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The relationship of pretreatment pulping parameters with respect to selectivity: optimization of green liquor pretreatment conditions for improved kraft pulping

Keywords:

Green liquor, pretreatment, chemical absorption, softwood, kraft pulping, central composite experimental design

Abstract

Green liquor (GL) was used as a sulfide rich liquor to impregnate Southern pine wood chips in a pretreatment step for kraft pulping. A central composite experimental design was applied to investigate relationships between pretreatment conditions, chemical absorption, pulping selectivity, and primary pulp qualities. The derived equations provided a correlation between the independent cooking variables and described their influence on chemical absorption, pulp qualities, and other pulping parameters. The results indicate that a higher concentration of pretreatment liquor has the most significant impact for improving pretreatment and pulping processes as well as enhancing various pulp qualities. Since the chemicals in GL display different absorption characteristics in wood, pretreatment conditions can be optimized for higher sulfide absorption ratios. The experimental results revealed some notable trends between chemicals absorption and pulp properties. Sulfide absorption not only correlates with delignification, but also influences pulping selectivity and pulp yield. The sulfide to alkali ratio absorbed in wood chips is critical for improving pulping selectivity and enhancing pulp qualities. Finally, a higher hydrosulfide to hydroxide ratio is a key parameter for the benefit of pulping.

Introduction

Owing to ongoing and increasingly restrictive environmental regulations for the North American pulp and paper industry, extended delignification in pulping followed by oxygen bleaching has become a favorable approach for increasing the efficiency of pulping process for modern pulping and bleaching operations. In fact, several of the

major modified cooking processes such as MCC and EMCC for continuous cooking system /1,2/ and RDH for batch systems /3–5/ have been increasingly applied in the pulping industry for improving pulping efficiency and economics. These latter technologies possess the common motive of applying black liquor as the chip pretreatment liquor before the actual kraft cook. The purpose of a black liquor pretreatment, of course, is to provide higher sulfide concentration in the initial cooking stage, a concept that is based on the time honored principle of extended delignification /6,7/.

Green liquor (GL) is like black liquor since it is a rich hydrosulfide source, and easily accessible in all kraft pulp mills. One of greatest features for its potential consideration in pulping is its naturally high sulfide to alkali ratio that makes it superior as a pretreatment liquor compared to black liquor. Recent investigations have reported the use of GL, either the original liquor or its crystallized form, for the impregnation of wood chips in a total kraft cooking process /8–11/. Svedman /9/ et al. have followed along these lines and reported that principal benefits of a GL pretreatment are higher delignification selectivity, improvement of pulp qualities, and chemical savings. For example, approximately 10–20% reduction in alkali consumption could be achieved using original or crystallized GL, with a concomitant 30 cm³/g increase in pulp viscosity and 10% increase in tear strength. Moreover, Klevinska et.al /10/. concluded that GL pretreatment resulted in a delignification selectivity increase under attenuated liquor to wood ratios. Finally, Chang et.al. /8,11/ confirmed the positive impacts of GL pretreatment for reducing both cooking and bleaching chemicals consumption and simultaneously enhancing delignification and carbohydrates stabilization.

Although these latter investigations have focused on pretreatment conditions such as green liquor charge, the liquor to wood ratio, and addition points, the relationship

of pretreatment conditions to chemical changes in the process and pulp qualities still remains unclear. The current work was, therefore, sought to evaluate the impact of the pretreatment parameters on the changes in the absorption of the chemical components of GL and their effect on pulp properties. Thus, a central composite experimental design was applied to systematically reveal the intrinsic impacts of pretreatment on chemical changes and pulp qualities, and to correlate the interactive effects of pretreatment conditions.

Experimental

Wood

US Southern pine chips were obtained from an industrial member of the Institute of Paper Science and Technology (IPST). The chips were screened to retain the 3×20×25–30 mm fractions that were used for all experiments. The relative dry moisture content of the wood chips was 43.24%. All bark and knots were removed before pulping.

Green Liquor (GL)

The GL used in all of the described experiments was provided from the same industrial sponsor. It was found to contain 15.91g/l NaOH, 25.15 g/l Na₂S, and 85.36 g/l Na₂CO₃ (all concentrations expressed relative to Na₂O) when analyzed by standard TAPPI Test methods (TM 624cm-85).

Pretreatment

Pretreatments were carried out in a multi-unit stainless steel bomb system that was home built at the pulping and bleaching labs of IPST. Eight different samples were able to be pulped simultaneously. The pretreatment

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temperatures were controlled by the computer programmed oil bath and temperature ramps were of the order of 1.2°C/min. Each bomb could accommodate a volume of 500 ml with approximately 50 ml of headspace and 60 g of wood chips (o.d.). Pretreatment conditions were varied based on the experimental design.

Cooking

After pretreatment, the GL was drained, and fresh white liquor was added for the post cook. The cooking conditions were as follows: the ratio of liquor to wood chips was 4:1 (liquor absorbed by wood chips was included); active alkali = 15% (Na₂O); Sulfidity = 30%; and temperature ramps were on the order of 1.3°C/min to reach 170°C in 90 minutes.

Analysis

Sodium hydroxide in the pretreatment liquor was analyzed by the ABC titration method as modified in-house, while its Sulfide and carbonate contents were analyzed by GC method [11]. All chemicals that were absorbed into wood or present in the pretreatment liquor were expressed as mol per kilogram wood.

Analysis of pulp viscosity and kappa numbers were based on TAPPI standard test methods T230 om-94 and T236 cm-85 respectively.

Design of experiments

In order to investigate the effects of parameters on pulping process and pulp qualities and establishing appropriate models that could be used to exhibit trends between pretreatment and pulp properties, a central composite experimental design was applied in this work. The investigation includes four variables: GL charge, liquor to wood ratio, pretreatment temperature, and time. All experimental variables and data are shown in Tables 1 and 2.

Results and discussion

Profile of pulp qualities

Fig. 1 demonstrates the influence of a series of independent pretreatment parameters (GL charge, liquor to wood ratio, pretreatment temperature, and time; see Table 1 for designation of X variables) on pulp screen yield. For this set of experiments, surprisingly, the pulp yield was found to decrease for an increase in the GL charge in the range of experiments done. As evidenced for most of the variables, both pretreatment temperature and time provided an optimal point to achieve the highest pulp yield. Yet, the

Table 1. Central composite experimental design vs results data (Pulp qualities).

No.	X(1) GL Charge l/kg wood	X(2) Liquor ratio to wood	X(3) Pretreat Temp.°C	X(4) Pretreat Time min	Y(1) Pulp yield %	Y(2) Kappa number	Y(3) Viscosity mPa.s	Y(4) Pulping selectivity
1	0.75	3	100	45	46.73	21.97	29.27	1.33
2	1.25	3	100	45	45.15	16.62	24.44	1.47
3	0.75	5	100	45	44.41	20.62	31.29	1.52
4	1.25	5	100	45	43.98	16.73	24.95	1.49
5	0.75	3	140	45	42.76	14.73	19.65	1.33
6	1.25	3	140	45	43.75	15.29	23.75	1.55
7	0.75	5	140	45	42.85	17.92	25.55	1.43
8	1.25	5	140	45	43.31	18.42	29.26	1.59
9	0.75	3	100	75	44.51	14.34	36.34	2.53
10	1.25	3	100	75	45.12	16.21	28.17	1.74
11	0.75	5	100	75	46.87	20.96	33.75	1.61
12	1.25	5	100	75	45.01	16.24	27.79	1.71
13	0.75	3	140	75	45.54	19.25	30.11	1.56
14	1.25	3	140	75	42.79	15.61	20.14	1.29
15	0.75	5	140	75	48.91	19.61	15.66	0.8
16	1.25	5	140	75	46	16.52	26.62	1.61
17	0.5	4	120	60	50.11	23.81	35.69	1.5
18	1.5	4	120	60	44.36	14.36	19.65	1.37
19	1	2	120	60	48.93	19.88	31.26	1.57
20	1	6	120	60	46.6	18.37	27.86	1.52
21	1	4	80	60	50.29	22.94	32.34	1.41
22	1	4	160	60	47.6	22.69	27.2	1.2
23	1	4	120	30	46.63	18.23	25.17	1.38
24	1	4	120	90	45.41	18.11	26.21	1.45
25	1	4	120	60	46.3	17.64	27.12	1.54
26	1	4	120	60	46.27	16.81	25.06	1.49
27	1	4	120	60	45.35	18.38	27.07	1.47
28	1	4	120	60	46.72	16.99	26.62	1.57
29	1	4	120	60	46.32	17.24	26.85	1.51
30	1	4	120	60	45.85	17.56	26.91	1.46
31	1	4	120	60	46.26	17.38	26.53	1.5

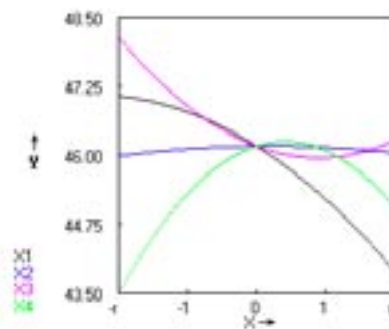


Fig. 1. Pulp yield vs. pretreatment parameters.

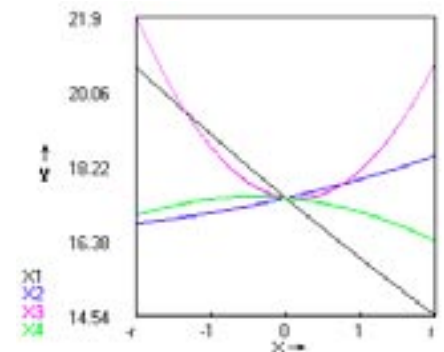


Fig. 2. Pulp kappa number vs. pretreatment parameters.

pretreatment liquor to wood ratio has no obvious influence on pulp yield. The equation derived from these sets of experiments that correlates the pretreatment parameters with the observed pulp yield is elucidated as follows:

$$Y (\text{pulp yield}) = 46.1528 - 0.7904 X_1 - 0.4687 X_3 + 0.3912 X_4 - 0.1256 X_1 X_2 - 0.3969 X_1 X_4 + 0.4669 X_2 X_3 + 0.7919 X_2 X_4 + 0.5831 X_3 X_4 - 0.1687 X_1^2 + 0.2588 X_3^2 - 0.4712 X_4^2 \quad (\text{Eq. 1})$$

Table 2. Central composite experimental design vs results data (Absorption profile).

No.	X(1)	X(2)	X(3)	X(4)	Y(5)	Y(6)	Y(7)	Y(8)
	GL Charge	Liquor ratio	Pretreat	Pretreat	S absorption	OH absorption	CO3 absorption	[HS]/[OH]
	l/kg wood	to wood	Temp.°C	Time min	mol HS/kg	mol OH/kg	mol CO3/kg	
1	0.75	3	100	45	0.2741	0.3696	0.6569	0.7419
2	1.25	3	100	45	0.3903	0.6119	1.1095	0.638
3	0.75	5	100	45	0.1882	0.3605	0.5052	0.5221
4	1.25	5	100	45	0.2575	0.5833	0.8688	0.4414
5	0.75	3	140	45	0.3042	0.385	0.7067	0.7902
6	1.25	3	140	45	0.507	0.6416	1.1119	0.7902
7	0.75	5	140	45	0.3042	0.385	0.603	0.7902
8	1.25	5	140	45	0.507	0.6416	0.9	0.7902
9	0.75	3	100	75	0.2838	0.3807	0.6694	0.7455
10	1.25	3	100	75	0.421	0.6416	1.1027	0.6562
11	0.75	5	100	75	0.1868	0.3657	0.495	0.5108
12	1.25	5	100	75	0.2254	0.6416	0.8293	0.3512
13	0.75	3	140	75	0.3042	0.385	0.7095	0.7902
14	1.25	3	140	75	0.4819	0.6416	1.0963	0.7511
15	0.75	5	140	75	0.2579	0.385	0.5627	0.6698
16	1.25	5	140	75	0.3218	0.6416	0.814	0.5015
17	0.5	4	120	60	0.1728	0.2567	0.4078	0.6732
18	1.5	4	120	60	0.3679	0.77	1.1564	0.4778
19	1	2	120	60	0.3824	0.5133	1.0755	0.7449
20	1	6	120	60	0.2167	0.5133	0.5963	0.4222
21	1	4	80	60	0.2546	0.4454	0.8042	0.5716
22	1	4	160	60	0.3491	0.5133	0.8719	0.6801
23	1	4	120	30	0.2889	0.5133	0.7504	0.5629
24	1	4	120	90	0.3895	0.5133	0.9195	0.7589
25	1	4	120	60	0.3067	0.5133	0.7612	0.5976
26	1	4	120	60	0.33	0.5133	0.7825	0.6428
27	1	4	120	60	0.3312	0.5133	0.772	0.6452
28	1	4	120	60	0.3055	0.5133	0.7805	0.5951
29	1	4	120	60	0.3431	0.5133	0.7579	0.6683
30	1	4	120	60	0.3366	0.5133	0.7806	0.6558
31	1	4	120	60	0.3284	0.5133	0.7758	0.6397

The above equation allows a quantitative elucidation of the interaction of each of the two pretreatment parameters and their influence on pulp yield. Although, the liquor to wood ratio did not exhibit an appreciable influence, it had significant correlation with other parameters. Overall, our results convincingly demonstrate that a lower GL charge with a higher liquor to wood ratio at lower temperatures for moderate treatment times increase pulp yield. This suggests that mild conditions favor the retention of carbohydrates partially through limited chemical degradation reactions, but probably more through endcapping reactions favoring the incorporation of sulfide in the carbohydrates. We are currently developing evidence to support this latter hypothesis through systematic elemental analyses of various pulps.

Fig. 2 in the same vein illustrates how pretreatment parameters can affect pulp kappa number. Notably, GL dosage during

pretreatment has a significant influence on delignification; as the GL dosage increases, the pulp kappa number linearly decreased. However, an increase in the pretreatment liquor to wood ratio resulted in a higher kappa number. These results indicate that GL charge and concentration in the pretreatment liquor play an important role in lignin removal during pulping process. Lignin removal can thus be facilitated by a lower liquor ratio during pretreatment. This is not unusual since the concentration gradient would more readily favor transfer of the active chemicals into the wood chips. Our previous work on chemical sorption profiles has adequately demonstrated a strong correlation for the uptake of hydroxide and sulfide as a function of concentration in the GL. This current data can, therefore, be used to derive an optimal equation which quantitates the influence of pretreatment parameters on pulp kappa number:

$$Y=17.4285-1.5275X_1+0.4158X_2-0.2850X_3-0.1583X_4-0.2900X_1X_2+0.4012X_1X_3+0.1363X_2X_3+0.1775X_2X_4+0.8013X_3X_4+0.9743X_3^2-0.1869X_4^2 \quad (\text{Eq. 2})$$

Fig. 3 illustrates that the same pulp kappa number can be reached by using less GL at a lower liquor ratio as compared to a higher GL charge at a higher liquor ratio. This fact clearly demonstrates that control of the GL concentration in the pretreatment liquor has a positive impact on pulping delignification. The results also show that pretreatment temperature has an optimal effect at approximately 120 °C for decreasing the pulp kappa number. Although the pretreatment time has no obvious influence on pulp kappa number as an independent parameter, it does display an interactive effect with other parameters and a longer pretreatment time is beneficial for delignification. In addition to delignification, vis-

cosity improvements were a criterion of high importance. In figure 4, the relationship of pretreatment conditions and pulp viscosity is shown. Among all the pretreatment parameters, pretreatment temperature exhibited the single most important influence on pulp viscosity. In the experimental range studied, as the pretreatment temperature increased from 80 °C to 160 °C, the pulp viscosity decreased as much as ~ 33% of the original. Besides pretreatment temperature, the increase of GL charge also shows a linear decrease in the pulp viscosity. It is not surprising, because stronger pretreatment conditions could encourage both delignification and carbohydrates degradation. Overall, a pretreatment condition using: a lower GL charge, higher concentration, lower temperature, and longer times would benefit pulp viscosity. Thus, an equation correlating optimal pulp viscosity and pretreatment conditions is expressed as follows:

$$Y = 26.5943 - 2.0242X_1 - 0.1583X_2 - 2.3142X_3 + 0.5283X_4 + 1.3275X_1X_2 + 2.1312X_1X_3 - 0.6112X_1X_4 + 0.2425X_2X_3 - 1.5550X_2X_4 - 1.3613X_3X_4 + 0.4912X_2^2 + 0.5437X_3^2 - 0.4763X_4^2 \quad (\text{Eq. 3})$$

Unavoidably, the delignification process is accompanied with carbohydrate hydrolysis. Thus, reduction of carbohydrate loss during lignin removal is the focus of any satisfactory pulping technology. Effective reduction in carbohydrate losses may be indexed by using the ratio of pulp viscosity to kappa number, known as the pulping selectivity. The equation from our experiments that elucidates optimal pulping selectivity is expressed as follows:

$$Y = 1.5057 - 4.7480X_2 - 0.1108X_3 + 5.3333X_4 + 0.1088X_1X_2 - 4.0000X_1X_4 + 2.7500X_2X_3 - 0.1087X_2X_4 - 0.1512X_3X_4 + 2.8154X_2^2 - 3.1845X_3^2 \quad (\text{Eq. 4})$$

Based on Eq. 4, Fig. 5 shows the impact of pretreatment parameters on the pulping selectivity. It is apparent from the data that the increase of GL charge shows some influence on pulping selectivity. The data imply that increasing the GL charge in the pretreatment phases mainly contributes to delignification rather than to carbohydrate preservation. In fact, Fig. 6 demonstrates that the highest pulping selectivity was achieved under a 0.5 L/kg wood GL charge and the lowest liquor to wood ratio. Not surprisingly, Eq. 4 indicates that higher pretreatment temperatures showed a negative effect on pulping selectivity, but longer

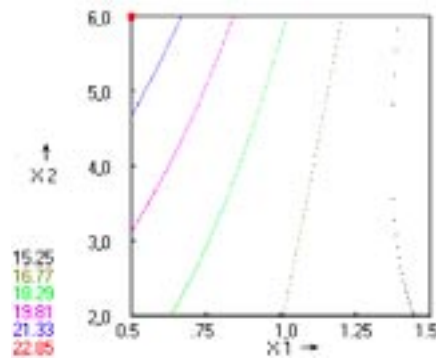


Fig. 3. Pulp kappa number vs. interaction of GL and liquor to wood ratio.

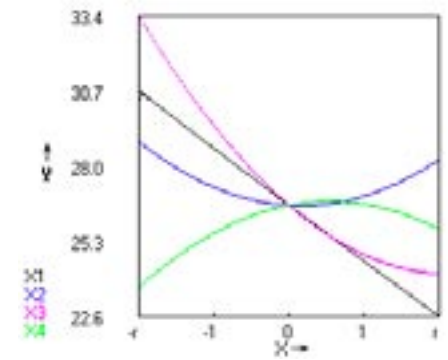


Fig. 4. Pulp viscosity vs. pretreatment parameters.

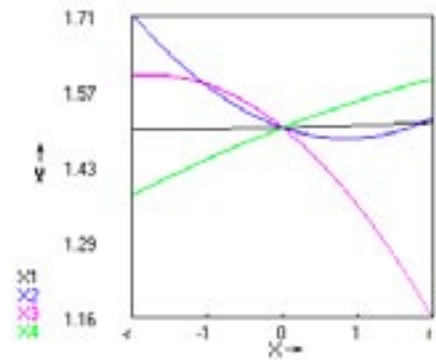


Fig. 5. Pulping selectivity vs. pretreatment parameters.

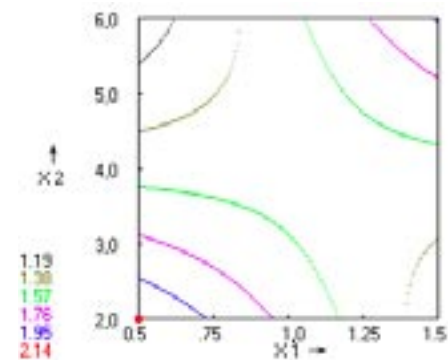


Fig. 6. Pulping selectivity vs. interaction of GL charge and liquor to wood ratio.

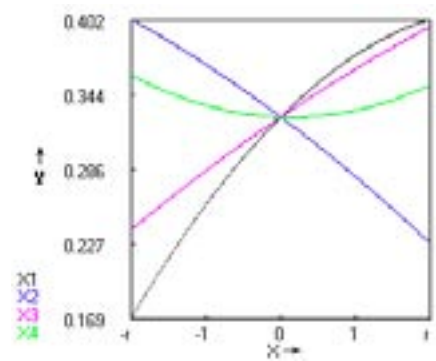


Fig. 7. Sulfide absorption vs. pretreatment parameters (as mol HS/kg wood).

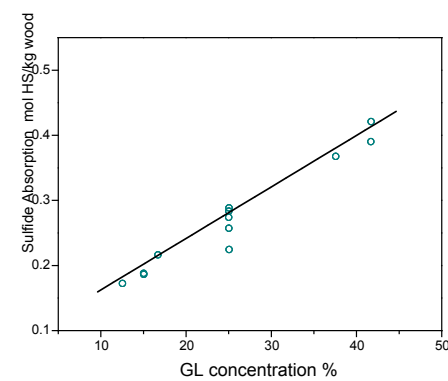


Fig. 8. Correlation of GL concentration with sulfide absorption (100 °C and 120 °C).

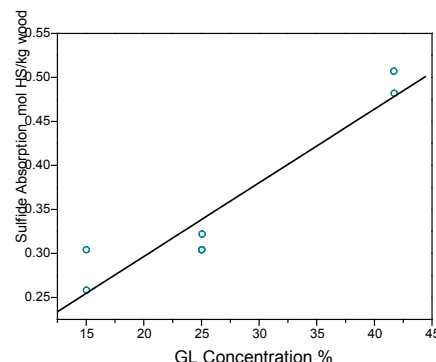


Fig. 9. Correlation of GL concentration with sulfide absorption (140 °C).

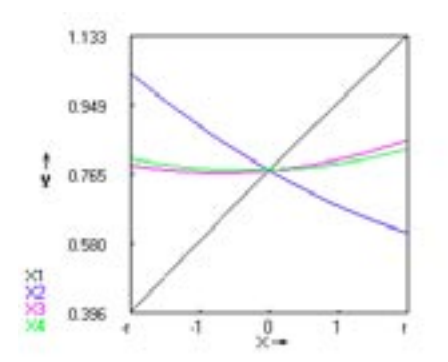


Fig. 10. Carbonate absorption (as mol CO₂/kg wood) vs. pretreatment parameters.

pretreatment time at the lower temperature benefits pulping selectivity.

Profile of chemicals absorption

Higher sulfide anion concentrations in the first cooking stage is known to enhance the overall pulping process and provide improved pulp qualities [6,7]. Based on this general principle, modified kraft pulping technologies have been developed in which black liquor pretreatment is a standard method of operation. GL is a naturally sulfide rich liquor produced from alkali recovery that can impregnate wood chips before the cook and enhance the impact of sulfide at the beginning of the postcook. Reasonably, the status of chemical absorption during the pretreatment critically correlates to the pulping results.

Fig. 7 clearly shows the impact of each independent pretreatment parameter on the mole absorption of sulfide into wood chips. The results demonstrate that as the GL charge is increased, sulfide absorption increased, but it almost leveled off after 1.0L/kg GL charge. Additionally, a decrease in the liquor to wood ratio used in pretreatment also resulted in an increase in the sulfide absorption. This fact indicated that control of the concentration and levels of pretreatment liquor is critical for sulfide absorption. Figs. 8 and 9 correlated the pretreatment liquor concentration with sulfide absorption by means of regression fitting, and the results demonstrate that a good linear relation existed. Therefore, efficiently enhancing sulfide content in wood chips may be accomplished by using a higher pretreatment liquor concentration other than by employing a higher GL charge. Sulfide absorption was also observed to display a linear concentration increase as a function of temperature. The pretreatment time exhibited a smaller influence on sulfide absorption, but surprisingly, the maximum sulfide absorption was achieved at a shorter time, 30 min. In general, a higher GL charge and concentration, as well as higher pretreatment temperature contributed to increase sulfide absorption in wood chips. Thus, the maximum sulfide absorption was achieved under 1.5 L/kg wood GL charge, 2.0 liquor-to-wood ratio, and 126°C for 30 minutes.

In the experiments done, almost all of the available sodium hydroxide in the GL was absorbed into the wood chips under most pretreatment conditions, but only 60–70% of the carbonate in the GL was absorbed during the pretreatment. Yet, since the carbonate content in GL is approximately three times higher than both sulfide and caustic alkali, relatively much

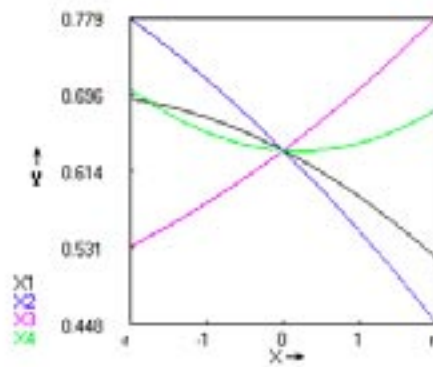


Fig. 11. The ratio of HS/OH vs. pretreatment parameters.

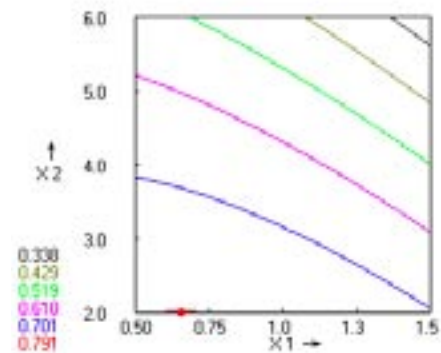


Fig. 12. The ratio of HS/OH vs. interaction of GL and liquor to wood ratio

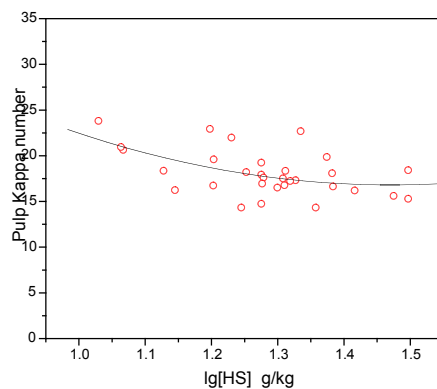


Fig. 13. Logarithm of sulfide absorption vs pulp Kappa number.

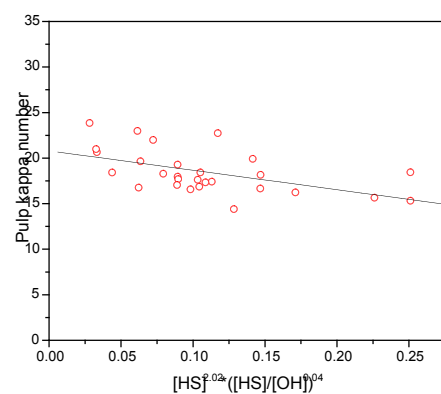


Fig. 14. Pulp Kappa number as function of sulfide absorption and [HS]/[OH].

more carbonate was absorbed into wood chips after pretreatment. The influence of various pretreatment parameters on carbonate absorption into wood chips is evident from Fig. 10. Only GL charge and its concentration showed an obvious impact on carbonate absorption; both higher GL charge and concentration enhanced carbonate absorption, but pretreatment temperature and time did not significantly influence carbonate absorption.

Besides the sulfide absorbed in wood chips, the ratio of sulfide ion to hydroxide ion plays a significant role in the pulping process [13]. Our previous work has investigated chemicals absorption during GL pretreatment [14]. Various GL chemicals showed very different absorption rates. An important fact arising from this work was that hydroxide absorbed into wood chips much faster than sulfide. In our current experiments, the influence of pretreatment parameters on sulfide to hydroxide ratio ([HS]/[OH]) absorbed into wood chips are shown in Figs. 11 and 12. The results indicate that the GL concentration in pretreatment liquor has the most significant impact on [HS]/[OH]; when the pretreatment liquor to wood ratio decreased from 6.0 to 2.0, the sulfide to hydroxide ratio increased from 0.45 to 0.78, which is over a 70% increase.

On the other hand, an increase in the GL charge resulted in a decrease in sulfide to hydroxide ratio. The lower sulfide absorption rate under the higher GL charge is probably a reason for the reduction of sulfide to hydroxide ratio. Furthermore, the higher temperature and the shorter time is preferred to achieve the higher hydroxide to sulfide ratio. The relationship of pretreatment parameters with sulfide absorption and sulfide to hydroxide ratio can be expressed by the following equations:

$$Y[\text{HS}] = 0.3260 + 0.0583X_1 - 0.0437X_2 + 0.0396X_3 - 0.0163X_1X_2 + 0.0180X_1X_3 - 0.0109X_1X_4 + 0.0191X_2X_3 - 0.0175X_2X_4 - 0.0165X_3X_4 - 0.0100X_{12} - 0.0028X_{22} - 0.0022X_{32} + 0.0072X_{42} \quad (\text{Eq. 5})$$

$$Y[\text{HS}]/[\text{OH}] = 0.6349 - 0.0430X_1 - 0.0821X_2 + 0.0618X_3 - 0.0057X_4 - 0.0110X_1X_2 + 0.0141X_1X_3 - 0.0170X_1X_4 + 0.0366X_2X_3 - 0.0308X_2X_4 - 0.0230X_3X_4 - 0.0076X_{12} - 0.0056X_{22} + 0.0050X_{32} + 0.0138X_{42} \quad (\text{Eq. 6})$$

Regularities between sulfide absorption and pulp properties

Based on current knowledge, to strengthen sulfide effect in order to benefit pulp qualities, pretreatment with sulfide-containing

liquor as a modified method has been discussed by many research efforts, but GL is complex chemical system (3 components) and the behavior of its chemicals with lignin and carbohydrates is still unclear. Our current work correlate chemicals absorption to pulping and primary pulp properties trying to establish the specific relationships between the pretreatment process and pulp qualities. Fig. 13 shows that with increasing sulfide absorption into wood, the pulp kappa number decreased, but in the GL system delignification should be impacted by multiple chemical factors. Considering the comprehensive effect of both sulfide and sodium hydroxide, the effect related to the chemical absorption and pulp kappa number can be described in Fig. 14. The decrease of pulp kappa number exhibited an approximate linear relationship with the function of sulfide absorption and sulfide to hydroxide ratio; the sulfide absorption demonstrated a tremendous influence on kappa number, while the sulfide to hydroxide ratio showed a slight positive impact on decrease of kappa. From the experimental results, it is concluded that the enhanced sulfide absorption during pretreatment with GL must be combined with the alkali absorption to improve delignification. Both higher sulfide absorption and sulfide to hydroxide ratio could enhance delignification, and give the lower pulp kappa number. In addition, the similar impacts of chemicals absorption on pulp viscosity were observed. Fig. 15 shows that the pulp viscosity generally decreased with the increase of the logarithm of sulfide absorption; furthermore, pulp viscosity not only correlates with sulfide absorption, but also with alkali absorption. Fig. 16 demonstrates that the increasing pulp viscosity could be correlated with the function of the logarithm of sulfide absorption and $[HS]/[OH]$ ratio. The higher $[HS]/[OH]$ ratio resulted in better pulp viscosity, but the higher sulfide absorption indicated little adverse effect on pulp viscosity. The data indicate that enhancing the sulfide absorption results in both lignin removal and carbohydrate hydrolysis. It seems that sulfide absorption did not prohibit carbohydrate decomposition.

Fig. 17 gives a plot between sulfide absorption and pulping selectivity. As apparent from the figure, the sulfide absorption did not show a definite correlation with pulping selectivity. However, Figs. 18 and 19 illustrate that pulping selectivity first decreases with increasing $[HS]/[OH]$ ratio and then increases linearly above a $[HS]/[OH]$ ratio of approximately 0.50. Fig. 20 further displays the synergistic effect of both sulfide absorption and the sulfide to hydroxide ratio

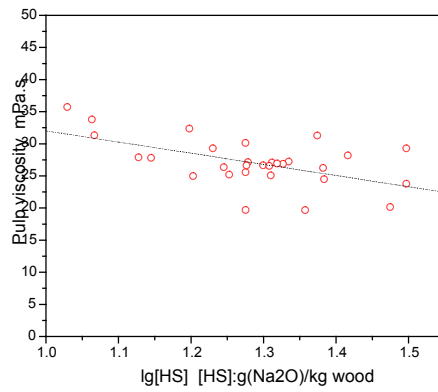


Fig. 15. Logarithm of sulfide absorption vs. pulp viscosity.

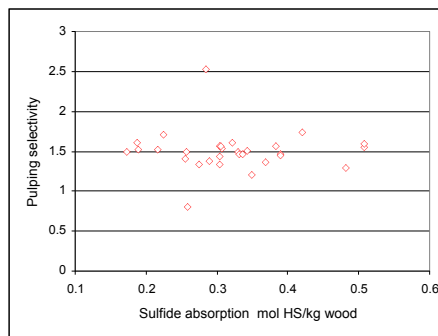


Fig. 17. Sulfide vs pulping selectivity.

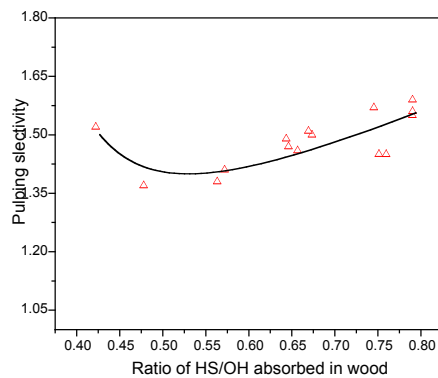


Fig. 19. Impact of the ratio of HS to OH absorbed in wood on pulping selectivity (120 °C, 140 °C).

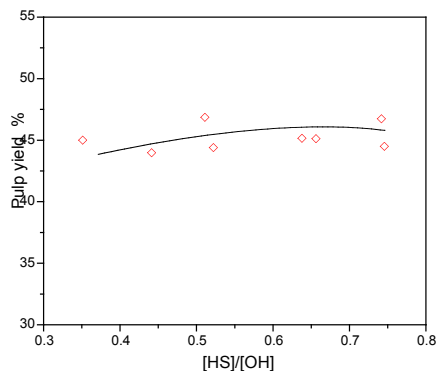


Fig. 21. Impact of Ratio of $[HS^-]$ to $[OH^-]$ absorbed in wood on pulp screened yield (100°C).

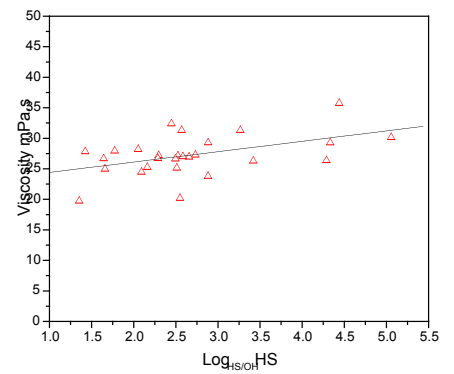


Fig. 16. Logarithm of sulfide absorption and $[HS^-]/[OH^-]$ vs pulp viscosity.

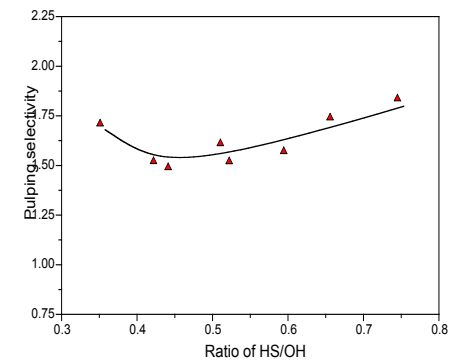


Fig. 18. Impact of the ratio of HS to OH absorbed in wood on pulping selectivity (100 °C).

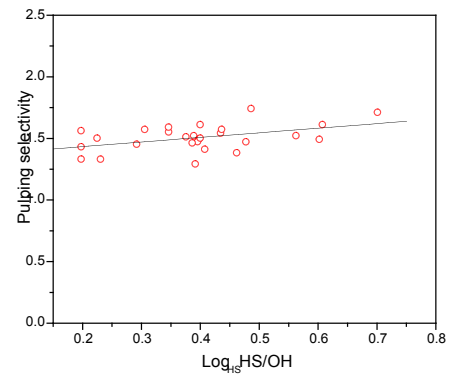


Fig. 20. Pulping selectivity as a function of Logarithm HS/OH based HS (HS as sulfide absorption mol/kg wood).

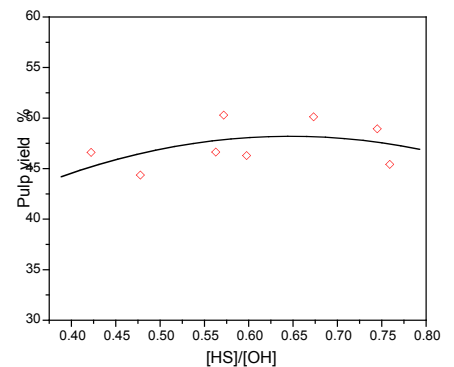


Fig. 22. Impact of ratio of $[HS^-]$ to $[OH^-]$ absorbed in wood on pulp screened yield (120°C).

with pulping selectivity. The facts suggest that a favorable alkalinity is necessary to ensure sulfide activity, and furthermore, the higher sulfide concentration in wood chips after pretreatment is critical to accelerate lignin degradation during post cooking.

In Fig. 21 and Fig. 22, the sulfide to hydroxide ratio also shows a positive influence on pulp screened yield in most cases. The higher the sulfide to hydroxide ratio during GL pretreatment, the higher will be the pulp yield.

Conclusions

In the summary, GL pretreatment parameters can make an important impact on pulping and pulp qualities. The increase of GL charge would result in the decrease of pulp kappa number and simultaneously lower pulp yield and viscosity. In the range of these experiments, the dosage of GL in the pretreatment did not exhibit a obvious impact on pulping selectivity. The lowest kappa pulps with the better viscosity could be obtained by using the highest concentration of pretreatment liquor which also gives the best pulping selectivity. Therefore, a low level of GL used at higher concentration for pretreatment, which is acceptable in industrial experience, would be the best for both pulp qualities and mill operation.

During the GL pretreatment, using the higher GL charge, and higher concentration at the higher temperature for longer time could result in a higher sulfide absorption into wood chips, but because of different absorption rate of each chemical composite in GL, a variety of pretreatment parameters would result in different sulfide to hydroxide ratios after pretreatment. In general, the higher GL charge would result in a lower sulfide to hydroxide ratio. However, higher concentration of pretreatment liquor, higher pretreatment temperature and longer time would be helpful to increase sulfide to hydroxide ratio. An increase in the carbonate absorption will be mainly affected by higher GL charge and concentration,

The results demonstrate that the different absorption characteristics of chemicals in GL would result in varied chemical absorption profiles under different pretreatment conditions, and it would significantly impact the cook and pulp properties. The synergistic impact of all chemicals in GL, not only sulfide, on pulping and pulp qualities can be ultimately realized.

The profile of chemicals absorption in GL pretreatment well correlate with pulping and pulp primary qualities. The experimental results conclude that the sulfide to

hydroxide ratio has a significant impact on pulping selectivity; a higher ratio would improve pulping selectivity. When the ratio reached approximately 0.5, a further increase in the ratio exhibited a positive linear relationship with pulping selectivity. The higher sulfide to hydroxide ratio also slightly increases pulp screened yield and a good linear correlation exists between the pulp primary properties, kappa number, viscosity, and pretreatment chemical absorption. The results indicate that the synergistic effect of sulfide and hydroxide ratio contribute to enhanced delignification.

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