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STUDY OF THE YIELD OF EUCALYPTUS KRAFT LIGNIN FRACTIONATION BY DIFFERENT ORGANIC SOLVENTS

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ABSTRACT

Lignin is the main organic compound present in residual liquors produced by pulping processes. It is estimated that only 1 to 2% of this lignin is used to generate value-added products, such as lignosulfonates produced by the sulfite process. The remaining 99% is incinerated to generate energy for the kraft process. The commercial application of kraft lignin is still underperformed due to the difficult workability of this polymer, which has low reactivity, high heterogeneity and great complexity. One of the ways used to increase the uniformity of molecular weight and, therefore, reduce polydispersity, is the fractionation technique with organic solvents. Thus, this study aims to evaluate the yield of eucalyptus kraft lignin fractionation in different organic solvents, in order to allow realizing the subsequent assembly of an eluotropic series suitable for sequential solvent fractionation of lignin. Two grams of kraft lignin were fractionated using 20mL of organic solvents ethanol, methanol, acetone, dichloromethane and a mixture of methanol/dichloromethane separately. The systems were subjected to stirring at 140rpm for 2 hours at room temperature. The suspensions were filtered through glass crucibles covered with vacuum-packed aluminum oxide and the retained fractions were subsequently dried in an oven at 105ºC to determine the masses of insoluble lignin. The filtrate was dried by the solvent recovery method in an extraction battery, and the residual material was weighed. The percentages of soluble and insoluble fractions of kraft lignin with each solvent were calculated based on the total mass of the material. The yields of the soluble fractions obtained for methanol, ethanol and acetone were 86.6%; 80.4% and 84.5%, respectively. These yields were considered high and satisfactory, being greater for methanol. Methanol obtained higher soluble fraction yields than ethanol, when comparing alcohols. The result is in accordance with the predicted, since, for a homologous series, the greater the carbon chain of the solvent, the smaller the solubility of kraft lignin. The methanol/dichloromethane mixture solubilized more lignin than each solvent separately. The conclusion is that methanol is the solvent that leads to the best yield of soluble fraction of eucalyptus kraft lignin. It is also observed that the three solvents are adequate to compose the eluotropic series for sequential fractionation. Finally, it is noted that dichloromethane and methanol act in quite different fractions of lignin.

Keywords: fractionation; organic solvent; lignin; kraft; eucalyptus

INTRODUCTION

Lignin is one of the main compounds present in wood and the second most abundant biopolymer on Earth (Duval et al., 2016). This polymer is the main organic compound present in the residual liquor produced by the pulping process (Tagami et al., 2019). It is estimated that only 1 to 2% of this lignin is used to generate products with high value-added, such as lignosulfonates produced by the sulfite process (Mohan et al., 2006). The remaining 99% is incinerated for power generation in the recovery cycle of kraft process (Gellerstedt et al., 2013). The energy generated is 60% higher than necessary to supply the internal energy demands of the manufacturing units (Sannigrahi et al, 2010). The burning of lignin also allows for the recovery

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of chemical pulping reagents, as mentioned by Duval et al. (2016) and Tagami et al. (2019).

In this context, the lignin biorefinery has become an increasingly important field of study, implying on its more profitable use (Theliander, 2008; Nowak et al., 2018). Examples of products that can be obtained from kraft lignin include polymers, adhesives, chemicals, carbon fibers, phenolic resins, stabilizers for plastics, composites and lignosulfonates (Domenek et al., 2013; Ragauskas et al., 2014; Lourençon et al., 2015; Aro et al., 2017; Park et al., 2018).

Lignin is an aromatic, branched and amorphous polymer. Kraft lignin has some characteristics that hinder its workability in biorefinery and consequent commercial application, such as its heterogeneity, which becomes even more evident after kraft processing (Tagami et al., 2019). In addition, lignin has a very complex chemical structure and undesirable properties for commercial application, like its low solvent solubility, amorphous structure and high polydispersity (Vishtal and Kraslawski, 2011; Park et al., 2018; Tagami et al., 2019).

The main methods used to increase the uniformity of the molecular weight of the lignin polymer and reduce its polydispersity are the fractionation techniques, which are most commonly applied by eluotropic series of organic solvents (Duval et al., 2016; Tagami et al., 2019), precipitation by the pH effect (Lourençon et al., 2015) and the use of membrane ultrafiltration (Toledano et al., 2010). These techniques make it possible to obtain more homogeneous fractions of lignin and, therefore, easier to be worked on.

The solvent fractionation technique uses the principle that some industrial solvents are capable of partially solubilizing kraft lignin, so that each solvent presents a soluble fraction of exclusive polydispersity. Several solvents in sequence allow the soluble fractions to have exclusive properties according to the structural characteristics of what is extracted (Duval et al., 2016, Tagami et al., 2019). The use of methanol, ethanol and acetone are interesting for this application because they have a low boiling point, which facilitates the recovery in the extraction stage of the soluble fraction and also prevents thermal degradation of fractionated lignin (Duval et al., 2016). In fact, the high recovery rate reduces waste and process costs since the solvent is reused. In addition, these chemicals have a minor risk for operators, as well as lower environmental damage when compared to chlorinated and aromatic chemicals that also have potential for lignin fractionation (Alfonsi et al., 2008).

This study aimed to evaluate the yield of eucalyptus kraft lignin fractionation in different organic solvents, in order to allow realizing the subsequent assembly of an eluotropic series suitable for sequential fractionation of lignin with the use of organic solvents.

METHODS

Eucalyptus kraft lignin was used to carry out this study. Lignin was chemically characterized prior to the fractionation screening.

Chemical characterization of lignin

The chemical characterization of the kraft lignin sample was carried out in duplicate, using the following analyses: total lignin (soluble and insoluble), carbohydrate content and ashes. The analytical procedures used are listed in Table 1.

Fractionation of kraft lignin

The fractionation of kraft lignin was carried out by using methanol, ethanol and acetone separately Two grams of kraft lignin were fractionated using 20mL of each organic solvent separately. The systems were subjected to stirring at 140rpm for 2 hours at room temperature. The suspensions were filtered through glass crucibles covered with vacuum-packed aluminum oxide and the retained fractions were subsequently dried in an oven at 105ºC to determine the masses of insoluble lignin. The permeate was dried by the solvent-recovery method in an extraction battery, and the residual material was weighed. The percentages of soluble and insoluble fractions of kraft lignin with each solvent were calculated based on the total mass of the material.

Finally, an alternative fractionation of kraft lignin was carried out using methanol, dichlorometane and metanol/ dichlorometane 1:1. The methodology was the same as that

Table 1. Analytical procedures used in chemical characterization

Parameter	Procedure
Soluble lignin	TAPPI UM 250
Insoluble lignin	TAPPI T 222 om-02
Carbohydrate content	SCAN-CM 71:09
Ashes	TAPPI 211 om-93

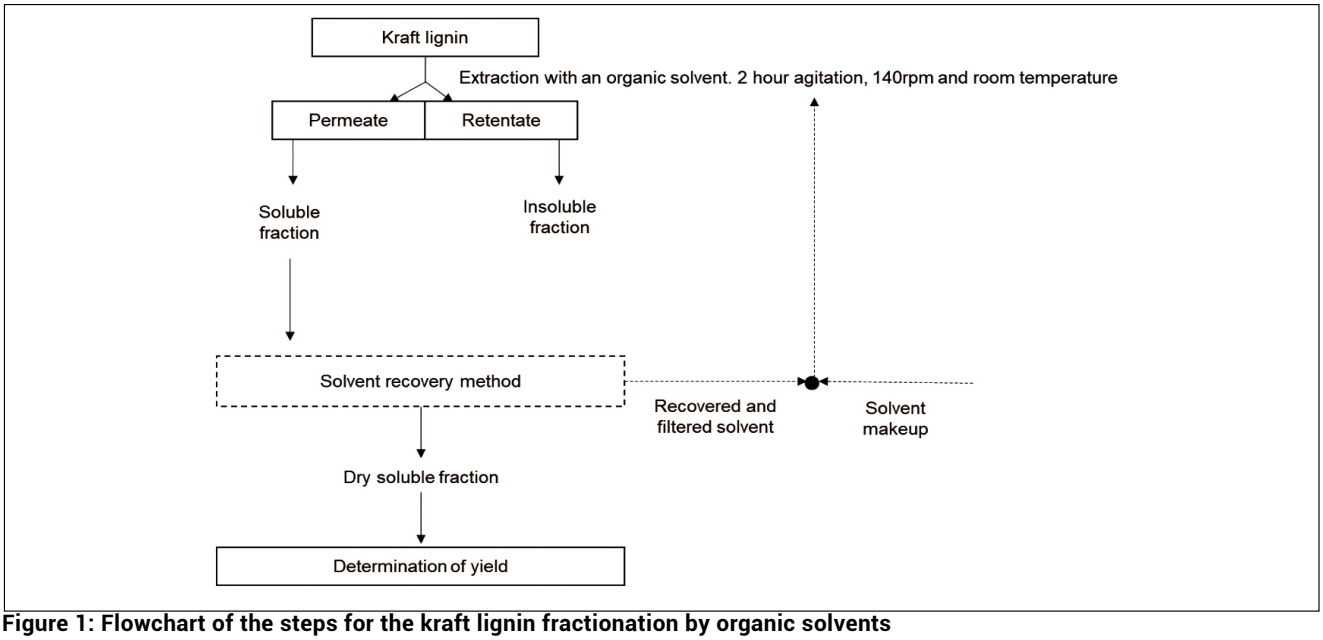

Figure 1: Flowchart of the steps for the kraft lignin fractionation by organic solvents

used with the previously listed solvents. To justify a safer use of dichloromethane, the yield of solvent recovery was also determined.

The flowchart described in Figure 1 shows all the steps performed in the fractionation method of kraft lignin by organic solvents.

RESULTS AND DISCUSSION

Chemical characterization of lignin

The results obtained for the chemical characterization of eucalyptus kraft lignin are shown in Table 2.

8.9% of acid-insoluble lignin and 86.7% of acid-soluble lignin was obtained, with a purity of 95.6%. These values are slightly below those found in literature and, therefore, are not ideal for applications in biorefinery (Zhou and Lu, 2014). It may indicate that there is a reasonable amount of contaminants and the process of purification and isolation of lignin was not perfect. Another possible explanation may be in the chemical composition of the wood, although such high values of ash are not so common in eucalyptus.

There is an amount of 4.4% of non-lignin components in the studied kraft Lignin. The ash content was higher than that reported in the literature as ideal for isolated kraft lignin (Tomani, 2010; Boschetti et al., 2019). It indicates that this eucalyptus kraft lignin does not present optimal levels of purity, which impairs the yield and possibly the biorefinery application properties.

Yield of eucalyptus kraft lignin fractionation by different solvents

The yields of soluble fraction of kraft lignin obtained for each solvent are shown in Table 3.

The yields of the soluble fractions obtained for methanol,

Table 2. Chemical characterization of eucalyptus kraft lignin

Parameter	Result
Acid-soluble lignin (%)	8.9
Acid-insoluble lignin (%)	86.7
Total lignin (%)	95.6
Sugars (%)	1.8
Ash (%)	2.6

Table 3. Yield of the eucalyptus kraft lignin fractionation by different solvents

Organic solvent	Yield of lignin insoluble fraction (%)	Yield of lignin soluble fraction (%)
Methanol	13.4	86.6
Ethanol	19.6	80.4
Acetone	15.5	84.5
Dichloromethane	79.4	20.6
Methanol/Dichloromethane	4.8	95.2

ethanol and acetone were 86.6%; 80.4% and 84.5%, respectively. These yields were considered high and satisfactory, being greater for methanol. As mentioned by Park et al. (2018), the solubility parameters are quite variable and can change according to the purpose of fractionation and the characteristics of the unfractionated lignin. Thus, different fractionation techniques can present quite divergent results in yield.

Methanol obtained higher soluble fraction yields than ethanol, when comparing alcohols. The result is in accordance with the predicted, since, for a homologous series, the greater the carbon chain of the solvent, the smaller the solubility of kraft lignin (Horvath, 2006).

It was possible to obtain a yield of soluble fraction with acetone greater than that with ethanol and quite close to that obtained with methanol. This was possible since kraft lignin is more soluble in ketones than in alcohols (Duval et al., 2016). However, methanol is more efficient than acetone because of the effect produced by the size of the carbon chain, which is greater in acetone and has an inverse effect on lignin solubility.

The soluble fraction yields obtained for dichloromethane and methanol/dichloromethane were 20.6% and 95.2%, respectively. The yield was very high for the solvent combination. From the result obtained for methanol/dichloromethane, it is noted that dichloromethane is capable of extracting lignin fractions complementary to methanol. The insoluble fraction of methanol has more-condensed and less-polar lignin than the soluble one, and part of that lignin is solubilized by dichloromethane. It is possible, therefore, that dichloromethane is capable of solubilizing fractions of greater molecular weight. When applied together, methanol solubilizes the fractions of lower molecular weight and probably facilitates the permeation of dichloromethane to the lignin fractions of greater weight that have not yet been solubilized.

It was possible to recover an average of 93.2% of the dichloromethane used to fractionate lignin. Thus, even though the use of dichloromethane is not so recommended due to operational and safety reasons, it was possible to ensure that a very large amount of the solvent was reused, reducing discards and the makeup in the system.

CONCLUSIONS

The conclusion is that methanol is the solvent that leads to the best yield of eucalyptus kraft lignin soluble fraction. It is observed that methanol, ethanol and acetone are adequate to compose the eluotropic series for sequential fractionation, since they were all able to fractionate kraft lignin with satisfactory yields. Finally, it is noted that dichloromethane and methanol act in quite different fractions of lignin. Therefore, it is believed that the materials fractionated by methanol and dichloromethane separately will present different properties and, consequently, might be applied in different applications.

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