Purification of Cellulose from Bleached Pulp by Lewis Base-enhanced High-temperature Liquid Water Treatment

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Applications of cellulose-based materials that require high-purity cellulose as a feedstock are becoming increasingly common. However, reported methods for hemicellulose removal are comparatively complicated. In this study, a Lewis base-enhanced high-temperature liquid water (HTLW) treatment was used to purify cellulose. The variation of carbohydrate content, average degree of polymerization (DP), and the crystalline index of specimens of the purified cellulose were investigated. After primary HTLW treatment, the alpha-cellulose content of specimens increased distinctly; also, the alkali solubility decreased. The DP of the specimens decreased dramatically after HLTW treatment. The incorporation of a Lewis base was beneficial for maintaining DP and for removing hemicellulose selectively. Simultaneously, the results of Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) showed that the chemical and crystal structure of the specimens were unchanged. Based on the experimental results, Lewis base-enhanced HTLW is a promising method to prepare high-purity cellulose.

Keywords: Cellulose purification, High-temperature liquid water (HTLW); Lewis base; Carbohydrate content of cellulose

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INTRODUCTION

As one of the most abundant natural polymers, cellulose is widely used to prepare various chemicals or chemical derivatives. However, pure cellulose is difficult to obtain due to the coexistence of hemicellulose in naturally occurring cellulose fiber (Gehmayr and Sixta 2012). Thus, cellulose fiber must be purified if it is to be used for the preparation of cellulose-based materials (Roselli *et al.* 2014). Kraft pulping is a conventional and widely used method for purifying cellulose (Buzała *et al.* 2017). However, kraft pulp has the drawback that its cellulose is low-purity.

The main components of bleached kraft pulp are celluloses and hemicelluloses. A small amount of lignin also exists in pulp. In order to obtain high-purity cellulose, hemicellulose in the pulp should be eliminated. Unfortunately, due to its structure, hemicellulose is difficult to selectively remove from cellulose, even though hemicelluloses exhibit higher reactivity than celluloses. Reported methods for hemicellulose removal are comparatively complicated (Liu *et al.* 2011; Chen *et al.* 2015). Hence, a simple and practical method is required for purifying cellulose.

High temperature liquid water (HTLW) is defined as compressed liquid water from

160 °C to 300 °C (Dunn and Savage 2005). In comparison with ambient-temperature water, HTLW exhibits different physical properties (Dunn and Savage 2005). For instance, the hydrogen bonding within the water becomes weaker and less persistent with increasing temperature and decreasing density (Akiya and Savage 2002). Since Bobleter *et al.* (1976) used HTLW in biomass processing, HTLW has been widely investigated for different uses (Liu and Charles 2003; Ramsurn and Gupta 2012; Boakye-Boaten *et al.* 2015). Various components of lignocellulosic biomass exhibit different reactivity (Mok and Antal Jr. 1992; Phaiboonsilpa *et al.* 2011). Recently, many methods to enhance the efficiency of HTLW treatment have been reported (Mosier *et al.* 2005; Hunter and Savage 2007). While cellulose is more stable than hemicellulose under HTLW conditions, it may suffer from depolymerization during this process.

The accumulation of degraded products inhibits the further degradation of carbohydrates in lignocellulosic biomass. Normally, hemicellulose is easier to degrade than cellulose. If degraded hemicellulose products accumulate in a reaction mixture, the degradation of hemicellulose is inhibited, causing a decrease in degradation selectivity. The acidic degradation products can react with basic compounds and then be further converted. Basic compounds could be added into the mixture to reduce the accumulation of degradation products. However, the peeling reaction of cellulose will occur more rapidly with the increasing pH and temperature of the reaction. Peng *et al.* (2010) showed that alkali and alkaline earth metal chlorides, unlike ordinary basic compounds, have no significant influence on the conversion of cellulose. Therefore, alkalescent inorganic salts, which can reduce the accumulation of degraded products but exhibit little influence on the degradation of cellulose, were investigated in this work.

In this study, bleached softwood sulfate pulp was treated with HTLW. Sodium bicarbonate ($NaHCO_3$) and disodium phosphate (Na_2HPO_4) were added to the HTLW reaction to enhance its efficiency. The variation in carbohydrate contents, chemical structure, crystal structure, and average degree of polymerization (DP) were examined.

EXPERIMENTAL

Materials

Bleached softwood sulfate pulp (average DP was 1023, and the alpha-cellulose content was 82.03%) was purchased from Hongta Renheng Paper Co., Ltd. (Zhuhai, China). Potassium bromide (spectroscopic grade) was purchased from Damao Chemical Reagent Co., Ltd. (Tianjin, China). $NaHCO_3$, Na_2HPO_4, and other reagents were analytically-pure and purchased from Tianli Chemical Reagent Co., Ltd. (Tianjin, China).

Methods

Treatment of cellulose fiber

Bleached softwood sulfate pulp fibers were swelled with deionized water for 12 h at room temperature. Following soaking, the fibers were dispersed by a deflaker. Approximately 30 g of swelled cellulose fiber was treated with 1000 mL of water with varied $NaHCO_3$ or Na_2HPO_4 loading in a digester at 180 °C for 30 min. After treatment, specimens were washed to a neutral pH with deionized water, air dried, and placed into valve bags. Untreated fiber was used as the original specimen (OS). Specimens treated by water at 180 °C for 30 min were used as the control specimens (CS). The specimens were treated with a 1.5 wt.% NaOH solution at 30 °C for 1 h, washed with deionized water, and air dried. The OS and CS were also treated with alkali to obtain OS-AT and CS-AT specimens, respectively. The experimental formulas and the serial number of specimens are listed in Table 1.

Table 1. Experimental Formula and Serial Number of Specimens

Concentration of Lewis Base (mmol/L)	Na_2HPO_4		$NaHCO_3$	
	Without Alkali Treatment	With Alkali Treatment	Without Alkali Treatment	With Alkali Treatment
25	P25	P25-AT	C25	C25-AT
50	P50	P50-AT	C50	C50-AT
75	P75	P75-AT	C75	C75-AT
100	P100	P100-AT	C100	C100-AT

X-ray diffraction (XRD) analysis

XRD patterns were recorded using a Bruker D8-Advance instrument (Karlsruhe, Germany) equipped with a Cu Kα radiation source (k = 1.54 A°) with an X-ray source operating (40 kV, 30 mA) at a scan rate of 0.1 per second in a 2θ range of 10 to 60°. XRD crystalline indices (CI) were determined using published methods (Segal *et al.* 1959; French 2014).

Fourier transform infrared spectroscopy (FTIR) analysis

FTIR spectra were detected on a Bruker Vertex 70 FTIR spectrometer (Karlsruhe, Germany) with a resolution of 4 cm^{-1} in the range of 4000 to 400 cm^{-1} using the KBr method.

Average DP determination

Average degree of polymerization (DP) values were measured using the viscosity method with cupriethylenediamine (CED) per TAPPI T230 om-99 (1999).

Alpha-cellulose and alkali solubility determination

Alpha-cellulose and alkali solubility (S_{10} and S_{18}) were measured according to TAPPI T203 cm-99 (1999) and T235 cm-00 (2000) methods, respectively.

RESULTS AND DISCUSSION

Variation of Carbohydrate Contents

Due to the different reactivity of cellulose and hemicellulose during HTLW treatment, the carbohydrate content of specimens exhibited remarkable variation, as shown in Table 2. After HTLW treatment, the carbohydrate contents of the specimens varied distinctly. The alpha-cellulose content of treated specimens was increased. What is more, the alpha-cellulose content of Lewis base enhanced high-temperature liquid water treated specimens was higher than those of CS. Obviously, the purifying effect of HTLW treatment was enhanced by the incorporation of Na_2HPO_4 or $NaHCO_3$. After alkali treatment, the alpha-cellulose of specimens increased, with OS exhibiting the most distinct increase, followed by CS.

For alkali solubility, S_{10} was identified as hemicellulose and short-chain cellulose; S_{18} was typical hemicellulose (gamma-cellulose). The difference, S_{10}-S_{18} was identified as beta-cellulose. The results showed that alkali solubility, including the solubility of S_{10}, S_{18}, and S_{10}-S_{18}, were all decreased after HTLW treatment. With the incorporation of Lewis bases, the alkali solubility of specimens exhibited a further decrease. This result indicated that the addition of Lewis base favored the purification of cellulose.

These results might be attributed to the buffering effect of Lewis bases. During HTLW treatment, hemicellulose is degraded at 180 °C, but cellulose is not dissolved when the temperature is below 230 °C（Mok and Antal Jr. 1992; Phaiboonsilpa *et al.* 2011). As the reaction proceeded, hemicellulose degradation products accumulated in the reaction mixture, which inhibited the further degradation of hemicellulose. When a Lewis base was added into the reaction mixture, degraded hemicellulose products might have reacted with these bases and were further converted. Therefore, hemicellulose could possibly be further degraded. Accordingly, the purity effect of HTLW was enhanced by the incorporation of a Lewis base.

Table 2. Effect of Lewis Bases Enhanced HTLW on the Carbohydrate Contents

Specimens	Alpha-cellulose Content (%)	S_{10} (%)	S_{18} (%)	S_{10}-S_{18} (%)
OS	82.05 ± 0.18	19.53 ± 0.13	15.88 ± 0.09	3.65 ± 0.22
CS	89.73 ± 0.25	10.93 ± 0.11	7.23 ± 0.04	3.70 ± 0.15
P25	91.70 ± 0.19	9.52 ± 0.14	7.00 ± 0.04	2.52 ± 0.18
P50	91.98 ± 0.22	9.37 ± 0.07	6.80 ± 0.03	2.57 ± 0.10
P75	92.38 ± 0.20	8.91 ± 0.02	6.50 ± 0.10	2.41 ± 0.12
P100	92.51 ± 0.17	8.62 ± 0.08	6.27 ± 0.15	2.45 ± 0.23
C25	91.73 ± 0.15	9.64 ± 0.19	7.23 ± 0.12	2.41 ± 0.31
C50	92.11 ± 0.24	9.39 ± 0.05	6.72 ± 0.05	2.67 ± 0.10
C75	92.04 ± 0.13	9.27 ± 0.07	6.59 ± 0.16	2.68 ± 0.23
C100	91.82 ± 0.03	9.12 ± 0.06	6.35 ± 0.07	2.77 ± 0.13
OS-AT	85.74 ± 0.28	16.22 ± 0.08	13.53 ± 0.05	2.69 ± 0.13
CS-AT	91.98 ± 0.19	9.68 ± 0.13	7.29 ± 0.22	2.39 ± 0.35
P25-AT	92.86 ± 0.10	7.50 ± 0.07	5.42 ± 0.10	2.08 ± 0.17
P50-AT	92.94 ± 0.13	7.94 ±0.08	5.46 ± 0.14	2.48 ± 0.22
P75-AT	93.05 ± 0.08	6.36 ± 0.16	4.95 ± 0.16	1.41 ± 0.32
P100-AT	93.82 ± 0.05	7.00 ± 0.02	5.20 ± 0.13	1.80 ± 0.15
C25-AT	92.54 ± 0.14	7.05 ± 0.17	5.97 ±0.09	1.08 ± 0.26
C50-AT	92.66 ± 0.22	7.62 ± 0.08	5.86 ± 0.13	1.76 ± 0.21
C75-AT	92.59 ± 0.16	7.66 ± 0.04	5.00 ± 0.05	2.66 ± 0.09
C100-AT	93.48 ± 0.08	7.23 ± 0.09	4.64 ± 0.18	2.59 ± 0.27

Table 3. Final pH Value of Liquid Products at 25 °C

Concentration of Lewis Base (mmol/L)	Final pH value of liquid products at 25 °C	
	Na_2HPO_4	$NaHCO_3$
0	4.13	
25	5.06	5.13
50	5.42	5.37
75	5.67	5.58
100	5.90	5.80

In addition, the carbohydrate content of specimens treated with different concentration of base were similar. For each Lewis base that was used, the pH value of solutions varied with the concentration of base scarcely between 25 and 100 mmol/L.

Hence, the buffering effect might be similar during these processes. What is more, the buffering effect of Na_2HPO_4 was better than that of $NaHCO_3$ according to the alpha-cellulose content of alkali treated specimens. These results might be attributed to the higher pH value of Na_2HPO_4 solution in same concentration.

Variation of DP

Normally, carbohydrates are depolymerized during HLTW treatment. To ascertain the variations in cellulose during this process, the DP of sample pulps was measured (Table 4). All treated specimens exhibited lower DP than OS. Except for CS, the DP values of all specimens were decreased slightly after further alkali treatment. This effect was attributed to the increasing H^+ concentration in the HTLW. Carbohydrates are hydrolyzed by HTLW due to the instability of glycosidic bonds in the presence of H^+ (Fukuoka and Dhepe 2006). Furthermore, the DP values of specimens treated with Lewis base-enhanced HTLW were much higher than those of CS. These results indicated that the incorporation of Lewis base prevented the degradation of cellulose to a certain degree. During HTLW treatment, the degradation of hemicellulose and cellulose is regarded as acid hydrolysis. In general, hemicelluloses are more sensitive to H^+ than celluloses. The concentration of H^+ in a reaction mixture might be reduced by the incorporation of Lewis base. Hence, cellulose might be more stable in Lewis base-enhanced HTLW treatments. Furthermore, the high DP value might suitable for obtain cellulose-based materials and derivatives of cellulose.

Table 4. Effect of Lewis Bases Enhanced HTLW on the DP

Specimens	DP of Specimens before Alkali Treatment	DP of Specimens after Alkali Treatment
OS	1004 ± 18	990 ± 3
CS	600 ± 5	604 ± 11
P25	935 ± 3	881 ± 3
P50	934 ± 15	892 ± 7
P75	886 ± 11	875 ± 8
P100	916 ± 13	853 ± 4
C25	902 ± 2	849 ± 9
C50	902 ± 16	859 ± 5
C75	922 ± 12	874 ± 7
C100	915 ± 6	898 ± 18

Variation of Chemical and Crystal Structure

Eight specimens (OS, CS, P100, C100, OS-AT, CS-AT, P100-AT, and C100-AT) were selected to examine variations in their chemical and crystal structure by FTIR and XRD, as shown in Figs. 1 and 2, respectively. The CI values are listed in Table 5.

The FTIR spectra of specimens exhibited no significant variations. No absorption peaks disappeared or emerged, indicating that no variation of chemical structure occurred during the treatment. The absorption band at 3343 cm^{-1} is -OH stretching associated with polar groups linked through intra- and inter-molecular hydrogen bonding; the peaks at 2900 and 1373 cm^{-1} are methyl, methylene and methine stretching vibrational bands; the bands at 1430 and 1318 cm^{-1} are attributed to the saturated C-H bending and wagging vibration, respectively (Li *et al*. 2015). The absorption bands at 1164, 1112, and 1059 cm^{-1}, which are due to C-O-C stretching vibrations, were considered to be the typical bonds of cellulose (Leung *et al*. 2011). The absorption band at 893 cm^{-1} is typical of the β-linkage within glucose polymer between sugar units (Nelson and O'Connor 1964; Kumar *et al*. 2010).

Furthermore, the absorption peaks near 1650 cm^{-1} is indicative of stretch vibration-absorption peaks from -CHO groups that are present exhibited significant elevation after treatments. In addition to reducing end groups, functional groups of cellulose were unable to be responsible for the absorption peak near 1650 cm^{-1}. Hence, the amount of reducing end groups, according to the elevation of absorption peaks near 1650 cm^{-1}, increased after treatments. This was attributed to the depolymerization of carbohydrates by HTLW, which increased the number of reducing end groups and thus changed the abundance of -CHO groups.

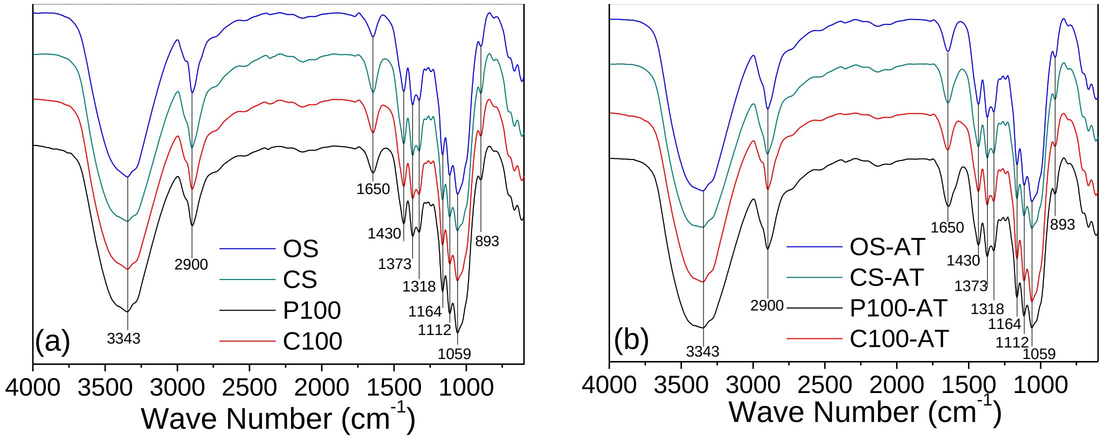

Fig. 1. FTIR spectra of specimens **(a)** without alkali treatment and **(b)** with alkali treatment

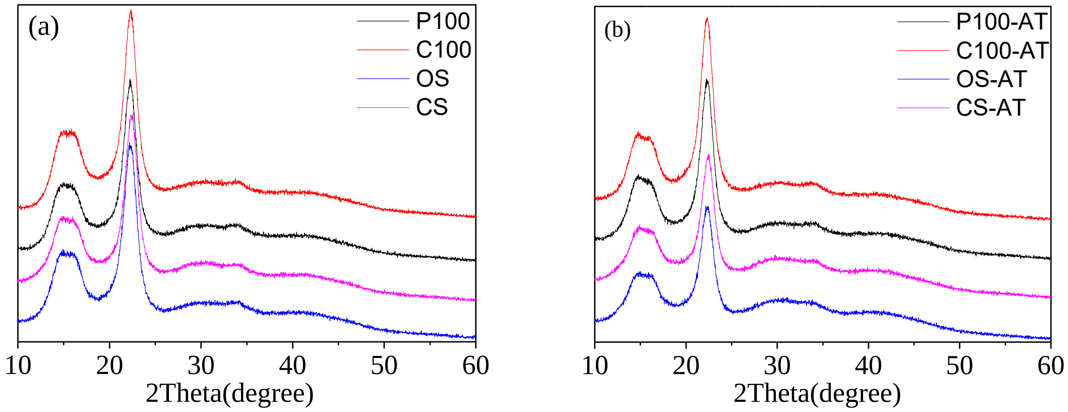

Fig 2. XRD patterns of specimens **(a)** without alkali treatment and **(b)** with alkali treatment

As indicated in Fig. 2, all XRD patterns showed the typical diffraction peaks of cellulose at $2\theta = 15.1°$, $16.4°$, and $22.6°$ due to the (1 -1 0), (1 1 0), and (2 0 0) planes of cellulose I, respectively. Except for the variations in diffraction intensity of the observed diffraction peaks, negligible changes were observed in the XRD patterns. Thus, the crystal form of cellulose did not vary during the treatments. However, the CI of CS increased in comparison with OS. With the incorporation of Lewis bases, the CI of specimens exhibited further increases. The CI of all the specimens decreased after further alkali treatment, while P100 and C100 showed a smaller decrease in CI than those of OS and CS. This result demonstrates that the incorporation of Lewis base in primary HTLW treatment was beneficial for maintaining the CI during further alkali treatment process. In fact, short-chain cellulose exists in the untreated pulps, and it could be removed during HTLW treatment process. On the other hand, short-chain cellulose is generated due to the hydrolysis effect of HTLW on cellulose during HTLW treatment process. With the incorporation of Lewis base, the amount of short-chain cellulose generated by the degradation of cellulose was decreased. Thus, the retention in CI of cellulose after alkali treatment explains the variation in cellulose during Lewis base-enhanced HTLW.

Table 5. Effect of Lewis Base-enhanced HTLW on the Crystallinity Indices (CI) of Different Lewis Bases

Specimens	CI before Alkali Treatment	CI after Alkali Treatment
OS	0.696	0.611
CS	0.703	0.622
P100	0.713	0.694
C100	0.724	0.719

Proposed Mechanism of HTLW Treatment

With elevated temperature, the pH value of water decreased gradually. Hydrolysis of carbohydrates occurred in the samples. Normally, hemicellulose is more sensitive to H^+ than cellulose. When the reaction proceeded to a certain degree, the degradation products of hemicellulose accumulated in the reaction mixture. Evidently, the accumulation of degraded products inhibited the further degradation of hemicellulose and resulted in the degradation of cellulose. When a Lewis base was added into the reaction mixture, the degraded products of hemicellulose might react with these bases and be further converted. Hence, hemicellulose could be further degraded. Accordingly, the degradation of cellulose was mitigated.

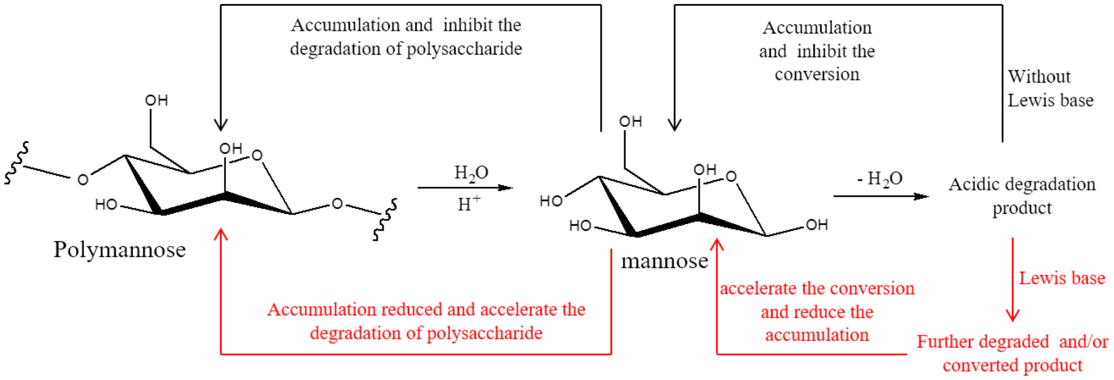

Fig. 3. Schematic representation of proposed mechanism (polymannose as a representation)

CONCLUSIONS

1. Cellulose was purified by high temperature liquid water (HTLW) and Lewis base-enhanced HLTW treatment. The incorporation of Lewis base favored cellulose purification and somewhat prevented its degradation.
2. No variation in chemical and crystal structure occurred during the treatment. However, the absorption peaks due to stretch vibrations of -CHO groups were strengthened after treatments, which was attributed to the decreased degree of polymerization (DP). Furthermore, the incorporation of Lewis base in primary HTLW treatment reduced the

decrease in the crystalline index (CI) of cellulose during the later alkali treatment process.

3. Due to the buffering effect of Lewis bases during the treatment, degraded products of carbohydrate might react with these bases and be further converted. In this case, hemicellulose was further degraded, while cellulose was not.

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