



# Assesment of technical lignins for uses in biofuels and biomaterials: Structure-related properties, proximate analysis and chemical modification



Oihana Gordobil<sup>a</sup>, Rosana Moriana<sup>b</sup>, Liming Zhang<sup>b</sup>, Jalel Labidi<sup>a,\*</sup>, Olena Sevastyanova<sup>b,c,\*\*</sup>

<sup>a</sup> Department of Chemical and Environmental Engineering, University of the Basque Country, Plaza Europa, 1, 20018 Donostia-San Sebastián, Spain

<sup>b</sup> Department of Fibre and Polymer Technology Department, KTH Royal Institute of Technology, Teknikringen 56-58, SE-10044 Stockholm, Sweden

<sup>c</sup> Wallenberg Wood Science Center, KTH Royal Institute of technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden

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## ABSTRACT

The potential of organosolv and kraft eucalyptus and spruce lignin as feedstock for polymeric materials and biofuel applications was assessed. Proximate analysis was used to predict the heating values and char formation. Chemical modification, based on the esterification reaction with methacryloyl chloride, was applied to introduce vinyl groups into the lignin macromolecules for enhanced reactivity. Kraft eucalyptus and spruce lignins had a more condensed structure than organosolv lignins, which resulted in greater thermal stability for these lignins. For different species within the same process, the thermal parameters showed a correlation with certain structural and compositional parameters (ash and sugars content, molecular weight and degree of condensation). Organosolv spruce lignin produced the highest heating value of 24 MJ/Kg, which is suitable for biofuel applications. The content of phenolic OH groups was higher for kraft lignins and especially higher for softwood lignins, both organosolv and kraft. The degree of methacrylation, estimated from the content of vinyl groups per C9 lignin unit, was significantly greater for organosolv lignins than for kraft lignins despite the higher OH-groups content in the latter.

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## 1. Introduction

Increasing interest in the commercialization of various types of technical lignins is due, first, to their increasing availability, as result of the development of second generation biofuel technologies, and, second, to the emergence of new biorefineries that focus their production on bio-based platform chemicals and commodities from lignocellulosic feedstock (Ragauskas et al., 2014). Indeed, the manufacture of ethanol from biomass alone is expected to result in an annual generation of up to 66 million tonnes of lignin, an amount that is greater than the total quantity of lignin wastes currently produced by the pulp and paper industry and that substantially exceeds the current yield of biofuels (Langholtz et al., 2014). Traditionally, lignin has been obtained as a by-product of the pulp and paper industry. Approximately 45 and 2 million tonnes/year of

kraft lignin and liginosulfonates, respectively, are generated as a by-product of chemical pulp production (Hu, 2002; Song et al., 2011; Sahoo et al., 2011). Most of the lignin is used internally as a low-grade fuel for the pulping operation, while only 1–2% of the total amount of technical lignin is used in high-value applications. However, current cellulosic ethanol projects have demonstrated that 60% more lignin is generated through combustion than is needed to meet internal energy requirements (Sannigrahi and Ragauskas, 2011; Boerjan et al., 2003). As a result, there is a need to develop new processes for the recovery, upgrade and modification of lignin derived from both paper-making and novel biorefinery processes to produce lignin with chemical and physical properties suitable for high-value utilization.

Lignin, which is the second most abundant biopolymer after cellulose, is an important structural component of lignocellulosic biomass. The main functions of lignin in plants are to provide rigidity and physical strength to the plants, to transport water and nutrients internally, and to protect the plants from microorganisms and insects (Chung and Washburn, 2012; Mishra et al., 2007). Lignin in biomass has a complex heterogeneous structure which consists mainly of phenylpropane units that come from

\* Corresponding author.

\*\* Corresponding author at: Wallenberg Wood Science Center, KTH Royal Institute of technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden.

E-mail addresses: [jalel.labidi@ehu.es](mailto:jalel.labidi@ehu.es) (J. Labidi), [olena@kth.se](mailto:olena@kth.se) (O. Sevastyanova).

three aromatic alcohols: *p*-coumaryl, coniferyl and sinapyl alcohols. The phenolic substructures that originate from these monolignols are called *p*-hydroxyphenyl (H, from coumaryl alcohol), guaiacyl (G, from coniferyl alcohol) and syringyl (S, from sinapyl alcohol) (Laurichesse and Avérous, 2014). The chemical structure of lignin has distinctive characteristics, depending on the origin and growing conditions of the plant (Morandim-Giannetti et al., 2012; Notley and Norgren, 2010). In general, softwood lignins are composed mainly of G-units whereas hardwood lignins are based on guaiacyl (G) and syringyl (S) units present in different ratios (Derkacheva, 2013; Schorr et al., 2014). The most common linkages in the lignin molecule are the  $\beta$ -O-4 ether linkages, followed by other types of ether and C-C linkages such as  $\alpha$ -O-4,  $\beta$ -5, 5-5, 4-O-5,  $\beta$ -1, and  $\beta$ - $\beta$ ' (Sjöström, 1993). Although the lignin structure has been studied intensively for many years, it is not yet fully understood. Different kinds of linkages in lignin, and the diversity of their functional groups, such as methoxyl, phenolic and aliphatic hydroxyl groups, result in a complicated macromolecule (Crestini et al., 2011). Those functional groups have a great impact on the reactivity of lignin (Macfarlane et al., 2014). The extraction processes also have a great influence on the final structure and properties of lignin (Canetti and Bertini, 2007; Vishtal and Kraslawski, 2011). Kraft lignins usually contain sulfur in an amount of less than 1–2%. Moreover, it contains a high number of condensed structures (highly condensed G-units and some linkages related to condensed structures like  $\beta$ -5, 5-5', 4-O-5) and a high percentage of the phenolic hydroxyl group. Of the various technical lignins, organosolv lignins, such as those produced during bioethanol production, differ significantly from other technical lignins. Structurally, organosolv lignins have a higher relative amount of phenolic hydroxyl groups and a more oxidized structure, yet possess low Tg's and are easy to process thermally (Kubo and Kadla, 2004). As a result, organosolv lignins have advantages over other industrial lignins when considering composite-material applications.

Lignin is an excellent energy source/power source and is suitable in the production of electricity, fuel, steam and syngas (Laurichesse and Avérous, 2014; Macfarlane et al., 2014). When considering biomass thermal conversion for energy production, proximate analysis is one of the most important characterization methods. Lignin, like other biomass components, is composed of moisture, ash and organic matter (volatiles and fixed carbon). This makes it attractive as a solid biofuel for pyrolysis, gasification and combustion processes. The increasing price of fossil fuels, as well as growing environmental concerns, make the biomass an important renewable energy source (García-Maraver et al., 2015). Biomass presents distinct advantages when compared to traditional fossil fuels, namely: the reduction of greenhouse gas emissions, low NO<sub>x</sub> and SO<sub>2</sub> emissions, its abundance and sustainability, and its economic competitiveness (García et al., 2014; Poddar et al., 2014; Shen et al., 2010). There are a limited number of studies available concerning assays of proximate analysis of lignin (Farag and Chaouki, 2015; Jin et al., 2013). Volatiles and fixed carbon content are two important parameters during thermal conversion of lignin (Moriani et al., 2014). Pyrolysis is inherently present in combustion and gasification processes and is one of the most applied techniques in thermal technology (Farag and Chaouki, 2015; Jin et al., 2013; Bridgwater, 2003) because it can directly generate solid (carbon), liquid and gaseous products (García et al., 2014; Farag and Chaouki, 2015). Moreover, it is important to note that the products and conversion yields depend mainly on the nature of the lignin, its composition and its functional groups, although processing conditions such as heating rate and temperature also have a strong influence (Shen et al., 2010; Ferdous et al., 2002). Lignins, in general, possess fewer volatiles and higher fixed carbon content than biomass (Shen et al., 2010; Won Kim, 2015). On the other hand, lignin also has a potential for use as a raw material in the

polymer industry. Several studies have shown that it is possible to incorporate lignin directly and without any modification into other commercial polymers, thereby introducing new or improved properties (Sahoo et al., 2011; Mishra et al., 2007; Morandim-Gandini, 2012; Pouteau et al., 2003, 2004; Alexy et al., 2000; Kaewtatip and Thongmee, 2013; Bhat et al., 2013). Also, lignin is used as the main component in the production of carbon fiber (Jin et al., 2013). The addition of lignin has an important influence on the thermal behavior of some polymers (Canetti and Bertini, 2007; Canetti et al., 2006; Bertini et al., 2012). Due to its structural features, lignin has a great potential for chemical modifications, which can result in improved reactivity and lead to value-added polymeric materials with specific properties (Dournel et al., 1988; Podkościelna et al., 2015). Usually, chemical modification is performed through the creation of new active sites or the functionalization of hydroxyl groups (Laurichesse and Avérous, 2014). The modifications are typically aimed at the derivatization of phenolic and aliphatic hydroxyl groups (OH phen and OH aliph) situated at the C- $\alpha$  and C- $\gamma$  positions of the propane side chain in order to introduce more reactive functional groups into lignin molecules. The ratio of OH phen to OH aliph varies depending on the origin of the lignin (hardwood or softwood) and on the pulping process (e.g., kraft, alkali or organosolv pulping), and, thus, a detailed knowledge of the chemical structure of lignin is important. For that, NMR techniques like <sup>31</sup>P and <sup>13</sup>C are appropriate. The following types of chemical modification reactions involving hydroxyl groups of lignin have been proposed: etherification, esterification, reaction with isocyanates, silylation, phenolation, and oxidation/reduction (Laurichesse and Avérous, 2014). For the esterification reactions, three types of reagents can be used: acidic compounds, acid anhydrides and acid chlorides, with the latter two being more reactive. Considering the reaction parameters and reactant used, the esterification is the easiest type of lignin modification to perform. The chemical compounds used for esterification are often bi-functional, which results in lignin-based polyester networks. Another goal of lignin modification is the introduction of reactive groups into its macromolecular structure so as to enable it to crosslink with other polymeric systems—the phenomenon known as chemical activation (Naveau, 1975). This study focused on the comparative characterization of lignin samples from spruce (softwood) and eucalyptus (hardwood) woods extracted by two different methods, i.e., kraft and organosolv processes. Thorough structural and thermal characterization of four extracted lignin samples using FTIR, <sup>31</sup>P NMR, <sup>13</sup>C NMR, SEC, DSC and TGA methods, as well as proximate analysis, was performed, and the results thereof were used to discuss the potential use of the lignin samples in different applications, such as bioenergy and biomaterials. Methacrylic derivatives of technical lignins were obtained from the reaction with methacryloyl chloride and characterized by FTIR and <sup>13</sup>C NMR. The results of the modification were discussed in relation to the structural differences of the lignin samples.

## 2. Materials and methods

### 2.1. Lignin isolation

Spruce (softwood) and eucalyptus (hardwood) were selected as raw materials for lignin extraction. Two different extractive methods were used to isolate lignin for each raw material, i.e., organosolv and kraft processes. For the organosolv extraction of spruce, a mixture of ethanol–water (50/50 w/w), with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) as a catalyst (1.2% w/w), was used (Pan et al., 2005). The treatment was carried out at 180 °C for 60 min in a 4 L pressure (20 Ba) stainless steel batch reactor with constant stirring (EL0723 Iberfluid) and with an electronic control unit for pressure and temperature

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