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Research paper

Using 2D NMR to characterize the structure of the low and high molecular weight fractions of bio-oil obtained from LignoBoost™ kraft lignin depolymerized in subcritical water

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ABSTRACT

In this work a multilevel analysis approach have been used for characterization of LignoBoost™ kraft lignin and bio-oil produced from LignoBoost™ kraft lignin using a process based on subcritical water (350 °C, 25 MPa). LignoBoost™ kraft lignin and the different fractions of the bio-oil (light oil, heavy oil and suspended solids) was characterized with high field NMR (18.8 T, 2D ^{13}C, ^{1}H-HSQC NMR and ^{13}C-NMR), GPC, GC-MS and elemental composition to improve understanding of the subcritical process. By using high resolution 2D HSQC NMR it was possible determine the chemical structures both on low and high molecular weight fractions of the bio-oil. It was confirmed that the signals from the aliphatic lignin inter-unit linkages, *i.e.* β-O-4′, β-β′, β-1′ and β-5′, had disappeared from all of the bio-oil fractions studied. This means that both the aliphatic carbon-oxygen (C—O) and to some extent carbon-carbon (C—C) bonds in LignoBoost™ kraft lignin have been cleaved and an effective depolymerization has occurred. However, re-polymerization into higher molecular weight (Mw) fractions takes place simultaneously. These higher Mw fractions (heavy oil and suspended solids) were found to be re-polymerized macromolecules, with new structural networks based on guaiacol/disubstituted aromatic ethers and polyaromatic hydrocarbon structures bound tightly together.

1. Introduction

Lignin is one of the three major components that form the structure of wood: approximately 20–30% of wood is composed of lignin. Lignin is a heterogeneous, random, aromatic macromolecule that is cross-linked by carbon-oxygen (C—O) and carbon-carbon (C—C) bond networks [1]. Although lignin structures vary, the main types are softwood, hardwood and annual plant lignin. Whilst the general characteristics of lignins are similar, there are variations in the frequencies of the different bonds and side groups. This paper deals with softwood lignin. Lignin, as mentioned above, is a heterogeneous, random, aromatic macromolecule, which means that its exact structure is unknown. However, a vast amount of work has already been carried out with the aim of defining its various building elements and type of bonds. The structure of native lignin has still to be clarified; the closest structure is currently regarded as being milled wood lignin (MWL) [2,3]. The MWL lignin from softwood has been found to be comprised of different phenyl-propane units, *i.e.* coniferyl alcohol (>95%) and *para*-coumaryl alcohol (<5%, Fig. 1) connected by aliphatic/aromatic C—C and C—O bonds (ether bonds, Fig. 1). The aliphatic inter-unit linkages found in softwood lignin are (Fig. 1) β-O-4′ (β-ether, 45–50%), α-O-4′ (α-ether, 6–8%) and β-β′ (pinoresinol, secoisolariciresinol, 3%) and the aliphatic-aromatic are: β-1′ (diphenyl ethane, 7–10%) and β-5′ (phenylcoumaran, 9–12%), whilst the aromatic connecting linkages are 4-O-5′ (diphenyl ether, 4–8%) and 5-5′ [biphenyl and dibenzodioxocine (5-5′-α, β-O-4′), 18–25%] [2,4]. During the kraft process lignin is solubilized by the cleavage

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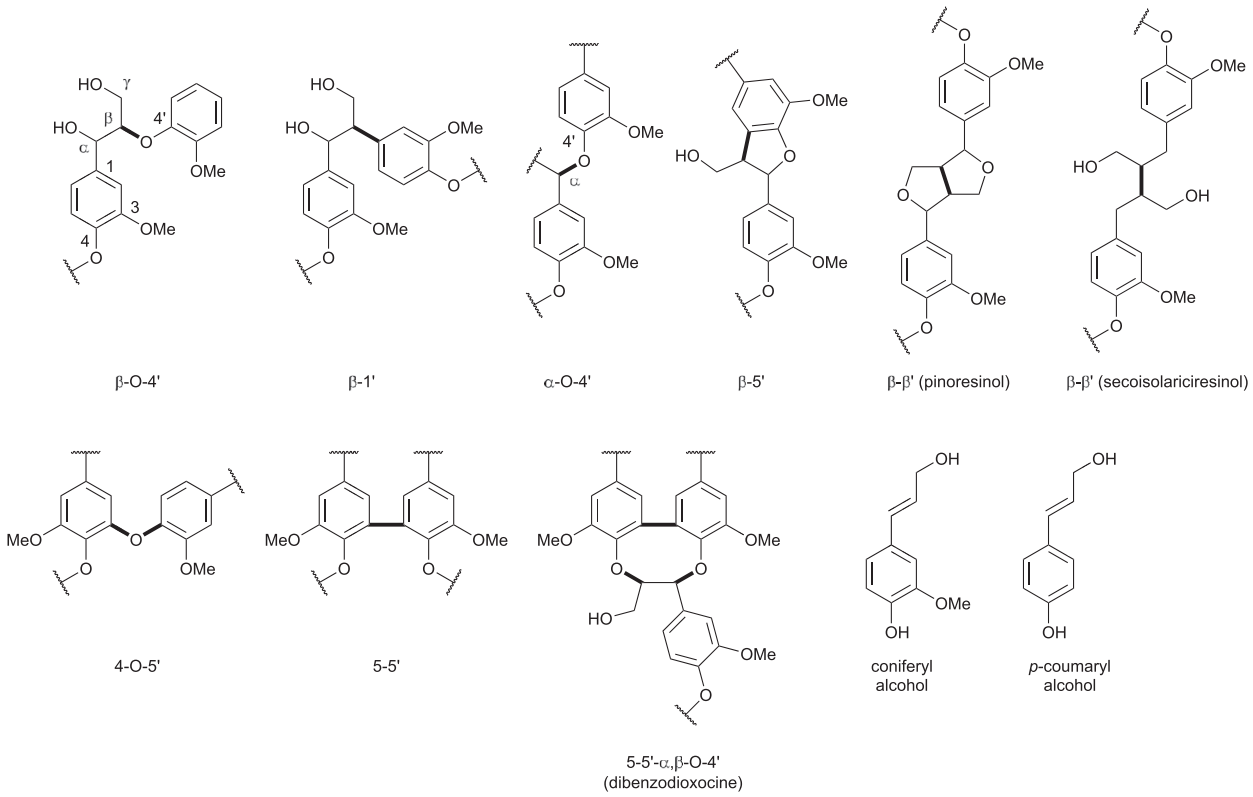

Fig. 1. Lignin linkages found in MWL softwood lignin and other common structural motifs. Bold face linkages indicate the carbon-carbon and carbon-oxygen bonds known to exist in lignin [1].

of ether bonds, yielding an introduction of phenolic groups. The most important structural change that occurs is the formation of phenolic hydroxyl groups, which enhance the water solubility of lignin in an aqueous solution. It is known that bonds such as β-O-4′, α-O-4'and β-1′ are hydrolyzed during the kraft process, and that 4-O-5′, 5-5′, β-β′ and β-5′ structures are usually more resistant to the alkaline environment of the kraft process and are therefore often found in kraft lignin (Fig. 1) [4–6]. The rather harsh conditions also cause other typical structural changes to the kraft lignin, such as new C–C bonds from condensation reactions, unsaturation (*i.e.* stilbene and vinyl ether structures) and a reduction in the lignin side chains of aliphatic structures [6–9]. The lignin obtained after a kraft cook has a rather high molecular weight (Mw, 3–17 kDa) and, due to the formation of C–C bonds, it is rather stable [10].

Today, large quantities of lignin are dissolved from wood in the production of paper pulp. This lignin is mostly combusted at present, and the heat used to produce steam. However, lignin is a natural source of aromatic rings, *i.e.* phenols, guaiacols and syringols, making it a potential renewable source for generating fuel and chemicals that could replace a part of the current demand for fossil fuels. A new, green, process technology for the separation and purification of kraft lignin from the black liquor generated from the kraft pulping process currently exists, and is known as the LignoBoost™ process [11]. LignoBoost™ kraft lignin is precipitated from alkaline black liquor with carbon dioxide, thereby generating a solid LignoBoost™ kraft lignin. This may be used in future biorefineries to develop new, high value, products from lignin. However, additional processes need to be developed if the kraft lignin is to be transformed into new, high value, products.

Recent years a huge effort for find a new thermochemical process technology for depolymerization of lignin to small aromatic structures *i.e.* pyrolysis, gasification, hydrogenolysis, chemical oxidation, catalysis and hydrolysis under sub and supercritical conditions have been studied. All these thermochemical process struggle with understanding the complex depolymerization mechanism, low yield and complex product mixtures of small aromatics as well as lignin repolymerization reactions to higher molecular weight (Mw) byproducts (*i.e.* residual lignin, char and coke) [12–15].

One promising technique for the depolymerization of lignin involves procedures based on subcritical water to generate bio-oil [12,14–18]. Water gains unique properties when it is close to its critical point (372.9 °C, 22 MPa): it resembles an organic solvent and can therefore be used in the solubilization of organic structures such as the phenolic lignin network. Water at these temperatures acts as reactant, catalyst and enhances solubility of both organic structures, inorganic ions and gases which yields exceptional opportunities for promoting lignin depolymerization with an environmental friendly solvent [19–22]. Another advantage is that in the reactor it is subcritical conditions and the reactions proceeds in “one phase”, but after the reactor, when the pressure and temperature has been lowered (<350 °C, <25 MPa) the system separates into two phase system *i.e.* bio-oil and water phase. By this means byproducts like: water, inorganic salts and more hydrophilic and reactive intermediates (carboxylic acids, aldehydes and alcohols) transports to the water phase This phase separation have been shown to be very beneficial for the bio-oil storage stability [23]. This opens up for the sustainable depolymerization of lignin by means of “green chemistry”.

Several studies of subcritical water have shown that the reaction rates for breaking the various bonds in lignin are very high: that of aryl-alkyl ethers (*i.e.* β-O-4 and α-O-4) is very high at 270–290 °C already [24,25]. Catalysts and/or higher temperatures are necessary for bonds with a bond strength, such as C–C bonds [21,26].