PRECIPITATION OF LIGNOSULPHONATES FROM SPORL LIQUID BY CALCIUM HYDROXIDE TREATMENT

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Precipitation of lignosulphonates from the liquor for sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) by addition of $Ca(OH)_2$ was investigated in this work. The experiment was conducted in a reaction temperature range of 20 to 75^oC for 90 minutes with $Ca(OH)_2$ charge varying from 20 to 90 g/L and a range of liquid enrichment ratio of 1 to 5. It was found that increased $Ca(OH)_2$ charge, duration time, reaction temperature, and liquor concentration each tended to improve lignosulphonates precipitation, but tended to hurt fermentable sugars conservation. Application of $Ca(OH)_2$ 20 g/L to SPORL liquid without enrichment at 30^oC for 90 minutes could be an optimal condition. Under this condition, 25.95% of the lignosulphonates was precipitated for further utilization, while calculated amounts of 106.46% of glucose and 60.25% of xylose were conserved for further fermentation.

Keywords: SPORL pretreatment; Spent liquor; Lignosulphonates precipitation; Fermentable sugars; $Ca(OH)_2$

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INTRODUCTION

Sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) was recently developed and is new to the biomass research community (Yang et al. 2011; Zhu et al. 2010, 2009; Wang et al. 2009). High enzymatic hydrolysis glucose yield, high removal of hemicellulose as well as lignin, and low amounts of fermentation inhibitors can be achieved in the SPORL pretreatment (Zhu et al. 2010). Furthermore, the existing mature equipment, technology, and infrastructure that have long been used in the pulp and paper industry can be fully used during SPORL treatment (Liu et al. 2011; Yang et al. 2011; Wang et al. 2009).

During the SPORL pretreatment, lignosulphonates, as well as fermentable sugars, which are mainly glucose and xylose, are released into the SPORL liquor phase. Lignosulphonates obtained from SPORL liquor phase have excellent dispersing properties and therefore they can be exploited as superplasticizers in concrete to maintain adequate fluidity (Yasuyuki 2005). As for the main fermentable sugars, glucose fermentation can produce fuels (e.g., ethanol) (Safi et al. 1986), and xylose fermentation can yield ethanol and process xylitol sugar substitute (Herskowitz 1985; Miroslav and Nancy 2004; Toivari 2004). Studies have been carried out for effective utilization of these resources. In industry, precipitation of lignosulphonates from spent liquor generated during sulfite pulping can be achieved by addition of lime to liquor phase to form the insoluble Calcium lignosulphonate compound:

$$(\text{Lignin–SO}_3)_2\text{Ca} + \text{Ca(OH)}_2 \rightarrow (\text{Lignin–SO}_3)_2\text{Ca} \bullet \text{Ca(OH)}_2 \downarrow \qquad (1)$$

It has been shown that utilization of a membrane process such as ultrafiltration, nanofiltration, or reverse osmosis can also obtain lignosulphonates from spent liquor (Bhattacharya 2005). Several reports have been published concerning simultaneous saccharification and fermentation processes (Gauss et al. 1976; Hamelinck et al. 2005; Wu et al. 1998), and simultaneous conversion of D-glucose and D-xylose into ethanol has been achieved by utilizing recombinant saccharomyces yeast (Lawford and Rousseau 1998). In addition, the detoxification of dilute-acid hydrolyzate by application of $Ca(OH)_2$ (overliming) and its effect on fermentation inhibitors removal and on fermentability of the detoxified hydrolyzates was also investigated (Millati 2002; Purwadi 2000, 2004). Nevertheless, limited studies have focused on the combination of lignosulphonates and fermentable sugars analysis. Accordingly, it is an object of the present work to find a combination between soluble lignin precipitation and fermentable sugars conservation in the SPORL liquor phase by $Ca(OH)_2$ treatment in order to utilize this biomass resource.

EXPERIMENTAL

SPORL Liquid

SPORL liquid was produced by SPORL pretreatment, with wheat straw used as the feed material. The pretreatment liquor was prepared by mixing sodium bisulfite with sulphuric acid. The ratio of pretreatment liquor to wheat straw (o.d.) was 4:1(v/w), and the pretreatment under the optimal condition of bisulfite charge of 3% (w/w) and sulphuric acid charge of 1.5% (w/w) on the untreated o.d. wheat straw at 180°C for 30 minutes. The characteristics of required constituents in the SPORL liquor phase are shown in Table 1.

Table 1. Constituents of Liquid from SPORL Pretreatment with 1.5% Sulfuric Acid Charges at 180°C for 30 minutes with 3% Sodium Bisulfite Charge (on o.d. untreated wood)

Lignosulphonates (g/L)	Fermentable sugars (g/L)		Total amount of soluble sugars in the liquor phase(g/L)		Solids content (%)	Liquor phase pH
	Glucose	Pentose	Glucose	Pentose		
8.51	1.6	26.44	2.25	29.14	5.51	3.11

* The solid-to-liquor ratio was 1:4 for every trial.

Liquid Enrichment

Desired liquid concentrations were achieved by using a rotary vacuum evaporator at 40°C and 50 rpm (RE-52AA, Shanghai Applied Chemical Instrument Ltd. China). The results for amounts of lignosulphonates and fermentable sugars content under different liquid concentration are shown in Table 2.

Table 2. The Content of Lignosulphonates and Fermentable Sugars under Different Liquid Concentrations

Liquid concentration	Lignosulphonates (g/L)	Fermentable sugars (g/L)	
		Glucose	Pentose
Untreated	8.51	1.6	26.44
2 times enrichment	18.04	3.0	49.26
3 times enrichment	30.58	4.5	75.97
4 times enrichment	41.08	6.8	110.22
5 times enrichment	49.53	11.7	147.78

Liquid Treatment by Addition of $Ca(OH)_2$

All experiments were conducted in 250 mL beakers. First, 200 mL of SPORL liquid was added to a beaker. Then, calcium hydroxide, at the desired concentration in the range of 20 to 90g/L, was added to form insoluble calcium lignosulphonates. The water bath was electrically heated to the desired reaction temperatures in the range of 20 to 75°C. The loaded beaker was then placed into a magnetic stirrer (DF – 101S, Shanghai Applied Chemical Instrument Ltd. China) inside the water bath. The stirring speed was 25 rpm to ensure good mixing of the $Ca(OH)_2$ with SPORL liquid inside the beaker. After a preset time was reached, the insoluble calcium lignosulphonates and supernatant were separated through centrifugation using a centrifuge (KH10 – 2.4A, Beijing Instrument Ltd. China). The supernatant was saved to determine the concentration of lignosulphonates and fermentable sugars.

Determination of Lignosulphonates and Fermentable Sugars

Concentrations of lignosulphonates were determined following the procedure of GB/T standard NO. 2677.8-1994 with the use of an ultraviolet spectrophotometer (756PC, Shanghai Optical Spectrum Instrument Ltd. China). Wavelength accuracy and photometric accuracy of the ultraviolet spectrophotometer were about 0.5 nm and ±0.5 percent T, respectively. Insoluble calcium lignosulphonates yields were calculated based on measured lignosulphonates concentration in the liquor phase after $Ca(OH)_2$ treatment, and then the difference relative to the initial lignosulphonates concentration was calculated. The content of glucose was determined directly with a commercial glucose analyzer (SBA 40-D glucose analyzer, Jinan, Shandong, China). Relative error is about 1%, based on manufacturer specifications. The concentration of xylose was analyzed according to the Douglas colorimetric method (Yu et al. 2007). The total amount of glucose and xylose in the SPORL liquid were determined as described by Sluiter et al. (2008). The results are summarized in Table 1.

Solids Content

The solids content of spent liquor was gravimetrically determined by drying samples at 105°C to constant weight.

RESULTS AND DISCUSSION

Effect of $Ca(OH)_2$ Charge on Lignosulphonates Precipitation and Fermentable Sugars Conservation

In this study, $Ca(OH)_2$ was added to SPORL liquor phase at 30°C with a duration varying from 0 to 90 minutes. As shown in Fig. 1, the results indicated that an increase in $Ca(OH)_2$ charge would improve lignosulphonates precipitation. 38.03% (percentage of initial concentration) of lignosulphonates was precipitated at a 90 g/L $Ca(OH)_2$ charge, while only 10.6% (percentage of initial concentration) of lignosulphonates was precipitated at a 10 g/L $Ca(OH)_2$ charge. This was because increased $Ca(OH)_2$ charge would improve formation of more insoluble calcium lignosulphonates in the liquid. On the other hand, reduced $Ca(OH)_2$ charge favored fermentable sugars conservation. The concentration of both glucose and xylose decreased by 58.96% and 57.68% (percentage of initial concentration), respectively, at a $Ca(OH)_2$ charge of 90 g/L, while 106.46% glucose and 60.25% xylose (percentage of initial concentration) would be conserved when the $Ca(OH)_2$ charge was reduced to 20 g/L. The content of fermentable sugars seriously declined when the $Ca(OH)_2$ charge increased, because of more monosaccharides (glucose plus xylose) were degraded by the alkaline conditions, producing numerous saccharinic acids (Yang and Montgomery 1996). The content of glucose increased under 20 g/L $Ca(OH)_2$ treatment, mainly because compared to degradation of glucose, alkaline hydrolysis of glucan held the dominant position.

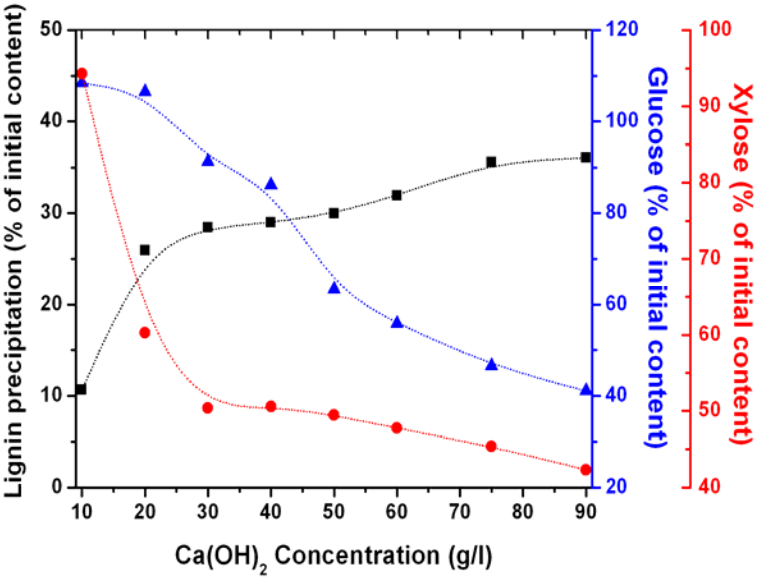

Fig. 1. Effect of $Ca(OH)_2$ charge on lignosulphonates precipitation and fermentable sugars conservation

It is noteworthy that excluding 10 g/L $Ca(OH)_2$ charge, where only 10.6% soluble lignin was precipitated, increased $Ca(OH)_2$ charge showed little influence on lignosulphonates precipitation but seriously hurt fermentable sugars conservation (Fig. 1). Therefore, a $Ca(OH)_2$ charge of 20 g/L is probably optimal for the combination of lignosulphonates precipitation and fermentable sugars conservation.

Time Courses of Lignosulphonates and Fermentable Sugars Concentration after Application of $Ca(OH)_2$ to Spent Liquor

In this study, 20 g/L of $Ca(OH)_2$ was added to SPORL liquid at 30°C with an duration varying from 0 to 90 minutes. The contents in terms of both lignosulphonates and fermentable sugars (glucose and xylose) were affected by duration time. As shown in Fig. 2, there was a general trend of decreased content of lignosulphonates and xylose. After 90 min treatment, the concentration of lignosulphonates decreased from 8.51 g/L to 6.30 g/L, while the content of xylose decreased from 26.44 g/L to 15.93 g/L. However, the glucose concentration began to rise and reached a maximum of 2.25 g/L at 15 minutes and then decreased with extended reaction time. The mainly reason may be that during SPORL pretreatment, a portion of soluble oligosaccharides, as well as monomeric sugars, was released into liquor phase (Table 1). After addition of $Ca(OH)_2$ to SPORL liquid, glucan hydrolysis held the dominant position (compared to alkaline degradation of glucose) during the first 15 min, and more monosaccharides were generated, while alkaline degradation of glucose held the dominant position with extended reaction time, which resulted in decreased content of glucose.

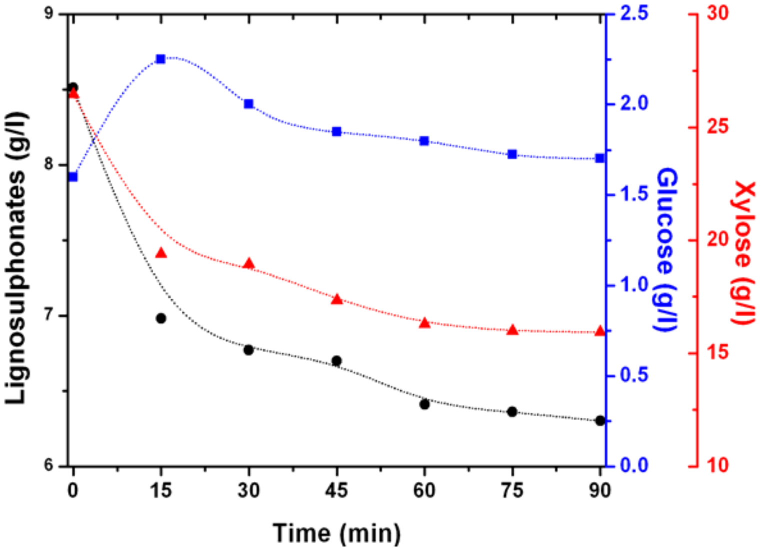

Fig. 2. Time courses of lignosulphonates, glucose, and xylose concentration in the spent liquor

Effect of Reaction Temperature on Lignosulphonates Precipitation and Fermentable Sugars Conservation

In this study, 20g/L $Ca(OH)_2$ was added to SPORL liquid at the reaction temperature in the range of 20 to 75°C for 90 minutes. As was shown in Fig. 3, the results indicated that increased reaction temperature favored precipitation of lignosulphonates.

There was a maximal amount of lignosulphonates precipitation at 75°C, where 35.96 % (percentage of initial concentration) soluble lignin was precipitation. However, $Ca(OH)_2$ treatment under higher reaction temperature would result in serious degradation of fermentable sugars. The concentration of glucose and xylose were decreased to 20.71% and 4.68% (percentage of initial concentration) respectively at 75°C for 90 min, while 106.46% glucose and 60.25% xylose (percentage of initial concentration) would be conserved at 20°C. The observed decrease in concentration of glucose and xylose under high temperatures was probably because of the formation of by-products and thermal decomposition of monosaccharides. It is noteworthy that excluding 20°C, where only 14.45% (percentage of initial concentration) soluble lignin was precipitation, increased reaction temperature beyond 30°C did not further improve lignosulphonates precipitation, but seriously handicapped fermentable sugars conservation. Therefore, a reaction temperature of 30°C is probably optimal to lignosulphonates precipitation and fermentable sugars conservation.

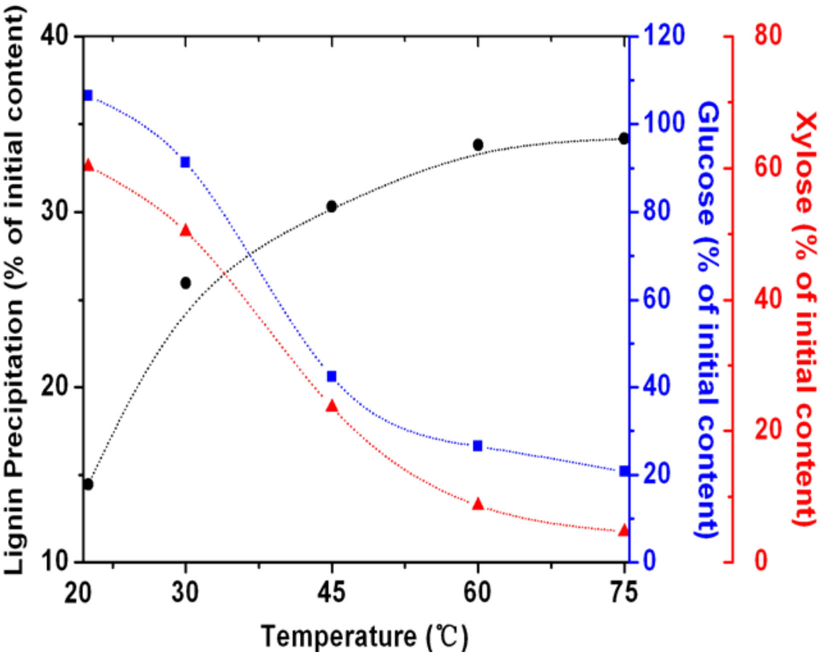

Fig. 3. Effect of reaction temperature on lignosulphonates precipitation and fermentable sugars conservation

Effect of Liquid Concentration on Lignosulphonates Precipitation and Fermentable Sugars Conservation

Figures 4 and 5 reveal how the liquid concentration factor influenced the lignosulphonates precipitation and fermentable sugars conservation. Firstly, SPORL liquid was titrated by $Ca(OH)_2$ and the relationship between the pH value of the spent liquor and $Ca(OH)_2$ concentration is shown in Fig. 4. The pH value of SPORL liquid was not obviously changed when the $Ca(OH)_2$ charge was in the range of 20 to 90 g/L. The result was largely because of the low solubility of $Ca(OH)_2$.

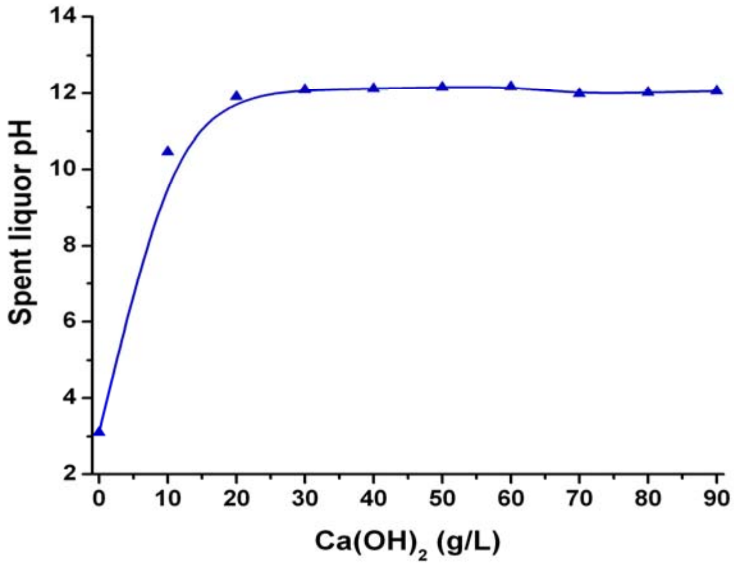

Fig. 4. The relationship between $Ca(OH)_2$ charge and liquid pH at 30°C

In order to maintain the same experimental conditions examined in this study, all the pH value of concentrated SPORL liquid was adjusted to 12 by application of $Ca(OH)_2$, and the reaction temperature was set to 30°C for a period of 90 minutes. As shown in Fig. 5, the results indicated that increased liquid concentration favored precipitation of lignosulphonates. 63.55% (percentage of initial concentration) lignosulphonate was precipitated when using 5-times-concentrated SPORL liquid, while only 25.95% (percentage of initial concentration) lignosulphonate was precipitated when using SPORL liquor without enrichment. Nevertheless, increased liquid concentration hurt fermentable sugars conservation and resulted in serious degradation of fermentable sugars.

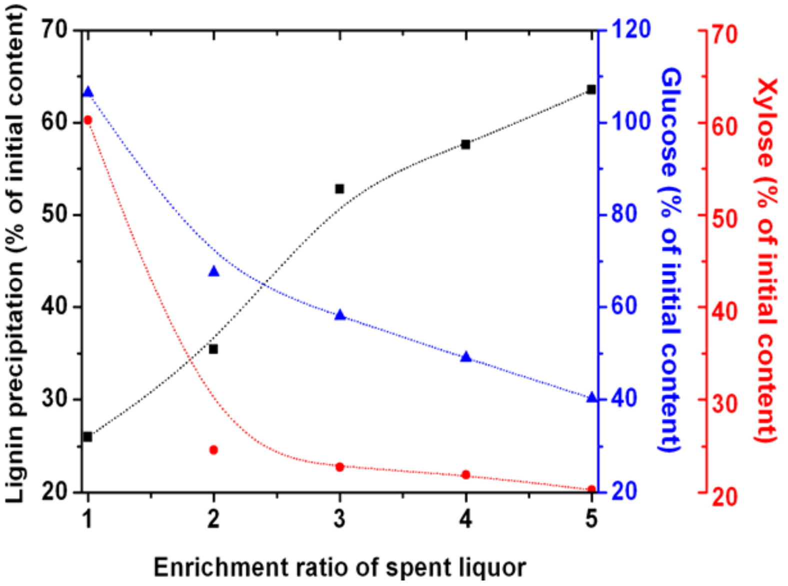

Fig. 5. Effect of spent liquor concentration factor on lignosulphonates precipitation and fermentable sugars conservation

The concentration of both glucose and xylose decreased to 40.26% and 20.3% (percentage of initial concentration), respectively, in the 5-times-concentrated SPORL liquid, while 106.46% glucose and 60.25% xylose (percentage of initial concentration) were conserved when using the selected liquid without enrichment. When the goal is to achieve a combination of lignosulphonates precipitation and fermentable sugars conservation, spent liquor without enrichment is probably the better selection.

Optimal Condition

Taking both lignosulphonates precipitation and fermentable sugars conservation into account, the following ideal condition was selected: application of $Ca(OH)_2$ 20 g/L to SPORL liquid without enrichment at 30°C for a period of 90 minutes. Under this condition, 25.95% (percentage of initial concentration) soluble lignin was precipitated for further utilization while 106.46% glucose and 60.25% xylose (percentage of initial concentration) were conserved for further fermentation.

CONCLUSIONS

1. Increasing $Ca(OH)_2$ charge, duration, temperature, and SPORL liquor concentration each tend to favor precipitation of lignosulphonates, but each hurt fermentable sugars conservation.
2. Taking both lignosulphonates precipitation and fermentable sugars conservation into account, application of $Ca(OH)_2$ 20 g/L to the liquor phase without enrichment at 30°C for 90 minutes could be an optimal condition. Under this process condition, 25.95% (percentage of initial concentration) lignosulphonates were precipitated, while 106.46% glucose and 60.25% xylose (percentage of initial concentration) were conserved for further utilization.

ACKNOWLEDGMENTS

The authors are grateful for the financial support of Tianjin colleges and universities science and technology fund, Grant. No. 20080522, and State Key Lab of Pulp and Paper open fund, South China University of Technology, Grant No. 200924.

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Article submitted: October 27, 2011; Peer review completed: December 10, 2011; Revised version received: January 1, 2012; Accepted: January 7, 2012; Published: January 10, 3012.