



Influence of membrane filtration on extraction and characteristics of lignin from a kraft dissolving pulp mill pre-hydrolysate

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ARTICLE INFO

Keywords:

Lignin
Pre-hydrolysate
Dissolving pulp
Extraction

ABSTRACT

During dissolving pulp production, the extraction of hemicellulose and other organics from hardwood chips prior to the kraft pulping process can be performed using steam or hot water. The pre-hydrolysate from this step is rich in sugars and contains a considerable amount of lignin. It is estimated that the lignin content in this stream can be as high as 28 t d^{-1} for a kraft dissolving pulp mill producing about 550 t d^{-1} of pulp. In this article, we report on the recovery of lignin and its characterization. The use of a membrane filtration system has been experimentally validated as an effective method for concentrating the pre-hydrolysate and extracting lignin. Three membranes with different molecular weight cut-offs (100, 10 and 1 kDa) have been tested. In a subsequent step, sulfuric acid was added to the concentrated pre-hydrolysate to precipitate the lignin. The recovered lignin was characterized with respect to purity, molecular weight distribution and other chemical properties. Approximately 99% retention of both sugars and lignin was achieved using the 1 kDa membrane, with about 44.4% of the total lignin being extracted by sulfuric acid precipitation method. The lignin was found to have a low molecular weight (2810 Da), high homogeneity ($M_w/M_n = 1.15$), and high purity (91%). These characteristics make the pre-hydrolysate lignin a very attractive candidate for niche applications.

1. Introduction

Between 2008 and 2025, the projected world demand for dissolving pulp is expected to increase from 4.1 to 6.1 million ADt y^{-1} (Flickinger et al., 2011). To meet this increased demand, several kraft pulp mills have considered converting their production lines to dissolving pulp. This conversion will allow these pulp mills to demonstrate the concept of forest biorefinery and diversify their product portfolio by making the best use of wood chips and produce new bio-products (Mabee et al., 2005; Thorp, 2005).

Kraft dissolving pulp mills have the opportunity to recover the pre-hydrolysate before it is mixed with black liquor and use it to produce value-added products. The pre-hydrolysate solution contains a large amount of hemicelluloses (pentoses (C5 sugars) and some hexoses (C6 sugars)), and lignin. The recovery of the lignin and the conversion of sugars into other high value-added products (such as furfural, ethanol, or xylitol) represent an attractive option for mills planning to move closer to a biorefinery operation conditions (Mabee et al., 2005; Thorp, 2005) and diversify their products.

In addition, lignin present in the pre-hydrolysate has not been in contact with any chemicals and has a high purity. However, there are

only a few studies that have been conducted on the extraction of lignin from the pre-hydrolysate. In most of these studies, the goal of this extraction was not to valorize the lignin (as in the case of lignin extraction from black liquor), but rather to facilitate the production of bioproducts such as ethanol and xylitol from hemicellulose because lignin was considered as an inhibitor during fermentative conversion of C5 and C6 sugars (Shi et al., 2011, 2012; Ajao et al., 2015a). Therefore, majority of the studies conducted on pre-hydrolysate solutions targeted lignin elimination and not its recovery.

Several techniques and methods have been proposed to remove lignin from pre-hydrolysate such as precipitation, centrifugation, filtration, activated carbon extraction, and complexation.

Yang et al. (2013) tested the extraction of lignin from the pre-hydrolysate by simple acidification to precipitate it. The pre-hydrolysate was acidified to pH = 2 using a 20% sulfuric acid solution. The precipitated lignin was recovered by centrifugation and then purified with distilled water. No information about the percentage of lignin extracted was reported. The lignin had a very low molecular weight ($M_w = 2975 \text{ Da}$) and a wide molecular weight distribution (polydispersity index $M_w/M_n = 3.7$). The same lignin extraction methodology and technique were adopted by Jahan et al. (2012) to extract the lignin

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from the pre-hydrolysate. The results obtained and the observations made were perfectly consistent with the findings of Yang et al. (2013).

Wang et al. (2014a) stated that the presence of lignin in the pre-hydrolysate could have a negative effect on the fermentation of xylose to ethanol or xylitol, and on the extraction of acetic acid and conversion of pentoses into furfural. Thus, they recommended its removal from the pre-hydrolysate. The idea was based on the use of an enzyme (laccase), followed by a flocculation and a filtration step. Laccase polymerizes lignin and increases its molecular weight. The polymerized lignin was flocculated with the coagulating agent polydiallyldimethylammonium chloride (polyDADMAC) and/or cationic polyacrylamide (CPAM) to facilitate its separation by filtration. Under the optimum conditions of temperature, pH, reaction time and concentration of laccase, the authors were able to recover between 50 and 58% of lignin (using laccase alone). This is consistent with a study published later by Wang et al. (2015) in which it was shown that using laccase alone leads to about 60% extraction of the lignin initially present in the pre-hydrolysate solution. In addition, Wang et al. (2014a) showed that the treatment of the pre-hydrolysate with polyDADMAC alone allowed removal of more than 23.6% of the lignin. However, the combined action of laccase and polyDADMAC removed up to 57% of the initial lignin. The addition of CPAM improved the removal of lignin by forming more compact sediment, thus facilitating the subsequent separation step. The possibility of increasing the molecular weight of lignin by 160% (polymerization caused by laccase) was demonstrated but with about 15% sugar loss. This is consistent with the results obtained by Wang et al. (2015), where recovered lignin had a high molecular weight (21,522 Da) and a significantly high polydispersity index (M_w/M_n : 5.32).

Another technique based on the pH increase of the pre-hydrolysate was proposed by Wang et al. (2014b). The principle is based on electrostatic interactions between lignin and sodium (Na^+) or calcium (Ca^{2+}), which are added as sodium hydroxide (NaOH) or calcium oxide (CaO). The addition of the alkaline compounds increases the pH of the solution and transforms the lignin from its non-ionized (protonated) form to the ionized form once the pH becomes higher than the pKa of the functional groups (phenolics, or carboxylic acids) of lignin. Thus, a maximum lignin yield of 28% was obtained when the pH of the pre-hydrolysate was increased to 10.5. Additional amount of sodium hydroxide did not result in any further lignin precipitation. On the other hand, the use of calcium oxide increased the yield of lignin extraction. Thus, when the pH of pre-hydrolysate was increased to 12.5, the precipitation of the lignin was around 48%. However, the results showed co-precipitation of about 90% of carbohydrates. This was attributed to the pKa of each compound. In fact, the pKa of hydroxyl groups in sugars is between 12 and 13, while the pKa of the phenolic groups of the lignin is between 9 and 11. Thus, in order to avoid co-precipitation of the sugars, the authors recommended precipitation of the lignin at lower pH than the pKa of the sugars. At pH = 11, 27% of lignin was precipitated and only 7% of the carbohydrates.

Although the techniques cited above demonstrate acceptable lignin extraction rates, they are still far from being optimal for recovering the pre-hydrolysate lignin for the following reasons:

- The techniques used do not take into account the valorization of lignin. The main purpose of these studies was to eliminate lignin which was considered a fermentation inhibitor. Therefore, it had to be removed before any utilization of hemicelluloses was possible (these techniques can be considered as detoxification steps).
- A considerable amount of non-recoverable complexing agents was required to remove the lignin, which can result in fairly high operating costs.
- In most cases, there were significant losses of carbohydrates.

Based on the discussion above, it appears that the recovery of lignin from the pre-hydrolysate does not seem to be a straightforward procedure. This is due to:

- Firstly, the total content of solids in the pre-hydrolysate is very low (3–5%) as compared to a value of 30%–40% solids in the black liquor. Black liquor is generally acidified, coagulated, and then filtered to obtain a lignin cake. The pre-hydrolysate solution is already acidic (pH 2–4). In addition, part of the lignin is in colloidal form and is difficult to coagulate and filter. Thus, further manipulations of the pre-hydrolysate solution are needed to recover the lignin.
- Secondly, the ionic strength of the solution plays a very important role in the lignin precipitation step. It is known that the precipitation of lignin is improved with increasing ionic strength (Norgren, 2000; Ohman, 2002; Merewether, 1961). The presence of inorganics such as Na_2SO_4 , Na_2CO_3 , Na_2S , and NaOH in black liquor facilitates lignin separation procedure. The content of inorganics is much lower in the pre-hydrolysate than in the black liquor, and this affects subsequent coagulation and filtration.
- Thirdly, it is well known in the literature (Ohman, 2002) that filtration and washing of lignin derived from hardwood are much more difficult than in the case of softwood. Kraft dissolving pulp mills that are currently in operation use mostly hardwood chips.

Accordingly, the aim of this study is to evaluate the potential of extracting lignin from the pre-hydrolysate and subsequently characterize it to determine suitable applications. To do that, a concentration step is necessary to increase the content of lignin in the pre-hydrolysate and, consequently, improve its recovery. In addition, the concentration step lowers the cost of lignin extraction since a smaller volume of pre-hydrolysate will be handled (Ajao et al., 2015b). The concentration step also results in lower energy consumption and investment costs for any subsequent pre-hydrolysate valorization.

2. Materials and methods

2.1. Wood chips

The wood chips mixture used in this study was a combination of maple (65 wt%) and aspen (35 wt%) from 30 year old trees (without bark) available in New Brunswick (Canada). They were provided by a Canadian dissolving pulp mill. The chips were screened on disc screen using a thickness fraction between 2 and 8 mm. The mass fractions of their solid contents were 60.5 and 37.3% for maple and aspen, respectively. The composition of the wood species in terms of cellulose, hemicelluloses, lignin, and extractives is presented in Table 1.

2.2. Generation of the pre-hydrolysis

In order to extract hemicelluloses from wood chips, the chips were subjected to a two-step treatment. The first step consisted of placing the chips in a 56 L-digester and then purging them three times with steam to remove air. In each time, the treatment lasted for three minutes under a pressure of 138 kPa. In the second step (the pre-hydrolysis), an initial liquor-to-wood mass ratio of 3:1 was employed. The pre-hydrolysis stage was carried out at a temperature of 170 °C for 90 min. About 15 dm³ of pre-hydrolysate solution were produced per batch. A typical composition of the pre-hydrolysate is given in Table 2.

2.3. Lignin and sugars extraction procedure

A schematic diagram of the lignin extraction and the sugar recovery

Table 1
Composition of aspen and maple wood chips by weight (dry basis).

Wood	Cellulose, %	Hemicelluloses, %	Lignin, %	Extractives, %
Aspen	50	23	24	3
Maple	44	23	31	2

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