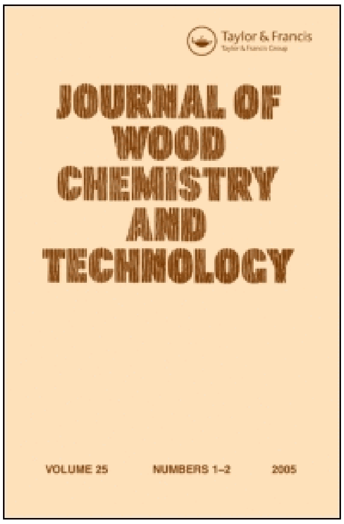

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EFFECTS OF CHEMICAL TREATMENTS ON ULTRA-HIGH-YIELD PULPING IV. THE INFLUENCE OF SULFITE LIQUOR pH ON NORWAY SPRUCE CMP

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ABSTRACT

The pH of sulfite treatments has a profound influence on the efficiency of fiber sulfonation of Norway spruce. Compared at the same pulp yield, the extent of sulfonation decreases in the order of pH value 7.5 > 9.5 > 4.5; the sulfonation reaction is improved significantly by using a two-stage treatment at pH 4.5 and 7.5. The degree of fiber sulfonation plays a dominant role in the tensile and tear strength improvement of these high-yield pulps.

INTRODUCTION

Sulfite-based treatments are the most widely used[1-3] in commercial production of high-yield chemimechanical pulps (CMP) or chemithermomechanical pulps (CTMP). This subject has continued to receive much attention in recent years[4-8]. It is well known that the dominant role of sulfite treatments is lignin sulfonation, which causes softening of cell wall matrix[9], facilitates the mechanical fiber separation process[10,11], and enhances the fiber bonding of high-yield pulps[10,12-16]. The sulfonation reaction can generally be accelerated by increasing the total SO_2 concentration, reaction temperature, or reaction time[15,17,18], but this will often result in a yield loss.

The pH of the cooking liquor also has a profound influence on the nature of the sulfonation reactions[19]. For example, sulfonation under neutral or alkaline conditions is virtually limited to the phenolic hydroxyl groups of lignin while sulfonation under acidic conditions may take place on both phenolic and etherified lignin units. Interestingly, the rate of initial fiber sulfonation at pH 4 is significantly lower than that at pH 7, but a higher degree of sulfonation can be achieved with extended treatments[17,18].

The pulping technology based on the use of sodium bisulfite[22] or sodium sulfite[15,23] in the pH range of 4-9 has been well documented for the production of CMP from softwood. However, to what extent the variation in liquor pH would affect the efficiency of sulfonation of softwood as related to the strength improvement has yet to be systematically investigated. Also, there are no general agreements among the published data of softwood related to pH-effects[14,20,21].

Beath and Mihelich[20] reported that the burst strength of softwood sulfite CMP (SCMP) increases with increasing pH of the sulfite treatments within the range of 3.7 to 13. However, the comparison was not made at the same yield level. A similar pH-effect was observed by Iwamida _et al._[14] when they compared the strength properties of SCMP obtained at 85% yield using three pH levels (1.8, 4.0, and 8.6).

On the other hand, Kojima and Kayama[21] observed an entirely different pH-effect. The tensile strength of spruce SCTMP, when compared at about 80% yield, decreased with the following order of treatments: bisulfite > neutral sulfite > alkaline or acid sulfite. However, Atack _et al._[12,13] concluded that the strength properties of ultra-high-yield SCMP and SCTMP fibers from black spruce (>88%) depended primarily on the sulfonate content of treated chips, and were not appreciably affected by the pretreatment pH within the range of 1.8-9.8.

This study was initiated to clarify the role of liquor pH in sulfite treatments of softwood with emphasis on the efficacy of fiber sulfonation. Norway spruce SCMP samples, prepared at three different pH levels using sodium bisulfite (pH 4.5), bisulfite-alkali (pH 7.5) and sodium sulfite (pH 9.5) solutions were characterized for their chemical and sheet properties. The chemical effect of a two-stage process, consisting of treatments at pH 4.5 and 7.5, was also explored.

EXPERIMENTAL

Analytical Methods

TAPPI standard methods were used to determine lignin contents (Klason plus acid-soluble lignin), and for the preparation and testing of handsheets.

Sulfonate and carboxyl group contents were determined according to a conductometric method described by Katz et al.[24].

Phenolic hydroxyl content was determined by the aminolysis method[25,26].

Chip Pretreatments

Sulfite treatments of Norway spruce chips were conducted in an M & K digester with a solution containing 3% SO_2 at a liquor-to-wood ratio of 6:1 in the temperature range of 145-165°C for 15-150 min. The chips were first impregnated with the cooking liquor at 100°C for one h prior to heating to higher temperatures. Three different pH levels were used, equivalent to sodium bisulfite (pH 4.5), sodium sulfite (pH 9.5), and a bisulfite solution adjusted to pH 7.5 with sodium hydroxide.

The treatment conditions for eight samples are summarized in Table 1. Samples 7 and 8 were treated at two pH levels, 4.5 and 7.5. After the initial bisulfite treatment, the chips were washed with water to remove residual chemicals prior to the subsequent neutral sulfite stage.

After completion of the cook, the liquor was blown down and the cooked chips were subjected to refining without washing.

Refining

The first stage of chip refining was performed in a 12-in Sprout-Waldron laboratory refiner. The refining process consisted of four steps, with disc clearances of 1.0, 0.5, 0.2, and 0.1 mm, respectively. The coarse pulp was washed with water, and the pulp yield (Table 1) was determined in the usual fashion.

The second-stage refining of coarse pulps was conducted in a PFI mill at 10% consistency using samples equivalent to 30 g OD pulp.

RESULTS AND DISCUSSION

Table 1 summarizes the lignin, sulfonate and phenolic hydroxyl group content of eight SCMP samples obtained from Norway spruce by varying the liquor pH during the sulfite treatments of chips.

It was shown that pH had a moderate influence on the dissolution of wood components. A comparison of samples 1 and 4, as well as 3 and 5 shows that the rate of yield loss, under otherwise identical conditions, increased in the order of pH, 7.5 < 9.5 < 4.5. However, variation of pH within the range of 4.5-9.5 had little influence on the relative dissolution of lignin and carbohydrates.

Phenolic Hydroxyl Content

The data in Table 1 indicate that both the bisulfite (No. 2) and neutral sulfite (No. 4) treatments resulted in a large in-

Table 1

Conditions of Sulfite Treatments, Yield, Lignin, Sulfonate, and Phenolic Hydroxyl Group Content of SCMP from Norway Spruce

No.	1st stage at 145°C		2nd stage[a] pH	Pulp			
	pH	Time		Yield %	Lignin %	Acidic group, mmol/100g Sulfonate	Acidic group, mmol/100g Phenolic
U[b]	-	-	-	100	28.6	-	17.2
1	4.5	75	-	82.0	26.3	20.0	-
2	4.5	150	-	78.0	25.4	24.8	23.5
3	7.5	15	7.5	90.3	26.6	21.0	-
4	7.5	60	7.5[c]	86.5	25.9	23.4	22.8
5	9.5	15	9.5	88.2	27.9	21.0	-
6	9.5	15	9.5[c]	86.5	26.6	22.0	-
7	4.5	15	-	-	28.1	-	22.1
7A	4.5	15	7.5	89.2	26.5	26.5	-
8	4.5	15	7.5[c]	84.0	26.1	28.8	23.0

[a] Conducted at 165°C for 30 min.
[b] Untreated sample
[c] Treated for 60 min.

crease (50%) in the free phenolic hydroxyl groups based on the residual lignin content. A similar effect of neutral sulfite treatments was observed previously by Yang, et al.[27].

Interestingly, the mild bisulfite pretreatment (No. 7) also provided a significant increase (30%) in the free phenolic hydroxyl content, but it did not affect the overall phenolic hydroxyl content of the combined bisulfite-neutral sulfite sample (Nos. 8 vs. 4).

It should be noted that the nature of chemical reactions responsible for the generation of new phenolic hydroxyl groups varies with the level of pH used. In bisulfite treatments (at pH 4.5), the formation of phenolic hydroxyl groups is probably a result of the hydrolytic cleavages of benzyl aryl ether linkages which are very labile in an acidic medium[28]. On the other hand, the sulfitolytic cleavages of some phenolic β-aryl ether linkages are probably involved in the neutral sulfite treatments as judged from the behavior of model compounds[19].

Sulfonate Group Content

As indicated, in Table 1, fiber sulfonation was rapid when conducted in the pH range of 7.5-9.5 at 165°C. The reaction was nearly complete within 30 min. An extension of the treatment from 30 to 60 min. gave only a 5-11% increase in sulfonate content (Nos. 3 vs. 4; 5 vs. 6). While an extension of the bisulfite treatment from 75 to 150 min, which was conducted at a lower pH (4.5) and temperature (145°C), resulted in a large increase (24%) (Nos. 1 vs. 2).

The samples prepared at two different pH levels (Nos. 7A and 8) had the highest sulfonate content. A comparison of Nos. 3 and 7A shows that the mild bisulfite pretreatment (at 145°C for 15 min.) resulted in a 26% increase in sulfonation after the subsequent neutral sulfite treatment. The same chemical effect of a bisulfite pretreatment was observed previously[16] in conjunction with an alkaline sulfite treatment at pH 10.7.

It is intriguing that both the neutral sulfite (No. 4) and bisulfite-neutral sulfite (No. 8) samples had virtually the same phenolic hydroxyl content, but the latter two-stage treatment achieved a 26% increase in sulfonation. Thus, it appears that fiber sulfonation is also controlled by factors other than the free phenolic hydroxyl content. The extent to which a mild bisulfite pretreatment can effect sulfonation of etherified units or reduce potential lignin condensation reactions is of special interest and warrants further exploration.

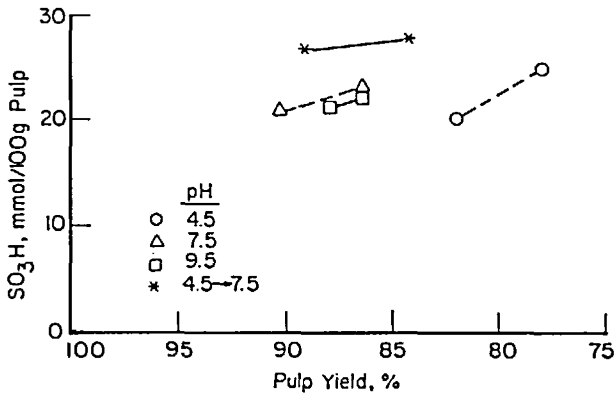

FIGURE 1. Effect of pH and pulp yield on the sulfonate content of Norway spruce SCMP.

Sulfonate Group Content-Yield Relationship

Figure 1 shows that pH has a significant effect on the degree of fiber sulfonation as related to pulp yield. Compared at the same yield, the sulfonate content of SCMP increases in the order of pH used, 4.5 < 9.5 < 7.5. The difference in sulfonate content between bisulfite and neutral sulfite samples was estimated to be about 30% when compared at an 85% yield. As indicated previously, the sulfonate content-yield relationship of the neutral sulfite samples could be improved by including a mild bisulfite pretreatment, e.g. a 15% increase in sulfonate content at 85% yield.

Rate of Beating

Figure 2 shows the influence of liquor pH on the beatability of the resulting SCMP fibers as indicated by the development of tensile strength after beating in a PFI mill for 14,000 revolutions. It is evident that the variation in beatability among the

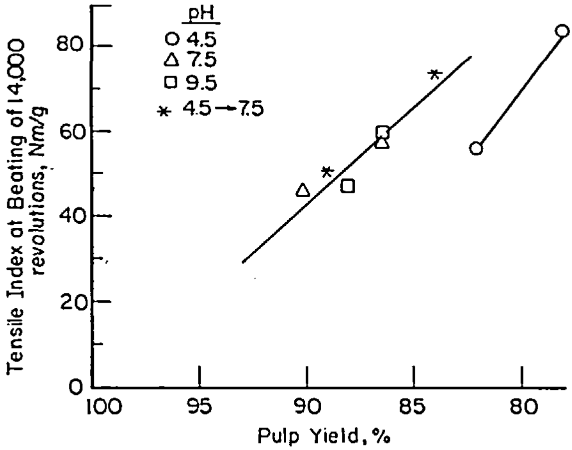

FIGURE 2. Effect of pH and pulp yield on tensile index development of Norway spruce SCMP after PFI beating of 14,000 revolutions.

six SCMP samples prepared at pH 7.5 and 9.5 can be directly related to pulp yield.

Compared at the same pulp yield, the SCMP prepared at pH 4.5 was substantially weaker than pulps prepared at a higher pH. A difference of about 80% was found at the 85% yield level. The difference between the bisulfite and neutral sulfite SCMP was particularly pronounced in the high-yield (82-95%) region, and diminished as the yield was reduced.

Strength-Yield Relationship

The relationship of tensile or tear index and pulp yield is illustrated in Figure 3 for eight SCMP. The tensile index was determined at the same CS freeness (500 mL) and the tear index was compared at the same tensile index (60 N m/g).

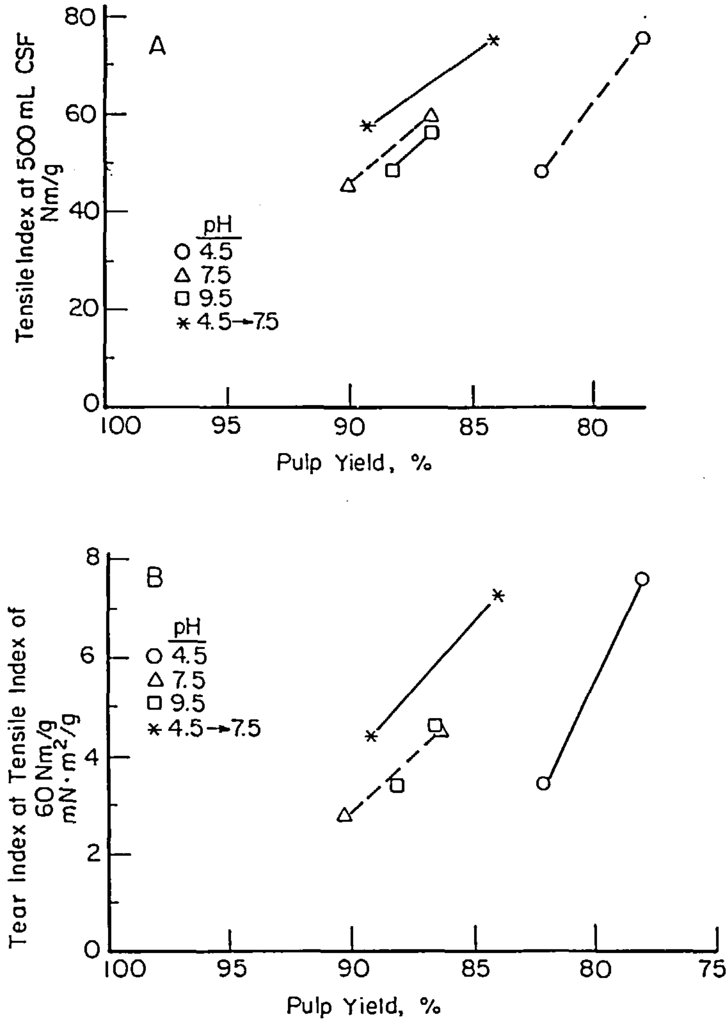

FIGURE 3. Effect of pH and pulp yield on the tensile index (at 500 mL freeness) (A), and tear index (at 60 Nm/g tensile index) (B) of Norway spruce SCMP.

Compared at the same pulp yield, the treatments at pH 7.5 and 9.5 were more effective than that at pH 4.5 in promoting both tensile and tear development, especially in the high yield region (82-92%). It is noteworthy that the observed pH-dependence diminishes rapidly as the yield decreases below 80%.

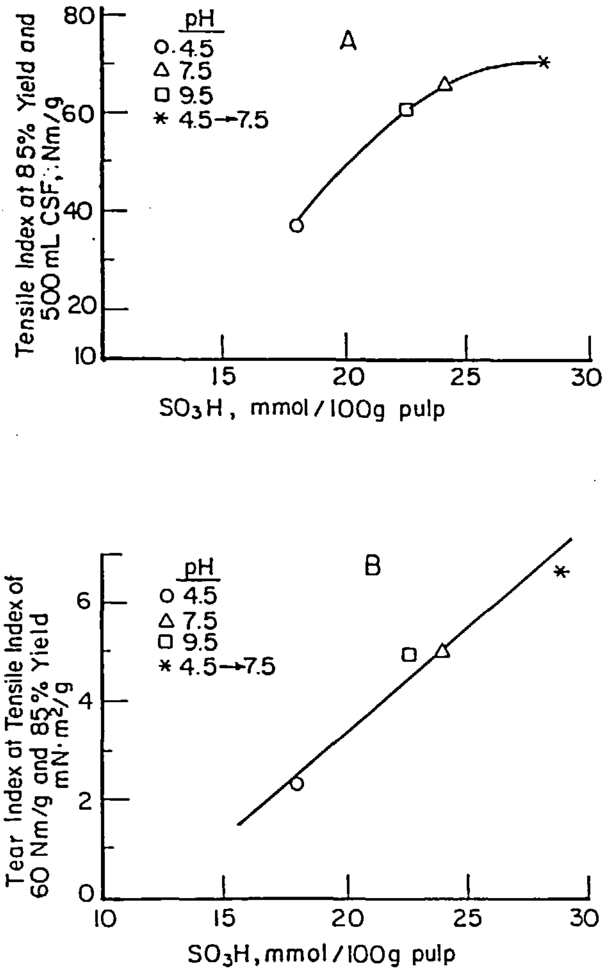

FIGURE 4. Effect of fiber sulfonation on the tensile (at 500 mL CSF) (A) and tear (at 60 Nm/g tensile index) (B) indices of Norway spruce SCMP estimated at 85% yield.

Interestingly, both the tensile and tear strength of the neutral sulfite CMP can be further improved by a mild bisulfite pretreatment without an additional yield loss. An improvement of 10 and 30% for tensile and tear index, respectively, was found at an 85% yield.

Role of Fiber Sulfonation

Figure 4 illustrates the influence of fiber sulfonation on strength improvement of SCMP fibers, where the tensile index (at 500 mL CSF) and tear index (at the tensile index of 60 N m/g) of various samples were extrapolated to 85% yield.

In the case of tear index, the pH of the sulfite liquors appears to have had little influence. The tear index was directly proportional to the sulfonate content of SCMP fibers. This finding further confirms the important role of sulfonation in high-yield pulping, notably in the development of the overall tensile-tear property of SCMP fibers.

The tensile index also increased with the sulfonate content but it appeared to level off at about 27 mmol/100 g pulp. This 2.16%, or 0.24 sulfonate groups per C_9 unit, assuming that a C_9 unit has a weight of 230 g[14]. The observed behavior further supports the contention that chemical reactions other than sulfonation contribute to the tensile strength development of SCMP fibers, especially those with a high sulfonate content.

For example, the beneficial effects of mild bisulfite pretreatments observed for the two-stage process (Nos. 7A and 8) may be ascribed partly to disruption of the lignin net-work as a result of the hydrolytic cleavages of benzyl aryl ether linkages.

Also, as discussed previously[16], controlled degradation of polysaccharides appears to be beneficial for the strength development of SCMP from Norway spruce.

Optical Properties

As shown in Figure 5A, the brightness of beaten SCMP (at 500 mL CSF) is significantly affected by both the pH of the sulfite

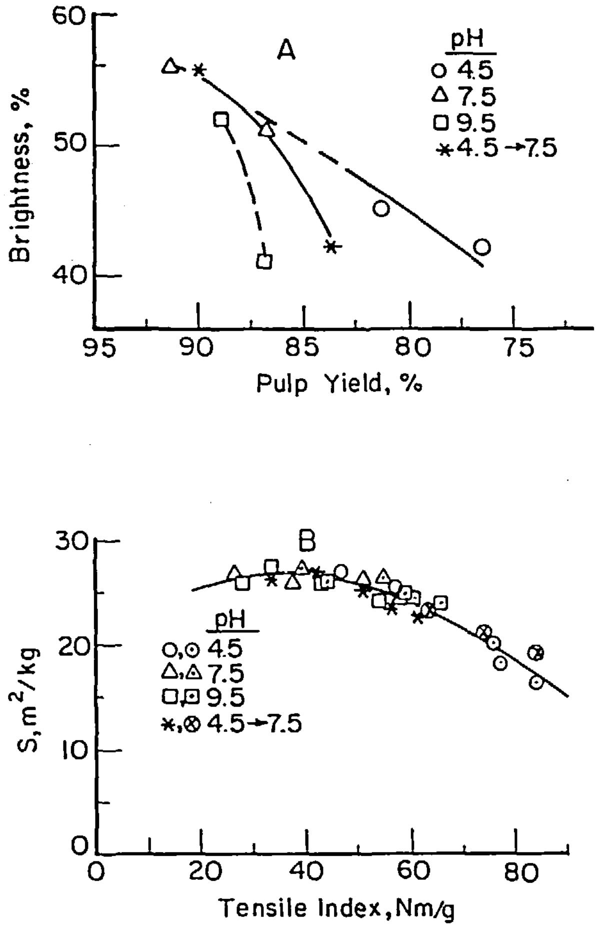

FIGURE 5. Effect of pH on the brightness (A) and scattering coefficient (B) of Norway spruce SCMP.

treatments and the pulp yield. In general, the brightness decreased with the treatment pH from 4.5 to 9.5; it decreased with a decrease in yield. However, it appears that pH had little influence on the pulp brightness in the high-yield region (> 90%). On the other hand, there was little variation among eight SCMP fibers in scattering coefficient when compared at the same tensile index (Figure 5B).

CONCLUSIONS

The present study clearly shows that variation of the liquor pH in sulfite treatments of Norway spruce chips has a profound influence on the efficiency of chemimechanical pulping.

Compared at the same pulp yield, both the tensile and tear strength of SCMP prepared at pH 7.5 and 9.5 are substantially higher than that of pulp prepared at pH 4.5. This pH dependence is closely related to that of the fiber sulfonation-yield relationship.

The performance of SCMP prepared at pH 7.5 is improved significantly by including a mild bisulfite pretreatment. This two-stage treatment improved the fiber sulfonation and strength development.

It appears that the overall tensile-tear property of SCMP can be further upgraded by the development of a more effective sulfonation process.

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