Integration of hemicellulose recovery and cold caustic extraction in upgrading a paper-grade bleached kraft pulp to a dissolving grade

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ABSTRACT

In this study, a hemicellulose recovery process was integrated with a cold caustic extraction (CCE) process in upgrading paper-grade bleached kraft pulp to dissolving grade. Under the conditions of 15% NaOH, 10% pulp consistency, 30 °C and 1 h, a paper-grade softwood bleached kraft pulp was purified to a dissolving-grade pulp with 97.57% α-cellulose and 1.67% pentosan contents. The spent liquor from the cold caustic extraction process was sequentially extracted with ethanol to precipitate and recover the dissolved hemicelloses, followed by evaporation to recover the ethanol. After the recovery of hemicelluloses and ethanol, the spent liquor can be reused as the caustic solution for the CCE process without compromising the resulting pulp properties. The results demonstrated that it is feasible to integrate hemicellulose production with the cold caustic extraction process of dissolving pulp production, based on the concept of biorefinery.

Key words: Hemicellulose; Recovery; Dissolving pulp; CCE; Ethanol precipitation; Reutilization

1. INTRODUCTION

Dissolving-grade pulps are purified bleached pulps with high cellulose content of 90-99% for the production of regenerated cellulose fibers and cellulose derivatives, which has great market growth over the last ten years. For high quality of dissolving pulp, the hemicelluloses, lignin and extractives contents have to be low.1 Cold caustic extraction (CCE) can be a good approach to upgrade prehydrolysis kraft pulp to acetate grade dissolving pulp under the 20–50 °C temperature in 10–20% alkaline solution, aiming to selectively dissolve short chain carbohydrates, mainly hemicelluloses.2-5 One main challenge of CCE is the recovery of the relatively high concentration of alkaline solution, due to the presence of hemicelluloses in the CCE filtrate. It has been proposed that a sequential extraction process may be performed to isolate the hemicelluloses from the CCE filtrate for value-added products,6 and then the caustic liquor can be reused for the CCE process. So the two processes can be integrated by the concept of biorefinery. However, few results have been reported in the literature.

In this study, we systematically investigated the effect of CCE process parameters including temperature, alkaline concentration and pulp consistency on resulting pulp properties and the recovery of hemicelluloses. The CCE filtrate was sequentially extracted with various concentrations of ethanol (25%-50%-75%) to recover the hemicelluloses dissolved in the CCE process, and the recovered hemicelluloses were characterized by HPAEC. After hemicelluloses were recovered, the spent liquor was recycled back to the CCE process.

2. MATERIALS AND METHODS

2.1 Materials

A commercial bleached softwood kraft pulp was obtained from a paper mill in China. The pulp sheets were torn into small pieces manually and stored in a sealed plastic bag at room temperature.

2.2 Cold Caustic Extraction (CCE)

The CCE experiments were carried out according to a 3-factor Box-Behnken design, as shown in Table 1. The three factors were: pulp consistency (PC), alkali concentration (AC) and temperature (T). The CCE treatment of the pulp was carried out in polyethylene bags heated in a water bath for 60 min. The bags were taken out every 15 minutes for mixing by kneading manually for 10–15 s. After the CCE treatment, the pulp samples were filtered and the filtrate was collected for further analyses.

2.3 Hemicellulose Recovery

A 3-step sequential extraction process was applied to recover the hemicelluloses from the spent CCE liquor. In the first step, 35 ml of 95% ethanol was added slowly to 100 ml of the CCE filtrate at room temperature under constant stirring to deposit the first fraction of the dissolved hemicelluloses. The first hemicellulose fraction (labeled as H1) precipitated from above process was separated from the liquid phase by centrifugation, washed with 95% ethanol, and vacuum dried at 60 °C. The clear liquid phase was labeled as AL1. In the second step, another 50 ml of 95% ethanol was added to 100 mL of AL1 to obtain the second hemicellulose fraction (labeled as H2), in the same way as in the first step. The clear liquid phase was labeled as AL2. Similarly, in the 3rd step, another 125 ml of 95% ethanol was added to 100 ml of AL2 to obtain the third hemicellulose fraction which was labeled as H3.
clear liquid from the 3rd step was marked as AL$_3$ which was saved for ethanol recovery and caustic recycling.

2.4 Reutilization of the CCE Filtrate

The AL$_3$ liquid was evaporated under vacuum to recover the ethanol, and the remaining caustic liquor was reused for the CCE process as mentioned in the section 2.2. The alkali concentration of the recovered caustic solution was determined by titration with double indicators.

2.5 Pulp Properties Analyses

The viscosity, and the $\alpha$-cellulose, $\beta$-cellulose, $\gamma$-cellulose and pentosan contents of the pulp samples were determined according to Tappi standard methods (T230 om-04, T203 cm-09 and T223 cm-10). The initial pulp’s viscosity was 742 mL/g, and its $\alpha$-cellulose and pentosan contents were 8.632% and 5.44%, respectively.

2.6 Carbohydrates Analysis

The constituent neutral sugar and uronic acids in the recovered hemicelluloses were determined by high-performance anion exchange chromatography (HPAEC). The neutral sugars and uronic acids in the recovered hemicelluloses were liberated by hydrolysis with 72% H$_2$SO$_4$ for 45 min at 25 $^\circ$C followed by a high temperature hydrolysis at 105 $^\circ$C for 2.5 h by dilution to 3% H$_2$SO$_4$. After hydrolysis, the samples were diluted and injected into the HPAEC system (Dionex ISOC 3000, USA) with an amperometric detector, a CarbopacTMPA-20 column (4 mm x 250 mm, Dionex), and a guard PA-20 column (3 mm x 30 mm, Dionex). Neutral sugars and uronic acids were separated in isocratic 5 mM NaOH (carbonate free and purged with nitrogen) for 20 min, followed by a 0.75 mM NaAc gradient in 5 mM NaOH for 15 min with a flow rate of 0.4 mL/min. Calibration was performed with standard solutions of L-arabinose, D-glucose, D-xylose, D-mannose, D-galactose, glucuronic acid, and galacturonic acid.

3. RESULTS AND DISCUSSION

3.1 Effect of CCE Conditions on Treated Pulp Properties

The pulp properties after the CCE treatments under various conditions were listed in Table 1. Before the CCE treatment, the pulp’s viscosity was 742 mL/g, and its $\alpha$-cellulose and pentosan contents were 8.632% and 5.44%, respectively. In all cases, the CCE treatment increased the $\alpha$-cellulose content and decreased the pentosan content markedly. The $\alpha$-cellulose content represents the level of un-degraded and higher-molecular-weight cellulose, while the pentosan content indicates the amount of hemicelluloses as impurity, which should be kept as low as possible for dissolving pulp. The results in Table 1 show that after the CCE treatment, the $\alpha$-cellulose content of the pulp increased from 86.72% up to 97.67%, and the pentosan content decreased from 5.44% to as low as 1.67%, a reduction of almost 70%, while the viscosity change was relatively small.

Table 1 Characteristic of dissolving pulp under different CCE conditions

| No | T $^\circ$C | PC % | AC % | Vis mL/g | $\alpha$-cellulose % | Pentosan % |
|----|------------|------|------|----------|---------------------|------------|
| 1  | 20         | 10   | 10   | 732      | 96.32               | 3.03       |
| 2  | 20         | 20   | 5    | 721      | 96.21               | 4.28       |
| 3  | 20         | 20   | 15   | 753      | 96.29               | 2.77       |
| 4  | 20         | 30   | 10   | 717      | 92.72               | 2.03       |
| 5  | 30         | 10   | 5    | 734      | 92.67               | 3.86       |
| 6  | 30         | 10   | 15   | 758      | 97.57               | 1.67       |
| 7  | 30         | 20   | 10   | 730      | 94.10               | 2.73       |
| 8  | 30         | 30   | 5    | 742      | 93.72               | 4.82       |
| 9  | 30         | 30   | 15   | 732      | 93.89               | 4.78       |
| 10 | 40         | 10   | 10   | 712      | 93.65               | 2.27       |
| 11 | 40         | 20   | 15   | 740      | 95.50               | 2.54       |
| 12 | 40         | 20   | 5    | 715      | 90.98               | 4.61       |
| 13 | 40         | 30   | 10   | 700      | 91.79               | 4.89       |

Table 2 shows the statistical analyses of a single CCE parameter’s effect on the resulting pulp properties ($\alpha$-cellulose, pentosan and viscosity). It can be seen that increasing the temperature from 20 to 30 $^\circ$C benefited the viscosity and $\alpha$-cellulose content, probably due to increased removal of short chain carbohydrates. However, further increasing the temperature had negative effect on the viscosity and $\alpha$-cellulose due to alkaline degradation. These results are in agreement with those reported earlier.

For the effect of pulp consistency on the CCE performance, the analyses in the Table 2 indicate that the CCE performed best at the lowest pulp consistency. This is understandable if we consider the fact that at a lower pulp consistency more caustic solution was available for treating a given amount of fibers. The caustic concentration had a positive effect on the CCE performance: the higher the caustic concentration, the higher the viscosity and $\alpha$-cellulose, and the lower the pentosan content of the resulting pulp. Similar effect of enhanced alkaline concentration was reported earlier on the extraction of hemicelluloses.

In general, mild reaction temperature, low pulp consistency and high alkalinity favored the CCE process in purifying the pulp, which is in accordance with the results in Table 1 (30 $^\circ$C, 15% alkalinity with 10% pulp consistency). Under these conditions, a high grade of dissolving pulp can be produced with high viscosity, high $\alpha$-cellulose content and low pentosan content.

3.2 Recovery of Hemicelluloses from CCE Filtrate

To recover the dissolved hemicelluloses, the filtrate from the CCE process (30 $^\circ$C, 15% alkalinity with 10% pulp consistency) was treated by a sequential extraction process with ethanol of different concentration. Hemicelluloses are essentially insoluble in ethanol/water solution, depending on the molecular weight of hemicelluloses and the ethanol concentration.
The high-molecular-weight fraction of the hemicelluloses can be firstly separated from the CCE filtrate by deposition at a low ethanol concentration. And then lower Mw fractions of hemicelluloses can be separated sequentially by raising the ethanol concentration in the system by stepwise.

### Table 2 Mean values of treated pulp properties under each single parameter

| T °C | Σ Vis/n mL/g | Σα-cellulose/n % | Σ Pentosan/n % |
|------|--------------|------------------|----------------|
| 20   | 731          | 93.89            | 3.03           |
| 30   | 739          | 94.35            | 3.57           |
| 40   | 717          | 92.98            | 3.58           |

| PC % | Σ Vis/n mL/g | Σα-cellulose/n % | Σ Pentosan/n % |
|------|--------------|------------------|----------------|
| 10   | 734          | 95.05            | 2.71           |
| 20   | 732          | 93.42            | 3.39           |
| 30   | 723          | 92.98            | 4.13           |

| AC % | Σ Vis/n mL/g | Σα-cellulose/n % | Σ Pentosan/n % |
|------|--------------|------------------|----------------|
| 5    | 728          | 91.84            | 4.39           |
| 10   | 718          | 93.72            | 2.99           |
| 15   | 746          | 95.81            | 2.94           |

### Table 3 Polysaccharides contents (%*) of recovered hemicelluloses

| w/w  | H₁   | H₂   | H₃   |
|------|------|------|------|
| Ara  | 2.51%| 1.75%| nd   |
| Gal  | 3.60%| 3.31%| nd   |
| Glu  | 11.56%| 11.36%| nd |
| Xyl  | 46.92%| 43.20%| nd |
| Man  | 35.12%| 40.38%| nd |
| GluA | 0.27%| nd   | nd   |
| GalA | 0.02%| nd   | nd   |
| Yield %^ | 3.87 | 6.88 | nd |

*Neutral sugars and uronic acid contents calculated based on the total neutral sugars and uronic acid. Ara: arabinose; Gal: galactose; Glu: glucose; Xyl: xylose; GluA: glucuronic acid; GalA: galacturonic acid.

^based on the OD pulp;

nd —— not detected;

As shown in Table 3, about 3.87% and 6.88% of hemicelluloses were separated from the CCE spend liquor in 1st and 2nd extraction stages, respectively. No carbohydrates were found in the H₃ fraction, suggesting that two stages of ethanol extraction were sufficient to isolate most of the hemicelluloses dissolved in the CCE spent liquor. This finding was in agreement with those reported by Peng et al. The recovered hemicelluloses consisted mainly of xylose and mannose, which is in accordance with the findings by Tian et al. The recovered hemicelluloses may be further treated by an enzymatic saccharification and hydrolysis process to isolate the main monosaccharide for high-value application.

Aromatic lignin and hemicelluloses may be further treated by an enzymatic saccharification and hydrolysis process to isolate the main monosaccharide for high-value application. It is interesting to note that the GluA and GluA were only identified in the H₁ fraction, but not in other fractions. These results indicated that the recovered hemicelluloses from the H₁ fraction consisted more branched xylen (i.e. arabinogluconoxylan). Meanwhile, the Ara/Xyl ratio of the H₁ fraction was higher than that for the H₂ fraction, also confirming that more branched xylans were recovered in the 1st stage at a lower ethanol concentration.

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NaOH to Na₂CO₃ during the treatment; ii) reaction of NaOH with ethanol to form CH₃COONa. When the recovered CCE caustic solution was applied to the CCE process to replace the fresh caustic solution, the resulting pulp had similar properties as the pulp treated with fresh alkali liquor, in terms of viscosity, α-cellulose and pentosan contents.

These results demonstrate the feasibility of applying the CCE process to an existing paper-grade softwood kraft pulp mill to produce dissolving grades of pulp to meet market demands. As shown in Fig. 1, with the integrated CCE technologies, the pulp mill can produce dissolving grades of pulp, as well as high value products from hemicelluloses.

4. CONCLUSION

Hemicellulose recovery was successfully integrated with the CCE process for dissolving pulp production. The optimal CCE process conditions were found to be 30 °C, 10% pulp consistency and 15% caustic concentration. The dissolved hemicelluloses in the CCE process can be recovered and fractionated by sequential precipitation at different levels of ethanol concentrations. It was found that the recovered hemicelluloses consisted mainly of xylose and mannose which can be potentially converted to high value products. More branched xylans were separated in the first isolation stage at a lower ethanol concentration. The CCE spent liquor can be reused after the recovery of the hemicelluloses and ethanol, without affecting the resulting pulp properties in terms of viscosity, α-cellulose and pentosan contents.

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