/h)	635.83	635.83	592.50	43.33	43.33	19.09	24.24	24.24	8.24	22.66	0.00	9.82	9.82	2.42	7.40	1.00
Mass Frac-H ₂ O	9.96E-01	9.96E-01	1.00E+00	9.46E-01	9.46E-01	1.00E+00	9.04E-01	9.04E-01	1.93E-02	9.67E-01	0.00E+00	1.62E-02	1.62E-02	2.41E-04	2.15E-02	0.00E+00
Mass Frac-Guaiacol	2.36E-04	2.36E-04	1.99E-04	7.45E-04	7.45E-04	8.86E-05	1.26E-03	1.26E-03	0.00E+00	2.96E-05	0.00E+00	3.05E-03	3.05E-03	1.24E-02	3.97E-08	0.00E+00
Mass Frac-Vanillin	4.13E-04	4.13E-04	5.66E-05	5.28E-03	5.28E-03	1.11E-06	9.45E-03	9.45E-03	0.00E+00	4.42E-16	0.00E+00	2.33E-02	2.33E-02	9.46E-02	1.15E-12	0.00E+00
Mass Frac-AcetVanillon	1.31E-04	1.31E-04	1.38E-05	1.73E-03	1.73E-03	1.30E-07	3.10E-03	3.10E-03	0.00E+00	3.33E-05	0.00E+00	7.57E-03	7.57E-03	3.07E-02	6.42E-14	0.00E+00
Mass Frac-BisPhenol	3.15E-03	3.15E-03	1.76E-05	4.60E-02	4.60E-02	7.28E-10	8.23E-02	8.23E-02	0.00E+00	5.79E-06	0.00E+00	2.03E-01	2.03E-01	8.24E-01	3.71E-24	0.00E+00
Mass Frac-EtAc	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.81E-01	3.30E-02	0.00E+00	7.47E-01	7.47E-01	3.85E-02	9.79E-01	1.00E+00

Q reaction (kcal/h)	5827.0
E-1 (kcal/h)	0.8
HDR (kcal/h)	694.5
HDC (kcal/h)	1351.0

Figure 3. Distillation tower in detail.



	Reflux	To Condenser	Boilup	To Reboiler
Vapour Fraction	0.0	1.0	1.0	0.0
Temperature (°C)	18.9	19.2	124.1	28.6
Pressure (bar)	0.1	0.1	0.11	0.11
Mass Flow (kg/h)	5.2	12.6	4.3	6.8
Mass Frac (H ₂ O)	2.15E-02	2.15E-02	1.70E-02	1.10E-02
Mass Frac (Guaiacol)	0.00E+00	0.00E+00	2.00E-02	1.73E-02
Mass Frac (Vanillin)	0.00E+00	0.00E+00	3.26E-03	3.59E-02
Mass Frac (AcetVanillon)	0.00E+00	0.00E+00	4.25E-04	1.13E-02
Mass Frac (BisPhenol)	0.00E+00	0.00E+00	0.00E+00	2.95E-01
Mass Frac (E-Acetate)	9.79E-01	9.79E-01	9.59E-01	6.30E-01

Table 2 presents the monomer losses in the whole low-molecular-weight components recovery process. The main losses occurred in Flash 1 due to the extreme decompression from 260 bar to 4.7 bar in valve V-1. Although the losses of guaiacol were important (80.1%) and the losses corresponding to vanillin and acetovanillone were also considerable (12.7 and 10.7%, respectively), the total monomer losses were only of 6.9%. Thus, a high monomer recovery (93.1%) was achieved, making this process promising for the continuous recovery of light oil.

Table 2. Low-molecular-weight compounds total losses in the continuous product fractionation process.

	BCD Products (kg/h)	Light oil product (kg/h)	Losses (%)
Guaiacol	0.2	0.0	80.0
Vanillin	0.3	0.2	12.8
Acetovanillone	0.1	0.1	10.7
Bisphenol	2.0	2.0	0.5
Total	2.5	2.3	6.9

This work was focused on the separation of light oil fraction, containing monomers, dimers and trimers, from the lignin oligomers, as it was performed in the laboratory in the previous Chapters. However, it would be interesting to separate monomers from dimers and trimers, as well as purify monomers of high value, such as vanillin or acetovanillone. Vigneault et al. [4] have proposed an interesting strategy to separate monomers combining adsorption, vacuum distillation, liquid chromatography and crystallization. Membrane separation could also be a good alternative to separate di-trimers from monomers. As it can be deduced, several stages are required to separate phenolic compounds. Trying to separate those components in a single step is most likely impractical. An interesting future work would be to study the post-treatment of the light oil for monomers purification, which requires a large amount of experimental work.

3.3. Economic balance, market and applications of the light oil product.

Table 3 shows the cost per hour of the raw materials based on the current market prices. Table 4 presents the utilities cost. Freon 12 was chosen as refrigerant for the distillation column condenser. Table 5 shows the operation cost of all units, as well as the equipment type of every unit. In table 6 can be seen the global economic balance, being the total cost per year of 600,000 € during the first 5 years operating 8766 hours per year. After this period, the capital cost will be zero, being the total cost reduced to 79 €/year. The cost of the SCW depolymerization process was not considered in this economic balance since it would be negligible installing a steam injection gas turbine in the process as explained in the work of Danilo et al. 2015 [6]. With this technology, the heating and compression costs in the SCW process can be suppressed. The capital cost of that process is negligible in comparison to the low-molecular-weight compounds recovery process.

Table 3. Raw materials cost (Current Market Prices).

Raw materials				
Name	Rate	Rate Units	Cost per Hour	Cost Units
Water	633.3	kg/h	1.1	€/h
NaOH	5.1	kg/h	2.7	€/h
H ₂ SO ₄	0.5	kg/h	0.1	€/h
Ethyl acetate	0.8	kg/h	1.2	€/h

CHAPTER IV

Table 4. Utilities cost.

Utilities					
Name	Fluid	Rate	Rate Units	Cost per Hour	Cost Units
Electricity	-	49.3	kW	3.8	€/h
Refrigerant - Freon 12	Refrigerant	3.4E-02	Ton/h	5.8E-03	€/h
Steam @690KPa	Steam	1.4E-03	Ton/h	2.5E-02	€/h

Table 5. Unit operation cost.

Unit Operation				
Name	Equipment type	Equipment Cost [€]	Installed Cost [€]	Utility Cost [€/h]
Flash 1	Vertical process vessel	19,400	121,200	0
Flash 2 + Acidification + Filtration	Vertical process vessel + cartridge filter (5 micron cotton)	24,400	132,100	0
LLE Unit	Vertical process vessel (1 stage)	38,800	222,200	0
Vacuum Distillation Column	Multiple diameter, trayed or packed column, 2 stages (Condenser/Reboiler: TEMA shell and tube exchanger)	15,900	132,900	0
P-1	Centrifugal single or multiple-stage pump	4,120	27,000	0

Table 6. Global economic balance.

Capital cost (€/year)	600,000
Utilities (€/year)	33,776
Raw materials (€/year)	45,255
Total cost (€/year)	678,578

Considering an annual light oil production of 21.0 Ton, the minimum selling price of this product during the first 5 years of operation would be 33 €/kg to have no economic losses. After this period of 5 years required to recover the equipment cost and the installation cost, the minimum price of the bio-oil will be reduced up to 4 €/kg, which could be a reasonable price. If interesting applications would be found for this bio-oil, its selling price could be higher in the future market, giving important incomes.

Our oily product containing lignin monomers, dimers and trimers could be of special interest for laboratories working on the synthesis of high value products such as vanillin or acetovanillone. From our product, which is free of water, the purification of monomers via adsorption, liquid chromatography and/or crystallization would be possible. Other possible application of this product is the production of gasoline blending components.

Energetic integration studies of the lignin product fractionation process are required in order to reduce the cost of the process, and in consequence, the cost of our product and do this process economically feasible. In addition, an optimization of this process must be performed in order to minimize the monomer losses.

4. Conclusions.

In this work, a strategy to separate the low-molecular-weight compounds obtained as products from the lignin depolymerization process in alkaline SCW has been proposed, with the main objective of performing the whole process in continuous and approaching this process to the real industry. The process proposed here combines flash separators to remove most of water of the BCD mixture, liquid-liquid extraction (LLE) in order to recover the low-molecular-weight compounds and vacuum distillation to recover the solvent. Simulation showed that about 95 wt% of water in the BCD products coming out from the SCW process could be removed in only 2 flash separators, but with the consequent monomeric losses. In the first flash unit, up to 32% of monomers were lost in the vapour phase because of the previous sudden decompression (from 260 bar to 5 bar) to stop the de-/repolymerization lignin reactions. On the other hand, simulation revealed that with a 1-stage extractor, a 99.6 wt% of monomers can be recovered using ethyl acetate. After the LLE unit, simulation demonstrated that a 3-stages vacuum distillation column is required to remove almost completely the solvent (98.7 wt%) and to obtain a concentrated light oil containing the low-molecular-weight compounds of interest. However, the light

oil fraction, which is still a mixture of monomers, dimers and trimers, would require additional operations to separate monomers from dimers and trimers such as adsorption, and further distillations and crystallizations for monomers purification. Only LLE was tested in the laboratory. Thus, additional laboratory experiments are needed to prove the technical feasibility of the flash and distillation units, as well as the solvent recycling, and make this simulation more relevant.

In addition, the economic profitability of the process was studied. The minimum price of the bio-oil would be 4 €/kg, which could be a reasonable price considering the market of the pure monomers. If interesting applications would be found for this bio-oil, its selling price could be higher in the future market, giving important incomes.

References.

1. Islam, M.N., et al., *Yield of Phenolic Monomers from Lignin Hydrothermolysis in Subcritical Water System*. Industrial & Engineering Chemistry Research, 2018. **57**(14): p. 4779-4784.
2. Pérez, E. and C.O. Tuck, *Quantitative analysis of products from lignin depolymerisation in high-temperature water*. European Polymer Journal, 2018. **99**: p. 38-48.
3. Erdocia Iriarte, X., Corcuera Maeso, M. A., Labidi Bouchrika, J., *Novel method for the depolymerisation of lignin*. 2015.
4. Vigneault, A., D.K. Johnson, and E. Chornet, *Base-Catalyzed Depolymerization of Lignin: Separation of Monomers*. The Canadian Journal of Chemical Engineering, 2007. **85**(6): p. 906-916.
5. Altshuller, A.P. and H.E. Everson, *The Solubility of Ethyl Acetate in Water*. Journal of the American Chemical Society, 1953. **75**(7): p. 1727-1727.
6. Cantero, D.A., et al., *Energetic approach of biomass hydrolysis in supercritical water*. Bioresource Technology, 2015. **179**: p. 136-143.

CONCLUSIONS

LIGNIN DEPOLYMERIZATION BY
SUPERCRITICAL WATER
ULTRAFAST HYDROLYSIS.

In this thesis, the valorisation of lignin using hot-pressurized water was thoroughly studied. The investigation begun with the depolymerization of Kraft lignin using sub and supercritical water at short times and ended up with the application of the previously optimized ultra-fast alkaline supercritical water technology to real paper and biorefineries residues and the development of a continuous downstream process to recover low-molecular-weight products from the reaction mixture.

1. Search for optimal operating conditions for lignin depolymerization using sub and supercritical water.

1.1. Kraft lignin was successfully degraded into low-molecular-weight products at the optimal operating conditions of 386°C and 170 ms. A yield of 44.6% to light oil containing monomers, dimers and trimers was obtained, suppressing almost totally the formation of repolymerization products. The monomeric selectivity in guaiacol, vanillin, acetovanillone and homovanillic acid was 9.9%.

1.2. The repolymerization reactions were more favoured at higher temperatures and reaction times.

1.3. Changing the reaction conditions from sub- to supercritical, as well as the reaction time, strongly influenced the lignin degradation reactions into phenolic monomers. A more comprehensive study would be required for understanding the mechanism of those reactions.

2. Improvement of the lignin depolymerization process using supercritical water by addition of NaOH as catalyst.

2.1. The addition of NaOH to the reaction allowed to increase the lignin concentration up to 5 times, and even reacting a higher amount of lignin, higher monomeric yields were achieved than in the case of non-alkaline SCW reactions. At 300 ms, 386 °C and 0.2M NaOH, the light oil yield was 60 wt% with a selectivity in 8 key monomers around 20 wt%.

CONCLUSIONS

2.2. Analysis and quantification of the reaction products allowed distinguishing the different stages of the reaction: Depolymerization starts with a very rapid dehydration step followed by cleavage of C-O and C-C bonds up the optimum point. Low-molecular-weight fragments start to repolymerize at longer reaction times to yield char. Organic sulfur is incorporated to the latter at the last stages of the reaction.

This novel technology for converting lignin into high value-added products has been patented under the Title 'Ultra-fast Lignin Depolymerization Process' (European Patent Office, Application number 17382892.2 - 1109).

3. Application of the ultra-fast base-catalysed supercritical water technology to real pulping and biorefinery residues for its valorisation.

Different lignins were depolymerized using base-catalysed SCW at a reaction time of 300 ms. Since they were extracted from different biomasses using different methods, their behaviour in the depolymerization reaction differed, obtaining different yields at the same conditions of temperature and reaction time, as well as different major depolymerization products.

3.1. Promising results were obtained for Kraft lignins (both softwood and hardwood lignins) with yields of bio-oils (light oil + heavy oil) of up to 92 wt% and a selectivity in aromatic monomers of up to 16 wt%.

3.2. Organosolv-hardwood lignin depolymerization via alkaline SCW also seemed to be a promising route for obtaining high yields in bio-oils (28.5 %wt light oil and 62.8 %wt heavy oil) with a high selectivity in aromatic monomers (8.1 wt% in light oil).

3.3. Non-wood lignins isolated via biomass hydrolysis, seemed to be less convenient for the obtention of aromatic low-molecular-weight compounds.

3.4. All lignins suffered dehydration during the base-catalyzed SCW process, and the lignin aromatic structure after repolymerization was not altered. Repolymerization could be controlled thanks to the low reaction time applied, and as result, the amount of char formed was low in all cases. However, the

reaction time should be further optimized for each lignin in order to obtain the highest recovery of monomers and the minimum formation of char.

3.5. The ultra-rapid SCW treatment was directly applied to diluted black liquors. It was found to be equally effective than when using Kraft lignin.

Thus, this is a promising methodology to incorporate into a kraft process, giving the possibility to obtain bio-oils suitable for fuel and chemical production with no need of catalyst addition.

4. Development of a strategy to recover low-molecular-weight products from the lignin product mixture in a continuous process.

A strategy to separate the low-molecular-weight compounds from the product mixture obtained after the alkaline SCW process has been proposed, with the main objective of performing the downstream process also in continuous, saving operational costs and approaching this process to the real industry. The process proposed combines two flash separators to remove most of water of the products mixture, 1-stage liquid-liquid extraction (LLE) in order to recover the low-molecular-weight compounds and 3-stages vacuum distillation to recover the solvent used in the LLE.

4.1. Simulation showed that only 6.9% wt of monomers, dimers and trimers were lost, indicating that this strategy is promising for the continuous recovery of light oil fraction. However, additional operations to separate monomers from dimers and trimers would be required, followed by further distillations and crystallizations for monomers purification.

4.2. In addition, the economic profitability of the process was studied, concluding that the minimum light oil price should be 3.8 €/kg, which could be a competitive price in the future market if interesting applications were found for this bio-oil.

ANNEX I:

PATENT

ULTRA-FAST LIGNIN

DEPOLYMERIZATION PROCESS

ULTRA-FAST LIGNIN DEPOLYMERIZATION PROCESS

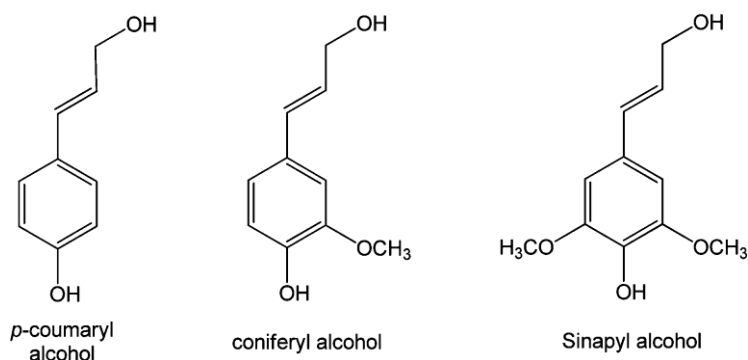
FIELD OF THE INVENTION

The present invention relates to the field of lignin valorization, in particular to the conversion of lignin products into added value small organic molecules useful in a range of industrial fields such as the cosmetic or food industries, pharmaceutical industry or for obtaining building block molecules.

BACKGROUND OF THE INVENTION

Lignin is a natural resource which exists in woody materials, agricultural residues and other plant materials (so-called lignocellulosic materials). Lignocellulosic materials generally comprise 10–30% lignin by weight, the exact proportion depending on the source of the lignocellulosic material. Softwoods are known to contain higher contents of lignin, followed by hardwoods and then grasses.

Lignin is a complex natural polymer resulting from oxidative coupling of, primarily, 4-hydroxyphenylpropanoid units, and more particularly of the three major phenylpropanoid building units *p*-coumaryl, coniferyl and sinapyl alcohols (depicted below). These units are randomly connected in lignin by several interunit ether and carbon-carbon linkages in different proportions, forming a randomized three-dimensional amorphous polymer structure.



Lignin has so far mainly been used as an energy source in combustion processes. In fact, less than 5% lignin is used for other purposes. Because of its polymer structure, lignin is considered a potential renewable resource of high-value chemicals, in particular of small, generally monomeric, phenolic compounds which find widespread applications such as in the cosmetic or food industries, or as building blocks of pharmaceuticals. Examples of such compounds are vanillin or syringol.

A considerable amount of research has focused on the depolymerization of lignin. A number of methods have been developed with such purpose, including pyrolysis, gasification, hydrolysis or biochemical processes. Particular attention has been paid to the hydrolysis of lignin in supercritical fluids.

Document WO 2015/075290 discloses the depolymerization of lignin in black liquor at temperatures of 250-500°C and pressures of 5-30 MPa. However, the process reported therein requires very long reaction times (30 minutes to 2 hours) and leads to low yields and low selectivity of important monomeric phenols (0.03% guaiacol, 0.2% vanillin, or 0.07% acetovanillone). Furthermore, the document only refers to a non-continuous (i.e. batch) process. These represent important drawbacks, as reduced depolymerization times and continuous flow processes are eagerly desired from an industrial standpoint.

Attempts at achieving lower depolymerization times with continuous flow setups, especially ultra-fast depolymerization rates under the second, have so far proven rather unsuccessful. Matsumara *et al.* (Industrial & Engineering Chemistry Research, 2012, 51, 11975-11988) studied the continuous conversion of lignin employing supercritical water and reaction times of 0.5 s or higher. However, whilst rapid lignin decomposition was recorded at 0.5 s, the decomposed lignin was mainly transformed into char (roughly 60% yield char) instead of into the desired phenolic compounds of interest.

Thus, there is still a need for developing efficient and selective, rapid, and industry-oriented processes for the production of high value small organic compounds from lignin.

SUMMARY OF THE INVENTION

It has now surprisingly been found that high value phenolic compounds can be produced from lignin in very good yields and selectivities, with depolymerization times below the second, when employing the process of the present invention. Furthermore, this process can be used in a continuous flow setup and is therefore highly suited to its use at an industrial level.

In particular, the process of the present invention is a process for the depolymerization of lignin comprising the following steps:

- a) Providing a lignin solution or suspension;
- b) Bringing the solution or suspension resulting from step a) to a temperature from 350 to 430°C and to a pressure of at least 220 bar, and maintaining, simultaneously, said pressure and temperature for a time of between 40 and 450 ms, in order to obtain a depolymerized lignin mixture comprising oligomeric and monomeric phenolic compounds.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. a) Simplified schematic depiction of a system for carrying out the process of the present invention as a continuous flow process; b) closer detail of a mixing means, reactor, and cooling/ decompression means suitable for carrying out the process of the present invention as a continuous flow process.

Figure 2. Schematic depiction of a representative phenolic oligomer and/or phenolic monomer isolation process according to the present invention.

Figure 3. Effect of temperature on a) first phenolic oil yield; and b) final solid phase; in the absence of base.

Figure 4. Effect of time on phenolic oil yield in a) the absence; and b) the presence of base.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention is a process for the depolymerization of lignin. In the context of the present invention, the term “lignin” has the meaning generally recognized in the art, which was described hereinabove.

The depolymerization of lignin refers to the degradation of the lignin macromolecule into smaller fragments. The depolymerization involves, amongst others, the cleavage of ether bonds, in particular aryl ether bonds, in the lignin macromolecule, along with other reactions such as dealkylations. The mixture of products obtained from lignin depolymerization depends on the process of lignin depolymerization employed and is generally difficult to characterize in full. However, as new processes of lignin depolymerization are developed, different lignin depolymerization product mixtures can be obtained. In particular, new processes of lignin depolymerization can favour higher proportions of specific lignin depolymerization products which may be of high value and/or commercial interest.

In a preferred embodiment the depolymerization of lignin refers to the conversion of the lignin macromolecule into phenolic oligomers and phenolic monomers. The term “phenolic oligomers” refers to compounds which comprise at least two and up to ten phenol functional groups. The oligomer is preferably a tetramer (four phenol functional groups), a trimer (three phenol functional groups) or a dimer (two phenol functional groups).

In a more preferred embodiment the depolymerization of lignin refers to the conversion of the lignin macromolecule into phenolic monomers. The term phenolic monomer refers to compounds which present a single phenol functional group. Examples of phenolic monomers include phenol, guaiacol, alkyl guaiacols such as creosol, 5-methylguaiacol or 4-ethylguaiacol, 4-vinylguaiacol, guaiacyl acetone, eugenol, isoeugenol, 4-hydroxybenzaldehyde, vanillin, vanillic acid, homovanillic acid, homovanillyl alcohol, acetovanillone, propiovanillone, syringaldehyde, 3,4,5-trimethoxybenzyl alcohol, 4-hydroxyacetophenone, 4-hydroxybenzoic acid, syringol, acetosyringone, syringic acid, ferulic acid, caffeic

acid, dehydrozingerone, sinapyl alcohol, coniferyl alcohol or *p*-coumaric acid.

In a particularly preferred embodiment the depolymerization of lignin refers to the conversion of the lignin macromolecule into guaiacol, creosol, vanillin, acetovanillone, homovanillic acid, 5-methyl guaiacol, acetosyringone, syringaldehyde and/or syringol. More preferably, it refers to the conversion of the lignin macromolecule into syringol, vanillin and/or homovanillic acid. In a preferred particular embodiment, it refers to the conversion of the lignin macromolecule in black liquor into syringol, syringaldehyde and vanillin. In another preferred particular embodiment, it refers to the conversion of the lignin macromolecule in Kraft lignin into vanillin and/or homovanillic acid.

In a preliminary step of the process of the present invention, a lignin product is provided, i.e. a product comprising lignin. The lignin product of the preliminary step of the present invention can comprise any lignin known in the art. Preferably the lignin is Kraft lignin or organosolv lignin. Other kinds of lignins known in the art are Brauns' lignin, cellulolytic enzyme lignin, dioxane acidolysis lignin, Klason lignin, periodate lignin, lignosulfates, lignosulfonates, and steam explosion lignin.

Lignin can also be classified based on the biomass submitted to a fractionation process.

In an embodiment, the lignin is hardwood lignin, i.e. lignin obtained from the fractionation of hardwood. Examples of hardwoods are eucalyptus, aspen or birch wood.

In another embodiment, the lignin is softwood lignin, i.e. lignin obtained from the fractionation of softwood. Examples of softwoods are spruce, pine, fir, larch or hemlock wood.

In another embodiment, the lignin is plant lignin, more particularly grass (Poaceae or Gramineae) lignin, i.e. lignin obtained from the fractionation of plant/grass material. Examples of plant material from which lignin can be obtained are the tobacco plant, cereal straw (e.g. wheat straw) or beet pulp.

In an embodiment, the lignin in the lignin product is obtained from a mixture of different lignocellulosic biomasses, preferably from a mixture of wood (softwood or hardwood) and plant material, in particular wood (softwood or hardwood) and grass.

In an embodiment, the lignin product is black liquor obtained from wood and/or plant material.

In an embodiment, the lignin is neither acylated nor alkylated prior to subjecting it to depolymerization.

In a preferred embodiment, the lignin product comprises at least 0.1% lignin by weight with respect to the total weight of the lignin product. In a particular embodiment, the percentage of lignin by weight with respect to the total weight of the lignin product is at least 1%. In a particular embodiment, the percentage of lignin by weight with respect to the total weight of the lignin product is at least 5%. In a particular embodiment, the percentage of lignin by weight with respect to the total weight of the lignin product is at least 10%. In a particular embodiment, the percentage of lignin by weight with respect to the total weight of the lignin product is at least 20%. In another particular embodiment this percentage is at least 30%. In another particular embodiment it is at least 40%. In another particular embodiment it is at least 50%. In another particular embodiment it is at least 60%. In another particular embodiment it is at least 70%. In another particular embodiment it is at least 80%. In another particular embodiment it is at least 90%. In another particular embodiment it is at least 95%. In another particular embodiment it is at least 99%. In another embodiment, the lignin product consists of lignin.

In a preferred embodiment the lignin product comprises at most 50% cellulose by weight with respect to the total weight of the lignin product. In a particular embodiment, the percentage of cellulose by weight with respect to the total weight of the lignin product is at most 40%. In another particular embodiment this percentage is at most 30%. In another particular embodiment it is at most 20%. In another particular embodiment it is at most 10%. In another particular

embodiment it is at most 1%. In another embodiment, the lignin product comprises no cellulose.

In a preferred embodiment the lignin product comprises at most 50% hemicellulose by weight with respect to the total weight of the lignin product. In a particular embodiment, the percentage of hemicellulose by weight with respect to the total weight of the lignin product is at most 40%. In another particular embodiment this percentage is at most 30%. In another particular embodiment it is at most 20%. In another particular embodiment it is at most 10%. In another particular embodiment it is at most 1%. In another embodiment, the lignin product comprises no hemicellulose.

In the context of the present invention, lignin, hemicellulose and cellulose content are determined by the method described herein below (see working example Determination of Structural Composition of Biomass).

The above amounts of lignin and/or cellulose and/or hemicellulose may be combined to arrive at combined embodiments. For instance, in a particular embodiment, the lignin product comprises at most 50% cellulose by weight and at least 50% lignin by weight, with respect to the total weight of the lignin product.

Lignin products comprising the above amounts of lignin and/or cellulose and/or hemicellulose are known in the art. These products are commercially available (e.g. from Sigma-Aldrich, CAS 8068-05-1) or can be prepared by methods well known in the art, such as by fractionation of lignocellulosic biomasses.

As used herein, “biomass” refers to a renewable energy source generally comprising carbon-based biological material derived from living organisms. The organisms may be plants, animals, fungi, etc. The term “biomass” as used herein does not include fossil fuel sources.

As used herein, “lignocellulosic biomass” refers to a biomass, preferably a plant biomass, comprising cellulose and/or hemicellulose, and lignin. Lignocellulosic biomass can be obtained from a variety of sources, for example from: agricultural

waste, including corn stover and sugarcane bagasse; or wood, including hardwoods (such as eucalyptus, aspen or birch wood) and softwoods (such as spruce, pine, fir, larch and hemlock wood).

A prominent example of lignocellulosic biomass fractionation is the pulping process. Different kinds of pulping processes are known, such as the Kraft process, the sulfite process, or organosolv pulping. These methods generally refer to the treatment of a lignocellulosic biomass with a cooking liquor to break the bonds that link lignin, hemicellulose, and cellulose, and result in the production as a by-product of pulping liquors comprising lignin and hemicellulose, from which lignin can be precipitated.

The Kraft pulping process involves treatment of the lignocellulosic biomass with a mixture of water, sodium hydroxide, and sodium sulfide (the so called white liquor) at a temperature of above 100 °C, for example at a temperature between 140 and 180 °C. The white liquor solubilises lignin and hemicellulose to form the so called black liquor, which is separated from cellulose. Black liquor is thus a liquid lignin product obtainable from the treatment of a lignocellulosic biomass with the Kraft process.

The lignin in Kraft black liquor is usually burnt in the recovery boiler at mills, thus providing the energy needed for further pulping. However, the present inventors have surprisingly found that black liquor can be employed as a lignin product in the process of the present invention. Furthermore, the black liquor can be employed directly, i.e. without any treatment or modification, in the process of the present invention. Thus, in an embodiment, the black liquor is neither dried nor concentrated prior to subjecting it to step c) of the present invention. In another embodiment, the black liquor is dried or concentrated in order to increase the lignin concentration therein prior to subjecting it to step c) of the present invention.

Alternatively, the solubilized lignin in black liquor can be precipitated from the black liquor, for example by addition of any pH decreasing acidifying agent, such as sulfuric acid or carbon dioxide, to the black liquor, and then isolated by means

of filtration and/or centrifugation. Lignin thus obtained is referred to as Kraft lignin. Kraft lignin products are lignin products that consist of lignin, or comprise at least 80% lignin, preferably at least 90% lignin, or more preferably at least 95% lignin by weight with respect to the total weight of the lignin product.

The sulfite process on the other hand involves treatment of the lignocellulosic biomass with sulfite or bisulfite salt solutions such as aqueous solutions. In these salts the counterion is typically an alkaline earth metal (e.g. calcium, magnesium) or an alkali metal (e.g. sodium, potassium) or ammonium. The sulfite process is generally carried out at a temperature of above 100 °C, for example at a temperature between 130 and 160 °C. The sulfite or bisulfite salt solution solubilizes lignin and hemicellulose to form the so called brown liquor (also known as red liquor, thick liquor or sulfite liquor), which is separated from cellulose. Lignin can then be separated from hemicellulose by acidification to precipitate lignin, and the precipitated lignin is recovered by means of filtration and/or centrifugation. Brown liquor is thus a liquid lignin product obtainable from the treatment of a lignocellulosic biomass with the sulfite process.

The organosolv pulping process is also known as a means for fractionating biomass and recovering lignin. Organosolv pulping involves contacting a lignocellulosic biomass with an aqueous organic solvent at temperatures ranging from 140 to 220 °C to solubilize lignin and hemicellulose, the organic solvent then being separated from cellulose. Solvents used include acetone, methanol, ethanol, butanol, ethylene glycol, formic acid and acetic acid. Lignin can then be separated from hemicellulose by acidification to precipitate lignin, and the precipitated lignin is recovered by means of filtration and/or centrifugation. Such lignin is known as organosolv lignin.

Other methods of lignocellulosic biomass fractionation are known in the art and are described, for example, in US 2013/0145995 A1.

Subsequently, in step a) of the invention, the lignin product of the preliminary step, or more specifically the lignin in the lignin product of the preliminary step is dissolved or suspended in a solvent to respectively provide a solution or

suspension. In the context of the present invention, the solution or suspension includes solutions or suspensions wherein the lignin in the lignin product is partially dissolved or suspended.

In an embodiment, the lignin in the lignin product is dissolved or suspended in dioxane, acetic acid, THF, DMSO, DMF, an alcohol such as methanol or ethanol, water or a mixture thereof. Preferably, the lignin in the lignin product is dissolved or suspended in an alcohol such as methanol or ethanol, water or a mixture thereof. In a most preferred embodiment, the lignin in the lignin product is dissolved or suspended in water. The degree of dissolution or suspension of the lignin in water can be adjusted by means known by the person skilled in the art, such as by adjusting the temperature of the water, a higher temperature providing higher dissolution. The choice of lignin product can also affect the solubility of the lignin in the solution or suspension.

In an embodiment, where the lignin product of the preliminary step or the lignin in the lignin product of the preliminary step is already in the form of a solution or suspension, it may either be employed as the lignin solution or suspension of step a), or it may be further processed (e.g. further diluted) to provide a new solution or suspension. This is for instance the case with black liquors. The dissolution or suspension of the lignin product of the preliminary step can be advantageous where lignin product flow problems are encountered or expected in apparatuses wherein the process of the invention is carried out or to be carried out.

In a preferred embodiment, a base is added to the solution or suspension of step a). The base is preferably an alkali metal hydroxide or an alkali metal bicarbonate. Preferred alkali metals are sodium or potassium, more preferably sodium. A most preferred base is sodium hydroxide.

In an especially preferred embodiment, the solution or suspension resulting from step a) is an aqueous solution or suspension which comprises sodium hydroxide or sodium bicarbonate, preferably sodium hydroxide.

The addition of the base can be carried out after preparing the solution or

suspension of the lignin product; or the base can be added to the dissolving or suspending medium prior to dissolving or suspending the lignin product; or the base can be added to the lignin product prior to dissolving or suspending.

The concentration of base in the solution or suspension resulting from step a) is generally low and depends on the means by which step b) is carried out, in particular the means by which the temperature increase in step b) is carried out. Said concentration of base is preferably one which is between 0.01 M and 2 M, preferably between 0.1 and 0.5 M, at a point in time when the solution or suspension reaches the temperature described in step b), namely a temperature of from 350 to 430 °C. This is because the temperature increase of step b) can be effected by addition to the solution or suspension resulting from step a) of a fluid (such as water), thus leading to a dilution of the base. The skilled person knows how to select the appropriate base concentrations in the solution or suspension resulting from step a) and the appropriate amount of temperature-increasing fluid of step b) to arrive at the desired base concentration in step b). In an embodiment, the concentration of base in the solution or suspension resulting from step a) is between 0.1 M and 5 M.

If the temperature increase in step b) is effected not by addition of a fluid (i.e. not by dilution), then the concentration of base in the solution or suspension resulting from step a) is generally the same as that in step b) at the point in time when the solution reaches the temperature of from 350 to 430 °C, allowing for an up to 20% increase in concentration due any to solvent evaporation that may occur.

As regards the concentration of lignin in the solution or suspension resulting from step a), this again depends on whether or not a fluid is added to exert the temperature increase in step b). Other parameters such as flow rate or tubing/reactor volume in continuous flow setups can also be considered, for instance where tubing or reactors can suffer from clogging, then lower lignin concentrations can be employed. In an embodiment, the concentration of lignin in the solution or suspension resulting from step a) is between 10 and 0.1% by weight with respect to the total weight of the solution or suspension. In another

embodiment, said concentration is between 5 and 0.1% by weight with respect to the total weight of the solution or suspension. In another embodiment, said concentration is between 2 and 0.3% by weight with respect to the total weight of the solution or suspension. Alternatively, the concentration of lignin in the solution or suspension resulting from step a) is one which leads to a concentration of lignin of between 0.01 and 1%, or of between 0.1 and 0.5%, with respect to the total weight of the solution or suspension, at a point in time when the solution or suspension reaches the temperature described in step b), namely a temperature of from 350 to 430 °C.

The point in time when the solution or suspension reaches the temperature described in step b) is for instance in continuous flow setups the point in time at which the solution or suspension enters the reactor.

Step b) of the process of the present invention involves bringing the solution or suspension resulting from step a) to a temperature of from 350 to 430 °C and to a pressure of at least 220 bar, and maintaining, simultaneously, said pressure and temperature. The solution or suspension resulting from step a) is at a temperature and pressure below the temperature and pressure to which it is brought in step b). Preferably, the solution or suspension resulting from step a) is at a temperature below 300 °C, more preferably below 150 °C, more preferably it is at room temperature (20-25 °C).

In an embodiment, the solution or suspension resulting from step a) is firstly brought to a temperature of from 350 to 430 °C, and then to a pressure of at least 220 bar. In another embodiment, the temperature and pressure increase can totally or partially coincide in time. In a preferred embodiment, the solution or suspension resulting from step a) is firstly brought to a pressure of at least 220 bar, and then to a temperature of from 350 to 430 °C. Whilst such a temperature alone can induce undesired reactions of the lignin in the solution or suspension resulting from step a), such a pressure alone does not typically induce said undesired reactions, or does so to a far lesser extent.

The solution or suspension resulting from step a) is brought to a pressure of at

least 220 bar. In another embodiment the pressure is between 220 and 500 bar, or between 220 and 400 bar, or between 220 and 300 bar. Preferably, it is between 255 and 275 bar.

The solution or suspension resulting from step a) is brought to a temperature of from 350 to 430 °C. In another embodiment, the temperature is from 370 to 430 °C. In another embodiment, the temperature is from 370 to 405 °C. In another embodiment, the temperature is from 370 to 395 °C. In another embodiment, the temperature is from 370 to 390 °C. Preferably, the temperature is from 383 to 389 °C.

It is understood that any and each combination of the above preferences for pressure and temperature ranges is also preferred. For example, a pressure between 220 and 500 bar, or between 220 and 400 bar, or between 220 and 300 bar in combination with a temperature of 370 to 395°C are also specific embodiments of the present invention.

In a preferred particular embodiment, the solution or suspension resulting from step a) is brought to a pressure of between 255 and 270 bar, and to a temperature of from 383 to 389 °C.

Preferably, the bringing of the temperature of the solution or suspension resulting from step a) to a temperature of from 350 to 430 °C (or to any of the above recited temperatures) is carried out as quickly as possible. This is because time is an important factor in the depolymerization of lignin. The present inventors have observed that lignin undergoes several depolymerization-repolymerization processes which can occur within seconds, or even within the second. Therefore, a precise control over reaction time has proven important in the context of the present invention. The slower the target temperature is attained, the more lignin in the solution or suspension starts reacting before the target temperature and pressure is attained, thus negatively impacting on the yields of the desired lignin depolymerization products.

Thus, the temperature increase from the temperature at which the solution or suspension resulting from step a) is, to the temperature of from 350 to 430 °C

preferably occurs within 150 ms (i.e. at most 150 ms), more preferably within 100 ms, more preferably within 50 ms, more preferably within 10 ms, even more preferably within 3 ms.

In particular embodiments, the temperature increase occurs between a time of 0.1 and 150 ms, more particularly between 0.1 and 100 ms, more particularly between 0.1 and 50 ms, more particularly between 0.1 and 10 ms, more particularly between 0.1 and 3 ms.

In preferred particular embodiments, the temperature increase occurs between a time of 1 and 150 ms, more particularly between 1 and 100 ms, more particularly between 1 and 50 ms, more particularly between 1 and 10 ms, more particularly between 1 and 3 ms.

In particular embodiments, the temperature increase occurs between a time of 3 and 150 ms, more particularly between 3 and 100 ms, more particularly between 3 and 50 ms, more particularly between 3 and 10 ms.

This temperature increase can be carried out by means known to the person skilled in the art. In a preferred embodiment, the temperature increase within these timeframes is effected by adding to the solution or suspension resulting from step a) a fluid (most preferably water) which is at a temperature higher than from 350 to 430 °C, or more specifically higher than whichever specific temperature or temperature range is selected from said 350 to 430 °C range. The higher the temperature of the fluid added in step b), the quicker the temperature of from 350 to 430 °C is attained, but the higher the risk of side-reactions is. Thus, the temperature of the fluid added in step b) is preferably between 400 and 500 °C, provided that the temperature of the added fluid is higher than whichever specific temperature or temperature range is selected from said 350 to 430 °C range.

The pressure increases of step b) need not be as quick as the temperature increase of step b).

Step b) then involves maintaining the lignin solution or suspension brought to the desired temperature and pressure (as described in any of the above

embodiments) at said temperature and pressure for a time of between 40 and 450 ms (milliseconds). The present inventors have surprisingly found that an ultra-fast and efficient depolymerization of lignin takes place within this timeframe at the specified temperature and pressure. Under said times, small amounts of the desired products (phenolic oligomers and monomers) are obtained, and above said times lignin repolymerization and char formation events start competing with lignin depolymerization. This finding allows attaining desired product yields in times far below those considered necessary in the prior art.

In an embodiment, the desired temperature and pressure maintenance is for a time of between 100 and 425 ms. In another embodiment, it is for a time of between 100 and 400 ms. In another embodiment, it is for a time of between 100 and 375 ms. In another embodiment, it is for a time of between 100 and 350 ms. In another embodiment, it is for a time of between 125 and 425 ms. In another embodiment, it is for a time of between 125 and 400 ms. In another embodiment, it is for a time of between 125 and 375 ms. In another embodiment, it is for a time of between 125 and 350 ms. In another embodiment, it is for a time of between 150 and 425 ms. In another embodiment, it is for a time of between 150 and 400 ms. In another embodiment, it is for a time of between 150 and 375 ms. In another embodiment, it is for a time of between 150 and 350 ms.

In a preferred embodiment, the solution or suspension resulting from step a) is an aqueous solution or suspension to which a base, in particular a base as described above, has not been added, and which in step b) is maintained at the desired temperature and pressure (as described in any of the above embodiments) for a time between 140 and 320 ms.

In another preferred embodiment, the solution or suspension resulting from step a) is an aqueous solution or suspension comprising a base as described above, and which in step b) is maintained at the desired temperature and pressure (as described in any of the above embodiments) for a time between 140 and 370 ms, preferably between 210 and 370 ms.

As soon as the desired maintenance time of step b) has elapsed, the temperature

and pressure of the depolymerized lignin solution are rapidly reduced. Again, this is to ensure an accurate control over the depolymerization reaction and to avoid or reduce to a minimum any subsequent lignin repolymerization or char formation event. Therefore, temperature and pressure decrease times as low as possible are desired.

In an embodiment, a temperature reduction of between 125 and 300 °C, is effected in a time of at most 300 ms, or at most 100 ms, or preferably at most 10 ms, or more preferably at most 1 ms. In particular embodiments, this temperature reduction is effected in a time of between 0.1 and 300 ms, or of between 0.1 and 100 ms, or preferably of between 0.1 and 10 ms, or more preferably of between 0.1 and 1 ms. In preferred particular embodiments, this temperature reduction is effected in a time of between 0.01 and 300 ms, or of between 0.01 and 100 ms, or preferably of between 0.01 and 10 ms, or more preferably of between 0.01 and 1 ms. In other embodiments, these times apply but the temperature reduction is of between 200 and 300 °C.

In an embodiment, a pressure reduction of 100 bar or more is effected in a time of at most 300 ms, or at most 100 ms, or preferably at most 10 ms, or more preferably at most 1 ms. In particular embodiments, this pressure reduction is effected in a time of between 0.1 and 300 ms, or of between 0.1 and 100 ms, or preferably of between 0.1 and 10 ms, or more preferably of between 0.1 and 1 ms. In preferred particular embodiments, this pressure reduction is effected in a time of between 0.01 and 300 ms, or of between 0.01 and 100 ms, or preferably of between 0.01 and 10 ms, or more preferably of between 0.01 and 1 ms. In other embodiments, these times apply, but the pressure reduction is of between 100 and 300 bar, or of between 100 and 270 bar, and more preferably it is a pressure reduction down to atmospheric pressure.

Preferably, these degrees and times of decompression and cooling are carried out simultaneously. This can be achieved for instance by flash evaporation, or in continuous flow setups through the use of a high temperature decompression valve. These degrees and times of simultaneous decompression and cooling can

be achieved through any means making use of the Joule-Thompson thermodynamic effect.

In an embodiment, the decompressed and cooled depolymerized lignin mixture is then further cooled, preferably to room temperature, and/or decompressed, preferably to atmospheric pressure, after step b) and, if oligomeric and/or monomeric phenolic compounds are to be isolated or purified from said mixture, before isolating or purifying the oligomeric and/or monomeric phenolic compounds.

In a preferred embodiment, the process of the present invention is a continuous flow process, which is advantageously suited to the implementation of the process of the invention in an industrial setting. Flow rates of the different components of the process of the invention, in particular of the lignin solution or suspension resulting from step a) and of any fluid employed to bring said solution or suspension to the temperature of step b), can be adjusted by the person skilled in the art, such that the desired temperature increase, maintenance and/or decrease times are achieved within the timeframes mentioned hereinabove. Examples 1, 2 and 3 describe such a continuous process. Figure 1 schematically depicts a system for carrying out such a continuous process.

In a preferred continuous flow embodiment, the solution or suspension of step a) is prepared in a tank or reservoir (1), the latter being in fluid communication with an input end of a reactor (5). The depolymerization of step b) takes place in the reactor (5)

In a preferred continuous flow embodiment, the reactor (5) comprises or is coupled to, at its output end, means (7) for effecting the sharp cooling and decompression according to the present invention, such as a high temperature decompression valve. The reactor is provided at said output end with discharge means for discharging the decompressed and cooled depolymerized lignin mixture (10). In an embodiment, the decompressed and cooled depolymerized lignin mixture is further cooled, such as with a cooler (11) and/or decompressed.

Where the temperature increase of step b) is carried out by addition of a hot fluid,

the reactor further comprises or is coupled to, at its input end, mixing means (6) such as a T- or Y-junction, where the solution or suspension resulting from step a) and the hot fluid meet and then enter the reactor. The hot fluid can be supplied to the reactor from a tank or reservoir (2). Thus the tank or reservoir (1) is in fluid communication with a first entry port of the mixing means (6), and the tank or reservoir (2) is in fluid communication with a second entry port of the mixing means (6).

In a continuous flow embodiment, the solution or suspension of step a) in the tank or reservoir is pumped towards the reactor by means of a first pump (3). In a continuous flow embodiment, the hot fluid is pumped towards the reactor by means of a second pump (4). In a continuous flow embodiment, the hot fluid is initially not hot, and is heated to the desired hereinabove mentioned temperatures as it is being pumped towards the reactor, for instance by the use of heat exchangers (8) or heaters (9) past which the fluid flows.

In a preferred continuous flow embodiment, these continuous flow embodiments are combined, except where embodiments are mutually exclusive. The person skilled in the art is aware of parameters and means for implementing and modulating such a continuous flow system. For instance, fluid communication may be achieved through the use of tubing of the appropriate length, diameter and material, which will generally be chosen based on the amount of material to be depolymerized and the nature of the material itself, as well as the flow rate which is desired. Flow rates in turn can further be controlled by the pumps employed, or the length and diameter of the reactor and/or mixing or cooling/decompression means employed. The process of the invention may be for instance carried out in a system such as that described in Cantero, Bioresource Technology, 2013, 135, 697-703.

The present inventors have advantageously found that the depolymerization process of the present invention (steps a) to b)) can be efficiently carried out by employing only water (in the presence or absence of base as described hereinabove), in particular by employing only water as the dissolving or

suspending medium for the lignin in the lignin product and/or as the fluid for achieving the temperature increase of step b). Thus, in a particular embodiment the depolymerization process of the present invention is carried out in the absence of acid. In another particular embodiment it is carried out in the absence of a non-base catalyst, and more particularly it is carried out in the absence of a metal catalyst, thus providing a clean lignin depolymerization process. In an embodiment, the metal catalyst comprises a transition metal, in another embodiment the metal catalyst comprises a noble metal, and in another embodiment the metal catalyst comprises Si, Al, Zr, Fe, Pt, Pd, Ni, La, Ce, Mo, Ru or Cu. In another particular embodiment the depolymerization process of the present invention is carried out in the absence of a biocatalyst. In another embodiment, the depolymerization process of the present invention is carried out in the absence of an ionic liquid, such as those comprising an alkyylimidazolium (e.g. methylimidazolium) moiety. In another embodiment, the depolymerization process of the present invention is carried out in the absence of a capping agent. Capping agents are well known in the field of the present invention as compounds which are able to prevent or minimize the repolymerization of depolymerized lignin. In an embodiment, the capping agent is a capping agent other than a base as used in step a) of the present invention. In a particular embodiment, the capping agent is an ester. In another particular embodiment it is a silylating agent. In another particular embodiment, the capping agent is a cresol, more particularly *p*-cresol.

The process of the present invention can comprise a final step of isolating or purifying the oligomeric and/or monomeric phenolic compounds from the depolymerized lignin mixture. In an embodiment, said final step comprises isolating from the depolymerized lignin mixture a mixture which has a higher amount of the oligomeric and monomeric phenolic compounds than the depolymerized lignin mixture. In an embodiment, said final step comprises isolating from the depolymerized lignin mixture a mixture which comprises not less than 5%, not less than 10%, not less than 15%, not less than 20%, not less than 25%, not less than 30%, not less than 35%, not less than 40%, not less than 45%,

or not less than 50% by weight of oligomeric and monomeric phenolic compounds, or preferably of monomeric phenolic compounds, with respect to the total weight of the isolated mixture. In an embodiment, the isolated mixture is an oil, and more particularly it is the first phenolic oil described hereinafter. Oligomeric and/or monomeric phenolic compounds in the isolated mixture can generally be isolated or quantified by standard purification methods known to the skilled person, such as those described in the experimental section hereinafter.

The isolation or purification of the oligomeric and/or monomeric phenolic compounds from the depolymerized lignin mixture can be achieved for instance by adding an acid (11) to the decompressed and cooled depolymerized mixture (12) to obtain a first liquid phase (13) and a first solid phase (14). The first liquid phase comprises the greatest part of the phenolic oligomers and/or phenolic monomers.

The acid is preferably a mineral acid, such as sulphuric acid. The acid is preferably added dropwise to the decompressed and cooled depolymerized mixture. The acid is preferably added to the decompressed and cooled depolymerized mixture until the pH of said depolymerized mixture is between 1 and 4, preferably about 2.

In an embodiment, where the decompressed and cooled depolymerized mixture resulting from step b) already contains a first liquid phase (13) and a first solid phase (14), the addition of acid in step c) can be omitted. The decompressed and cooled depolymerized mixture resulting from step b) typically already contains a first liquid phase (13) and a first solid phase (14) when the pH of the mixture is acidic, i.e. under pH 7, for instance when it is at pH 6 or lower. This can be the case where a base is not added to the solution or suspension of step a).

The first liquid phase and the first solid phase are preferably then separated, preferably by centrifugation followed by removal of the first liquid phase.

In a preferred embodiment, in order to further purify the phenolic oligomers and/or phenolic monomers, the separated first liquid phase is extracted with an

organic solvent, such as ethyl acetate or DCM to obtain a first final organic phase (15) and a final aqueous phase (16). It is the first final organic phase which contains the phenolic oligomers and/or phenolic monomers. The first final organic phase can be evaporated and/or dried to remove the organic solvent therefrom, which typically results in an oil highly pure in phenolic oligomers and/or phenolic monomers (herein referred to as the first phenolic oil). By employing the process of the present invention, yields of first phenolic oil as high as 75% by weight with respect to the weight of lignin in the initial lignin product can be achieved. In a preferred embodiment, the extraction of the first liquid phase is repeated, for example once, twice or thrice.

The amount of phenolic monomers in the first phenolic oil can be higher than that observed for other lignin depolymerization products in the art. Thus, the present invention also refers to a product, in particular an oil, which comprises between 5 and 50% weight phenolic monomers with respect to the total weight of the product, or in particular of the oil. In another embodiment said weight of phenolic monomers is between 5 and 25%, or between 5 and 20%. In another embodiment said weight of phenolic monomers is between 10 and 50%, or between 10 and 25%, or between 10 and 20%. In another embodiment said weight of phenolic monomers is between 15 and 50%, or between 15 and 25%, or between 15 and 20%. The expression "weight of phenolic monomers" refers to the sum of all phenolic monomers in the product, in particular in the oil. In an embodiment "weight of phenolic monomers" refers to more than one phenolic monomer. In an embodiment, the product, or in particular the oil, comprises two, three, four or five phenolic monomers selected from guaiacol, creosol, vanillin, acetovanillone, homovanillic acid, syringol and syringaldehyde, and the combined weight of said two, three, four or five phenolic monomers with respect to the total weight of the product, or in particular the oil, is any of those specified above in this paragraph. The present invention also refers to the use of said product, or in particular oil, in cosmetic or food products.

The final aqueous phase typically contains inorganic salts produced during the process of the invention.

In an embodiment, the separated first solid phase is optionally washed with water, for example once, twice or thrice. The optionally washed separated first solid phase is then extracted with an organic solvent, such as ethyl acetate or DCM to obtain a second final organic phase (17) and a final solid phase (18). The extraction can be repeated, for example once, twice or thrice. The second final organic phase can be evaporated and/or dried to remove the organic solvent therefrom to obtain a second phenolic oil. The second phenolic oil contains phenolic oligomers and/or phenolic monomers to a lesser degree and in an impurer form as compared to the first phenolic oil, but may nevertheless be further processed to purify the phenolic oligomers and/or phenolic monomers. It should be noted that the amount of phenolic oligomers and/or phenolic monomers in the second phenolic oil has not been incorporated in the calculation of the above stated first phenolic oil yields.

The further processing of the first solid phase is typically not carried out when no base has been added to the solution or suspension of step a) of the invention.

The final solid phase typically contains residual lignin and char produced during the process of the invention.

A phenolic oligomer and/or phenolic monomer isolation process according to the present invention is depicted in Figure 2.

In a preferred embodiment, the isolation of the phenolic oligomers and/or phenolic monomers is also carried out as a continuous flow process.

In another embodiment, any of the phenolic oligomers and/or phenolic monomers is isolated from the phenolic oil. This can be achieved by standard purification techniques known to the skilled person.

In another aspect of the invention, the present invention refers to a product obtainable by any of the process embodiments of the present invention.

Unless expressly stated, the terms used herein are intended to have the plain and ordinary meaning as understood by those of ordinary skill in the art.

The following examples are provided for the purpose of illustrating, not limiting,

the invention.

Example 1: Continuous process for the depolymerization of lignin in the absence of base.

Materials.

The lignin used was Kraft lignin (CAS 8068-05-1) from Sigma-Aldrich. This lignin was chosen due to its good water solubility. Distilled water was used as the reaction medium to run the experiments.

Method.

The continuous process used to carry out the lignin depolymerization was that schematically depicted in Figure 1. The depolymerization was carried out at temperatures between 300 °C to 400 °C (300, 370, 386 and 400 °C \pm 2.1 °C) and a pressure of 260 \pm 8.1 bar, with reaction times between 60 ms and up to 4.6 s. The reaction time was controlled by changing the input flow to the reactor and the reactor volume. The feeding lignin concentration was 0.3% w/w (0.1 \pm 0.02 % w/w at reactor input). This low concentration was chosen to minimize the chances of clogging problems in the high temperature valve used for the decompression. The water flow was varied from 3.5 L/h to 5.1 L/h and the lignin solution flow was varied from 1.6 to 2.5 L/h at the operating pressure of 260 bar. Different reactors were made with volumes between 0.5 and 12.3 cm³. The reaction was stopped by sharp temperature reduction using the high temperature valve. Once the reaction finished, the depolymerized mixture was further processed in order to recover the different products formed and contained therein. Firstly, a first solid phased contained in the mixture was separated from a first liquid phase by centrifugation (10 min, 7000 rpm). The first liquid phase was recovered carefully by pipette without disturbing the solid. Then, the wet solid was washed with milli-Q water and dried in an oven at 45 °C, obtaining the first solid phase in dry form. The first liquid phase was subjected to a liquid-liquid extraction process with ethyl acetate to give a first final organic phase and a final aqueous phase. The ethyl acetate was evaporated from the first

final organic phase to give the first phenolic oil, which is the product of interest of the present invention.

Results.

The effect of temperature on the yields at a constant reaction time of 170 ms was studied at temperatures of 300, 370, 386 and 400 °C. As can be seen in Figure 3a, at 300 °C the yield of first phenolic oil was negligible, indicating that depolymerization had hardly taken place. Then, the oil yield increased dramatically up to 54.8% at 386 °C. At 400 °C, the yield was reduced drastically (16.6%). In accordance with these results, the yield of final solid phase (char and residual lignin) was 7.0% at 386 °C but increased greatly to 55.1% at 400 °C, as can be observed at Figure 3b).

After unexpectedly finding that high first phenolic oil yields could be achieved at a time under the second, in particular under half a second, the effect of reaction times between 70 and 360 ms was investigated. In Figure 4a it can be observed that the first phenolic oil yield in fact peaked at 290 ms, reaching 52.1%), and then decreased dramatically, presumably because of the repolymerization reactions occurring at longer times. With regard to the final solid phase formation, it was less than 7% at all timepoints beyond 90 ms. At 90 ms, residual lignin was the main product (12.3%). It was thus surprisingly found that a major first depolymerization can be induced under half a second, in clear contradiction to prior art assumptions such as those of Matsumara *et al.*

Example 2: Continuous process for the depolymerization of lignin in the presence of base.

Materials.

Materials employed were the same as those in Example 1. Sodium hydroxide technical grade pellets were acquired from Panreac and were used in solution in distilled water. The calibration standards used in the GC/MS analysis (guaiacol, vanillin, acetovanillone, homovanillic acid and creosol) and the internal standard

(2-phenyl ethanol) were purchased from Sigma-Aldrich (USA). The ethyl acetate for carrying out the liquid-liquid extractions and the acetone used as solvent to analyze by GC/MS were also purchased from Sigma-Aldrich.

Method.

The continuous process used to carry out the lignin depolymerization was that schematically depicted in Figure 1. In this study, the depolymerization was carried out at 386 ± 2.6 °C and 260 ± 5 bar with reaction (depolymerization) times of 38-490 ms. The reaction time was controlled by changing the inlet flow to the reactor and the reactor volume. The flows were varied between 1.4-2.6 L/h for the aqueous NaOH lignin solution, and 3.4-4.4 L/h for the water employed to bring the lignin solution to 386 °C. Two reactors were employed with volumes of 1.15 and 0.64 cm³, each coupled at their input end to a T junction in which the hot water and the basic lignin solution were mixed, and further comprising another T junction with a thermocouple to measure the reactor temperature, and a high temperature decompression valve at the output end of the reactor. The lignin concentration at the input end of the reactor was 5000 ppm (0.5% w/w) in a basic solution of NaOH at pH 13 (0.2 M).

Once the reaction finished the depolymerized mixtures were treated in order to simplify the analysis. A procedure was developed to separate the mixture into four phases. The scheme of this procedure is shown in Fig.2. Firstly, the depolymerized mixture was acidified by adding concentrated H₂SO₄ (96%) dropwise until the solution was at pH 2 to give a brown suspension. Then, the sample was centrifuged for 10 minutes at 7000 rpm to give a clear yellow liquid (the first liquid phase) on top of a dark brown solid (the first solid phase). The first liquid phase was recovered carefully by pipette without disturbing the solid and the wet solid was shaken with H₂O at pH 2 three times. The first solid phase was extracted three times with ethyl acetate (1:1 volume of sample/volume of ethyl acetate used in each extraction) to give a second final organic phase and a final solid phase. The solvent in the second final organic phase was evaporated with a rotary evaporator at 40 °C and was dried in an oven at 50 °C to give the

second phenolic oil. The water of the final solid phase was eliminated with a rotary evaporator at 80 °C and dried in an oven at 50 °C. The first liquid phase was extracted three times with ethyl acetate (1:1.25 volume of the sample/volume of ethyl acetate used in each extraction) to give the first final organic phase and the final aqueous phase. The solvent was evaporated from the first final organic phase with a rotary evaporator at 40 °C and dried in an oven at 50 °C to give the first phenolic oil. Finally, the water was removed from the final aqueous phase in a rotary evaporator at 80 °C and dried in an oven at 50 °C. The main product of interest in this study was the first phenolic oil. The final aqueous phase contained the salts formed (Na_2SO_4) during the sulfuric acid addition in order to precipitate the solid fraction.

Characterization of the products.

The products obtained after the fractionation procedure were analysed by different techniques. The first phenolic oil was characterized in order to establish the nature of the phenolic compounds. For this purpose, the oil was analysed by a gas chromatograph equipped with a quadrupole mass spectrometer detector (5977A-Agilent Technologies, USA). Data of the chromatographic separations were acquired using a capillary column HP-5ms, 30 m x 0.250 mm x 0.25 μm (Agilent Technologies, USA). The equipment was in splitless mode. The oven temperature was programmed as follows: initial temperature was set at 32 °C and kept for 10 min, then temperature was raised to 52 °C at 2 °C/min, and kept for 2 min; to 65 °C at 2 °C/min, and kept for 2 min; to 93 °C at 4 °C/min, and kept for 2 min; to 230 °C at 2 °C/min and kept for 3 min; and finally, to 300 °C at 15 °C, and kept for 3 min. To eliminate the acquisition of the solvent (acetone) by the MS, a solvent delay was programed at 3.70 minutes after confirming that no compounds were removed with the solvent. For compound identification, the data obtained in the GC-MS analysis were compared with m/z values compiled in the spectrum library Wiley. Data analysis was performed using the Agilent MassHunter software (Agilent Technologies, USA). Validation of compound identification was carried out by comparison of their MS spectra and their retention times with standards. Quantification was carried out using standard

calibration curves with a polynomial fit for guaiacol (100-800 ppm), vanillin (100-500 ppm), acetovanillone (100-500 ppm), homovanillic acid (100-500 ppm) and creosol (100-500 ppm). In order to eliminate instrumental variations, the peak area of each compound was normalized to the peak area of the internal standard, 2-phenyl ethanol (70 ppm). The normalized values were used for data analysis.

Results.

The yield of first and second phenolic oils was analysed at different timepoints. As can be seen in Figure 4b the yield of first phenolic oil increased with reaction time until reaching a maximum of 67% at 239 ms, and it decreased drastically after 348 ms, from 54% to a constant value of oil production of 12-14% at the higher reaction times. These results are in accordance with those observed for Example 1.

The following table shows the first phenolic oil composition at different depolymerization times. Values are weight % over the weight of the first phenolic oil.

Compound	Reaction time (ms)								
	38	62	146	239	296	350	423	450	490
Guaiacol	0.00	1.91	0.61	1.07	3.89	2.56	0.00	1.92	0.64
Creosol	0.00	0.97	0.20	0.37	1.98	1.00	0.00	1.23	0.56
Vanillin	1.54	1.03	0.53	0.96	4.14	0.91	0.82	2.65	1.77
Acetovanillone	1.85	1.30	0.60	0.84	3.31	1.31	1.72	0.11	2.43
Homovanillic acid	4.72	2.07	1.07	1.55	4.23	1.71	3.04	1.23	2.51
Total	8.12	7.28	3.01	4.78	17.55	7.49	5.58	7.14	7.90

It is important to note that in addition to these compounds, other compounds in a minor amount were also detected, such as 5-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, syringol, eugenol, isoeugenol, homovanillyl alcohol, propiovanillone, acetosyringone, syringaldehyde or dehydrozingerone. It was

also observed that the amount of phenolic monomers isolated was greater than that obtained in Example 1. Thus, it has been surprisingly found that the use of NaOH favoured depolymerization selectivity towards phenolic monomers.

As regards the second phenolic oil, it is composed mainly of monomers also presented in the first phenolic oil, but in a minor amount. It is hypothesized that these are just monomers remaining in the first solid phase that could not be separated from the solid in the centrifugation and washing steps.

Example 3: Continuous process for the depolymerization of black liquor in the presence of base.

Materials.

The black liquor used was obtained from eucalyptus wood and comprised low weight lignin with respect to the weight of the black liquor. Rest of materials were as specified for Example 2.

Method.

The procedure followed was similar to that described for Examples 1 and 2. A 0.5 M NaOH solution was prepared, and the black liquor was dissolved therein until a 1.2% w/w lignin solution was attained. Depolymerization parameters were as follows: 386 ± 2.6 °C, 260 ± 5 bar and 300 ± 8 ms.

Results.

The first phenolic oil was obtained in a yield of 51.3% by weight with respect to the amount of lignin in the lignin solution at the reactor input. The first phenolic oil composition is shown in the following table. Values are weight % over the weight of the first phenolic oil.

Compound	Yield % w/w
Guaiacol	2.7
Vanillin	0.6
Acetovanillone	1.6
Syringol	3.0
Creosol	0.8
Syringaldehyde	2.2

Example 4: Determination of Structural Composition of Biomass.

Cellulose and hemicellulose content.

The structural composition of biomass can be determined by extracting the cell wall of biomass and analyzing the content of cellulose, hemicellulose, and lignin. Samples are dried and milled to 212-500 μm size. The plant material is homogenized in 80 % (v/v) ethanol using a Polytron Homogenizer (Fisher, USA) at high speed for 2-3 minutes. Homogenate is heated for 1 hour at 80 °C, cooled down to room temperature, and centrifuged at 12000 times gravity (G) for 30 minutes. Pellets are resuspended in 80% ethanol, and the procedure is repeated. Pellets are washed three times with 85% acetone, and air dried. Dry pellets are suspended in 0.5% aqueous sodium dodecyl sulfate (SDS) overnight. The residue is recovered and washed with water by filtration, washed with a 1:1 mixture of chloroform and methanol, rinsed with acetone, and air-dried. The resulting cell wall material (CW) is analyzed.

The cellulose content is determined by treatment of CW (10 mg) with acetic-nitric reagent (80% acetic acid:concentrated nitric acid, 10:1). Unhydrolyzed pellets are washed several times with water, followed by acetone, air-dried and weighed. Cellulose content is calculated in the percentage of total cell wall.

The hemicellulose content is estimated by hydrolysis of CW with 2M trifluoroacetic acid (TFA). Unhydrolyzed pellets are washed several times with

water, followed by acetone, air-dried and weighed. Acid soluble hemicellulose content is calculated in the percentage of total cell wall.

Lignin Content.

The lignin content is determined by the analysis method TP-510-42618 of NREL (U.S. National Renewable Energy Laboratory) (Version 08-03-2012).

CLAIMS

1. A process for the depolymerization of lignin, comprising the following steps:
 - a) Providing a lignin solution or suspension;
 - b) Bringing the solution or suspension resulting from step a) to a temperature of from 350 to 430°C and to a pressure of at least 220 bar, and maintaining, simultaneously, said pressure and temperature for a time of between 40 and 450 ms, in order to obtain a depolymerized lignin mixture comprising oligomeric and monomeric phenolic compounds;
 - c) Isolating the oligomeric and monomeric phenolic compounds from the depolymerized lignin mixture.
2. Process according to claim 1, comprising a preliminary step prior to step a) of preparing a lignin solution or suspension from a lignin product.
3. Process according to claim 2, wherein the lignin product of the preliminary step comprises at most 50% cellulose by weight with respect to the total weight of the lignin product.
4. Process according to any one of claims 2 to 3, wherein the lignin product of the preliminary step comprises at least 10% lignin by weight with respect to the total weight of the lignin product.
5. Process according to any one of claims 1 to 4, wherein the solution or suspension of step a) comprises a base.
6. Process according to claim 5, wherein the base is an alkali metal hydroxide or an alkali metal bicarbonate.

ANNEX I: PATENT

7. Process according to any one of claims 1 to 6, wherein the concentration of lignin in the solution or suspension resulting from step a) is between 10% and 0.1% by weight with respect to the total weight of the solution or suspension.
8. Process according to any one of claims 1 to 7, wherein the bringing of the solution or suspension resulting from step a) to a temperature of from 350 to 430°C is achieved by adding to said solution or suspension a fluid, wherein the fluid is at a temperature higher than from 350 to 430°C.
9. Process according to any one of claims 1 to 8, wherein the bringing of the solution or suspension resulting from step a) to a temperature of from 350 to 430°C is effected within a time of 10 ms.
10. Process according to any one of claims 1 to 9, wherein immediately after the time of step b) has elapsed, a temperature reduction of between 125 and 300 °C is effected within a time of 1 ms.
11. Process according to any one of claims 1 to 10, wherein no metal catalyst is used during steps a) to b).
12. Process according to any one of claims 1 to 11, wherein no capping agent is used during steps a) to b).
13. Process according to any one of claims 1 to 12, wherein the process is a continuous flow process.
14. Process according to any one of claims 1 to 13, wherein step c) comprises:
 - i. If the depolymerized lignin mixture of step b) does not comprise a first liquid phase and a first solid phase, adding an acid to the

depolymerized lignin mixture to obtain a first liquid phase and a first solid phase;

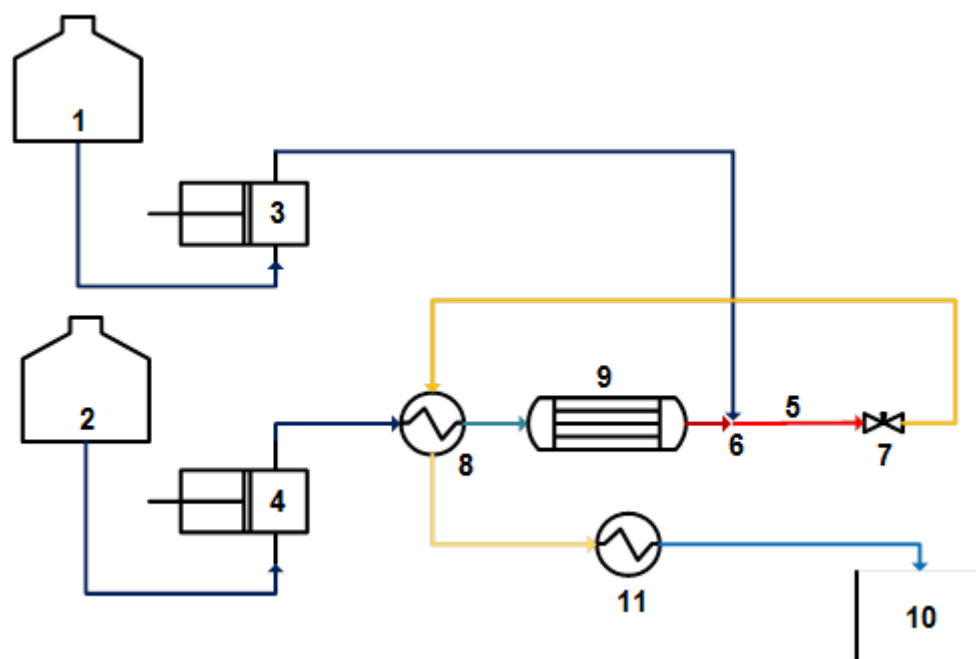
- ii. Separating the first solid phase from the first liquid phase and extracting the first liquid phase with an organic solvent to obtain a final organic phase comprising the oligomeric and monomeric phenolic compounds.

- 15. Process according to any one of claims 1 to 14, wherein the solution or suspension of step a) is black liquor or a solution or suspension of Kraft lignin.

ABSTRACT

The present invention refers to a process for depolymerizing lignin in times under the second and at elevated temperature and pressure. The process of the invention can be carried out as a continuous flow process and provides high yields of high-value oligomeric and monomeric phenolic compounds derived from lignin.

a)



b)

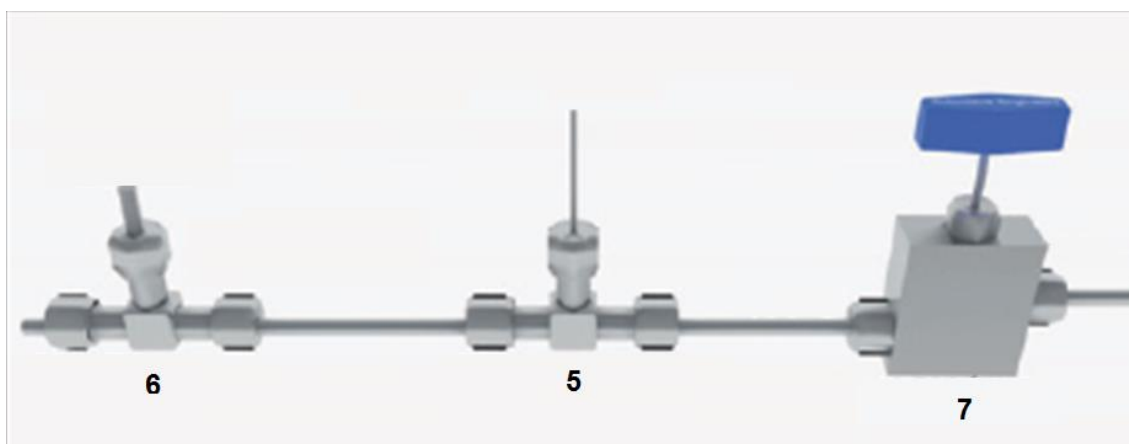


Figure 1

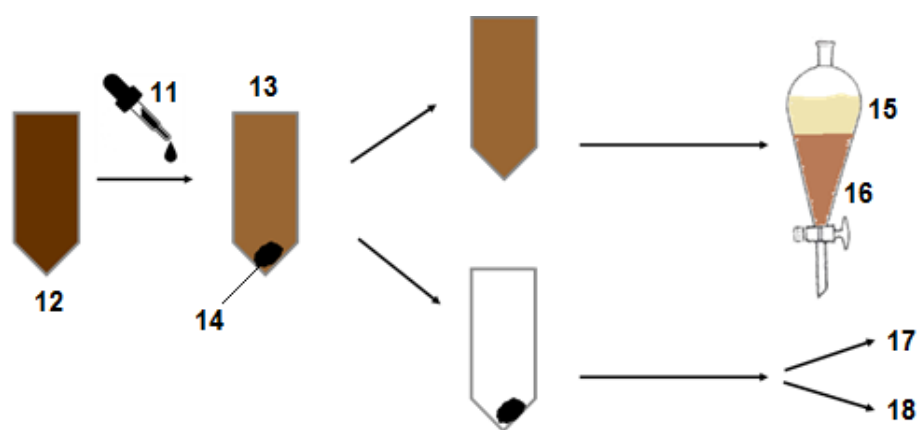
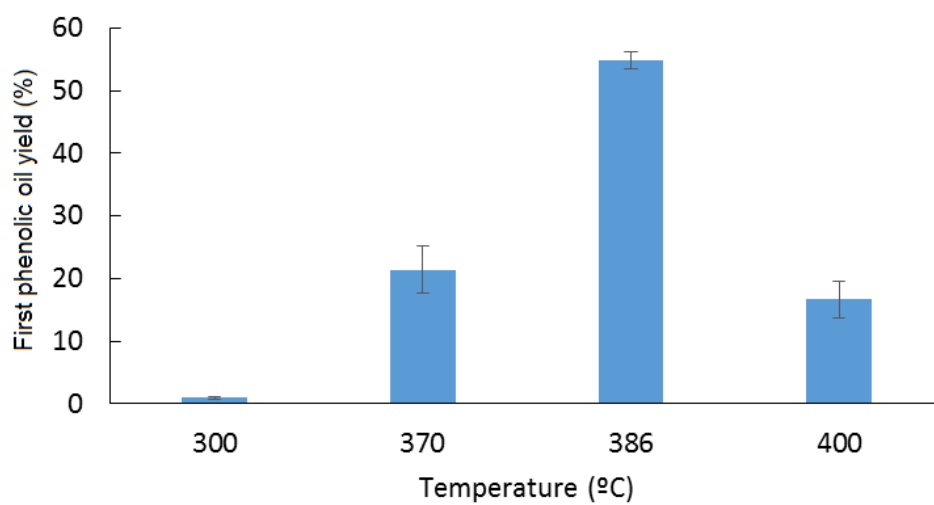
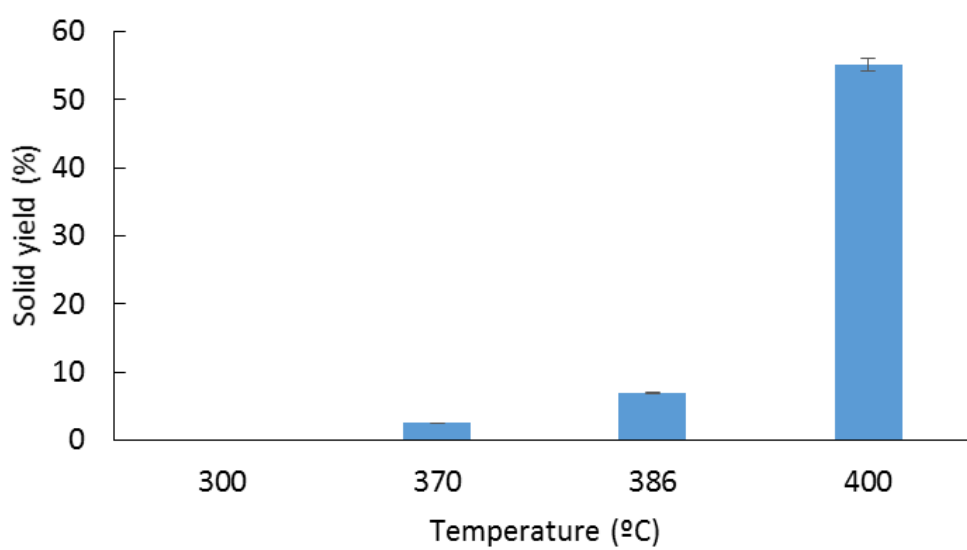


Figure 2

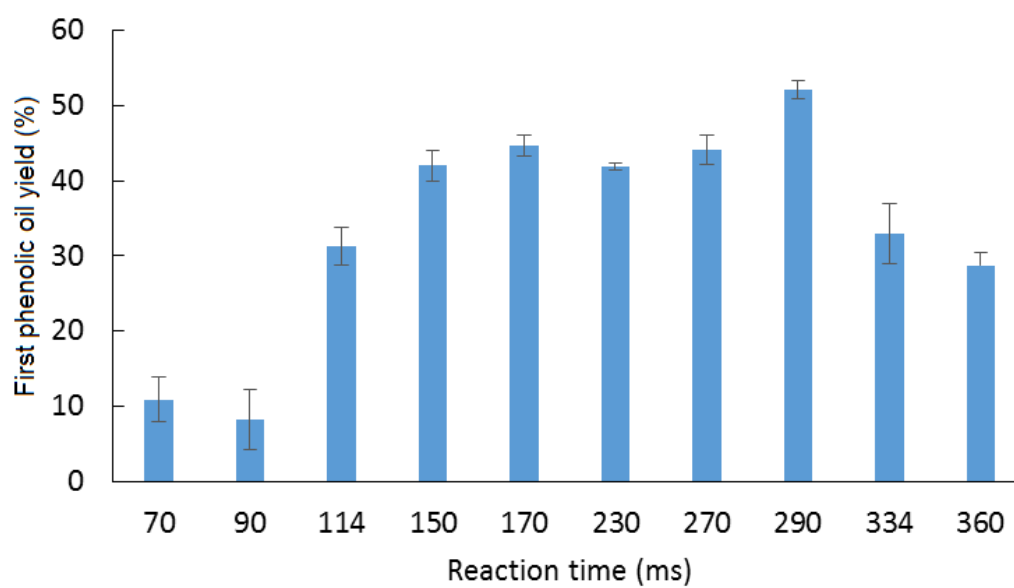
a)



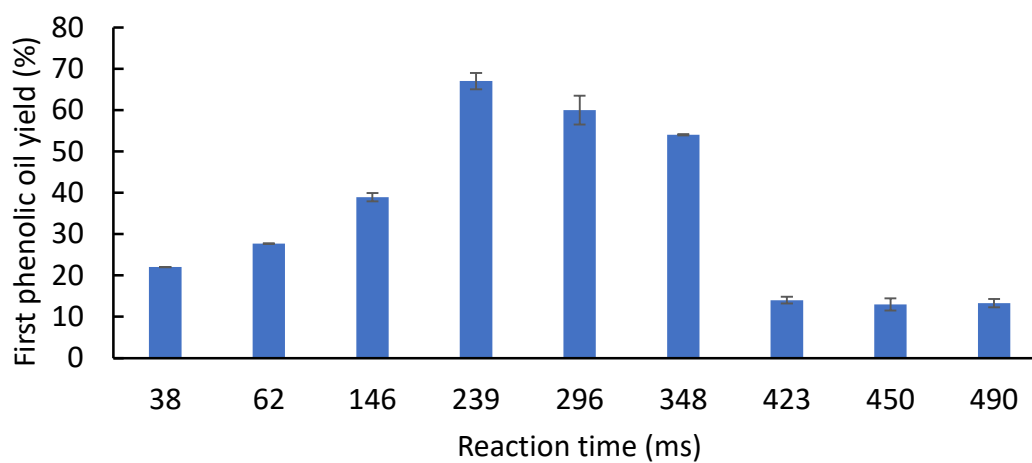
b)

**Figure 3**

a)



b)

**Figure 4**

RESUMEN

DESPOLIMERIZACIÓN DE
LIGNINA MEDIANTE HIDRÓLISIS
ULTRA-RÁPIDA EN AGUA
SUPERCRÍTICA.

Sobrevivir en un planeta provisto de recursos limitados para apoyar a nuestra población creciente es el mayor desafío al que la humanidad se ha enfrentado hasta ahora. El principal problema se basa en que nuestra economía está impulsada por muchas tecnologías que no son sostenibles en absoluto. Esta necesidad de desarrollar tecnologías sostenibles capaces de enfrentar tales desafíos, junto con la creciente preocupación por la protección del medio ambiente y las dudas sobre la disponibilidad futura de materia prima petroquímica, han impulsado a la investigación y al desarrollo hacia nuevos materiales a partir de recursos renovables sostenibles y respetuosos con el medio ambiente. En este contexto, la lignina surge como un candidato prometedor para estos fines.

La lignina es el tercer componente fundamental de la biomasa lignocelulósica, presentándose entre el 15% y 35% de su peso. Es un polímero de naturaleza aromática con una estructura amorfa y altamente ramificada que tiene como base estructural unidades de fenil-propano unidas entre sí por enlaces condensados y enlaces éter en una estructura helicoidal. El número de grupos funcionales y tipos de enlaces en la molécula difiere entre una biomasa y otra. Además, su estructura también depende del proceso de extracción desde biomasa lignocelulósica empleado (e.g. Kraft, organosolv, hidrólisis de biomasa...).

Su abundancia y su carácter aromático indican el gran potencial de esta molécula para ser aprovechada en la producción de compuestos de alto valor añadido. Sin embargo, hoy en día, las aplicaciones existentes de ligninas técnicas se limitan en gran medida a productos y aplicaciones de bajo valor añadido. Así por ejemplo, en industrias papeleras, la lignina es obtenida como subproducto en un licor negro, el cual se quema para la producción de energía para la misma industria.

Teóricamente, un proceso de despolimerización puede romper la molécula en estructuras fenólicas, como la vainillina o el guaiacol, que son químicos de alto valor debido a sus propiedades, aplicaciones farmacológicas y uso como intermediarios químicos para la síntesis de otros productos de interés. Sin embargo, a pesar de la extensa investigación sobre la descomposición de esta molécula con

diferentes estrategias, la transformación selectiva de la lignina en productos de alto valor sigue siendo difícil de alcanzar debido a la complejidad de su estructura y las reacciones indeseadas de repolimerización que tienen lugar en la mayoría de los procesos por las severas condiciones de temperatura y tiempo empleadas. En los últimos años, se ha investigado sobre el uso de fluidos supercríticos, el cual parece tener un efecto positivo sobre la despolimerización de lignina a moléculas pequeñas. El agua supercrítica (T_c : 374 °C y P_c : 22 MPa) es un solvente alternativo ambientalmente benigno para la despolimerización rápida de la lignina.

El objetivo de esta tesis fue valorizar esta molécula obteniendo productos aromáticos de bajo peso molecular de alto valor a través de una tecnología hidrotérmica ultra-rápida respetuosa con el medio ambiente que emplea principalmente agua sub y supercrítica como disolvente y bajos tiempos de reacción para lograr altos rendimientos y alta selectividad, lo que ha sido un verdadero desafío hasta el día de hoy.

Para alcanzar dicho propósito, se definieron los objetivos parciales descritos en los 4 capítulos que constituyen la tesis.

Objetivos.

1. Búsqueda de las condiciones de operación óptimas para la despolimerización de lignina utilizando agua sub y supercrítica.

- Despolimerización de lignina Kraft utilizando reactores de expansión súbita continua a diferentes temperaturas (300-400 °C) y diferentes tiempos de reacción (60 ms - 4.6 s).
- Determinación de las condiciones óptimas de operación para obtener el máximo rendimiento monomérico.

2. Mejora del proceso de despolimerización de lignina utilizando agua supercrítica mediante la adición de NaOH como catalizador.

- Despolimerización de lignina Kraft a la temperatura óptima y diferentes tiempos de reacción por debajo de 0,5 s usando agua supercrítica alcalina para aumentar el rendimiento monomérico.
 - Determinación del tiempo de reacción óptimo para obtener el máximo rendimiento monomérico.
 - Estudio de los mecanismos de reacción de la despolimerización de lignina en agua supercrítica alcalina.
3. Aplicación de la tecnología ultra-rápida de agua supercrítica alcalina a residuos reales de biorrefinería e industria del papel para su valorización.
- Despolimerización de diferentes ligninas obtenidas de diversas biomásas y métodos de aislamiento utilizando agua supercrítica alcalina en las condiciones óptimas de operación determinadas para la lignina Kraft.
 - Tratamiento directo de los licores negros Kraft con agua supercrítica en las condiciones óptimas de funcionamiento determinadas para la lignina Kraft.
 - Estudio de la influencia de la naturaleza de la lignina en el proceso de despolimerización en agua supercrítica alcalina y en el tipo de productos de lignina.
 - Estudio de mecanismos de reacción en lignina de diferente naturaleza.
4. Desarrollo de una estrategia para recuperar los productos de interés de la mezcla de productos de lignina mediante un proceso continuo.
- Simulación de un proceso aguas-abajo continuo para separar productos de bajo peso molecular de la mezcla de productos de lignina utilizando Aspen HYSYS.
 - Optimización del proceso aguas-abajo para minimizar las pérdidas monoméricas.
 - Estudio de la viabilidad del proceso.

Discusión de los resultados.

En el **capítulo uno**, titulado 'Depolymerization of kraft lignin using sub- and supercritical water', se estudió el efecto de los parámetros críticos que controlan la despolimerización hidrotérmica de la lignina: la temperatura y el tiempo de reacción. Para este estudio, se eligió como materia prima lignina comercial Kraft, como ejemplo del subproducto de la industria del papel. Se estudiaron diferentes temperaturas entre 300 y 400°C y tiempos de reacción tan cortos como 60 ms en un sistema continuo ultra-rápido que emplea agua sub- y supercrítica como medio de reacción (Figura 1).

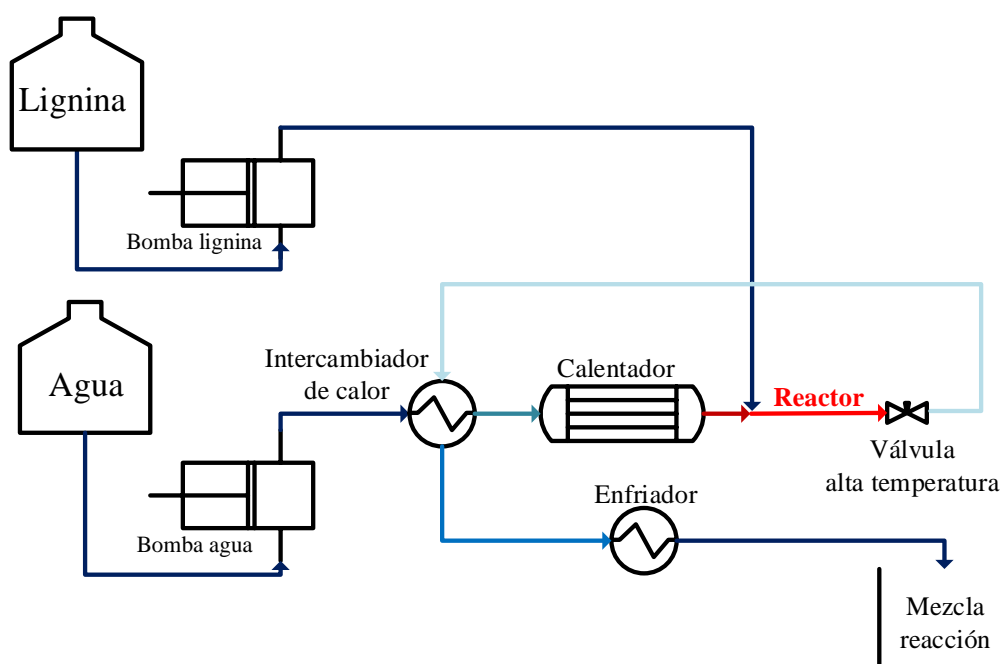


Figura 1. Esquema simplificado del proceso utilizado para despolimerizar lignina usando agua sub y supercrítica.

En la mayoría de los casos se obtuvieron dos productos principales de la mezcla de reacción: un aceite ligero, que contiene compuestos de bajo peso molecular, principalmente monómeros tales como guaiacol, vainillina, acetovanillona y ácido homovanílico, y un residuo sólido, producido por las reacciones de repolimerización. Un aumento en el tiempo de reacción a cada temperatura estudiada promovió tales reacciones secundarias de repolimerización. Esas reacciones indeseadas fueron más relevantes a medida que aumentaba la temperatura. A 386°C y 170 ms, se logró el mayor rendimiento en aceite ligero

(44,6%), así como la mayor selectividad en monómeros aromáticos (9,9%), con una pequeña formación de residuo sólido de sólo 3,5% (Figura 2).

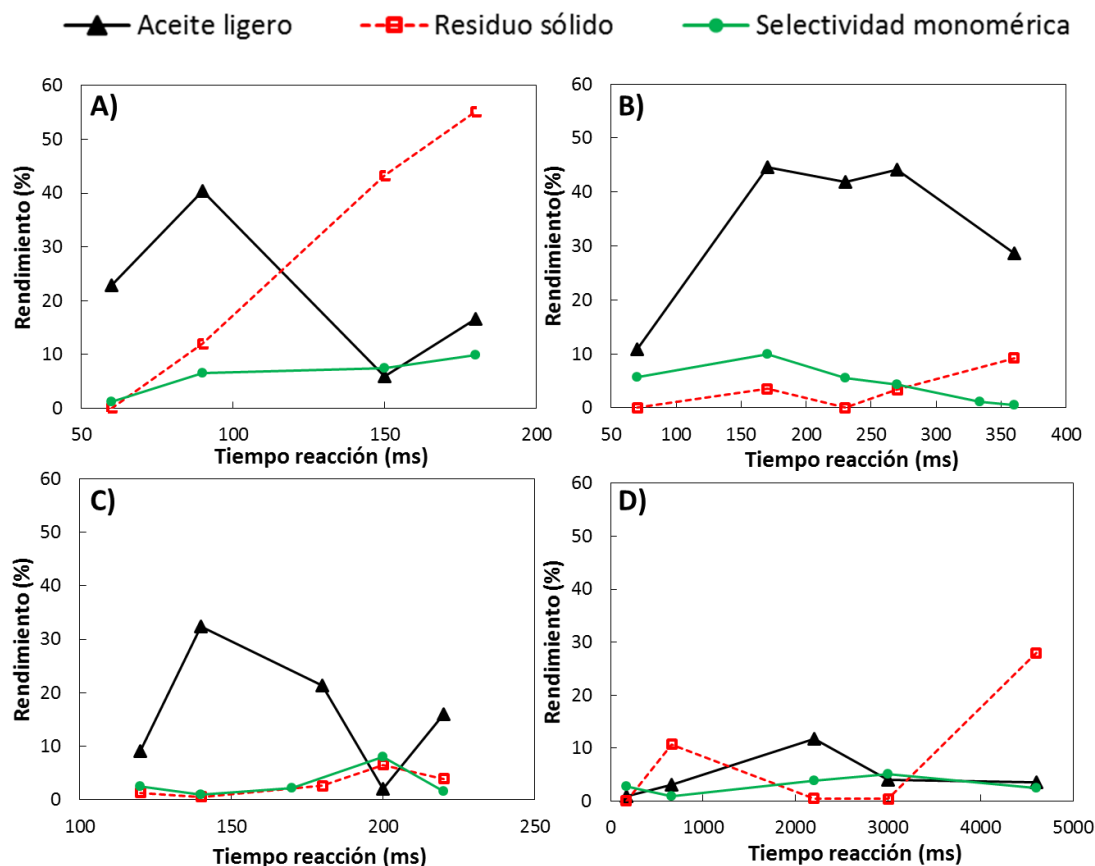


Figura 2. Rendimiento de aceite ligero, rendimiento de residuo sólido y selectividad monomérica en guaiacol, vainillina, acetovanillona y ácido homovanílico referida al aceite ligero frente al tiempo de reacción a diferentes temperaturas: A) 400 °C, B) 386°C, C) 370°C y D) 300°C.

El **capítulo dos**, titulado 'Obtention of aromatic monomers from lignin through ultrafast reactions in water using a base catalyst', se basó en intentar aumentar tanto el rendimiento de aceite ligero como la selectividad monomérica en la despolimerización de lignina Kraft agregando NaOH en baja cantidad como catalizador a la temperatura óptima de 386°C, ya que se sabe que las bases ayudan a romper los enlaces éter β -O-4 de la molécula de lignina. Se estudiaron diferentes tiempos por debajo de 0,5 s. En este caso, se obtuvieron tres productos principales de la mezcla de reacción, pues el residuo sólido fue dividido en dos fracciones: un aceite ligero, que contiene compuestos de bajo peso molecular, un aceite pesado, que contiene oligómeros, y char, producido por las reacciones de

repolimerización. Usando agua supercrítica alcalina, la reacción alcanzó un óptimo a 300 ms con un rendimiento de aceite ligero del 60% y una selectividad en compuestos clave tales como guaiacol, creosol, vainillina, acetovanillona y ácido homovanílico de alrededor del 20%, siendo la formación de char en este punto sorprendentemente baja (4%) (Figura 3).

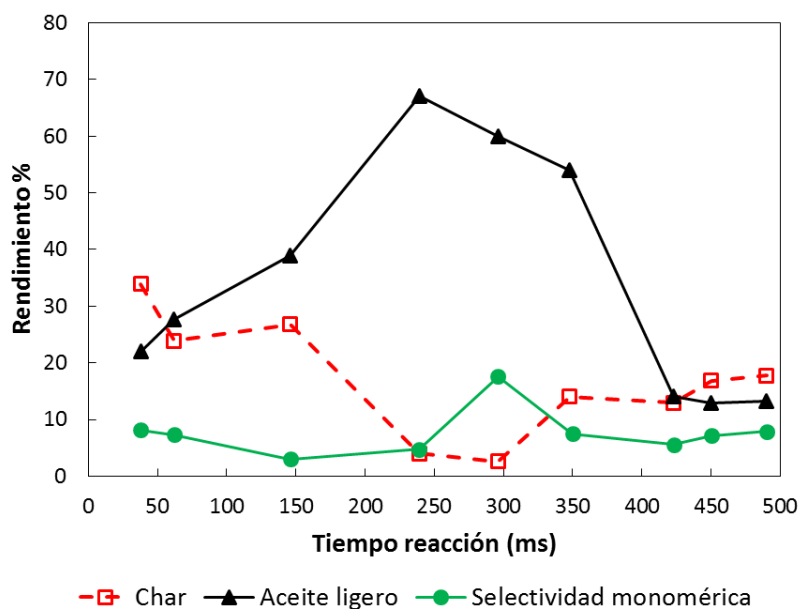


Figura 3. Evolución de la reacción de despolimerización de la lignina Kraft en agua supercrítica alcalina (386°C) frente al tiempo. Rendimiento de aceite ligero, char, y selectividad monomérica en guaiacol, creosol, vainillina, acetovanillona y ácido homovanílico.

Además, mediante técnicas como 2D NMR, se pudo observar la desaparición de los grupos -OH alifáticos después del proceso tanto empleando agua subcrítica como agua supercrítica, lo que es indicativo de que reacciones de deshidratación han tenido lugar. Sin embargo, por debajo del punto crítico, el agua tiene un producto iónico de varias órdenes de magnitud superior, por lo que la deshidratación tendrá lugar por medio de reacciones iónicas. Por otro lado, a temperaturas por encima del punto crítico predominarán los mecanismos radicalarios. A las temperaturas intermedias estudiadas en este trabajo (370 y 386°C) sería plausible asumir una combinación de ambos mecanismos.

En el **tercer capítulo**, titulado 'Base-catalyzed depolymerization of lignins: influence of lignin nature and valorization of pulping and biorefinery residues',

se estudió la influencia de la naturaleza de la lignina en el proceso de despolimerización mediante agua supercrítica alcalina, además de estudiar la viabilidad del proceso para la valorización de distintas ligninas. Se aplicó la tecnología a residuos reales de biorefinería, así como a licores negros y ligninas obtenidos en industrias papeleras.

Las ligninas obtenidas de diferentes fuentes (maderas duras, madera blanda y residuos de cultivos) y aisladas por diferentes procesos (kraft, organosolv o hidrólisis) fueron despolimerizadas en agua supercrítica alcalina (SCW: 386 °C y 260 bar) para producir compuestos de alto valor añadido en sólo 300 milisegundos de tiempo de reacción. El rendimiento monomérico más alto se obtuvo a partir de la despolimerización de la lignina kraft comercial de madera blanda estudiada en los capítulos previos, con 9,4 %, seguido de ligninas de madera dura kraft y organosolv con rendimientos fenólicos de 3,1 y 2,3 %, respectivamente. Las ligninas obtenidas del fraccionamiento de residuos de cultivo mediante hidrólisis de biomasa no fueron tan adecuados para la obtención de monómeros fenólicos como las ligninas técnicas extraídas de madera, con rendimientos monoméricos inferiores a 1,0%. Por otro lado, se pudo comprobar mediante distintas técnicas que tuvieron lugar reacciones de deshidratación en todas las ligninas estudiadas.

Una gran ventaja de esta tecnología es que se puede utilizar para tratar directamente licores negros con bajo contenido en lignina obtenidos como residuos de la industria papelera (Tabla 1). Se encontró que era igualmente eficaz que cuando se utilizan ligninas técnicas y aún mejor que la lignina correspondiente aislada de los propios licores, obteniéndose un rendimiento monomérico de hasta 9,2%.

Tabla 1. Rendimientos con respecto a la lignina inicial de aceite ligero, monómeros, aceite pesado y char obtenidos de la despolimerización en agua supercrítica alcalina (386°C, 300 ms) de la lignina Kraft comercial y de un licor negro obtenido de una industria papelera con bajo contenido en lignina.

	Lignina Kraft comercial	Licor negro Kraft
Aceite ligero	60,0	51,3
Monómeros	9,4	9,2
Aceite pesado	12,6	45,0
Char	2,6	5,0

El **cuarto capítulo**, titulado ‘Simulation of a continuous recovery of low-molecular-weight lignin depolymerization products’, se centró en el desarrollo de una estrategia para recuperar el aceite ligero (producto de interés) a través de un proceso continuo, lo cual hasta ahora se había llevado a cabo en discontinuo. Para ello, se ha propuesto y simulado un método factible con Aspen HYSYS V10. La estrategia de separación combina separadores de flash, extracción líquido-líquido y destilación a vacío (Figura 3). La simulación confirmó que hasta un 93,1% de compuestos de bajo peso molecular contenidos en el aceite ligero podría recuperarse de la mezcla de productos de despolimerización de lignina con nuestra estrategia. La inversión total de capital calculada fue de unos 2,9 M € para una capacidad de la planta de 15 toneladas de materia prima/día. El precio mínimo estimado del aceite ligero fue de 3,8 €/kg, que podría ser un precio competitivo en el mercado si se encontraran aplicaciones de interés de este bio-aceite. Una optimización energética del proceso, así como un amplio estudio en las aplicaciones de nuestro producto serán necesarios para impulsar nuestra tecnología en el futuro y hacer que la misma tenga potencial para la valorización de lignina.

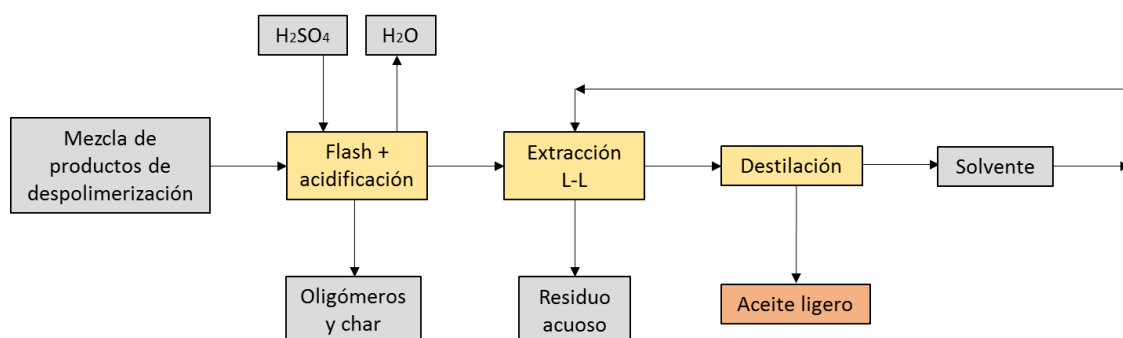


Figura 3. Diagrama de bloques del proceso continuo propuesto para la recuperación en continuo del aceite ligero de la mezcla de reacción obtenida del proceso de despolimerización mediante agua supercrítica alcalina: 1) Evaporación de agua + precipitación de oligómeros; 2) Extracción líquido-líquido de los compuestos de bajo peso molecular; 3) Destilación para la recuperación del solvente; 4) Recirculación del solvente.

CONCLUSIONES

En esta tesis se intentó valorizar la lignina mediante un proceso hidrotérmico ultra-rápido amigable con el medio ambiente usando agua caliente-presurizada e hidróxido de sodio como catalizador. La investigación comenzó con la despolimerización de lignina comercial Kraft a distintas temperaturas (300-400°C) y tiempos cortos de reacción (a partir de 60 ms) sin catalizador, con el objetivo de determinar las condiciones óptimas para obtener el mayor rendimiento de monómeros de lignina tales como guaiacol y vainillina, controlando las reacciones indeseadas de repolimerización. Tras determinar 386°C y 300 ms como las condiciones óptimas, NaOH se añadió a la reacción para aumentar los rendimientos de despolimerización. Tales rendimientos se aumentaron 1.5 veces, llegando a alcanzar un rendimiento del 70% en compuestos de bajo peso molecular (mezcla de monómeros, dímeros y trímeros). Esta novedosa tecnología permitió tratar directamente licores negros obtenidos como sub-productos en industrias papeleras, obteniendo monómeros de interés con rendimientos de hasta 9.2%. Además, se estudiaron mecanismos de reacción de lignina en agua supercrítica, llegando a concluir que sea cual sea la naturaleza de la lignina, tienen lugar reacciones de deshidratación. En el futuro, sería de

RESUMEN

especial interés llevar a cabo la optimización energética del proceso, estudiar las posibles aplicaciones de nuestro producto (aceite ligero), así como optimizar la relación lignina/NaOH, para poder impulsar nuestra tecnología hacia la futura valorización de lignina en la industria.

ABOUT THE AUTHOR



Nerea A.F. (Palencia-Spain, 1991) started the studies of Chemical Engineering at the University of Valladolid (Spain) in 2009 and graduated in 2015. She gained a scholarship financed by the Ministry of Education (Spain) for doing part of the last year of her master's degree (2014-15) in the University of Arizona (USA), where she could obtain a quality training in sonochemistry collaborating in a project financed by the Davis-Monthan Air Force Base (USA). That project consisted in degrading fire-fighting foam containing perfluorinated compounds (PFCs), toxic and persistent chemicals, by applying ultrasounds. Those 8 months spent as a researcher in USA inspired her to start the PhD in the High Pressure Processes Group at the University of Valladolid (Spain). From September 2015, Nerea has developed different process engineering activities, but she has intensely trained in biomass valorization and supercritical fluids. From April to July 2018, she was working in the Department of Bioproducts and Biosystems in Aalto University (Finland), where she was involved in a biorefinery project. During those years of research, Nerea has published 5 scientific articles in different scientific fields, she has developed an international patent in lignin valorisation and she has participated in 5 international scientific congresses. Today, she's an expert in research and development, and currently she is working as process engineer in the Technological Center 'José Lladó' of Técnicas Reunidas, S.A. (Madrid-Spain) from December 2018, where she is strongly involved in biomass valorization projects.

ACADEMIC TRAINING

- Master's degree in Chemical Engineering at the University of Valladolid (Spain), 2009-2015.

STAYS IN FOREIGN RESEARCH INSTITUTES

- Department of Chemical and Environmental Engineering, University of Arizona (USA). November 2014 – June 2015. Topic: Sonochemical degradation of perfluorinated compounds (PFCs).
- Biorefineries Group, Department of Bioproducts and Biosystems, Aalto University (Finland). April – July 2018. Topic: Lignin extraction from biorefinery residues and characterization of bio-oils by Nuclear Magnetic Resonance (NMR).

LIST OF PUBLICATIONS

- Aromatics from lignin through ultrafast reactions in water. **N. Abad**, E. Pérez, and M. J. Cocero. *Green Chemistry*, 2019.
- Tailoring the structure and morphology of low-molecular-weight cellulose produced during supercritical water hydrolysis. Jean Buffiere, **Nerea Abad**, Patrik Ahvenainen, Jinze Dou, María José Cocero, and Herbert Sixta. *ACS Sustainable Chemistry and Engineering*, 2018.
- Redefining conventional biomass hydrolysis models by including mass transfer effects. Kinetic model of cellulose hydrolysis in supercritical water. Luis Vaquerizo, **Nerea Abad**, Rafael B. Mato, and María José Cocero. *Chemical Engineering Journal*, 2018.
- Understanding biomass fractionation in subcritical & supercritical water. María José Cocero, Álvaro Cabeza, **Nerea Abad**, Tijana Adamovic, Luis Vaquerizo, Celia M. Martínez, and María Victoria Pazo-Cepeda. *The Journal of Supercritical Fluids*, 2018.
- Sonochemical degradation of perfluorinated chemicals in aqueous film-forming foams (AFFFs). Lucia Rodriguez-Freire, **Nerea Abad-Fernández**, Reyes Sierra-Alvarez, Christiane Hoppe-Jones, Hui Peng, John P. Giesy, Shane Snyder, and Manish Keswani. *Journal of Hazardous Materials*, 2016.

- Effect of chemical structure on the sonochemical degradation of perfluoroalkyl and polyfluoroalkyl substances (PFASs). **Nerea Abad Fernández**, Lucia Rodriguez-Freire, Manish Keswani, and Reyes Sierra-Alvarez. *Environmental Science: Water Research & Technology*, 2016.

PATENTS

- Ultra-fast lignin depolymerization process. **N. Abad**, E. Pérez, and M. J. Cocero. European Patent. Application number: 17382892.2 – 1109.

ORAL COMUNICATIONS

- Intensified depolymerization of lignin and black liquor in supercritical water. Influence of nature of the starting material. **N. Abad-Fernández**, E. Pérez, and M. J. Cocero. *International Symposium on Advances in Hydroprocessing of Oil Fractions (ISAHOF 2019)*. 9-12 June 2019, México City. Submitted.
- Lignin depolymerization in supercritical water at short residence time. **N. Abad**, E. Pérez, and M. J. Cocero. *6th International Congress on Green Process Engineering (GPE 2018)*. 3-6 June 2018, Toulouse (France).
- Effect of reaction time in the hydrolysis process of lignin via supercritical water using ultrafast reactors. **N. Abad**, E. Pérez, and M. J. Cocero. *10th World Congress of Chemical Engineering (WCCE10)*. 1-5 October 2017, Barcelona (Spain).
- Demonstration of an efficient biomass to sugars transformation process by ultrafast reactors in supercritical water. Celia M. Martínez, Danilo A. Cantero, Juan García-Serna, María José Cocero and **Nerea Abad-Fernández**. *24th European Biomass Conference and Exhibition (EUBCE 2016)*. 6-9 June 2016, Amsterdam (Netherlands).

POSTER COMUNICATIONS

- Depolymerization of lignin using supercritical water. **N. Abad**, E. Pérez, and M. J. Cocero. *15th European Workshop on Lignocellulosics and Pulp (EWLP 2018)*. 26-29 June 2018, Aveiro (Portugal).
- Hydrolysis of lignin in sub and supercritical water using an ultrafast reactor to improve selectivity: Effect of temperature. **N. Abad**, E. Pérez, and M. J. Cocero. *16th European Meeting on Supercritical Fluids (EMSF 2017)*. 25-28 April 2017, Lisbon (Portugal).

ACKNOWLEDGEMENTS

Thanks to María José and Eduardo, my directors, for all the scientific support, encouraging me to overcome and reach new goals.

Thanks also Rafa, for helping me with the last chapter of this thesis. Thanks to all the professors who helped me at some moment in this path either academically or personally.

Thanks to Herbert Sixta, who welcomed me warmly in his group during my stay in Finland. Thanks Mikhail Balakshin for all the knowledge shared. I am so grateful for your patience and dedication.

Thanks to the lab technicians who helped me, from whom I learned a lot. They are an essential part of this research. Especially, thanks to Isa and Jose María for all your support in the laboratory. Without you, this work would not have been possible.

Thanks to my friends, all of them. During this time, they made me feel in a big family. Especially, thanks to Celi, Nuri, Yoana, Ruti y María, my best friends, for all the moments shared. Thanks Tai, a lot. My friend of other life, the best thing Finland gave me.

Gracias a mi familia (Imelda, Jorge y Laura) por estar siempre a mi lado y apoyarme en todo momento. Sin ellos, nunca hubiera conseguido mis metas. Gracias a mi tía Sina, por enseñarme las cosas esenciales de la vida y demostrarme cada día lo que es el amor. Y gracias a mi yaya Montse, que sé que siempre me cuida allá donde vaya. Mai t'oblidaré.

Grazie Gian, mio compagno di vita, per ogni momento, per ogni consiglio, per tutto l'amore che mi hai sempre dato. Grazie anche alla mia famiglia italiana, Vito e Luciana, per prendervi cura di me dal primo momento come se fossi vostra figlia.

Gracias Vicente y Lourdes, por valorarme y motivarme para continuar con mi carrera de investigación. Seremos un gran equipo.

Thanks to people I did not name here, but who was there, sharing so many great moments and laughs. A million thanks!

ACKNOWLEDGEMENTS

And finally, I wish to acknowledge the Spanish Ministry of Science, Innovation and Universities for the scholarship/predoctoral contract FPU15/00409.

