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Relationship between the Kraft Green Liquor Sulfide Chemical Form and the Physical and Chemical Behavior of Softwood Chips during Pretreatment

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Chemical pretreatment of softwood chips with kraft mill green liquor results in the selective retention of various chemicals in the chips. It was found that each chemical component in the green liquor exhibits a different physicochemical behavior in the wood. For example, sulfide was determined to exist in wood chips in three distinct forms: free (in the bulk), adsorbed (physically entrained in the solid matrix), and chemically bonded (that cannot be leached). The ratios among these forms are a function of the pretreatment conditions employed. For example, high temperatures and high sulfide concentrations increase the amounts of both the adsorbed and chemically bonded forms. Meanwhile, surfactants, anthraquinone (AQ, a pulping catalyst), and polysulfide (PS, an active pulping chemical) added to a green liquor pretreatment scheme augment the levels of the chemically bonded form. This investigation into the influence of the pretreatment conditions on sulfide behavior demonstrated that lignin dissolution is increased as the levels of sulfide in the wood chips are increased. In fact, of the three forms of sulfide available for wood chip interactions, the free sulfide form exhibited a negative influence on lignin removal during pretreatment, whereas the adsorbed and chemically bonded forms correlated directly with higher lignin dissolution.

Introduction

The pretreatment of wood chips with various sulfide-rich liquors has been widely investigated as a powerful modification of kraft cooking and has been shown to be an efficient method for providing benefits in pulping selectivity and pulp qualities.^{1–5} In general, pretreatment technologies target chemical and/or physical modifications of the wood chips to facilitate chemical penetration and reactions in subsequent cooking stages. Nevertheless, the advancement of such technologies has been very slow given the lack of robust data on the chemistry occurring during the pretreatment. One of the stipulations for higher-efficiency kraft cooking technologies that was promulgated several years ago states that the sulfide (technically, the hydrosulfide anion) is the active species upon dissolution) content for the kraft cook should be high at the onset of the cook to derive the maximum physical and chemical benefits attainable for the wood chips. Pretreatment can therefore be thought of as a means to address this stipulation under fairly mild conditions relative to the strong caustic, high-temperature conditions of the kraft cook.

Therefore, the most critical issue for the continued development of improved pulping technologies is to ensure high sulfide contents in the initial cooking stage. Yet, the deployment of a pretreatment stage before the kraft cook has not received sufficient investigation given its value to the whole pulping operation. Such a stage could, in theory, minimize lignin condensation reactions. Condensation reactions in lignin can be defined as the formation of increased aromatic dimer or higher-order unit bonds in the form of 5,5-phenyl units (or higher-

order aromatic bridges) or diphenyl methane functionalities. Reducing the level of such condensed lignin structures is therefore tantamount to diminishing the activation barrier necessary to degrade the highly complex, three-dimensional lignin polymer. If the lignin polymer is less condensed, the opportunity to degrade it under less forceful conditions is likely enhanced, and thus, improvements in pulping selectivity can be obtained, e.g., less damage to the carbohydrate portion of the pulp occurs.

Previous investigations have reported that sulfide adsorption incrementally increases as a function of increasing pretreatment temperature, time, sulfide concentration in the pretreatment liquor, and ionic strength.^{4–6} To obtain sulfide adsorption benefits, Olm et al. concluded that the ratio of hydrosulfide to hydroxide ions should be 6–7 for absorption.⁵

Therefore, the objectives of this present work were to investigate the physical and chemical behavior of wood chips as a function of the sulfide forms that exist in wood chips under various pretreatment conditions and thus provide greater insight into approaches that can be used to optimize a pretreatment stage for increased benefits in kraft pulping technologies. One of the methods commonly used to assess the general utility of the pretreatment technology is to measure the dissolution of lignin, which was done in the present work.

Experimental Section

Wood Chips. U.S. southern pine wood chips from industrial supporting members of the Institute of Paper Science and Technology (IPST) were obtained. The chips were screened to retain the fractions with lengths between 16 and 32 mm and thicknesses below 10 mm. The dry content of all of the wood chips was determined

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to be 45.25%, and all bark, knots, and resinated chips were removed to keep the chip morphology as uniform as possible for all pulping work.

Green Liquor. The green liquor (GL) used in all of the experiments was provided by industrial sponsors of IPST. The chemical concentrations of its components were as follows: 26.45 g/L NaOH, 27.84 g/L Na₂S, and 78.27 g/L Na₂CO₃ (all concentrations expressed relative to Na₂O). These concentrations were analyzed by a standard ABC titration method (see TAPPI Method T626 cm-85).

Pretreatment. Pretreatment and cooking were carried out in a multi-unit stainless steel bomb digestive system. Six different samples could be treated simultaneously. Pretreatment procedures were controlled by a computer-programmed electric heater, with temperature ramps on the order of 1.5 °C/min. Each bomb could accommodate a volume of 1000 mL, and approximately 100 mL of headspace was allowed after the moist wood chips (equivalent to 100 g of oven-dried chips) were placed in each bomb. Pretreatment conditions were as follows: The ratio of pretreatment liquor to wood chips was 4:1 or 2:1. The GL charge on the wood chips was 1.0 L/kg, and the GL concentration varied from 25 to 50% (volume percent of GL in the total pretreatment liquor) based on the various ratios of liquor to wood, i.e., 33.14 g/L total chemicals and 6.96 g/L sulfide (both relative Na₂O) in the pretreatment liquor at the 4:1 ratio, and 66.28 g/L total chemicals and 13.92 g/L sulfide in the pretreatment liquor at the 2:1 ratio. The pretreatment temperatures were 90 and 120 °C, and the impregnating times varied from 15 to 120 min. Surfactants (SSAs) were provided for this work by Union Carbide and are referenced in this work according to their commercial designations. They were added in predetermined ratios to the wood chips during the pretreatment. TMN-10 corresponds to a 10-trimethylnonanol ethoxylate, whereas SS-15 surfactants are simple, secondary alcohol ethoxylates having a 13-carbon chain backbone. In general, the backbone contains variable-sized hydroxyl-end-capped ethylene oxide groups (up to 40) located in the middle of the alkyl chain.

Analysis. Sodium hydroxide in the pretreatment liquor was analyzed by the ABC titration method. Sulfide and carbonate in the pretreatment liquor were analyzed by GC.⁷ The concentrations of all chemicals that were adsorbed into the wood or present in the pretreatment liquor are expressed in units of moles per kilogram of wood.

After pretreatment, the pretreatment liquor was drained, and the void volume was measured. The amounts of the chemicals retained were calculated from the residual pretreatment liquor chemical analysis, i.e., amount of chemical retained = (total amount of chemical in the pretreatment liquor) – (amount remaining in the residual pretreatment liquor). The amounts of the chemicals adsorbed were calculated from the difference in chemical concentration between the remaining liquor in the wood chips and the residual pretreatment liquor, i.e., amount of chemical adsorbed = (amount of chemical retained) – (amount of free chemical). A discrete number of these wood chips were then washed in an ultrasonic washer with 0.05 M HCL solution followed by deionized water for about 12 h until no black deposit sediment could be detected by 0.1 M silver nitrate solution. The samples were oven-dried for standard elemental analysis, which was performed by Mi-

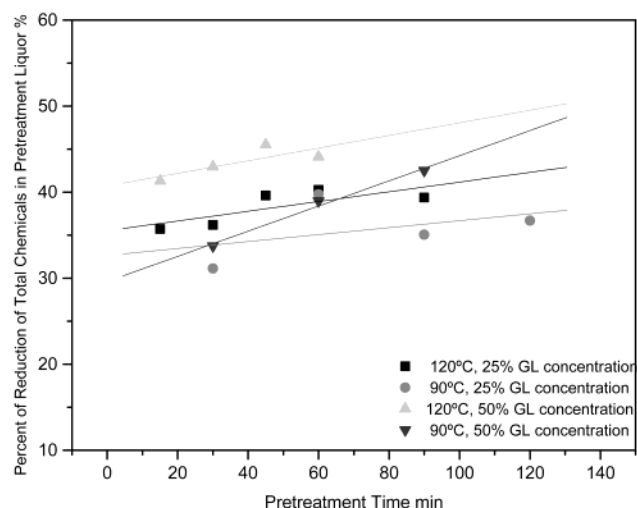


Figure 1. Change in concentrations of chemical components found in the pretreatment liquor. [The liquor-to-wood ratio was 4:1 for the 25% GL concentration and 2:1 for 50% GL concentration; the GL charge in all samples was 1.0 L/kg of chips (o.d.). These conditions also apply to the following figures]

cro Labs Atlantic (Norcross, GA). The sulfur content in the wood chips was calculated as the chemically bonded form.

Results and Discussion

Retention of Total Chemicals in Wood Chips.

Figure 1 shows the changes in total chemical contents in the wood chips under various pretreatment conditions. Overall, it was found that higher temperatures and pretreatment liquor concentrations provided higher levels of chemical sorption into wood chips within a certain impregnation time. However, the general increase in concentration of the chemicals in the wood chips had a threshold for each set of pretreatment conditions. This result suggests that penetration of the chemicals into the wood chips might be a rapid process. For example, it was found that, during wood chip pretreatment with green liquor, 80% of the total chemicals was consumed or retained in the wood chips within 15–30 min. Thus, for the purposes of chemical diffusion or penetration, long pretreatment times are not necessary. In the green liquor composite, sodium carbonate is the main component (almost two-thirds of the total chemical content), and its uptake changes little during the pretreatment, as will be discussed in detail later. Therefore, the changes in the concentration of the pretreatment liquor were attributed to changes in only hydroxide and sulfide, but the total concentration of the pretreatment liquor exhibited no obvious change.

Consumption of Hydroxide and Behavior of Carbocation in Pretreatment. As reported in our previous research,⁸ alkali is rapidly consumed by wood chips during pretreatment, which is partly due to the neutralization of organic acids in the wood, and the rest of the cations from the alkali are adsorbed onto the carbohydrates to accommodate charge neutrality. In the range of experiments performed thus far, the hydroxide ion was completely consumed in the pretreatment liquor within the initial 15 min, and the pH approached neutrality, as shown in Table 1. This fact indicates that the remaining sulfide acts on the wood chips as the hydrosulfide anion at a slightly alkaline or neutral pH for the majority of the pretreatment period under study.

Table 1. Changes in Pretreatment Liquor Alkalinity

sample no.	pretreatment conditions				liquor alkalinity after pretreatment	
	GL conc (%)	L/S ratio	temp (°C)	time (min)	pH	NaOH ^a (g/L)
1	25	4	120	15	9.6	0
2	25	4	120	30	8.9	0
3	25	4	120	60	7.7	0
4	25	4	120	90	7.8	0
9	25	4	90	30	11.47	0.084
10	25	4	90	60	11.24	0
11	25	4	90	90	10.6	0
12	25	4	90	120	10.45	0
5	50	2	120	15	8.2	0
6	50	2	120	30	7.3	0
13	50	2	120	45	7.2	0
14	50	2	120	60	6.8	0
15	50	2	90	30	11.36	0
16	50	2	90	60	11.16	0
17	50	2	90	90	10.48	0.26

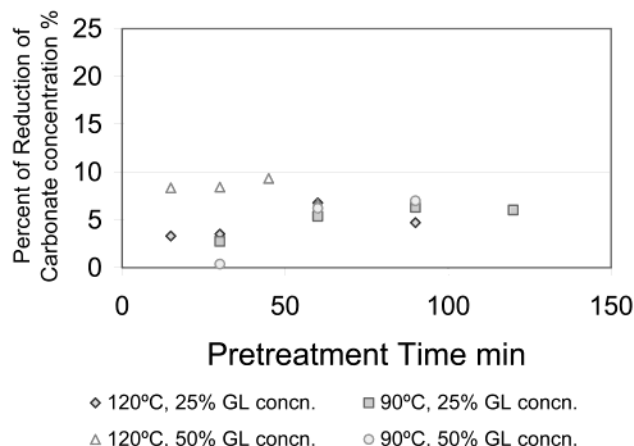
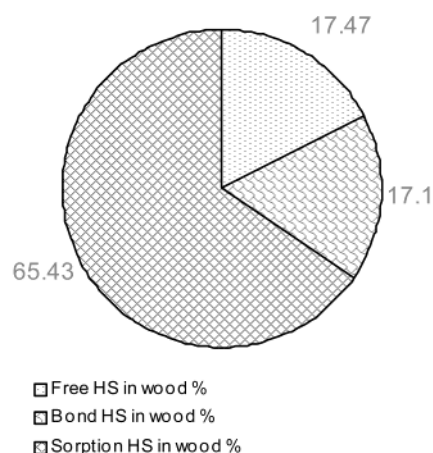
^a As Na₂O.**Figure 2.** Change in carbonate concentration during pretreatment under varying conditions.

Figure 2 illustrates the changes in the carbonate concentration in the pretreatment liquor during pretreatment. No obvious differences were observed between the carbonate concentrations in the liquor inside and outside the wood chips. The small differences in carbonate concentration might be due to decomposition of the bicarbonate ion under the neutral conditions. This latter result clearly indicates that carbonate does not behave in the manner demonstrated by sulfide during the pretreatment. The primary function of carbonate therefore appears to be increasing the ionic strength and assisting the sulfide activity.

Forms of Sulfide in the Wood Chips. During the impregnation of the wood chips with the chemical liquor, water and chemicals are absorbed into the wood chips until they gradually reach a moisture and mass equilibrium. The term "absorption" has typically been used to describe sulfide action during the pretreatment process in previous research, and the amount of sulfide "absorbed" has been calculated by obtaining the difference in the sulfide concentration in the pretreatment liquor before and after pretreatment. However, the concentration of sulfide in the wood chips does not take into account the profile of the sulfide forms that might exist there.

Thus, the term "adsorption" might be more appropriate for describing the chemical activity of sulfide within the wood chips. Adsorption is defined as the enrichment

**Figure 3.** Status of sulfide in wood chips after pretreatment with typical conditions (120 °C, 25% GL concentration, 60 min).

of a component in the interphase region compared to the bulk region,⁹ which is appropriate for the pretreatment case. Logically, there must be three chemical forms of sulfide that exist within the wood chips: free, adsorbed, and chemically bonded. The free form exists when there is no obvious difference in the concentration of a chemical component between the internal liquor in the wood chip (which enters through penetration) and the outside bulk liquor. Alternatively, when the internal liquor has a higher concentration of chemical component than the bulk liquor, i.e., when there is an enrichment of the chemical component concentration, the difference between the internal and bulk concentrations can be expressed as adsorption. The significant difference between the free and adsorbed forms is that adsorption occurs on the surface of carbohydrates, and free ions are present in the liquor both inside and outside the chips. A permanent adsorption event is one in which a chemical reaction occurs and a subsequent chemical bond is formed.

Figure 3 illustrates the amounts of the various forms of sulfide present in the wood chips under typical pretreatment conditions. As shown, most of the sulfide exists in the adsorbed form in the wood chips after pretreatment. These results reveal that sulfide, unlike hydroxide and carbonate, displays xylophilicity. Sulfide is selectively adsorbed into wood and therefore can be enriched within wood tissues. On the other hand, the chemically bonded form, although not present at any appreciable levels, confirms that sulfide can react with lignin under the given pretreatment conditions.

Impact of Pretreatment Conditions on Sulfide Form. In general, a higher pretreatment temperature results in more rapid penetration of the liquor into the wood, and therefore, more of the sulfide is retained in the wood chips after a given pretreatment time, as demonstrated in Figure 4. Another important factor influencing sulfide impregnation was observed by changing the ratio of pretreatment liquor to wood, i.e., changing the concentration of the green liquor contained in the pretreatment liquor. A higher green liquor concentration in the pretreatment liquor increases the sulfide content in the wood chips to a greater extent. Thus, in a practical sense, increasing the green liquor concentration in the pretreatment liquor is an efficient method of increasing the concentration of sulfide while remaining at a lower temperature.

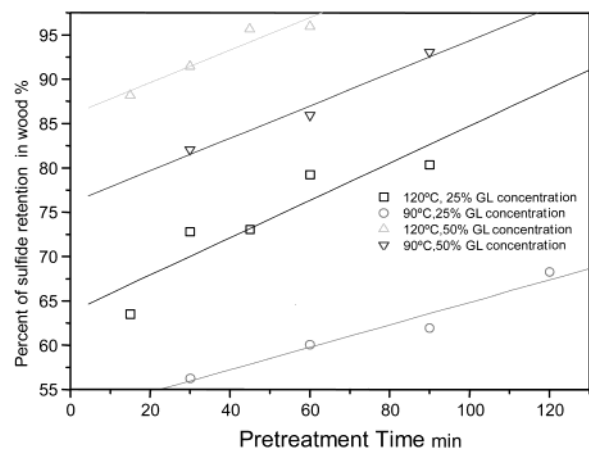


Figure 4. Percent of sulfide retained in the wood chips during pretreatment under varying conditions.

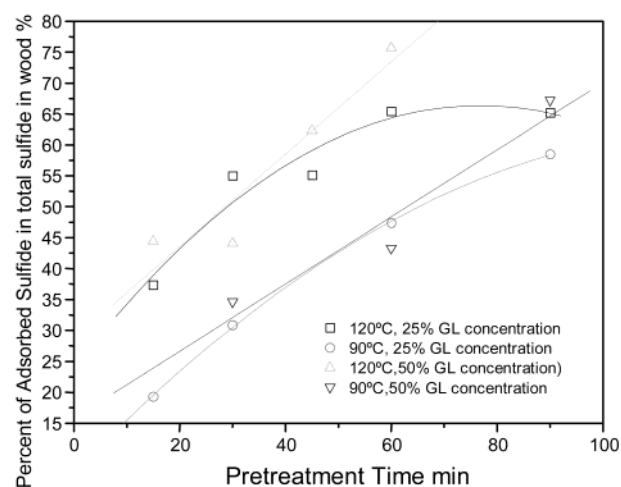


Figure 5. Comparison of sulfide adsorption in wood chips under various pretreatment conditions.

Similarly, Figure 5 demonstrates that both higher temperature and higher green liquor concentration can benefit sulfide adsorption. A higher green liquor concentration not only provides a higher sulfide content in the wood chips, but also increases the adsorption rate. Interestingly, the effects of the green liquor concentration and temperature can be compensated to give similar levels of sulfide adsorption. For example, similar levels of sulfide adsorption can be acquired by either a higher pretreatment temperature with a lower green liquor concentration or a higher green liquor concentration at a lower temperature.

Activity of Surfactant in the Pretreatment Process. As part of the overall plan to improve the kraft cooking process through a pretreatment phase, the question of enhanced penetration is a natural one for any improvements in the cooking process. Therefore, it was decided to employ surfactants to address the possibility of enhanced chemical penetration. Commercial surfactants were used in the current experiments: TMN-10 is a 10-trimethylnonan-1-ol ethoxylate, and SS-15 surfactants are simple, secondary alcohol ethoxylates having a 13-carbon chain backbone. The backbone contains variable-sized hydroxyl-end-capped ethylene oxide groups (up to 40) located in the middle of the alkyl chain.

For the same pretreatment conditions (120 °C, 30 min, 25% GL concentration), no obvious enhancement

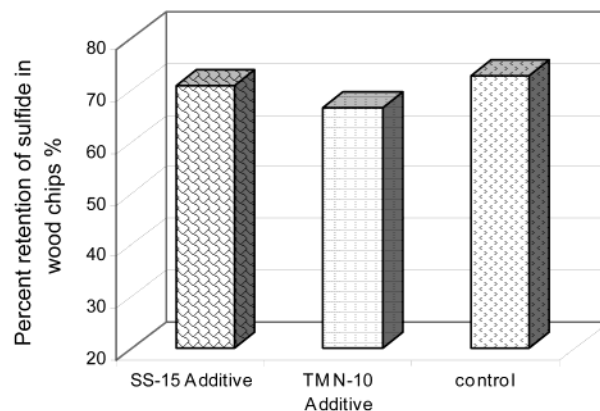


Figure 6. Percentage of sulfide retained in the wood chips for different surfactants.

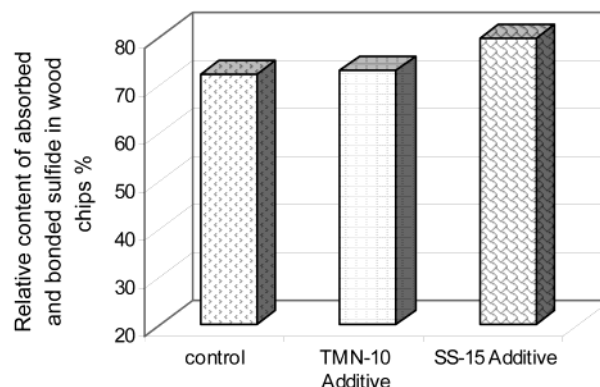


Figure 7. Relative contents of both adsorbed and chemically bonded sulfide in wood chips for different surfactants.

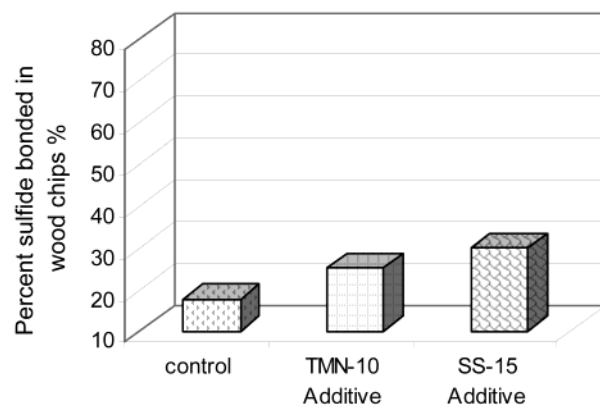


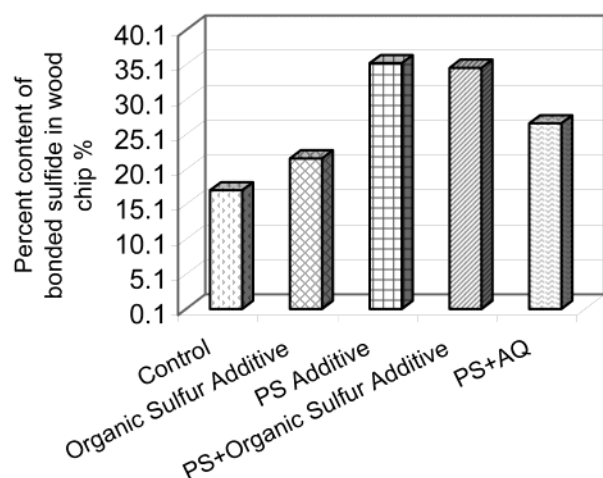
Figure 8. Percentage of chemically bonded sulfide in wood chips for different surfactants.

was observed in the overall retention of sulfide for either surfactant sample compared to that obtained with green liquor alone, as shown in Figure 6. These data suggest that neither surfactant assists in the penetration of the wood chips by the green liquor components. Figure 7 provides further detail on the impact of surfactants on sulfide adsorption: SS-15 provides higher sulfide adsorption than the control sample containing only green liquor, which indicates an improvement in the sulfide affinity with the wood components. However, TMN-10 appears to display no obvious positive influence on sulfide adsorption.

Furthermore, it appears that these surfactants influence the formation of sulfide chemical bonds, as shown in Figure 8. In general, the function of the surfactants is to reduce the surface tension between the liquor and

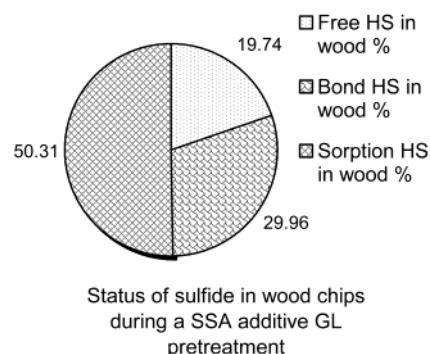
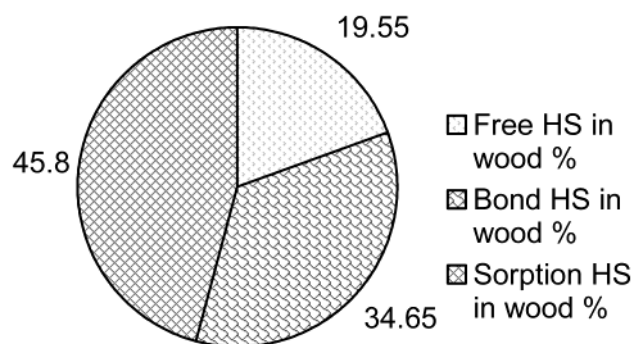
Table 2. Impact of Additives on Sulfide Form

	content in wood (%)		net sorption (%)	retention (%)
	free	bonded ^a		
control	17.47	17.095	65.43	79.24
AQ (0.05)	22.39	29.75	47.86	77.61
PS (1.0)	24.86	30.72	44.43	88.20
PS (1.0) + aliphatic thiols (1.0)	19.55	34.65	45.80	80.45
AQ (0.05) + aliphatic thiols (1.0)	23.048	26.69	50.26	76.95

^a As Na₂O.**Figure 9.** Percentage of chemically bonded sulfide for different pulping chemical additives (organic sulfur compound is from a series of related aliphatic thiols).

wood chips, thereby improving the penetration and diffusion of the chemical solution into the wood chips. Thus, a uniform distribution of the liquor can be achieved to provide beneficial pulp qualities. Some previous research has indicated that the addition of surfactant during pulping results in a significant decrease in rejects and a slight increase in pulp yield.^{10,11} However, the most obvious influence of surfactants on sulfide behavior in GL pretreatment under the current conditions is to strengthen sulfide chemical bonding, rather than to improve sulfide adsorption. A possible explanation for this phenomenon is that the surfactant in the pretreatment might help the sulfide to access and become enriched in concentration at the reaction sites. Werthemann,¹² for example, suggested a xylophilicity/hydrophilicity ratio concept for quinoid additives to describe their impact on delignification. Similarly, a hydrophilicity/hydrophobicity ratio for surfactants might be applicable in describing the influence of surfactant additives on the pretreatment process. Additional research in this area is required to develop this concept further.

Effects of Additives on Sulfide Status. Table 2 summarizes the impact of AQ and PS additives on the sulfide forms during GL pretreatment. The results indicate that not all additives can increase either sulfide retention or sulfide adsorption. However, the important influence of additives was observed for sulfide chemical bond formation, as shown in Figure 9. For either AQ or PS addition, the bonded sulfide form in wood chips increased by as much as 12–18% as compared with the control. These results indicate that the additives can exert a catalytic effect that strengthens the sulfide chemical reaction with lignin in wood under mild

**Figure 10.** Status of sulfide in the wood chips during an SSA (surfactant) additive GL pretreatment.**Figure 11.** Status of sulfide in wood chips during an additive GL pretreatment.

pretreatment conditions. The aspect of the catalytic behavior of AQ and PS in alkaline pulping for delignification and subsequent improved pulp qualities has been widely investigated previously, and the chemical mechanisms of their reactions with lignin and carbohydrates are well understood. However, most research in this area has focused on the cooking procedure, whereas the behavior of additives during pretreatment still remains unclear.

It is known, however, that the effectiveness of AQ is higher at lower sulfidity than at higher sulfidity when used during kraft pulping.^{13–15} The explanation for this behavior is still not fully clear. One possible explanation is that the efficiency of AQ might be attenuated by the chemical reactivity of sulfide under high sulfidity. Kutney¹⁵ reported that the addition of AQ can replace part of the active sulfide to achieve the same kappa number in kraft pulping. Yet, the general effect of additives on the behavior of the cooking chemicals, especially sulfide, has not received much attention. When AQ and PS are used in these pretreatments, lignin dissolution is not significant, but an obvious increase in the chemical bonding of sulfide in the lignin component is observed. This result demonstrates that AQ and PS can influence the form of sulfide in wood and enhance the chemical reaction of sulfide with lignin. The positive effect of this enhancement should therefore be exhibited in the post-cooking stage.

Figures 10 and 11 show the proportions of the forms of sulfide that are preserved in the wood chips following additive pretreatment with both surfactants and PS and aliphatic thiols. The main results shown here are the higher ratios of chemically bonded sulfide as compared to those obtained in the control green liquor pretreatment (Figure 3).

Relationship between Sulfide Form and Lignin Removal during Pretreatment. In general, the main

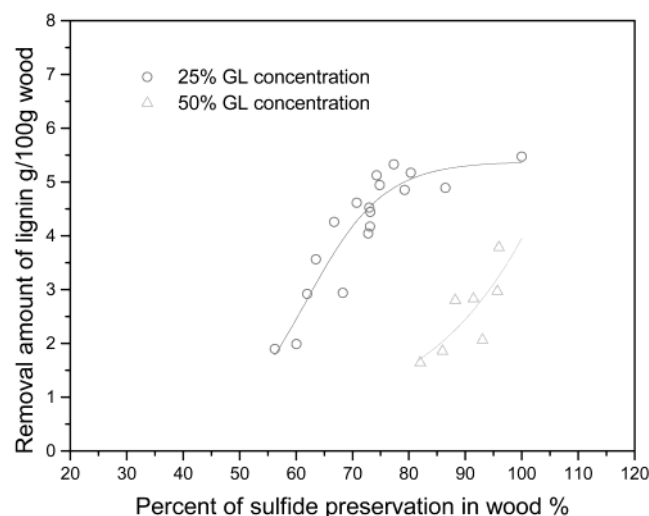


Figure 12. Lignin dissolution during pretreatment vs sulfide retained in the chips.

goal for pretreatment with sulfide-containing liquors is to preserve sulfide in the wood chips to acquire a higher sulfide concentration for increased delignification. As in the initial stage of kraft cooking, lignin should be dissolved from the wood chips during the pretreatment process. Unfortunately, not much information has been collected on the removal of lignin from wood chips during pretreatment. One investigation reported that a significant amount of lignin could be removed with a hot black liquor pretreatment, corresponding to nearly 50% of the original lignin.¹⁶ Another work reported that only 3% of the original lignin was reduced during pretreatment with various sulfide-containing liquors.¹⁷ These differences might derive from different experimental and measurement methods. Nevertheless, the removal of lignin during the pretreatment process can be correlated with the whole delignification process and subsequent delignification in the bulk cooking stage.

Figure 12 clearly demonstrates the relationship between lignin removal and sulfide retention in wood chips. Higher sulfide retention in wood results in a higher level of lignin removal during pretreatment, as observed at both the 25 and 50% green liquor concentrations. Any further increases in sulfide retention beyond 80% resulted in only a slight increase in the dissolution of lignin.

Although higher sulfide retention in pretreatment correlates to a higher ratio of lignin removal, different forms of sulfide in the wood chips play different roles in lignin removal. Figure 13 demonstrates the influence of various concentrations of sulfide in the free form on lignin dissolution. Interestingly, an increase in free sulfide has a negative impact on lignin removal during the pretreatment process. These results indicate that sulfide that is retained in the wood in the free form does not function as an effective delignification agent. The data thus reveal that effective lignin removal can be achieved only when sulfide is retained in the wood chips in the adsorbed and chemically bonded forms, as shown in Figure 14.

Furthermore, Figure 15 reveals a very novel and heretofore undiscovered result: a strong trend of the removal of lignin with the level of chemically bonded sulfide in the wood chips. Overall, an increase in the chemically bonded form of sulfide in wood chips results in higher lignin dissolution during pretreatment under

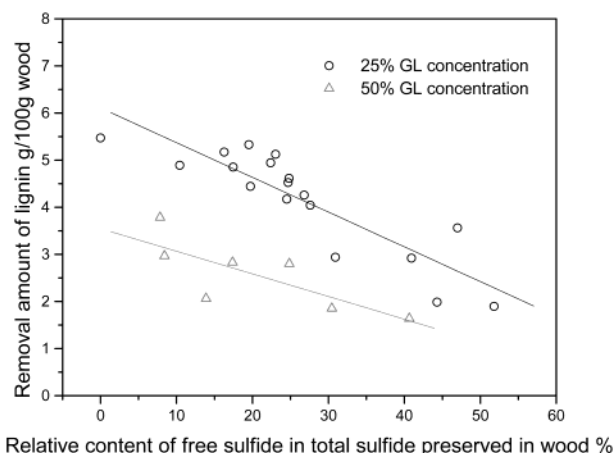


Figure 13. Lignin dissolution during pretreatment vs relative content of free sulfide in the wood.

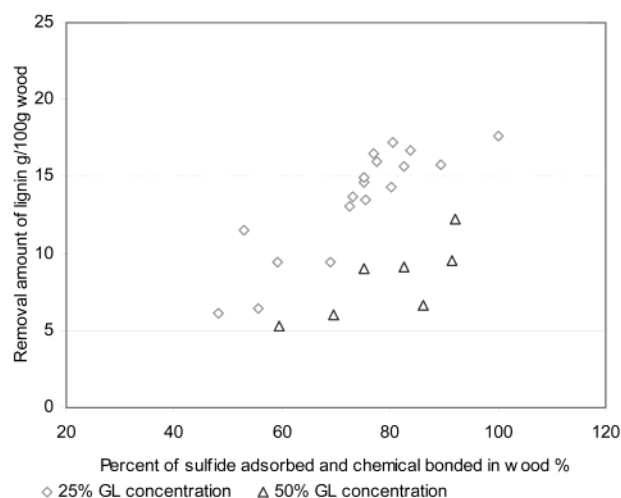


Figure 14. Lignin dissolution during pretreatment vs percent of sulfide adsorbed and chemically bonded.

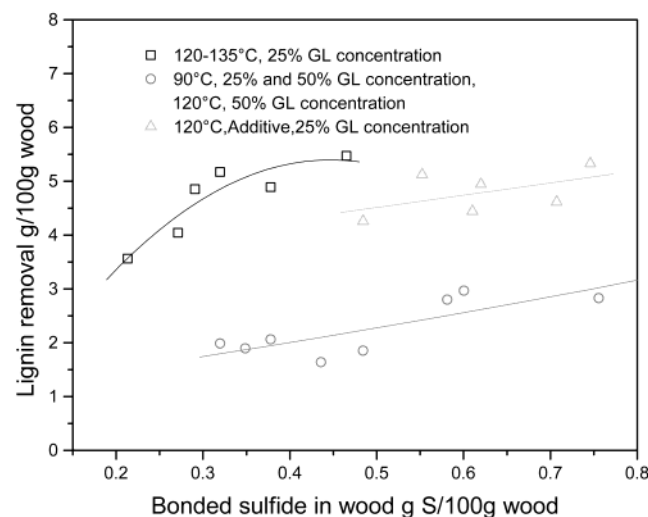


Figure 15. Lignin dissolution during pretreatment vs chemically bonded sulfide content.

various pretreatment conditions. Otherwise, the pretreatment conditions, especially the concentration of green liquor in the pretreatment liquor and the pretreatment temperature, have a significant influence on lignin removal. It was found that a higher pretreatment temperature is especially beneficial for lignin dissolu-

tion, whereas a high green liquor concentration strengthens both pretreatment liquor penetration and sulfide adsorption (see Figures 4 and 5). However, a high green liquor concentration was found to not assist in lignin removal during pretreatment. A possible explanation for this latter phenomenon is that a higher green liquor concentration in the pretreatment liquor corresponds to less liquor used in the pretreatment at a given green liquor charge, which results in a higher lignin concentration in the pretreatment liquor. Thus, this large concentration gradient would tend to hinder lignin dissolution, although these results do not necessarily translate into a negative influence in the kraft cooking phase.

Conclusions

This work has undertaken a careful investigation of the chemical behavior of various chemical components in kraft green liquor during a formal pretreatment phase of softwood chips. Alkali (hydroxide), for example, is known to be consumed rapidly during pretreatment as a result of neutralization and adsorption on carbohydrates. Sodium carbonate appears to behave as an inert component during green liquor pretreatment. This investigation demonstrated that sodium carbonate exists in wood in an unbound, free form, with no adsorption or chemical bonding observed. Sulfide, on the other hand, whose study comprised the bulk of this work, can be retained in wood chips, and it is able to maintain three distinct forms: free, adsorbed, and chemically bonded. A high temperature and a high green liquor concentration in the pretreatment liquor were shown to result in higher contents of the adsorbed and chemically bonded forms of sulfide.

Higher sulfide retention in the wood was found to correlate well with higher lignin dissolution during pretreatment. Remarkably, the different chemical forms of sulfide in the wood demonstrated different contributions to lignin removal; for example, the free sulfide form exhibited a negative impact on lignin removal, whereas high levels of the sulfide in the adsorbed and chemical bonded forms can be related to higher lignin dissolution.

Finally, the aspect of understanding the dynamics of lignin dissolution through the sulfide forms in the pretreatment phase was investigated using surfactants and other pulping agents. Surfactants, AQ, and PS appear to have a profound impact on both the sulfide form and lignin dissolution. Specific surfactants enhance sulfide chemical bonding rather than contributing to sulfide adsorption. Additionally, AQ and PS accelerate the formation of sulfide chemically bonded forms and, therefore increase lignin dissolution.

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