

## Lignin valorisation using supercritical water technology. Lignin repolimerización.

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### 1 Introduction

Lignin is a by-product of different biorefineries and its valorization is an important contribution to their economic development. The production of aromatic compounds is hereby the most attractive way for lignin valorization. However, the repolymerization reaction of depolymerization products was reported to be the main challenge for a better recovery of aromatic compounds from lignin using different technologies.

### 2 Materials and Methods.

Supercritical water (SCW) has been demonstrated as an excellent reaction media for the lignin depolymerization. At subcritical conditions, the ionic product is  $10^{-12}$ , what makes this reaction medium favors ionic reactions. However, at supercritical conditions, for example at 450°C and 25MPa, the density is 109.0 kg/m<sup>3</sup> and the ionic product  $10^{-18.1}$ [1]. Under these conditions, the reaction medium favors radical reactions, as we have demonstrated in previous works [2]. The reaction medium provides conditions to improve the processes intensification and the selectivity over other solvents, but, on the other hand, the reactions are very fast and, as soon as the products are formed, they are hydrolyzed and selectivity is lost. So, we have used our ultrafast SCW technology to control the selectivity of the lignin depolymerization [3]. Nevertheless, the selectivity can be control by the precise control of reaction time that is one of the main features of SCW sudden expansion reactor develop in our research group, that allows to work with residence time well below 1s. The description of the pilot plant can be found in reference [3].

### 3 Results and discussion

Lignin structure is an important point in the lignin depolymerisation that provide information of potential of lignin type to undergo depolymerization reaction. Lignin is based on the three main monomeric units: coniferyl alcohol, p-coumaryl alcohol and sinapyl alcohol. Their structures differ by the substitute on the positions three and five of the aromatic ring. The aromatic rings of monomers correspond to guaiacyl unit – G unit (derived from coniferyl alcohol), syringyl unit – S unit (derived from sinapyl alcohol) and p-hydroxyphenyl unit – H unit (derived from p-coumaryl alcohol). Oxidative coupling of lignin monomers among each other and with the growing polymer result in the formation of three-dimensional lignin polymer. The distribution of lignin monomers varies depending on the lignin origin. Coniferyl alcohol is the main monomer presented in softwood lignins, coniferyl alcohol and sinapyl alcohol are the main monomers of hardwood lignin, while all three monomers, coniferyl, sinapyl and p-coumarin alcohol are presented in lignins from grasses.

Lignin units are connected by C-O (ether) linkages or C-C linkages.  $\beta$ -O-4 ( $\beta$ -aryl ether) ether linkage is the most dominant one, with the contribution of 40-60% in softwood and hardwood. This bond is crucial for lignin depolymerization and its predominance arises from the reactivity of phenoxy C- $\beta$  position. Other important ether bonds in lignin are  $\beta$ - $\beta$  (resinol unit),  $\alpha$ -O-4 ( $\alpha$ -Aryl ether), 5-O-4 (diaryl ether). Examples of condense C-C bonds are  $\beta$ -5 (phenylcoumaran unit), 5-5 (biphenyl unit),  $\beta$ -1 (1,2-Diarylpropane). The distribution of different linkages, as in the case of the three main building blocks, depends on lignin origin. C-C linkages are much less reactive than ether linkages, thus their proportion in lignin determines its reactivity [4].

The amount of different functional groups in lignin also affects lignin reactivity. Functional groups presented in lignin are: phenolic hydroxyl, aliphatic hydroxyl, benzyl alcohol, noncyclic benzyl ether, carbonyl groups and methoxyl groups. The high reactivity of various functional groups in lignin is a key factor for the production of chemical pulps used in high-quality paper production. Lignin phenolic and aliphatic hydroxyl groups are important in lignin biosynthesis and degradation reaction. Phenolic hydroxyl groups are related to the degree of pulp brightness and stability while ring conjugated carbonyl groups are related to a darker pulp

color. The degradation reaction in lignin normally starts from the benzyl position, thus benzyl ether and benzyl alcohol groups are important in lignin chemical reactions [5].

Understanding the repolymerization reaction is a key factor in developing the strategy for its suppression. Our approach to follow the repolymerization reactions in supercritical water was to study the reactivity of lignin depolymerization products among each other and with lignin. Sulfonated kraft lignin (SKL) and main lignin monomers isolated in depolymerisation reaction were used in this study. Indulin as kraft lignin with a well-known structure was also employed as the reference for a better understanding of the repolymerization reaction.

The main reaction that happened on the structure of SKL lignin during the supercritical water process desulphonation. The 2D-NMR analysis confirms the presence of diarylmethanes structures in the solid residue of each sample, indicating that those structures could be responsible for the repolymerization reaction.

No big changes are determined in the structure of Indulin lignin in its solid residue after the supercritical water process, indicating that the main reaction happens in the fraction of low molecular products.

#### 4 Conclusions.

The presence of diarylmethanes structures in solid fraction of sample indicate that they their formation could be responsible for lignin repolymerization in supercritical water. To reduce the repolymerization and recover the high yield of monomers in the SCW process, light oil fraction enriched in monomers should be separated from the reaction mixture as soon as it is produced.

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