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# Insight into the Chemical Behavior of Softwood Carbohydrates during High-Sulfidity Green Liquor Pretreatment

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About 20% of the total wood carbohydrates removed from softwood chips from a pretreatment with a high-sulfidity, carbonate-rich solution known as green liquor (GL) are mainly derived from glucose and mannose. The salient chemical events occurring during GL pretreatment are sugar readsorption in a neutral or slightly alkaline environment and substantial mannan dissolution. However, it appears that pentose saccharides are more easily adsorbed onto fibers than hexose saccharides. Mannose, for example, undergoes degradation easily, with no obvious readsorption during the entire process. A higher GL concentration can enhance both tendencies of reabsorption and degradation. A striking finding is that, during the pretreatment phase, hydrogen sulfide appears to react with wood composites to form a very tight bond that appears to be chemical in nature. The apparent chemical bonding behavior of sulfur in wood correlates with carbohydrates retention: a higher level of bonded sulfur results in higher carbohydrates retention. Finally, various additives applied during GL pretreatment were found to exert a significant influence on sugar retention.

## Introduction

During the past several decades, technological strides in improving the efficiency of kraft pulping have been significant. One of the major improvements has resulted from the impregnation of wood chips with sulfide-containing liquors such as black liquor, based on one of the well-established pulping principles demonstrated by STFi (Swedish Pulp & Paper Research Institute) researchers.<sup>1–3</sup> The principle states that a high hydrogen sulfide ion concentration in the first cook stage relative to the hydroxide ion concentration benefits delignification selectivity (the ratio of pulp viscosity to kappa number) based on fundamental pulping chemistry considerations. Since then, many research efforts have been directed toward substantiating and utilizing this principle. Green liquor (GL), a process liquor from the black liquor recovery system in kraft pulping mills that naturally contains high sulfide levels, is superior as a pretreatment liquor compared to black liquor because of its higher sulfide content and ratio of sulfide to alkali. Several investigations have confirmed the benefits of using GL pretreatment to improve the delignification selectivity, pulp yield, and strength and to reduce chemical consumption.<sup>4–6</sup> However, previous investigations focused mainly on the technical conditions of the pretreatment and their impact on the qualities of the pulp. The mechanism of the pretreatment process is still unclear. The chemical changes occurring in the pulp carbohydrates during pretreatment have never been reported and warrant further work to understand the basis of the chemistry of GL pretreatment. Our previous work investigated the retention of carbohydrate components in various GL-pretreatment-modified kraft pulps by means of anion-exchange chromatography and the impact of GL pretreatment on carbohydrate retention.<sup>7</sup>

An increase in pulp yield that can arise, for example, from increased carbohydrate retention is one of the main priorities for the pulp and paper industry. Thus, a better understanding of the mechanism of carbohydrates retention in GL pretreatment is paramount for further improvements in pulping efficiency. The objective of the present work is to demonstrate the behaviors and functional changes of pulp carbohydrates under different pretreatment conditions. Investigating the impact of pretreatment parameters on the changes in carbohydrates in wood chips was the key driving force in this work.

## Experimental Section

**Wood Chips.** U.S. Southern pine wood chips were obtained from industrial supporting members of the Institute of Paper Science and Technology (IPST). 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 to be 45.25%, and all bark, knots, and resinated parts were removed to keep chip sizes 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 26.45 g/L NaOH, 27.84 g/L Na<sub>2</sub>S, and 78.27 g/L Na<sub>2</sub>CO<sub>3</sub> (all concentrations expressed as Na<sub>2</sub>O), as determined by the ABC titration method (see TAPPI Method T 626 cm-85).<sup>8</sup>

**Pretreatment.** Pretreatment and cooking were carried out using a stainless steel bomb digestive multi-unit system. Six different samples could be treated simultaneously. Pretreatment procedures were controlled by a computer-programmed electric heater; temperature increases (ramps) were on the order of 1.5 °C/min, and each digestive unit could accommodate a volume of 1000 mL while allowing a headspace of approximately 100 mL after wet wood chips (equivalent

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**Table 1. Experimental Conditions Investigated in This Work**

sample ID	pretreatment conditions					liquor properties after pretreatment			
	L/S ratio	GL conc (%)	temp (°C)	time (min)	additive, conc (%)	concentration <sup>a</sup> (g/L)			
						pH	NaOH	Na <sub>2</sub> S	Na <sub>2</sub> CO <sub>3</sub>
1	4	25	120	15		9.6	0	3.56	17.54
2	4	25	120	30		8.9	0	2.537 414	17.5
3	4	25	120	60		7.7	0	1.86	16.909 06
4	4	25	120	90		7.8	0	1.76	17.29
5	2	50	120	15		8.2	0	3.62	33.25
6	2	50	120	30		7.3	0	2.62	33.22
7	4	25	120	45		7.3	0	2.4	16.56
9	4	25	90	30		11.47	0.08	3.91	17.64
10	4	25	90	60		11.24	0	3.57	17
11	4	25	90	90		10.6	0	3.4	15.35
12	4	25	90	120		10.45	0	2.83	17.05
13	2	50	120	45		7.2	0	1.33	32.9
14	2	50	120	60		6.8	0	1.24	33.87
15	2	50	90	30		11.36	0	5.5	36.14
16	2	50	90	60		11.16	0	4.32	34.03
17	2	50	90	90		10.48	0.26	2.13	33.74
18	4	25	135	30		8.3	0	1.21	18.19
19	4	25	120	60	TS, 2.0	8.1	0	0	17.54
20	4	25	120	60	AQ, 0.05	8.1	0	2.92	14.43
21	4	25	120	30	TMN-10, 0.5	8.4	0	3.56	15.16
22	4	25	120	30	SS-15, 0.5	8.3	0	2.87	14.87
23	4	25	120	60	PS, 1.0	7.9	0	3.26	14.54

<sup>a</sup> Chemicals in pretreatment liquor expressed as Na<sub>2</sub>O.

to 100 g of oven-dried chips) had been placed in each bomb. The bombs were heated at a set heating rate until the designated temperatures were reached at (ramp period). Then, the temperatures were held for a specific time (impregnating period) during the pretreatment. The pretreatment conditions were as follows: the ratio of the pretreatment liquor to the wood chips was 4:1 or 2:1; the GL charge on the wood chips was 1.0 L/kg; and the GL concentration was varied from 25 to 50% (percent volume content 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 as Na<sub>2</sub>O) 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 used were 90 and 120 °C, and the impregnating times were varied from 15 to 120 min at the designated temperature. Surfactants (SSA) 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 surfactant, whereas SS-15 surfactants are simple, secondary alcohol ethoxylates having a 13-carbon chain backbone. The backbone generally contains variable-sized hydroxyl-end-capped ethylene oxide groups (up to 40) located in the middle of the alkyl chain.

All experimental conditions are reported in Table 1.

**Chemical Analysis.** Sodium hydroxide in the pretreatment liquor was analyzed by the ABC titration method. Sulfide and carbonate in the pretreatment liquor were analyzed by the GC method described in an earlier report.<sup>8</sup>

**Sample Preparation.** The hydrolyses of the pulp samples were accomplished by a two-step acid hydrolysis procedure as reported in the literature.<sup>9</sup>

**Chromatography.** The high-performance anion-exchange chromatograph (HPAEC) used was equipped with a GP40 gradient pump and an AS40 autosampler,

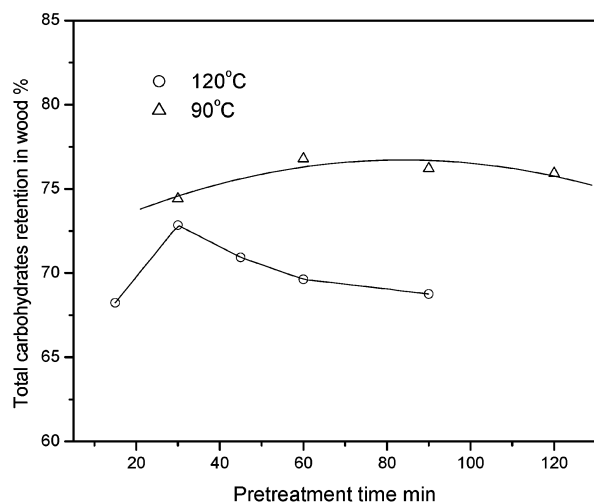
**Table 2. Carbohydrates and Wood Yields after Pretreatment**

sample ID	yield (%)		sample ID	yield (%)	
	carbohydrates	wood <sup>a</sup>		carbohydrates	wood <sup>a</sup>
1	61.82	75.93	15	67.44	78
2	65.96	75.97	16	84.74	77.81
3	64.7	74.03	17	64.02	75.8
4	66.64	73.79	18	76.94	71.97
5	66.71	75.8	19	74.17	72.87
6	65.02	74.75	20	69.2	75.01
7	65.17	74.87	21	75.04	76.33
9	63.67	80.4	22	68.36	75.55
10	64.65	81.69	23	70.17	74.64
11	67.32	77.87	24	70.1	72.33
12	66.61	78.4	25	72.53	72.48
13	65.24	74.14	wood	68.79	100
14	67.08	73.38			

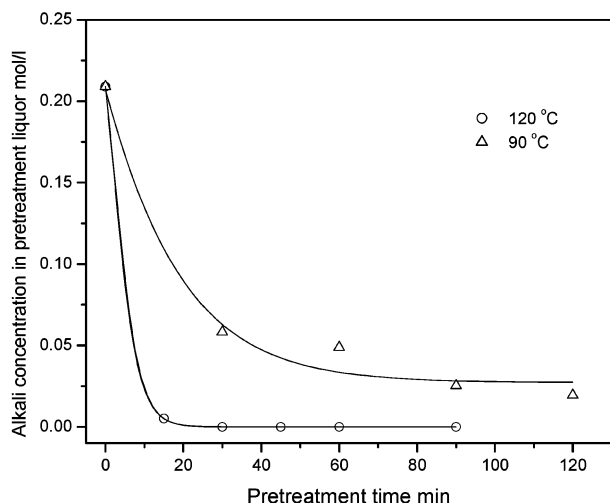
<sup>a</sup> After pretreatment.

whereas an ED40 pulsed amperometric electrochemical detector (PAD) was used for the analysis of carbohydrates. Typical operating conditions included an eluent flow of 1.0 mL/min, with eluent 1 being 2 mM NaOH and eluent 2 being 200 mM NaOH, for a duration of 17 min including cleaning and equilibration or 40 min for separation.

Carbohydrate retention in the experiments was calculated on the basis of the sugar amount in the samples [normalized to 100% based on chromatographic data and carbohydrate yield from hydrolysis (Table 2)] and was compared to the saccharide contents in the wood. All experimental trials were duplicated to ensure reproducibility. The standard deviation of the experimental runs was found to be 4.8%. The descriptions and measurements of carbohydrate identity in the pine wood (e.g., glucan) followed approved TAPPI standards and should not be confused with more rigorous terminology for individual saccharides. For example, the saccharides arabinose and galactose, although not found as these forms in pinewood, are nevertheless referred to as arabinan and galactan on the basis of the calculations



**Figure 1.** Change in total carbohydrates during GL pretreatment. [Note that the GL concentration in all figures is 25% (ratio of wood to liquor of 1:4) unless indicated otherwise.]

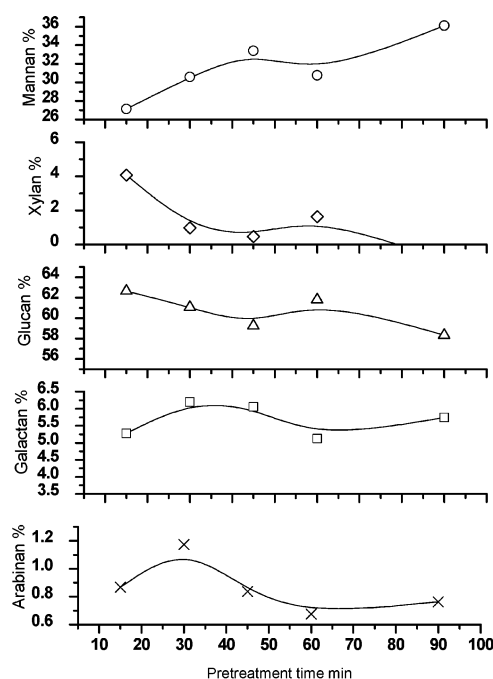


**Figure 2.** Change in alkali concentration during GL pretreatment at different temperatures.

performed in this work and in accord with TAPPI conventions.

## Results and Discussion

**Stabilization of Carbohydrates at Different Pretreatment Temperatures.** The general change in total carbohydrates during GL pretreatment is shown in Figure 1. As indicated in this figure 1, a higher pretreatment temperature results in a higher carbohydrate loss; indeed, one-third of the carbohydrates were removed from wood chips at the end of the first 15 min of the pretreatment period at 120 °C. However, in the next 15 min, the carbohydrates retention increased rather than exhibiting the natural tendency to decrease, a phenomenon observed at both the lower and higher temperatures. The rationale for this phenomenon in all likelihood is based on the changes in the pretreatment pH, as confirmed by Figure 2. In Figure 2, the changes in alkali concentration in the pretreatment liquor correlate quite well with the changes in carbohydrates. Alkali in the pretreatment liquor was thoroughly consumed in the first 15 min at 120 °C and, therefore, resulted in a slightly alkaline or neutral environment. A portion of the alkali-soluble saccharides could then

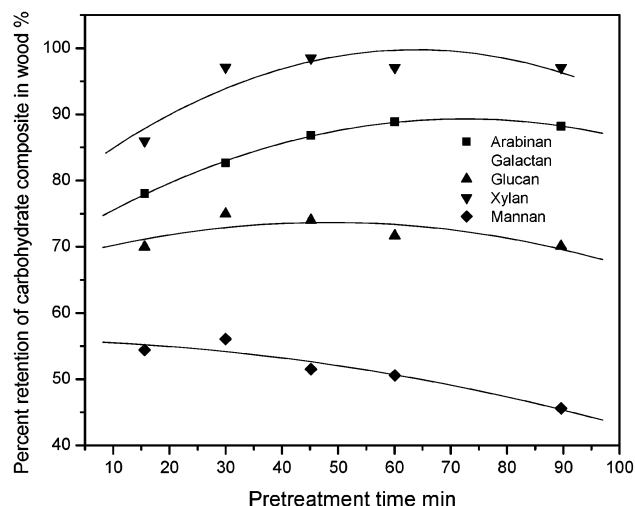


**Figure 3.** Saccharides in removed carbohydrates (pretreatment temperature of 120 °C).

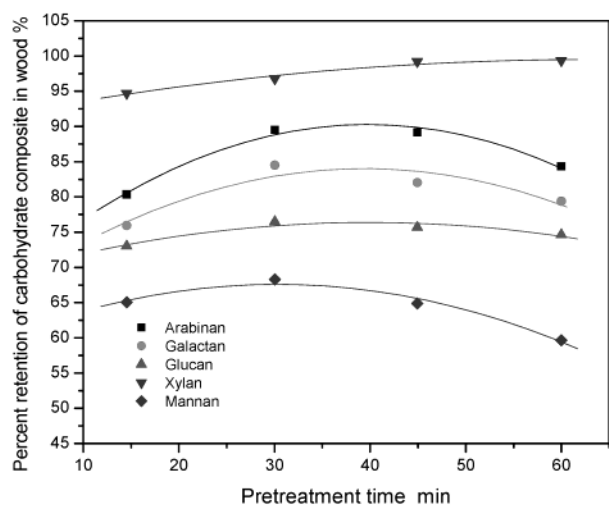
precipitate and be readsorbed at the pulp surface. This tendency was observed for all of the pretreatment times at the lower temperature. Because the decrease of the alkali concentration in the pretreatment liquor at the lower temperature was not as significant as that observed at the higher temperature, the readsorption of carbohydrates was not as pronounced. Therefore, a reduced alkalinity in the pretreatment stage is favorable to carbohydrate readsorption onto the fibers, which results in an increase in the level of carbohydrate retention during the pretreatment process.

Furthermore, carbohydrate retention slowly diminished during the remainder of the pretreatment period at the lower temperature. Compared to pretreatment at the higher temperature, pretreatment at the lower temperature resulted in higher carbohydrate retention, as much as 5–7 absolute percentage points.

**Analysis of Saccharides in the GL Pretreatment Liquor.** The compositional data for the saccharides in the dissolved carbohydrate fraction illustrated in Figure 3 are relatively significant. First, the main monosugar saccharides dissolved during the GL pretreatment are glucose (from glucan oligosaccharides) and mannose (from mannan oligosaccharides), approximately 60 and 30%, respectively. The observation of the mannose loss in the pretreatment is not surprising, given that galactoglucomannans are the principal hemicelluloses in softwood.<sup>10</sup> However, because the galactose/glucose/mannose molar ratio in galactoglucomannans is about 1:1:3,<sup>10</sup> it is reasonable to conclude that the bulk of glucose removal occurring during the pretreatment must derive from the degradation of cellulose. The lower galactan retention can be ascribed to its side linkage, which would allow this sugar to be more easily removed. Second, each of the saccharides demonstrated a unique behavior: The loss of xylan was reduced and was almost inconsequential. In contrast to xylan, mannan was continuously dissolved from the wood during the entire pretreatment process. In comparison to other saccharides, the retentions of glucan and galactan were



**Figure 4.** Changes in retention of sugar components (pretreatment temperature of 120 °C).



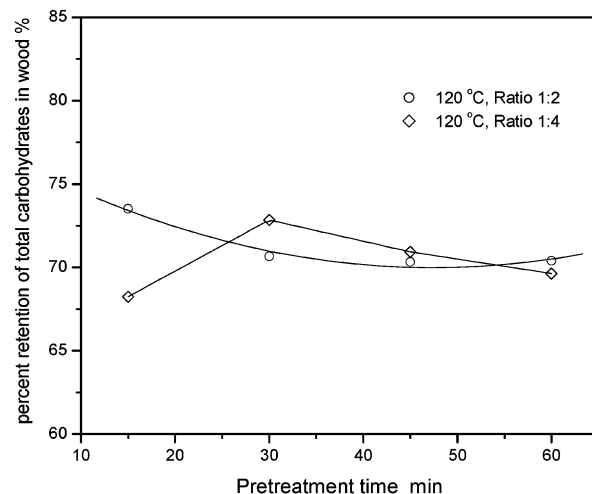
**Figure 5.** Changes in retention of sugar components (pretreatment temperature of 90 °C).

slightly reduced as the pretreatment proceeded, whereas arabinan behaved similarly xylan, as the retention ratio increased during the pretreatment. These startling results demonstrate that pentose-based saccharides are more easily readsorbed onto fibers than hexose-based saccharides. The changes in saccharide composition at the higher temperature compared to those observed at the lower temperature are shown in Figures 4 and 5, respectively. Similar trends for each of the saccharides were observed at both temperatures, but the changes were not as pronounced at the lower temperature.

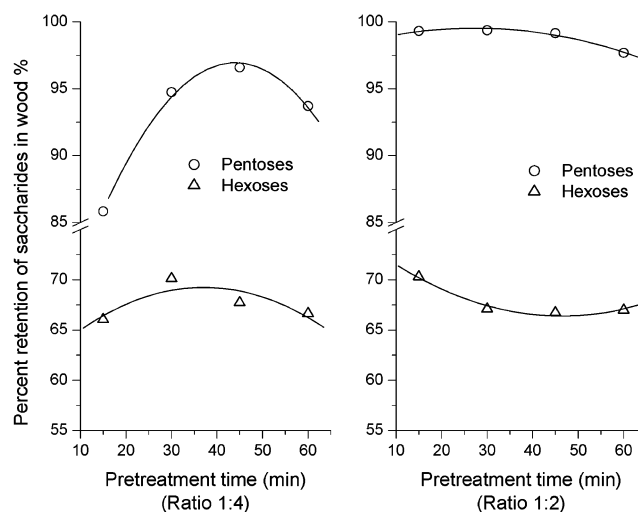
Although the pentoses, xylan and arabinan, engaged in readsorption, the pronounced loss of the hexoses, especially mannan, at higher temperatures resulted in an overall decrease in the total carbohydrates following the pretreatment period (as shown in Figure 1). Also, the lower losses of mannan and glucan under the mild pretreatment conditions (90 °C) and subsequent readsorption of the pentoses resulted in a slightly higher increase in total carbohydrates retention. From the experimental data, it can be concluded that a strong readsorption of xylan accompanied by a significant removal of mannan describes the salient changes for softwood carbohydrates during GL pretreatment.

#### Impact of GL Concentration on Carbohydrates.

The ratio of wood to liquor in the pretreatment is an



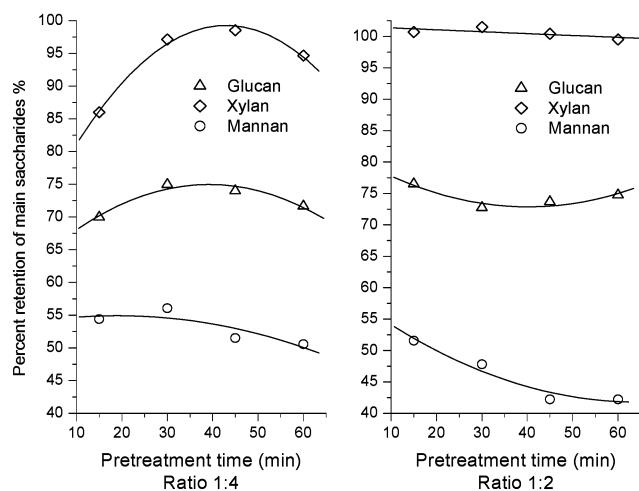
**Figure 6.** Comparison in total carbohydrates retention at various GL concentrations (pretreatment temperature of 120 °C).



**Figure 7.** Comparison in pentose and hexose retentions at various GL concentrations (pretreatment temperature of 120 °C).

important parameter, given that it controls the GL concentration in the process liquor. The changes in total carbohydrates in the pretreatment at wood-to-liquor ratios 1:4 and 1:2 are plotted in Figure 6. Compared to the results observed for the ratio of 1:4, i.e., 25% GL concentration in the pretreatment liquor, at a ratio of 1:2 (50% GL concentration), the retention of total carbohydrates in the first 15 min at 120 °C was higher, and no carbohydrate retention was observed. However, this does not indicate that readsorption of saccharides did not occur in the process at the high GL concentration. In comparison to the changes in alkalinity in the two cases (see Table 1), at the wood-to-liquor ratio of 1:2, the alkali and sulfide were completely adsorbed, and the alkalinity in the pretreatment liquor reached a neutral pH compared to a slightly alkaline pH at the 1:4 ratio. Because of a more rapid alkali adsorption at the higher GL concentration, saccharide readsorption should occur at an earlier stage as compared to the lower GL concentration. Figure 7 further illustrates the comparison of changes in the pentoses and hexoses in the pretreatment with varied liquor ratios. As much as 100% of the pentoses were retained at the higher GL concentration, which can be attributed to strong readsorption at an earlier pretreatment stage. These results indicate that the process with the lower liquor-to-wood



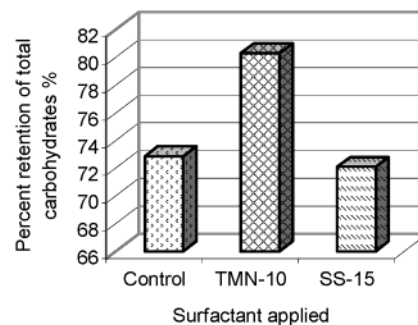


**Figure 8.** Comparison in changes of major saccharides at various GL concentrations as a function of pretreatment time (pretreatment temperature of 120 °C).

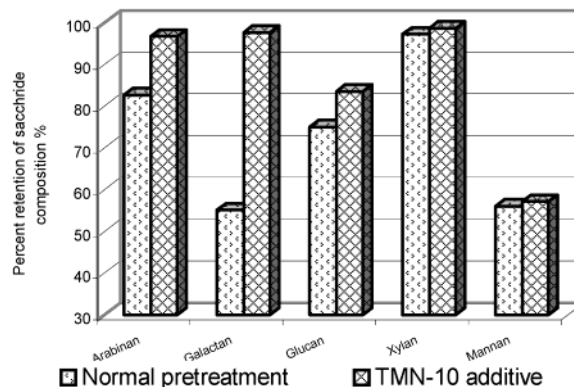
ratio is conducive to pentose retention. The behaviors of the three main saccharides in the pretreatment at both high (1:4) and low (1:2) ratios are shown in Figure 8. In addition to the high xylan retention in the low-liquor-ratio process from readsorption as discussed above, the mannan retention decreased more quickly by as much as 8 absolute percentage points at the end of pretreatment compared to that for the process with the high liquor-to-wood ratio. In both cases, the change in glucan retention was not notable during the impregnating period, which indicates that glucan was mainly removed before this period.

In summary, a pretreatment process having a lower ratio of liquor to wood demonstrated a significant impact on the carbohydrate behavior. It was found, for example, that a higher GL concentration exerted a stronger chemical effect by maintaining a higher level of dissolved mannan whereas, conversely, a lower GL concentration resulted in higher readsorption onto the fibers.

**Impact of Additives on Carbohydrates.** Our earlier efforts indicated that the delignification afforded by a GL pretreatment could be enhanced by using specific chemical additives during the pretreatment to bolster chemical adsorption and influence the kinetics of chemical reactions.<sup>11</sup> A follow-up study examined the influence of these additives on the final chemical compositions in the wood chips.<sup>12</sup> Investigating the impact of various additives on carbohydrate behavior during the pretreatment process was therefore a reasonable extension of our past work. Surfactants give rise to different chemical activities depending on the molecular structure and functional group balance of lipophilicity/hydrophilicity. Two ethoxylate-based surfactants, referred to as TMN-10 and SS-15 (see Experimental Section), were used during the GL pretreatment and have been described previously.<sup>12</sup> Figure 9 illustrates a comparison of the surfactant-modified GL pretreatment with the normal GL pretreatment. A remarkable increase of approximately 8 absolute percentage points in the total carbohydrate retention compared to that obtained with the normal GL pretreatment was observed upon TMN-10 addition. In contrast to TMN-10, SS-15 did not exhibit any positive effect on carbohydrate retention. These results are consistent with our previous report on an investigation of the changes in pulp carbohy-



**Figure 9.** Comparison of total carbohydrates retention under control and surfactant pretreatments (surfactant charge of 0.5% of the wood charge on a bone-dry mass basis).

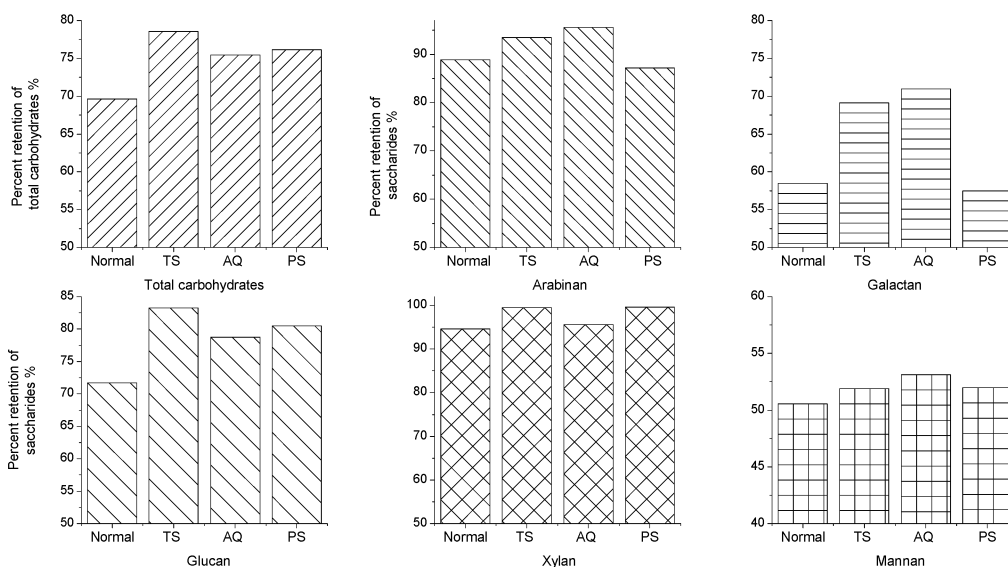


**Figure 10.** Comparison in saccharide compositions in wood from GL pretreatments with and without surfactants.

drates,<sup>7</sup> in which we found an 8 absolute percentage point increase in carbohydrates retention for kraft pulp with TMN-10-additive GL pretreatment. The chemical behavior of the surfactant in the pretreatment might be related to its molecular weight, as TMN-10 is a smaller, more branched ethoxylate than SS-15 and might thus be more surface active.

To further clarify the contribution of the surfactant to increased carbohydrate retention, the sugar compositions in both TMN-10-additive and normal GL pretreatments are compared in Figure 10. No obvious differences for either xylan and mannan retention is apparent; however, a significant increase in the retentions of arabinan, galactan, and glucan can be observed. Because glucan is the predominant component in wood carbohydrates, it can be confidently asserted that the surfactant's positive effect on carbohydrate retention can be mainly ascribed to the stabilization of glucose in wood.

The effects of the other additives on saccharide retention in GL pretreatment are shown in Figure 11. All three additives applied in the GL pretreatment, namely, polysulfide (PS), anthraquinone (AQ), and an unsaturated organic sulfur compound (TS), showed a positive impact on carbohydrate retention. The rank of additive efficiency in total carbohydrates retention is as follows: TS, is the highest (12 percentage points increase), followed by PS (9 percentage points increase) and then AQ (8 percentage points increase). The effect of PS and AQ on carbohydrate protection can be attributed to the oxidation of the end groups in the polysaccharides to carboxyl groups, as is widely accepted. Compared to the changes in the three main sugar components, as shown in Figure 11, the behavior of mannan was not significantly influenced by any

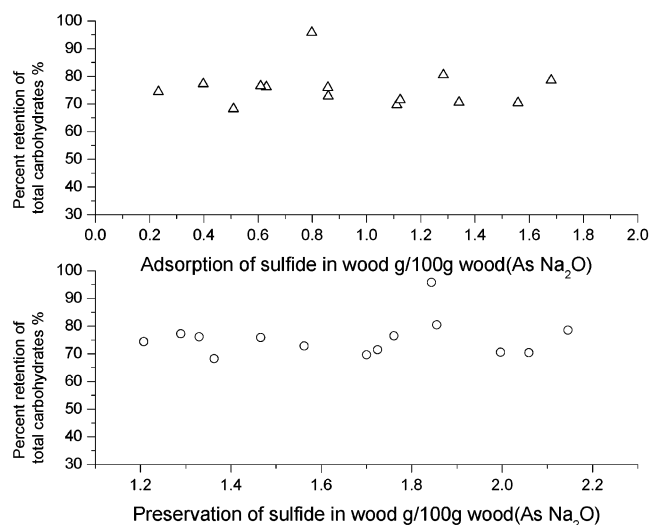


**Figure 11.** Impact of additives on carbohydrates retention in GL pretreatment.

additive process; however, the glucan retention due to the additives was increased and correlated well with an increase in the retention of total carbohydrates. Furthermore, the effects of the various additives on each wood saccharide are quite different. PS strongly increased the glucose and xylose retentions (12 and 5 percentage points, respectively) but did not have any positive influence on the retentions of galactose and arabinose. AQ significantly increased the retentions of galactose (21 percentage points) and glucose and arabinose (almost 10 percentage points for glucose and almost 8 for arabinose) but had no obvious effect on xylose. TS showed a positive impact on all saccharides. These results demonstrate that the improvement of carbohydrate retention achieved using additives in the GL pretreatment mainly results from the reduction of cellulose degradation, rather than from an increase in hemicellulose retention.

**Correlation between Carbohydrate Retention and Chemical Behavior in the Pretreatment.** As reported previously, the total sulfide preserved in wood chips following GL pretreatment has three chemical states: free, adsorbed, and bonded.<sup>12</sup> The free form is characterized by 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. The adsorbed form can be characterized by a difference between the internal and bulk concentration. More specifically, it is the nonequilibrium state in which the internal liquor has a higher concentration of the chemical component compared to the bulk liquor, i.e., an enrichment of the concentration of the chemical component. The significant difference between the free and adsorbed states is that adsorption occurs on the surface of carbohydrates whereas free ions are present in the internal and bulk liquors. Finally, the chemical form is characterized by a very strong bond between the component and the pulp so that this form of sulfide cannot be removed by even severe solvent washes.

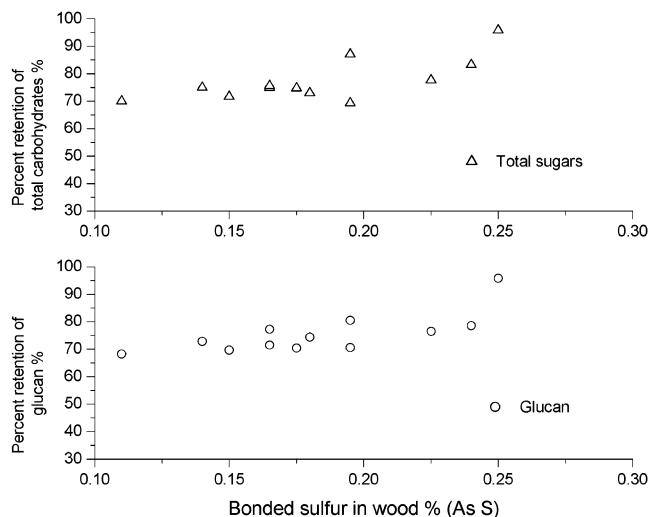
Further evidence to support the existence of these forms is that each of the forms was found to have a different effect on lignin removal. Overall, a higher sulfide retention (bonded form) in wood correlated strongly with higher lignin dissolution during pretreat-



**Figure 12.** Carbohydrates retention vs sulfide retention in GL pretreatment.

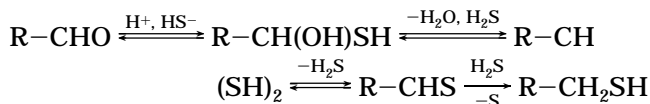
ment. Among the three sulfide states, the chemically bonded sulfide contributed the most toward enhanced lignin removal during pretreatment, followed by the adsorbed and free forms, respectively.

To identify the influence of sulfide behavior on the carbohydrates, the total carbohydrate retention was compared to the total sulfide retention and sulfide adsorption in the wood after GL pretreatment, as shown in Figure 12. Unlike lignin dissolution, no trend was found in these data to correlate carbohydrates retention with the form of sulfide and, consequently, with its retention in the pulp. The results appeared to indicate that the physicochemical behavior of sulfide in GL pretreatment has no direct effect on the carbohydrates. However, upon further investigation, it was determined that the bonded form correlated well with carbohydrates retention, as shown in Figure 13. The higher level of bonded sulfide resulted in higher carbohydrates retention. Interestingly, further clarification indicated that the bonded form was predominantly related to glucan retention to the exception of other saccharides (Figure 13). The results therefore strongly suggest that a reaction occurred between cellulose and sulfide during



**Figure 13.** Correlation of carbohydrates retention with bonded sulfur in wood.

the pretreatment, with the likely chemistry occurring at the reducing end groups of cellulose. Sjöström<sup>10</sup> suggested that the aldehyde end groups are reduced to thioalditols during pretreatment with hydrogen sulfide according to the following equations. The above mech-



anism might indeed be operative in our studies given the increased glucan retention. We are confident in asserting, therefore, that the hydrogen sulfide ion in the green liquor reacts with the carbohydrates and that the content of the bonded form of sulfide contributes to an increase in carbohydrates retention, specifically glucan retention, during the pretreatment.

## Conclusions

Approximately 15–20% of the carbohydrates in wood can be removed from wood chips during GL pretreatment. The bulk of this removal occurs during the earliest stage of the pretreatment, and glucan and mannan appear to be the main saccharides of the removed carbohydrates. In parallel with the removal, saccharide readsorption occurs during the pretreatment process, especially when the pretreatment system approaches a near-neutral pH. It further appears that pentoses are more readily readsorbed onto fiber than hexoses.

In general, the GL concentration in the pretreatment liquor influences both saccharide readsorption and chemical activity. A higher GL concentration results in stronger saccharide readsorption, especially for xylan,

but also leads to a sharp drop in the mannan concentration. To explore the behavior of the carbohydrate chemistry, additives were applied. Surfactants appear to impact carbohydrates retention to the point of increasing saccharide retention. A higher activity for a surfactant might be related to diminished size and higher branching to reduce surface tension, but further work needs to be done to validate this point. It was found that other classes of additives (PS, AQ, and TS) also demonstrate a positive influence on carbohydrates retention. These results indicate that additives can play a significant role during the chemistry of GL pretreatment to influence carbohydrates retention and subsequent delignification/pulping.

Finally, the presence of hydrogen sulfide ion on wood chips during pretreatment also influenced the carbohydrates retention. The bonded sulfur form resulted in higher carbohydrates retention likely as a result of the stabilization of cellulose reducing end groups, as supported by fundamental wood chemistry considerations.

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