ALKALI EXTRACTION OF HEMICELLULOSE FROM DEPITHED CORN STOVER AND EFFECTS ON SODA-AQ PULPING

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A biorefinery using the process of hemicellulose pre-extraction and subsequent pulping provides a promising way for the utilization of straw biomass and resolution of problems related to silicon. In this work, hemicellulose was extracted from depithed corn stover with sodium hydroxide solution before soda-AQ pulping. Components of the extracts were quantified by ion chromatography. The parameters (alkali concentration and temperature) affecting hemicellulose pre-extraction were optimized. The main constituent of hemicellulose in corn stover was xylan, which accounted for 18.1% of the depithed raw material. More than 90% of the xylan can be extracted under the optimal conditions: NaOH concentration of 10%, temperature of 75ºC, and time of 2h. Solid fractions after extraction were subjected to soda-AQ pulping. In comparison with control pulp obtained without extraction, it was found that alkali pre-extraction could improve the brightness and decrease kappa number of the subsequent pulp, causing a slight loss of yield, viscosity, density, and burst strength, but an obvious improvement of tear strength. Moreover, the silicon content was decreased by 79.8% when the extraction conditions were set at 75 ºC with alkali concentration of 8%, suggesting that pre-extraction of hemicellulose is a potential way to solve silicon problems associated with alkaline pulping of stover.

Keywords: Corn stover; Alkali pre-extraction; Hemicellulose; Silica removal; Soda-AQ pulping

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INTRODUCTION

Lignocellulosic biomass has been gaining increasing attention recent years owing to its great potential as sustainable feedstock for the production of biofuels and chemicals, a system for which the term biorefinery has been applied (Kamm 2004). Since there is a great risk of competition for raw materials with the pulping industry, the concept of an Integrated Forest Products Biorefinery (IFBR) was developed, suggesting a pre-extraction of hemicellulose prior to pulping (van Heiningen 2006). During kraft pulping, much of the hemicellulose, along with most of the lignin, is dissolved into the pulping liquor, and the mixture is finally burned in an alkali recovery system to produce steam and electricity. Considering that the heat value of hemicellulose is much lower than that of lignin (van Heiningen 2006), burning is not a good way to make full use of hemicellulose. Undergoing an IFBR process, the hemicellulose polysaccharides can be pre-extracted to produce ethanol or modified to manufacture advanced materials. Such approaches have significant potential to provide additional income for pulp or paper mills.

Several studies have focused on pre-extraction of hemicellulose using different methods of wood treatment, in combination with pulping. Mendes et al. (2009) performed an auto or acid-catalysed pre-hydrolysis treatment of eucalyptus before kraft pulping. The extracted hemicellulose polysaccharides could be further fermented to produce ethanol; meanwhile, the bleaching requirements and brightness reversion of pulp were found to be significantly decreased. Aldajani and Tschirner (2008) reported NaOH extraction of populus wood before kraft pulping. When the same yield and high quality of pulp were maintained, about 20%-25% of the hemicellulose can be recovered. Yoon et al. (2008) developed a hot-water pre-extraction technique with subsequent kraft pulping for IFBR of softwood, and over 40 kg hemicellulose per ton of aspen chips was extracted at 90^{o}C using 1.67mol/L NaOH, while yielding the same amount of pulp compared with the control cook.

Usually, hemicellulose exhibits higher solubility in alkaline solutions than in acidic ones with less degradation to furfural substances. Also, alkali pre-extraction generally requires much milder conditions of temperature, pressure, and chemical dosage than acidic conditions. Furthermore, no pH adjustment or water-washing is needed for subsequent alkaline (soda or kraft) pulping. When applied to non-wood biomass, an additional potential advantage is that the silicon problem, which refers to the increase in viscosity of pulping liquor due to dissolved silicon and formation of $Na_2O \cdot nSiO_2$, can be overcome. The IFBR process of woody biomass, such as eucalyptus, aspen, loblolly pine, etc., has been reported (Mendes et al. 2009; Aldajani and Tschirner 2008; Yoon et al. 2008). However, up to now, non-wood biomass materials with high content of hemicellulose such as wheat straw (Sun et al. 2000), corn stover (Gáspár et al. 2007), and sugarcane bagasse (Brienzo et al. 2009; Sun et al. 2004), have only been studied for hemicellulose extraction. To the knowledge of the authors, little work has focused on the subsequent pulping process using the pre-extracted biomass.

Corn stover is abundant in China, the US, and many other countries of the world, but this potential source of fibers has not been fully utilized, especially as papermaking raw materials, because of the significant amount of pith in it. The pith is mainly composed of carbohydrate reserves (oligosaccharides and polysaccharides containing arabinose, xylose, mannose, galactose, and glucose) which tend to absorb pulping chemicals and thus can be dissolved, leading to high chemical consumption and low yields; furthermore, the fine nature of residual pith after pulping significantly reduces the drainage rate of the resulting pulps, making washing and dewatering difficult. Finally, it has been noted that pith cells, if left in the final pulp, can result in reduced sheet opacity (Byrd 2005). Given these disadvantages, depithed corn stover was used in this study for hemicellulose extraction and soda-AQ (anthraquinone) pulping, noting that the pith from the corn stover can be used as animal feed. The yield and composition of hemicellulose polysaccharides were measured to investigate the effect of extraction temperature and chemical charge. The pulp properties of soda-AQ pulp with or without hydrogen peroxide bleaching as well as silicon content of pulping liquor were also examined to study the feasibility of an Integrated Forest Products Biorefinery for corn stover.

EXPERIMENTAL

Materials

Depithed corn stover was obtained from Shandong province, China, and was cut into pieces of 2 cm length. Before extraction, the material was washed with tap water to remove contaminants, and then air-dried (moisture content around 8%) and stored at room temperature.

Pre-Extraction of Hemicellulose

Extraction of hemicellulose from corn stover with alkali (NaOH) was performed in a 15-liter electrically heated and thermostatically controlled rotary digester (ZQS_1, Shaanxi University of Technology Machinery Factory, China). The solids loading of the feedstock was 300g (oven-dried weight), and the mass ratio of liquid to solid was 5:1. The alkali concentration and extraction temperature were varied within a range of 2% to 10% and 65°C to 95°C, respectively. The time to temperature and time at temperature were always set as 10 min and 120 min, respectively. After extraction, the residual solids and liquor were separated using a 200 mesh Nylon filter. The spent liquor was collected and stored at 4°C for further analysis, while the solid fractions were thoroughly washed with tap water and then air-dried for subsequent pulping.

Soda-AQ Pulping

The soda-AQ pulping was carried out in the same lab-scale batch digester for pre-extraction as described above. The cooking conditions were: 12% effective alkali (as NaOH), 0.05% AQ charge, liquor to solids ratio 4:1, time to maximum temperature 150 °C, 120 min, and time at 150 °C, 60 min.

After cooking, the pulp and liquor were separated by filtering through a 200 mesh Nylon filter. The pulp was extensively washed with deionized water to remove residual chemicals and other contaminants. All pulp samples were stored in moist form at 4 ºC before analyzing or bleaching. The pulping liquor was also stored at 4 °C for further analysis.

Peroxide Bleaching

In our previous work it was found that corn stover pulp was easy to bleach with hydrogen peroxide to achieve high brightness. The bleaching conditions in this work were as follows: Chelating treatment before hydrogen peroxide bleaching (Q): 10% (w/v) pulp consistency, 0.3% (w/w) EDTA, temperature 60°C, time 60min; alkaline peroxide bleaching (P): 10% pulp consistency, chemical dosage of 3% H_2O_2, 2% NaOH, and 0.15% $MgSO_4$. The pulp was mixed with bleaching agents and then maintained at a temperature of 90 °C for 4h.

Chemical Composition of Corn Stover

Ground particles in the range between 40 and 60 mesh were used for the determination of corn stover chemical composition. Moisture content was determined by drying a representative sample at 105°C in an oven overnight. Ash content and benzene/ethanol extractives were determined according to TAPPI standard methods T211 om-02 and T6 wd-73. Klason lignin, was determined according to a method by Effland (1977), while the acid soluble lignin content was determined by TAPPI method 250.

Before analysis of the monosaccharide content in the raw material, a two-step hydrolysis with 72% and 4% sulfuric acid, respectively, was done by the standard procedure recommended by NREL (Davis 1998). Then the hydrolysate was diluted and filtered through a 0.22μm syringe filter and analyzed by using an ion chromatography 3000 (Dionex Company, USA) with an electrochemical detector and a PA20 column.

Analysis of Polysaccharides in the Extract

The determination of the saccharides in the alkaline extraction liquor was also done with the IC3000 system. The liquor was adjusted to pH 5~6 using 6 mol/L HCl, and then hydrolyzed by 4% sulfuric acid at 121°C for 1h. The filtering and dilution steps were also done before injection into the IC system (Tunc and van Heiningen 2008a).

As can be expected for most non-wood hemicellulose, the main component of corn stover hemicellulose is xylan (Bastawde 1992), so the yield of xylan was used to estimate alkali extraction efficiency of hemicellulose in the experiment,

$$Y = \frac{c \times 10^{-3} \times n \times v}{m \times 18.1\%} \times \frac{132}{150} \times 100\% \quad (1)$$

where Y is the extraction yield of xylan (%); c is the concentration of xylose measured by IC (mg/L); n is dilution times; v is total volume of liquid in the extraction system (L); m is the o.d. weight of the corn stover (g), 132/150 is the stoichiometric factor between xylose and xylan, and 18.1% is the xylan content of the raw material.

Determination of Silicon Content

The silicon content dissolved in the extraction spent liquor was measured by silicomolybdate blue spectrophotometry (Tong et al. 2005). Silicic acid mixed with ammonium molybdate can form the silicomolybdate yellow complex compound under acidic conditions; reducing agent was used to reduce silicomolybdate yellow to silicomolybdate blue. A certain volume of 1g/L standard silicon solution was taken to mix with 10 mL 25%(v/v) nitric acid in the plastic beaker. Then 10mL of 10%(w/v) ammonium molybdate solution was added to the mixture. After uniform mixing of the solutions, the beaker was maintained in the water bath for 12 min under 30°C, then 40 mL 5%(w/v) oxalic acid was put into the beaker, 40 mL 4.5%(w/v) ammonium ferrous sulphate was added into the beaker successively, the mixture in the beaker was then put into a 250mL volumetric flask and made to constant volume, and the silica content was measured with an Aligent 8453 UV Spectrophotometer by using water as blank reagent.

Characterization of Pulps

The NaOH-AQ pulps with or without pre-extraction were characterized. The kappa number, brightness, viscosity, yield, and residual alkali were measured according to the standard testing methods. Refining of the pulps was done on a PFI device. Handsheets were prepared from the refined pulp according to TAPPI standard method T205. Physical properties, including density, breaking length, burst index, and tear index, of bleached pulps were characterized using TAPPI standard methods T494 cm-01, T403 om-02, and T414 om-04, respectively. All data reported were the mean value of at least 4 independent measurements.

RESULTS AND DISCUSSION

Effects of Temperature and Alkali Charge on the Yield of Hemicellulose

The chemical compositions of raw corn stover biomass are listed in Table 1. The main composition of the hemicellulose polysaccharides was xylan, which accounted for 18.1% of the o.d. weight of the raw materials. The content of arabinan was much lower (1.3%), while galactan, mannan, and galacturonic acid were undetectable. Therefore, hemicellulose recovery was calculated on the basis of xylan.

Table 1. Chemical Composition of Corn Stover Biomass (% on original material)

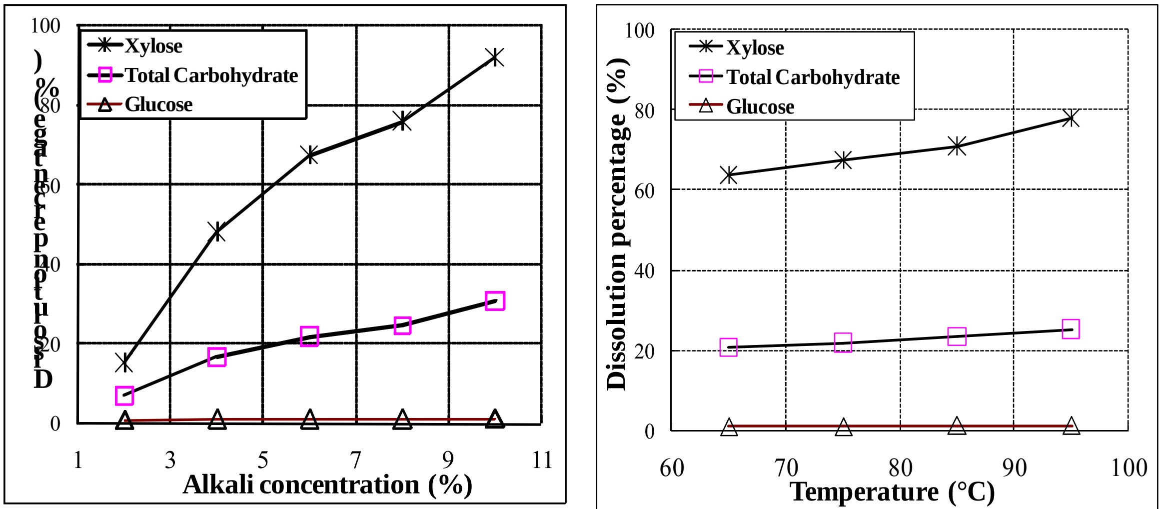
Component	Glucan	Xylan	Arabinan	Klason lignin	Acid soluble lignin	Benzene/ethanol extractives	Ash
Weight percent	50.7	18.1	1.3	15.5	1.4	7.4	3.8

The effects of initial alkali concentration (varied from 2% to 10%) on the dissolution of polysaccharides are shown in Fig. 1a. The data showed that the dissolution percentage of glucan was less than 1.3%, indicating that nearly all the loss of total carbohydrate (15%-30%) was due to the dissolution of hemicellulose. The dissolution of xylose was increased significantly with the increase of alkali concentration. When 10% of NaOH was applied, over 90% of the xylose could be extracted from solid substrates. As reported by Sun et al. (2001) 89.3% of the original hemicellulose can be extracted from partially delignified ground fast-growing poplar wood using 8.5% NaOH at 20°C for 16h. These results suggested that a considerable amount of hemicellulose could be extracted at low temperature despite the difference of raw materials.

The yield of hemicellulose from alkali extraction at various temperatures was also studied. The results (Fig. 1b) indicated that the yield of hemicellulose was improved by only 15%, meaning that it increased from 68% to 78% when the temperature was raised from 65°C to 95°C. Meanwhile, the dissolution of glucan was lower than 1.5%. Figure 1b also suggests that a considerable amount of hemicellulose could be obtained at even low temperature (<65°C). However, the objective of alkali pre-extraction is not only to yield hemicellulose but also to disrupt the cell-wall for improving pulping performance by dissolving lignin and silicon, hydrolysing uronic acid and acetyl groups, and swelling the cellulose. For an effective IFBR process, conditions with higher alkali concentration and temperature are more frequently used in order to minimize the time required for a high yield of hemicellulose.

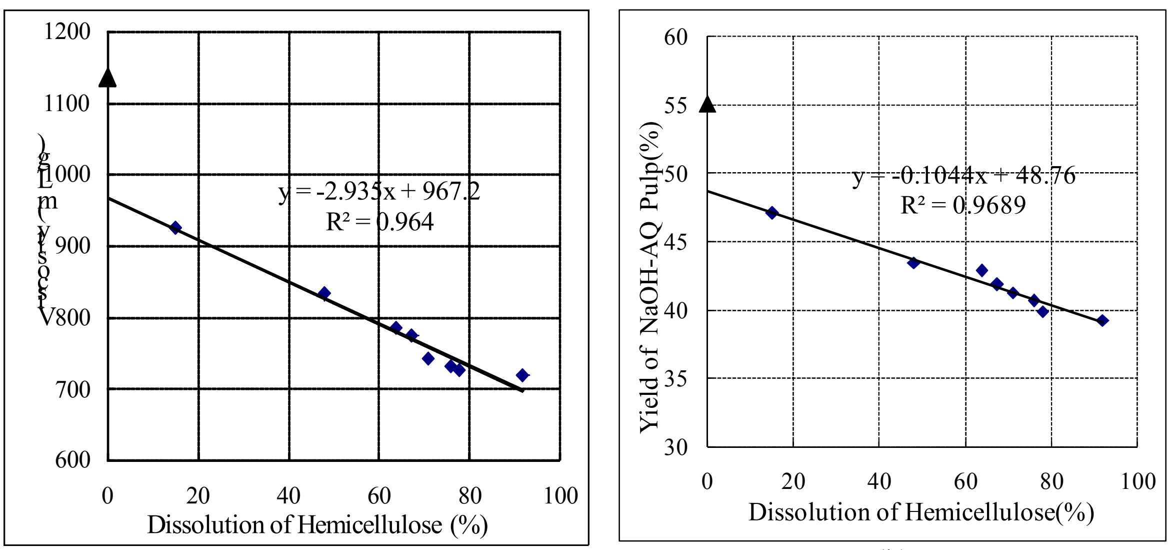
Effect of Alkali Pre-Extraction on Soda-AQ Pulping and QP Bleaching

Pre-extraction of hemicellulose from corn stover could cause a significant dissolution of carbohydrate, which may decrease the viscosity of subsequent NaOH-AQ pulp. Figure 2a shows that viscosity decreased linearly with increasing dissolution of hemicellulose. It could be seen that when the dissolution of hemicellulose increased from 15% to 90%, the viscosity of the pulp decreased from 924mL/g to 720 mL/g.



(a) (b)

Figure 1. Effects of alkali charge and extraction temperature on the dissolution yield of carbohydrate from corn stover: (a) Extraction temperature 75°C, time 2h; (b) Alkali charge 6%, time 2h.



(a) (b)

Figure 2. Effects of hemicellulose dissolution on viscosity (a) and yield (b) of subsequent NaOH-AQ pulp. The triangle symbol on the y-axis in Fig. 2 (a) represents the viscosity of the control pulp, 1135mL/g; while in Fig. 2 (b) it represents the yield of the control pulp, 55.1%.

A similar linear decreasing trend of pulping yield (calculated based on raw materials) with the increase of dissolution of hemicellulose was also observed (Fig. 2b). The dissolution of hemicellulose involved hydrolysis of ester and ether bonds that link the hemicellulose to lignin (Sjöström 1993), so lignin is subsequently much easier to dissolve during pulping of the pre-extracted material. This was confirmed by the kappa number and brightness of pulps (Table 2). The kappa number decreased significantly by 63%, even when 15% of hemicellulose was dissolved, compared with the control pulp. Dissolution of hemicellulose from 15% to 90% resulted in a decrease in the kappa number of subsequent NaOH-AQ pulp from 8.2 to 5.9. Table 2 also indicates that a more considerable amount of residual alkali was measured in the pulping liquor from pre-extracted lignocellulose than that from raw biomass. The reason was probably due to partial removal of lignin, uronic acid, and acetyl groups from corn stover lignocellulose via hemicellulose pre-extraction, thus reducing the demand for alkali in subsequent pulping. The results also suggest that an IFBR process combined hemicellulose pre-extraction with NaOH-AQ pulping can be used to substitute the process of extended delignification for a lower kappa number of pulp.

Table 2. Effect of Hemicellulose Pre-extraction on NaOH-AQ Pulp Properties

Pre-extraction		Kappa Number	Residual alkali (g/L)	Brightness (%ISO)	Density* (g/cm^3)	Breaking Length* (km)	Tear Index* ($mN \cdot m^2/g$)	Burst Index* ($KPa \cdot m^2/g$)
Alkali Concentration (%)	Temp. (°C)							
–	–	21.9	1.7	28	0.78	9.54	8.62	6.78
2	75	8.2	4.2	35.5	0.73	8.163	9.52	5.26
4	75	7.9	5.6	37.6	0.68	7.739	9.94	4.97
6	75	7.1	7.2	40	0.68	7.346	10.98	4.69
8	75	6.7	7.7	41.5	0.64	6.488	11.68	4.25
10	75	6.5	9.7	42.8	0.62	5.509	11.98	3.55
6	65	7.8	12.8	38.3	0.68	7.612	10.58	4.78
6	75	7.1	7.2	40	0.68	7.346	10.98	4.69
6	85	6.8	6.7	41.5	0.65	6.158	11.26	3.95
6	95	5.9	6.6	46.4	0.64	5.988	11.78	3.47

* Beating degree 42°SR.

Physical properties of the NaOH-AQ pulp and their corresponding QP bleached pulp are shown in Tables 2 and 3. High hemicellulose content is helpful for the bonding of fibers and can improve the bonding strength of the paper. From both Table 2 and Table 3 it could be found that as the extraction condition intensified, the density, burst index, and breaking length of both unbleached and bleached pulps were all decreased, as compared with the control sample. The main composition of corn stover hemicellulose is xylan, as confirmed by ICS. Xylan is a multi-hydroxyl compound. The refining process can increase the fibers swelling, hydration, and fibrillation degree and improve its flexibility, so bonding strength of the paper increases and physical properties are improved (Wang 2005). The reason for the decrease of the breaking length, burst index, and density of the paper was also attributed to the reduced xylose content from hemicellulose extracted material.

Table 3. Effect of Hemicellulose Extraction on QP Bleaching of the NaOH-AQ Pulp

Pre-extraction		Brightness (%ISO)	Density* (g/cm^3)	Breaking Length* (km)	Burst Index* (KPa·m^2/g)	Tear Index* (mN·m^2/g)
Alkali Concentration (%)	Temp. (°C)					
–	–	81.6	0.76	9.08	6.05	9.4
2	75	82	0.71	7.835	4.99	10.9
4	75	83.3	0.66	6.312	4.86	11.18
6	75	84.7	0.64	5.617	4.53	11.54
8	75	85.6	0.61	5.134	3.82	11.78
10	75	86.6	0.61	5.268	3.45	11.1
6	65	84	0.66	6.104	4.81	12.06
6	75	84.7	0.64	5.617	4.53	11.54
6	85	85.8	0.62	5.317	3.64	11.44
6	95	86.9	0.63	5.528	3.14	10.24

* Beating degree 42^{o}SR.

The effect of hemicellulose extraction on the tear index was different from the other strength properties. With the strong extraction conditions applied, tear index of the QP bleached handsheet increased first and reached the maximum when the alkali concentration was 8%. Tear index of the unbleached pulp was also increased, but lower than that of the bleached one. Tear index of all the extracted pulps was higher than that of the control. The result was in accordance with a previous study by Wang (2005).

It was found that after extraction, the pulp was much easier to be bleached than the control. Under the conditions used, brightness of the control sample was 81.6% ISO, while the brightness of the bleached pulp with 10% NaOH extraction before pulping reached 85.6% ISO.

Effect of Pre-extraction on Silicon Content in Black Liquor

The effects of pre-extraction conditions (alkali concentration and temperature) on silicon content in NaOH-AQ pulping black liquor are shown in Fig. 3. The removal percentage of silicon was significantly increased with the alkali concentration. When pre-extraction was performed at 75°C with 10% alkali concentration, the silicon content in black liquor was reduced by over 80%. The reason could be mainly ascribed to the pH change before and after the extraction. It has been reported that only if the pH value reaches 14, the majority of SiO_2 in the black liquor is in the form of SiO_3^{2-}, which is much easier dissolved in water (Tong et al. 2005). So higher alkali concentration promoted the dissolution of silicon in water during the extraction process.

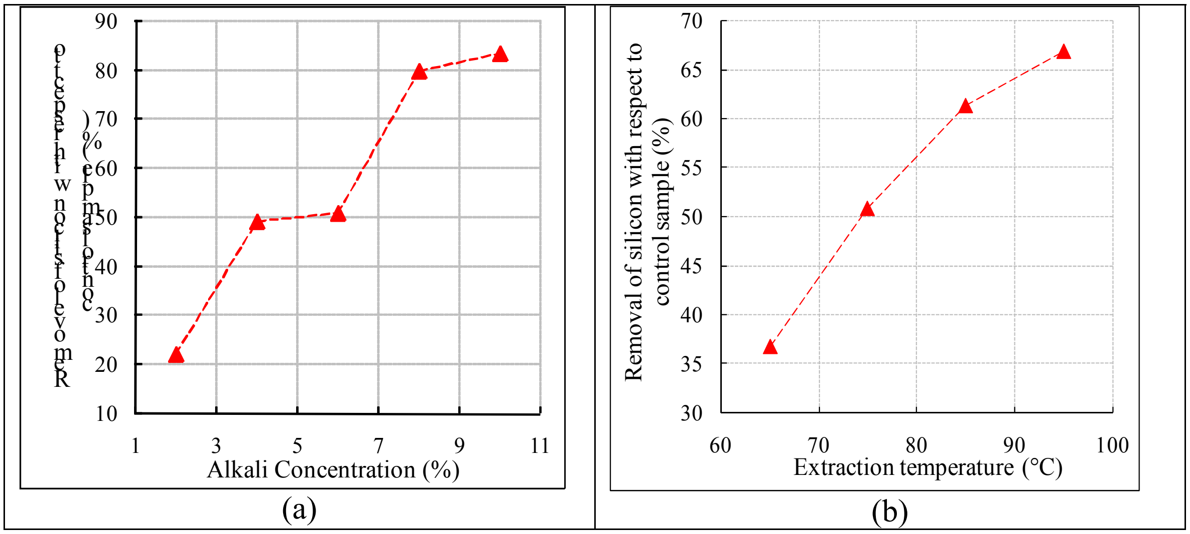


Figure 3. Effects of pre-extraction of hemicellulose on the removal of silicon from subsequent pulping liquor

The increase of extraction temperature could also promote the removal of silicon. An average rate of decrease of silicon can be obtained from the slope of the curve, indicating that the silicon content was decreased by 7.5% with a 10°C increase of temperature.

CONCLUSIONS

Sodium hydroxide was found to be an effective agent for the extraction of hemicellulose from corn stover. When extraction temperature was 75°C and alkali concentration was 10%, more than 90% of the original hemicellulose was dissolved. Combined with a subsequent NaOH-AQ pulping, alkali pre-extraction can significantly reduce the kappa number of the subsequent pulp. A loss of viscosity as well as breaking length and burst index was observed as a result of the dissolution of hemicellulose, while tear index was obviously improved. Moreover, alkali extraction of corn stover hemicellulose had important effect on silicon content in black liquor, achieving an over 80% reduction of the total silicon content in pulping liquor under conditions used.

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