Effects of Metal Chlorides on the Solubility of Lignin in the Black Liquor of Prehydrolysis Kraft Pulping

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The effects of $CaCl_2$, $MgCl_2$, $FeCl_3$, NaCl, and $AlCl_3$ on the solubility of lignin in the prehydrolysis kraft black liquor of Masson pine were studied using a focused-beam reflectance measurement (FBRM) instrument and UV spectra. The results showed that NaCl and $AlCl_3$ have no obvious effects on the coagulation or solubility of lignin in the prehydrolysis kraft black liquor at high effective alkalinity. However, $CaCl_2$, $MgCl_2$, and $FeCl_3$ have significant effects on the solubility of lignin in the black liquor. According to the reduction rate of UV absorbance, the effects of these chloride salts on the black liquor lignin solubility at high alkali content were as follows: $AlCl_3 \approx NaCl < MgCl_2 < CaCl_2 < FeCl_3$.

Keywords: Black liquor; Lignin solubility; FBRM; Particle size; Metal chlorides; Coagulation

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INTRODUCTION

Lignin is a three-dimensional cross-linked macromolecule (Nyman *et al*. 1986) that binds the fibers together in wood. During kraft cooking, delignification includes both chemical degradation and physical solubilization of lignin (Saltberg *et al*. 2009), which could be affected by inactive ions – those ions not reacting with wood chips (Bogren *et al*. 2009). Such ions may affect the physical solubilization of lignin. The solubility of lignin is adversely affected by said ion interaction. During the precipitation of lignin, delignification would decrease and the precipitated lignin would be adsorbed onto fiber surfaces, affecting the quality of pulp (Zhan *et al*. 2012). After cooking, the pulp is washed to remove black liquor. During pulp washing, the separation of fiber and lignin occurs. This will affect the kappa number of the washed pulp (Sundin and Hartler 2000), consequently affecting overall bleaching costs and paper properties. The higher the solubility of lignin is, the easier it is for the pulp to be washed cleanly.

Salt concentration is one of the factors that can affect the thermodynamic stability of lignin (Norgren *et al*. 2001). According to the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO), as the concentration of electrolytes in the black liquor increases, simultaneously, the electrical double layer compresses around the lignin gel particles, and the repulsive electrostatic forces reduce. As a result, the coagulation of lignin particles may occur (Sundin 2000). Therefore, to improve the cooking and washing processes, it is important to understand how different metal salts and concentrations affect the solubility of lignin in black liquor.

Focused beam reflectance measurement (FBRM) provides a unique ability to measure particles and droplets in suspensions and emulsions. These unique design features of FBRM ensure a repeatable and reproducible measurement of particle dimension and relative particle count despite highly concentrated and opaque solutions.

The effects of $CaCl_2$, $MgCl_2$, $FeCl_3$, NaCl, and $AlCl_3$ on the solubility of lignin in the prehydrolysis kraft black liquor of Masson pine were studied using an FBRM instrument and UV spectra. The lignin particle chord length variations in black liquor with the additions of metal chlorides were determined.

Two colloidal systems exist in black liquor. One of the systems consists of a molecular lignin colloid; also there are association colloids formed by fatty acids and resin acids salts (Hermans 1984). The fatty acids and resin acids are part of the extractives component of wood and they are present at much smaller quantities than lignin in wood chips. In this study, the black liquor was from the prehydrolysis kraft process. During the water prehydrolysis process, most of the hemicellulose and other water soluble substances in wood chips were removed and dissolved in the prehydrolysis liquor. Before kraft cooking, the prehydrolysis liquor was thoroughly drained from the chips, so the main part of colloids in the black liquor was lignin. The variation of particle size distribution (PSD) and the reduction of UV absorbance at 205 nm could reflect the coagulation of lignin in the black liquor.

EXPERIMENTAL

Materials

The black liquor was obtained from laboratory cooking of the prehydrolysis kraft pulp of Masson pine. The main conditions of the prehydrolysis process were as follows: liquor to wood ratio 6:1; maximum temperature 170 °C; heat-up time 90 min; and retention time at maximum temperature 90 min. After pre-hydrolysis, the liquor was thoroughly drained from the chips, and the prehydrolyzed chips were directly cooked using the following conditions: alkali charge 30% (as NaOH); sulfidity 30%; liquor to wood ratio 5:1; maximum temperature 170 °C; heat-up time 90 min; and retention time at maximum temperature 120 min. After cooking, the black liquor was separated from the pulp by filtration with a 260-mesh screen. The black liquor was then stored in a refrigerator for one or two days at approximately 4 °C to await further testing. The properties of the black liquor are given in Table 1.

Table 1. Characteristics of Prehydrolysis Kraft Black Liquor of Masson Pine

Baume degree	Total solids content (%)	Organics content (%)	Inorganics content (%)	Residual effective alkaline ($g \cdot L^{-1}$)
10.902	13.72	63.05	36.95	22.23

Methods

The particle dimensions, relative particle count, and particle size distribution of the black liquor were determined by focused-beam reflectance measurement (FBRM S400A, Mettler Toledo).

A 60-mL black liquor sample was transferred into a fixed beaker. Salt solutions were then added, followed by stirring at 150 rpm to mix the black liquor and salt solutions. The temperature was held constant at 18±2 °C.

The dissolved lignin content in the black liquor was determined by UV absorbance spectra (UV-2550, Shimadzu) at 205 nm (Shi 2010). Black liquor (30 mL) was transferred to a 50-mL tube and centrifuged at 9690 g for 10 min at 20 °C. The supernatant solution was decanted and filtered using an aqueous phase filter with a 0.45-μm pore size. Pure filtrate was then diluted 10,000 times with deionized water to determine its UV absorbance. The reduction rate of UV absorbance was calculated following Eq. 1,

$$\varepsilon = \frac{A_0 - A}{A_0} \times 100\% \qquad (1)$$

where ε is the reduction rate of UV absorbance, A_0 is the UV absorbance of the original black liquor, and A is the UV absorbance of the black liquor to which metal cations were added.

RESULTS AND DISCUSSION

Particle Size Distribution of Original Black Liquor from Prehydrolysis Kraft Cooking of Masson Pine

The trends of lignin particles in the original prehydrolysis kraft black liquor of Masson pine are given in Fig. 1. The predominate chord lengths of most particles in the black liquor were within the range of 1 to 150 μm. Particles of 10 to 50 μm in chord length were the largest proportion of the total particles.

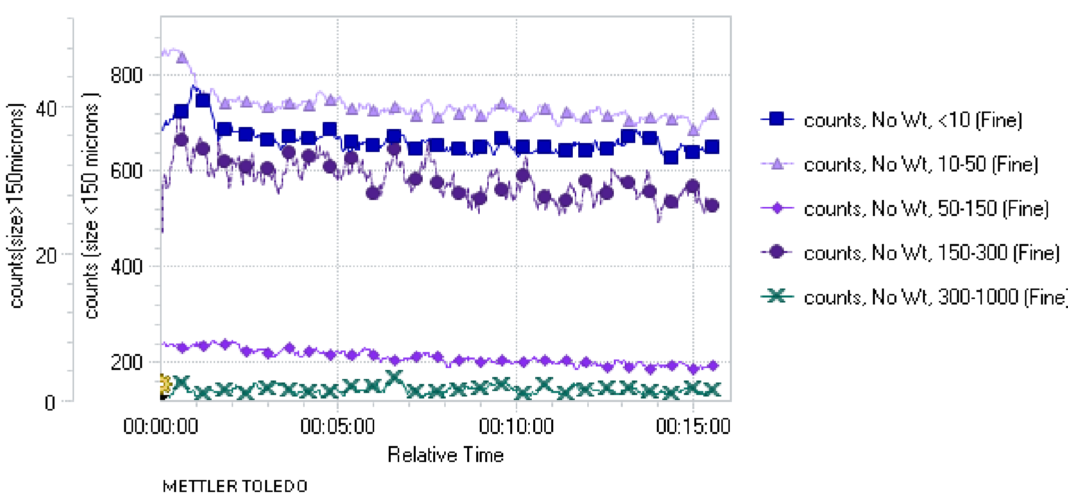

Fig. 1. The trends of lignin particles in original prehydrolysis kraft black liquor

Effect of Calcium Chloride

According to the change of the UV absorbance reduction shown in Fig. 2, it could be concluded that the solubility of lignin was reduced sharply with increasing concentration of calcium chloride. As can be inferred from the change in PSD of lignin particles in Fig. 3, as the calcium chloride concentration increased, the counts of lignin particulates (1 to 150 μm) increased. The counts of lignin particles with the size of about 10 μm increased, especially at high calcium chloride concentrations, suggesting that the coagulation degree of lignin increased with increasing concentration of calcium chloride.

From Figs. 2 and 3, it could be concluded that the higher concentration of calcium chloride exerted a negative impact on the solubility of lignin in the black liquor.

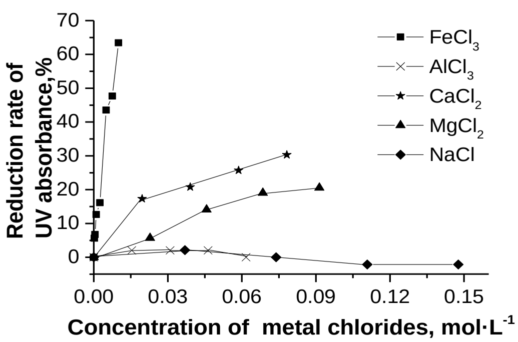

Fig. 2. The effect of different concentrations of metal chlorides on the reduction rate of UV absorbance

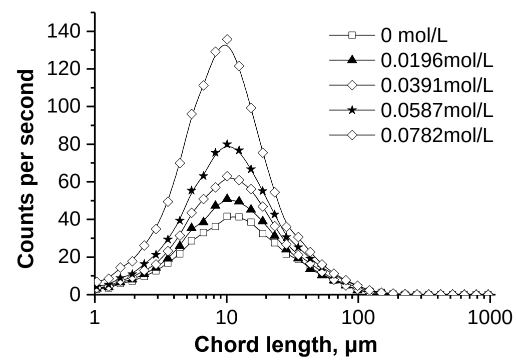

Fig. 3. The effect of different $CaCl_2$ concentrations on the PSD of lignin in the black liquor

Effect of Magnesium Chloride

Based on the PSD shown in Fig. 4, the counts of lignin sharply increased as $MgCl_2$ concentration increased. The increase in the count number had a close relationship with the chord length of lignin particles. Figure 4 indicates that particles with chord lengths of 1 to 300 μm increased with the addition of $MgCl_2$, with a peak chord length of around 10 μm. This suggests that the lignin started to coagulate and precipitate severely as the magnesium chloride content increased. The change in UV absorbance as a function of $MgCl_2$ content is given in Fig. 2. Clearly, the UV absorbance of lignin was reduced remarkably as $MgCl_2$ content increased, suggesting that lignin precipitated.

Compared to $CaCl_2$, similar amounts of $MgCl_2$ led to a smaller change in the reduction rate of UV absorbance. These results coincided with Lindström's suggested order of coagulation degree of kraft lignin solutions in the presence of magnesium and calcium ions (Lindström 1980).

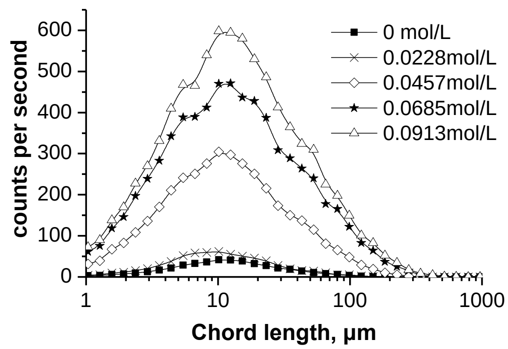

Fig. 4. The effect of different $MgCl_2$ concentrations on the PSD of lignin in the black liquor

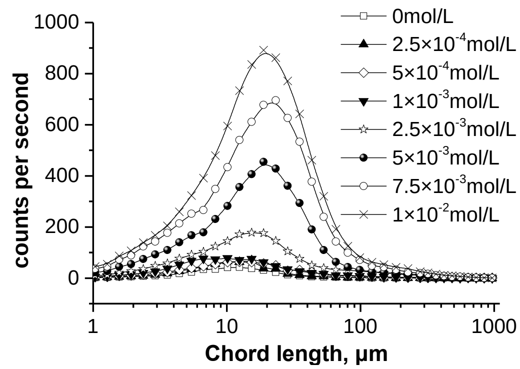

Fig. 5. The effect of different $FeCl_3$ concentrations on the PSD of lignin in the black liquor

Effect of Ferric Chloride

According to Figs. 2 and 5, the counts of lignin particles and the reduction rate of UV absorbance increased more with increasing ferric chloride concentration than with other metal chloride salts. Compared to the other chloride salts used in this study, ferric chloride impacted the lignin coagulation the most. The UV absorbance of lignin was reduced by approximately 60% by adding 0.01 M ferric chloride to the black liquor.

Effect of Sodium Chloride

Figure 6 shows that the PSD (1 to 1000 μm) of lignin particles in black liquor showed no significant change when the sodium chloride concentration was varied. Figure 2 demonstrates that with increasing sodium chloride concentration from 0 to 0.1477 M, the UV absorbance of lignin showed no noticeable change. It could be concluded that the concentration of NaCl had little effect on the solubility of lignin in black liquor containing high effective alkalinity. This conclusion coincides with Sundin's result for high pH solutions (Sundin 2000).

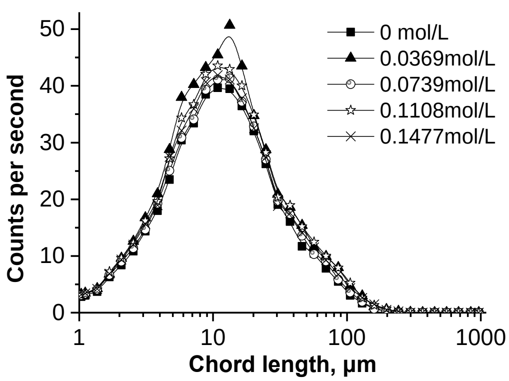

Fig. 6. The effect of different NaCl concentrations on the PSD of lignin in the black liquor

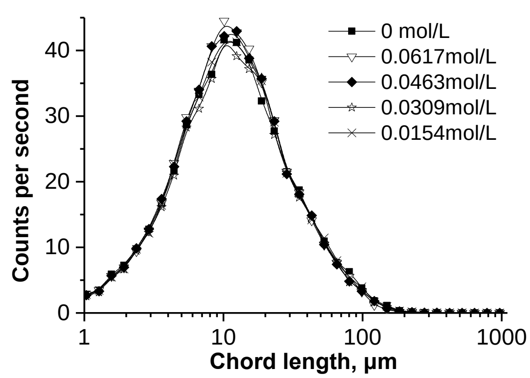

Fig. 7. The effect of different $AlCl_3$ concentrations on the PSD of lignin in the black liquor

Effect of Aluminum Chloride

Figure 7 shows no obvious change in the PSD as the aluminum chloride concentration was varied from 0 to 0.0617 M. As seen in Figure 2, UV absorbance displayed no change. Therefore, it can be inferred that aluminum chloride had no significant effect on the solubility of lignin in the prehydrolysis kraft black liquor containing high effective alkalinity (22.23 g/L as NaOH). It is well known that alum is a good coagulant at pH 5 to 6 (Dong and Chen 2004). However, under alkaline conditions, the Al^{3+} ions mostly exist as AlO_2^-. The ionic AlO_2^- could not function as an effective coagulant for negatively charged lignin particles.

Comparing the effects of five metal chloride salts (NaCl, $CaCl_2$, $MgCl_2$, $FeCl_3$, and $AlCl_3$) on the reduction rate of UV absorbance of lignin in the black liquor, it could be inferred that the effects on the solubility of lignin in black liquor with high alkalinity are as follows: $AlCl_3 \approx NaCl < MgCl_2 < CaCl_2 < FeCl_3$.

CONCLUSIONS

Sodium chloride and $AlCl_3$ had no obvious effect on the coagulation of lignin or the solubility of lignin in the prehydrolysis kraft black liquor.

Calcium chloride, $MgCl_2$, and $FeCl_3$ had a significant effect on lignin solubility in the black liquor. The lignin coagulation increased with increasing metal chloride concentration. As $CaCl_2$ or $MgCl_2$ concentration increased, the coagulation degree of lignin increased sharply. The UV absorbance of lignin was reduced by approximately 60% by adding 0.01 M ferric chloride to the black liquor.

According to the reduction rate of UV absorbance, the effects of NaCl, $CaCl_2$, $MgCl_2$, $FeCl_3$, and $AlCl_3$ on black liquor lignin solubility at high alkali content are as follows: $AlCl_3 \approx NaCl < MgCl_2 < CaCl_2 < FeCl_3$.

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