NITROGEN FIXATION AND CHELATING PROPERTY OF WHEAT AMMONIUM SULFITE PULPING SPENT LIQUOR

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Nitrogen fixation of wheat straw ammonium sulfite pulping spent liquor and the chelating property of nitrogen-fixed ammonium lignosulfonate were studied. Results showed that free ammonium nitrogen in spent liquor could be fixed by formaldehyde. When the amount of formaldehyde was 10% based on the dry weight of lignosulfonate, 30% of inorganic nitrogen was converted into organic nitrogen, of which 87.4% was ammonium lignosulfonate and 12.6% was urotropine. The proper chelating condition of nitrogen-fixed ammonium lignosulfonate was as follows: pH:3, hydrogen peroxide:10%, $FeSO_4$: 40.9%, and 50 ^{o}C for 30 min. Under this reaction condition, the chelating ratio of Fe^{2+} was measured as 15.1%. Chelation did not result in $Fe(OH)_3$ precipitation under alkaline conditions. Effects of H_2O_2 dosage on the structure of ammonium lignosulfonate were also studied. The content of carboxyl, phenolic hydroxyl, and conjugated carbonyl groups in lignosulfonate that could be chelated with metal ions increased after ammonium lignosulfonate was oxidized. Average molecular weight and distribution were also determined with GPC. Results showed that the proportion of higher molecular weight components increased after oxidation of ammonium lignosulfonate, indicating that oxidative degradation and condensation reaction proceeded during oxidative treatment and condensation was the main reaction. The increase of molecular weight could improve the chelating ability of ammonium lignosulfonate.

Key words: Ammonium lignosulfonate; Oxidation; Chelating reaction; Structure

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INTRODUCTION

The main pollutants in the paper-making industry originate from pulping spent liquor. Therefore to find a way to utilize such liquor is the prime requirement for the success of pulping process. Agricultural utilization of chemically modified sulfite pulping spent liquor can be the avaiable way to produce slow nitrogen releasing fertilizer, phosphate fertilizer activator, nitrogen fertilizer synergist, and seed dressing (Li 2006; Zhu et al. 2001; Fan et al. 1995; Liu et al. 1998; Meier et al. 1994). The main component of the spent liquor is lignosulfonate, which is a high-molecular network with high C/N ratio (~250) as well as active groups. Lignosulfonate can degrade slowly in soil, and the degradation product is the precursor of humic substances (Haider et al. 1998). Humic substances can promote plant growth, change the characteristics of soil water, and improve fertilizer efficiency of N, P, MgO, and Mn. Spent liquor also contains more than 10 kinds of trace elements that are necessary for agricultural crops (Jin 2002); thus, it

provides comprehensive nutrient elements. Lignosulfonate can be chelated with metal ions such as Fe, Cu, Mg, Ni (Jin 2002), and the metal ions will not precipitate in solution. The ability to adsorb metal ions is ascribed to the phenolic or hydroxyl groups and network structure of lignosulfonate. Because of the slow degradation rate of lignosulfonate, it can be used as chelated micro fertilizers (Flaig et al. 1974; Liu et al. 2002; Ma et al. 1999).

Ammonium sulfite pulping spent liquor contains inorganic nigrogen (ammonia and ammonium ion) and organically bonded nitrogen except lignosulfonate which can improve soil structure. But volatilization of free ammonia and decomposition of residual ammonium sulfite in ammonium lignosulfonate solution cause not only nitrogen release but generate air pollution. It has been recognized that if the spent liqour produced by ammonium sulfite pulping of either wood or non wood fiber sources need to be used as fertilizer it should contain bonded organic nitrogen to facilitate slow releasing of nitrogen. Therefore, we focused attention on the fixation of inorganic nitrogen on lognosulfonate and measured the molecular weight distribution of lignosulfonate to find suitable molecular distribution for the application of wheat straw ammonium sulfite pulping spent liqour as fertilizer.

EXPERIMENTAL

Materials

Wheat straw pulping spent liquor was collected from a pulp mill using AQ (anthraquinone) - ammonium sulfite pulping process. The pulp mill is operated by Shandong Tralin Paper Co., Ltd. The pulping condition was: NaOH charge: 3%, $(NH_4)_2SO_3$: 18%, urea: 4%, AQ: 0.05% (on the base of dry wheat straw). Wheat straw was first soaked with NaOH; then urea, $(NH_4)_2SO_3$ and AQ were added and rotated with straw to make chemicals mixed uniformly. The temperature was raised until the pressure was 3.5kg/cm^2 and gas was released until pressure was zero. Then the cooking tempera-ture was raised until the pressure was 7.5kg/cm^2, and this temperature was kept for 2 h.

The other chemicals were all analytical grade without further purification.

Raw Material Analyses

Water, ash, lignin content and pH value were measured according to the relevant TAPPI standard test methods.

Determination of Residual Ammonium Sulfite

In a conical flask containing 25 mL of 0.1mol/L I_2 solution, 5 mL of spent liquor solution (the sample solution was neutralized with 0.1mol/L H_2SO_4 if there was free ammonia in the test sample) was added and stirred to mix the solution uniformly. The mixture was titrated with 0.1mol/L $Na_2S_2O_3$ until pale yellow color appeared. Then, 1 to 2 mL of starch-iodide indicator were introduced, and the titration was continued until blue color disappeared upon addition of the indicator.

$$\rho = \frac{(v_1 c_1 - v_2 c_2) \times M / 1000}{5 / 1000}$$

(1)

In Eq. 1, ρ is the content of residual ammonium sulfite (g/L), v_1 is the volume of I_2 solution (mL), c_1 is the concentration of I_2 (mol/L), v_2 is the volume of $Na_2S_2O_3$ consumed (mL), c_2 is the concentration of $Na_2S_2O_3$ (mol/L), and M is the molar mass of $(NH_4)_2SO_3$, 116g/mol.

Determination of Free Ammonia

5 mL of test sample was placed in a conical flask containing 20 mL of distilled water, followed by addition of 20 mL of 3% H_2O_2 and 1 to 2 drops of methyl orange indicator. Then, the mixture was titrated by 0.1mol/L H_2SO_4 until it turned to reddish orange. The content of free ammonia was calculated on the basis of NH_3 (g/L).

$$\rho = \frac{2VCM / 1000}{5 / 1000}$$

(2)

In Eq. 2, V is the volume of H_2SO_4 consumed (mL), C is the concentration of H_2SO_4 (mol/L), and M is the molar mass of NH_3, 17g/mol.

Nitrogen Fixation Reaction

100 mL of wheat straw ammonium sulfite pulping spent liquor was placed in a 250 mL conical flask and a certain volume of formaldehyde was added (the amount of formaldehyde changed from 1% to 30% on the base of dry weight of lignosulfonate). The flask was sealed and put in a constant temperature oscillating water bath at 15 or 60℃ and oscillated for 30 min. The sample was then taken out for further determination.

Determination of Free Formaldehyde

2 mL of test sample was transferred into a 150 mL beaker. Then 50 mL of distilled water was added, and the sample was titrated by 0.1mol/L HCl to pH 4. Then 10 mL of 10% $NH_2OH \cdot HCl$ was introduced to the sample. The temperature was kept at 20 to 25 °C. Ten minutes later the sample was titrated with 0.1mol/L NaOH back to pH 4. 50 mL of distilled water was tested as the control.

$$F = \frac{(v_1 - v_2)C \times 0.03003}{2 / 1000}$$

(3)

In Eq. 3, F is the content of free formaldehyde (g/L), v_1 is the volume of NaOH consumed by the test sample (mL), v_2 is the volume of NaOH comsumed in the control test (mL), C is the concentration of NaOH standard solution (mol/L), and 0.03003 is the mass of formaldehyde for 1mL 1mol/L NaOH standard solution (g).

Determination of Sulfonic Group Content

The determination of sulfonic group content was carried out with conductometric titration. In a typical process, 300 mg of sample was dissolved in 50 mL distilled water, and the solution was treated with cation exchange resin two times. The ion exchange liquid was diluted to 250 mL, and from this solution 100 mL were titrated conductimetrically with 0.1mol/L NaOH under a N_2 atmosphere on a DDS-12A conductivity meter.

$$-SO_3H(\text{mmol/g sample}) = \frac{(Vs - Vo) \times C}{W} \tag{4}$$

In Eq. 4, C is the concentration of titrant (mol/L), V_s is the volume of NaOH consumed by sample (mL), V_0 is the volume of NaOH consumed by blank water (mL), and W is the sample weight (g).

Determination of Hydroxymethyl Group Content

0.1 g of accurately weighed sample was placed in an iodine flask containing 50 mL distilled water, and 25 mL I_2 solution was pipetted into the flask, followed by addition of 10 mL 0.1 mol/L HCl solution. The mixture was titrated with 0.1mol/L $Na_2S_2O_3$ to produce pale yellow color. Then, 1 to 2mL of starch-iodide indicator was introduced, and the titration was continued until blue color was disappeared. 50 mL of distilled water was tested as the control.

$$H\% = 1.03 \times [\frac{(V - V_0) \times 0.015 \times c}{W} \times 100 - F] \tag{5}$$

In Eq. 5, H is the content of hydroxymethyl groups (%), c is the concentration of $Na_2S_2O_3$ (mol/L), V is the volume of $Na_2S_2O_3$ consumed by the sample (mL), V_0 is the volume of $Na_2S_2O_3$ consumed by the blank test (mL), W is the dry weight of sample (g), and F is the content of free HCHO (%).

Oxidative Chelating Reaction of Ammonium Lignosulfonate

The nitrogen-fixed ammonium lignosulfonate was adjusted to pH 3 with 20% H_2SO_4 and then oxidized with H_2O_2 and $FeSO_4 \cdot 7H_2O$ at a given condition (H_2O_2:0-15%, 30-90°C, 15-60min). At the end of reaction, the pH of the sample was adjusted to 12 with 2 mol/L NaOH, and centrifugated to separate undissolved substances. Fe content in lignosulfonate was determined with the standard method for organic Fe fertilizer (NY/T 305.3-1995) and the chelate ratio was calculated.

Determination of Relative Molecular Weight Distribution

The relative molecular weight distribution was determined with Sephadex G-75 using 0.1 mol/L NaCl as eluent. The absorption value of effluent liquid at 280 nm was detected. A plot of eluent volume vs absorption value was obtained. Sulfonated polystyrene was used as reference sample to calculate molecular weight distribution and its proportion.

Determination of Carbonyl Group Content

Carbonyl content in lignin was determined with Ultraviolet reduction differential spectroscopy.

RESULTS AND DISCUSSION

Chemical Composition of Spent Liquor from Wheat Straw Pulping

The chemical composition of AQ-$(NH_4)_2SO_3$ pulping spent liquor was analyzed, and the results are listed in Table 1.

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Table 1. Chemical Composition of Spent Pulping Liquor

Specific gravity	pH	Total dry solids (g/L)	Ash (g/L)	Silica (g/L)	Acid soluble lignin (g/L)	Total Lignin (g/L)	Residual ammonium sulfite (g/L)	Free Ammonia (g/L)
1.029	7.62	80.1	12.8	0.4	26.3	28.5	22.8	1.12

Results showed that the total lignin content was 28.5 g/L. The spent liquor also contained 22.8 g/L of residual ammonium sulfite; this value was very high compared with the amount of lignosulfonate in spent liquor, indicating high inorganic ammonia in pulping spent liquor. Inorganic ammonia should be fixed to increase chemically bonded organic nitrogen, thus improving the slow-releasing property of fertilizer.

Effect of Formaldehyde Amount on pH of Waste Liquor and Nitrogen Fixation

Formaldehyde reacts with ammonium sulfite to produce $HOCH_2SO_3NH_4$ and proceeds via a sulfomethylation reaction with the phenolic unit of lignin (He et al. 1994), which results in the fixation of nitrogen. Figure 1 shows the reaction mechanism.
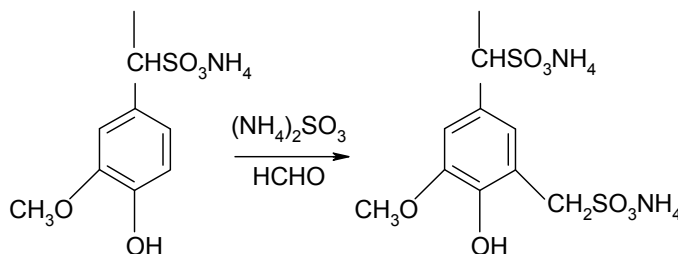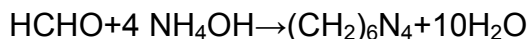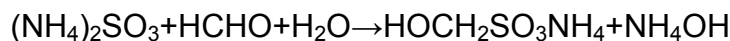
$$(NH_4)_2SO_3 + HCHO + H_2O \rightarrow HOCH_2SO_3NH_4 + NH_4OH$$

$$HCHO + 4\ NH_4OH \rightarrow (CH_2)_6N_4 + 10H_2O$$

Figure 1. Mechanism of nitrogen fixation by formaldehyde

According to the mechanism shown in Fig. 1, the pH value is controlled by adding formaldehyde. Free formaldehyde reacts with residual ammonia and ammonium sulfite to produce organically bonded nitrogen. The amount of formaldehyde should be controlled in order to prevent the pollution initiated from free formaldehyde.

Different dosages of formaldehyde were used in the experiment at temperatures of either 15°C and 60°C to observe the effects of formaldehyde on pH and nitrogen fixation. The results are illustrated in Figs. 2, 3, and 4.
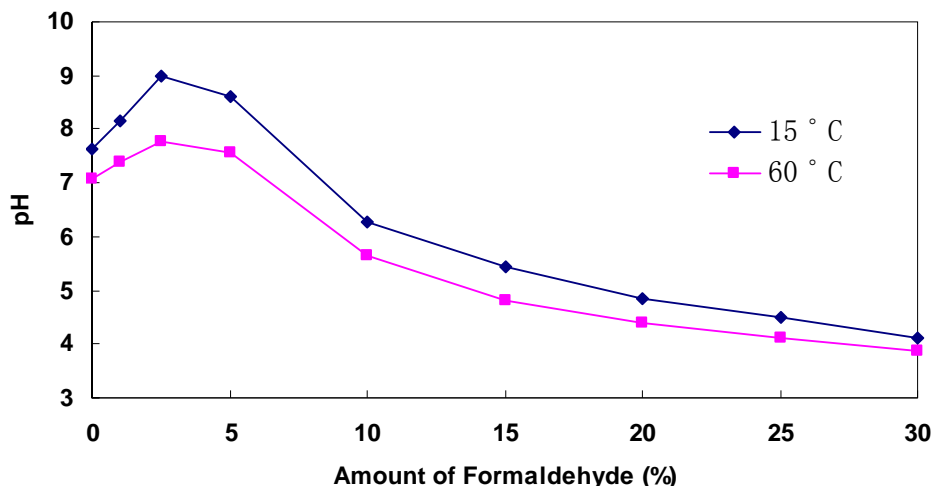
Fig. 2. Effects of formaldehyde charge on pH at different temperatures

As shown in Fig. 2, the pH of lignosulfonate solution intially increased with an increase of formaldehyde charge level and then started to decrease. The highest pH was 9. Higher temperature results in lower initial pH, but the temperature had no significant influence on the evolution of pH with the formaldehyde charge levels.
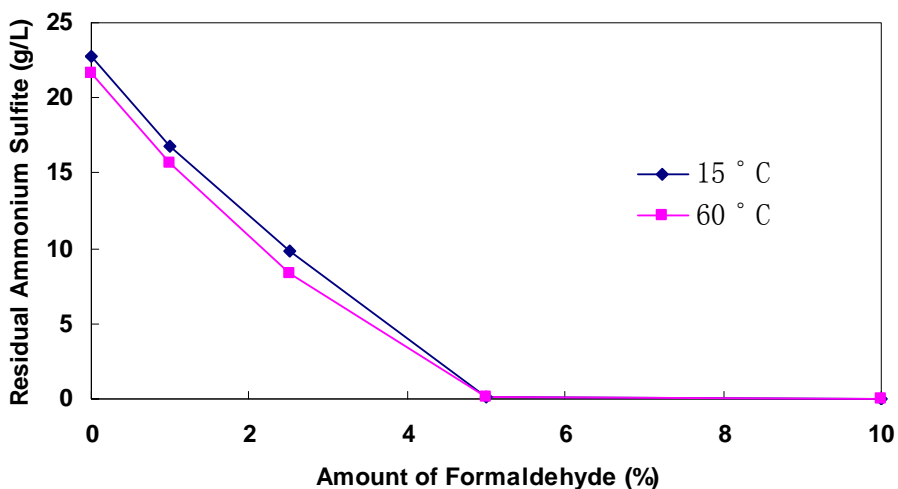
Fig. 3. Effects of formaldehyde charge on residual ammonium sulfite at different temperatures

Figures 3 and 4 show that the amount of residual ammonium sulfite was reduced nearly to zero at 5% of formaldehyde addition as a result of the reactions shown in Fig. 1, while the content of free ammonia reached its maximum at the same time. Further increase of formaldehyde charge levels from 5% to 10% would be used to fix the free ammonia. Figure 4 also indicates that the residual formaldehyde increased gradually when formaldehyde charge was higher than 5%. Excess addition of formaldehyde would result in the pollution of formaldehyde.
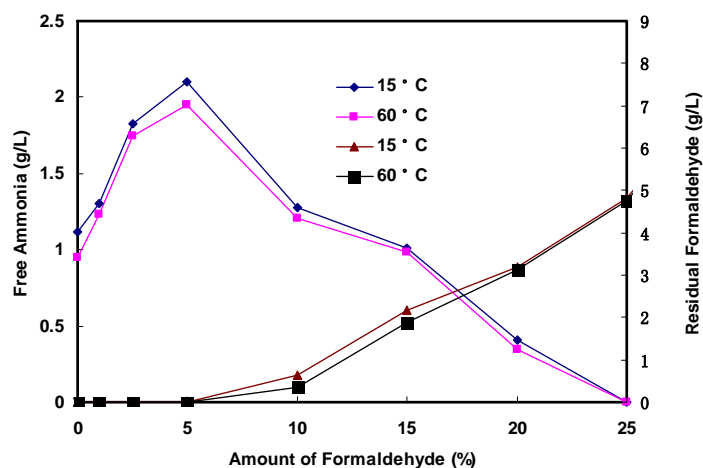

Fig. 4. Effects of formaldehyde charge on free ammonia and residual formaldehyde contents at different temperatures

Based on the results in Figs. 2 through 4 it was concluded that temperature did not impart significant influence on the variations of pH and nitrogen fixation. The pH increased first and then decreased as the concentration of formaldehyde increased. The reason may be that free ammonia was first produced in the reaction between formaldehyde and residual ammonium sulfite, and the subsequent reaction between the free ammonia and formaldehyde produced hexamethylenetetramine, which led to the decline of pH. This was also supported by the variations of the content of residual ammonium sulfite and free ammonia.

Considering the contents of residual ammonium sulfite, formaldehyde, and free ammonia, it can be expressed that the reactions were mostly completed at 10% of formaldehyde. The pH was between 6 and 6.5 at this point, which was the optimal value for effective nitrogen fixation with an appropriate amount of formaldehyde. In addition, the initial pH of the spent liquor was slightly lower at 60°C than at 15°C. This mainly resulted from the extravasation of some free ammonia.

The Content of Nitrogen Incorporated into Lignosulfonate by Nitrogen Fixation

Nitrogen content incorporated into lignin was calculated through the determination of hydroxymethyl group and ammonium sulfonate contents. From the principle of nitrogen fixation, it is known that the difference between the increase in the content of ammonium sulfonate and hydroxymethyl group before and after nitrogen fixation is the nitrogen incorporated into lignosulfonate.

Table 2. Results of Hydroxymethyl and Ammonium Sulfonate Determination

	Ammonium sulfonate mmol/g	Hydroxymethyl group mmol/g
Before nitrogen fixation	1.474	0.198
After nitrogen fixation	1.918	0.254
Increase	0.444	0.056

Note：The measured sample is the waste water with 10% of formaldehyde

Table 2 contains the results of the contents of hydroxymethyl group and ammonium sulfonate. As shown above, ammonium lignosulfonate was increased by 30.1% after nitrogen fixation. Ammonium hydroxymethylsulfonate and ammonium lignosulfonate accounted for 12.6% and 87.4% of the total increased ammonium sulfonate respectively.

Urea fertilizer usually contains about 30% nitrogen, but urea is easy to decompose into ammonia and CO_2 and escape from soil, resulting in low utilization ratio of urea. The nitrogen content in lignosulfonate fertilized was not high; however, nitrogen was fixed on the lignosulfonate macromolecule, and was difficult to volatilize into air. With the decomposition of lignosulfonate in soil, nitrogen was released slowly, and lignosulfonates turned into humic substances, which was good for soil structure.

Oxidative Chelating Reaction of N-fixed Ammonium Lignosulfonate

The effects of the amount of hydrogen peroxide, temperature and time on the degree of chelating reactions were studied under the condition of an overdose of Fe^{2+}. The proper condition of the chelating reaction could be determined by comparing the chelating rates in these different conditions.

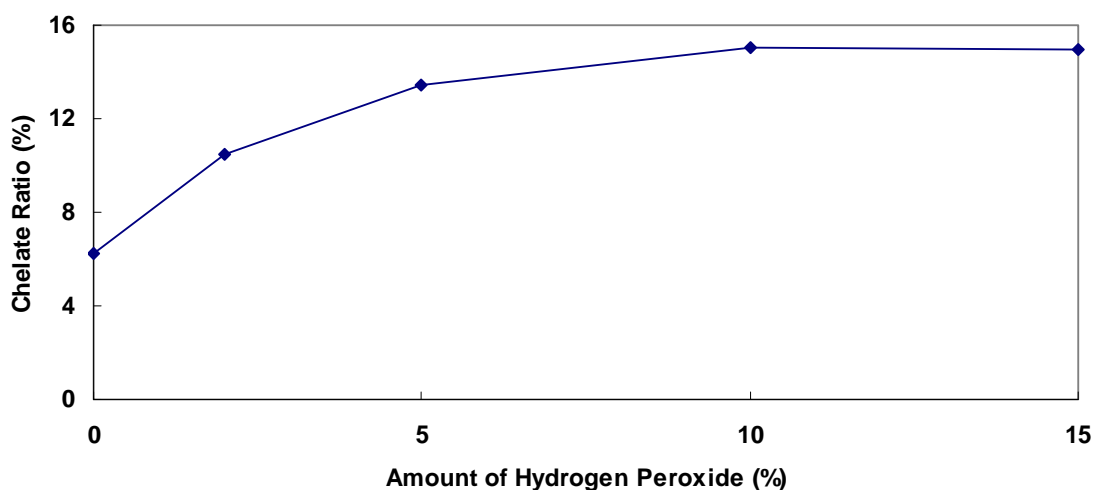The effects of H_2O_2 charge on the chelating ratio of lognosulfonate are shown in Fig. 5.

Fig. 5. Effect of hydrogen peroxide on chelating ratio (reaction condition: pH 3, 30 min, 50˚C)
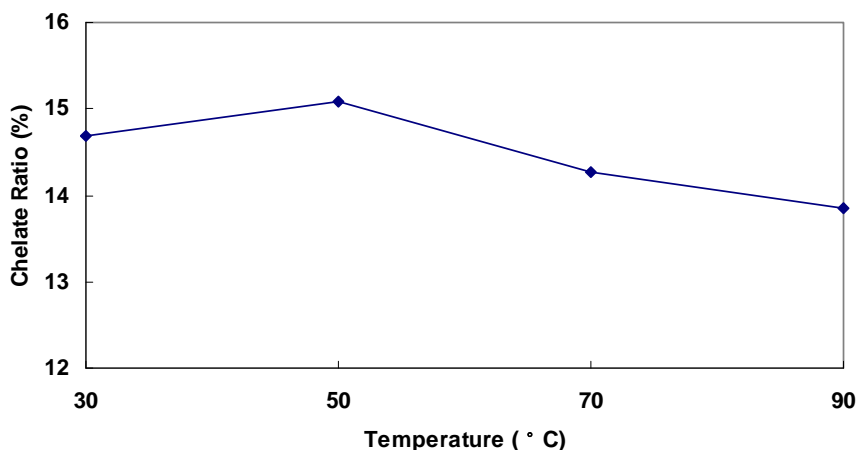
Fig. 6. Effect of temperature on chelating ratio (reaction condition: pH 3, 30 min, H_2O_2 10%)

The curve in Fig. 5 shows that the charge of H_2O_2 had a strong effect on chelating ratio, which was increased by increasing the charge of H_2O_2 and reached its highest value at 10% H_2O_2, but further increase was not observed after this high value. One possible reason for this is that excess H_2O_2 produced a high amount of ·OH when catalyzed with Fe^{2+} under acidic conditions. This improved the system's ability to attack lignin, resulting in an increase of functional groups that could be chelated with metal ion. However, this attacking ability was limited, and excess H_2O_2 would decompose. Therefore, the optimum H_2O_2 charge needs to be controlled in the chelating reaction.

Figure 6 shows the effect of temperature on chelating ratio. The chelating ratio did not change greatly at low temperatures, and its value was around 14%. It reached the highest value of 15.1% at 50˚C and then decreased significantly with temperature. This was due to the decomposition of H_2O_2 being faster at a higher temperature, while ·OH did not have enough time to react with lignin. This caused ·OH to disappear quickly, resulting in the decrease of chelating ratio. The proper temperature should be 50˚C.

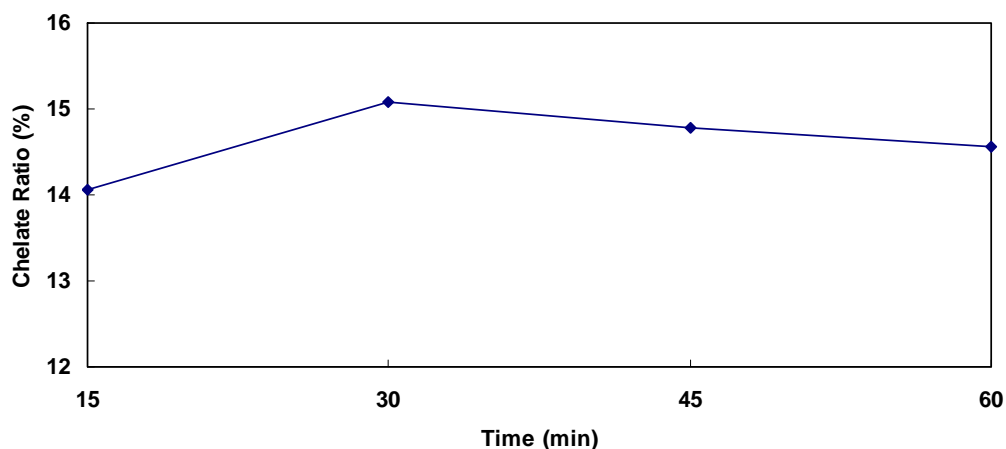Figure 7 shows the influence of time on chelating ratio.

Fig. 7. Effect of time on chelating rate (reaction condition: pH 3, 50˚C, hydrogen peroxide 10%)

As shown in Fig. 7, the reaction was fast and was not influenced remarkably by the reaction time. The optimum reaction time was 30 min.

According to results of the effects of different parameters on chelating ratio, the proper condition was determined as pH 3, H_2O_2 10%, 50°C, and 30 min. The highest chelating ratio was 15.1% under the optimized condition.

Effects of Oxidative Chelating on Characteristics of Ammonium Lignosulfonate

Results showed that the amount of H_2O_2 is the most effective parameter affecting chelating ratio. Chelating ratio increased with the increase of the H_2O_2 charge, and it changed little if the H_2O_2 amount charge was more than 10%. Reaction time and temperature had no significant effects on chelating ratio. Molecular weight of ammonium lignosulfonates oxidized with different charge of H_2O_2 was investigated in this part.

Active chelating groups, such as carbonyl, carboxyl, and phenolic hydroxyl groups, exist in the sulfonated lignin. The chelating behavior of a carboxylic group with a metal ion includes monodentate, bidentate, and bridging ligands. Oxygen in sulfonic, carbonyl, and phenolic hydroxyl groups could also form a ligand with metal ions. The content of the ligand group would affect the chelating ability of lignosulfonate with metal ions. The effects of oxidative chelating reaction on functional groups are shown in Table 3.

Table 3. Variation of Functional Groups' Contents in the Chelating Reaction

The amount of hydrogen peroxide/%	$-SO_3H$/ (mmol•g^{-1})	$-COOH$/ (mmol•g^{-1})	Ph-OH/ (mmol•g^{-1})	Carbonyl groups(×10^{-2})/(mmol•g^{-1})	Total groups/ (mmol•g^{-1})
0	1.19	0.71	0.31	4.10	2.25
2	1.01	0.73	0.42	4.77	2.21
5	1.00	0.83	0.40	4.79	2.28
10	0.94	0.93	0.47	4.99	2.39
15	0.99	0.85	0.33	4.56	2.22

It can be noted in Table 3 that the content of the sulfonic group in oxidized ammonium lignosulfonate declined, while the contents of phenolic hydroxyl, carbonyl and conjugate carbonyl groups increased slightly with the increase of H_2O_2 charge. The total amount of functional groups reached the maximum value when the dosage of hydrogen peroxide was 10%. As the highest chelating efficiency also appeared at the same dosage, it could be concluded that the content of different coordinate groups would affect the ability of lignosulfonate to chelate metal ions. The total amount of functional groups did not change remarkably from the maximum to other dosages of H_2O_2, but the corresponding chelating ratio varied greatly, which implied that the variation of functional groups would also have effects on the lignosulfonate's capacity to chelate metal ions. The effect of carboxyl, phenolic hydroxyl and carbonyl groups exceeded that of the sulfonic group. Therefore, the content of these functional groups that impart more effects should be increased to improve the capacity of chelating mental ions of ammonium lignosulfonate.

Results on GPC analysis are shown in Table 4. Molecular weight distribution parameters could be calculated from the respective molecular weight distribution curves.

Table 4. Mw Distribution of Lignin*

The amount of hydrogen peroxide/%	Proportion of different Mw %			
	<4950	4950-8000	8000-18300	>18300
0	69.43	9.23	17.59	3.77
2	50.59	10.76	25.51	13.00
5	49.47	13.34	22.18	14.90
10	45.52	10.91	23.01	20.53
15	47.28	10.11	22.52	20.02

* Mw : weight average molecular weight of Molecular Weight

From the molecular weight variation of reactive chelating products in Table 4, it was not difficult to find that the proportion of lignosulfonate fragments with molecular weight of less than 4950 decreased, while the proportions of fragments having molecular weight higher than 4950 increased after oxidation. The increased portion mainly involved molecular weights higher than 18,300 g/mole. It could be concluded that oxidation could increase the molecular weight of lignin on the whole. The increase of molecular weight did not change apparently when H_2O_2 amount was higher than 10%. Therefore, the increase of molecular weight could improve chelating ability of ammonium lignosulfonate.

CONCLUSIONS

1. Ammonium nitrogen in wheat straw ammonium sulfite pulping spent liquor could be fixed with formaldehyde. Formaldehyde mainly reacted with residual ammonia when its charge was lower than 5%. When the formaldehyde reached between 5% and 10%, nitrogen fixation of free ammonia dominated. The proper charge of formaldehyde was 10%. Temperature did not significantly affect nitrogen fixation. Ammonium nitrogen was converted into organic nitrogen by reacting with formaldehyde. The proportion of increased ammonium sulfonate was 30.1%, and 87.4% of which was ammonium lignosulfonate.
2. The charge of hydrogen peroxide had the largest effect on chelating ratio. The effects of temperature and reaction time were not apparent. The proper reaction conditions were: pH 3, with 10% hydrogen peroxide, 50 °C, and 30 minutes duration.
3. The sulfonic groups decreased, and the phenolic hydroxyl and carbonyl groups increase slightly. The proportion of high molecular weight fragments after oxidative chelation of lignosulfonate increased, and the increase is mainly concentrated on moleculaer weight s higher than 18,300. However, the role on molecular weight variation was not apparent when formaldehyde amount was more than 10%. Increasing molecular weight was helpful for improving chelating ability.

ACKNOWLEDGMENTS

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