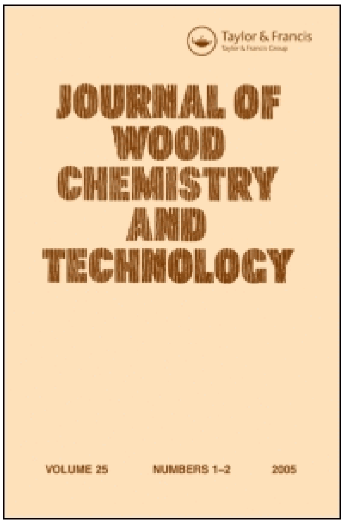

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EFFECTS OF CHEMICAL TREATMENTS ON ULTRA-HIGH-YIELD PULPING
VI. THE RELATIVE EFFECT OF LIGNIN OXIDATION AND SULFONATION

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ABSTRACT

The chemical properties and performance of aspen percarbonate (P) and sulfite (S) chemimechanical pulp (CMP) fibers are very comparable. The PCMP, when compared with SCMP of the same yield, has a slightly higher tear index, same beatability and light scattering coefficient, but a lower tensile index and brightness. The strength properties of these fibers are closely related to the total acidic group content resulting from lignin oxidation (carboxyls) and sulfonation (sulfonate).

INTRODUCTION

The strength improvement of refiner mechanical pulps (RMP) or thermomechanical pulps (TMP) is generally achieved by a chemical treatment of chips prior to refining.[1,2] The dominant process is the use of sulfites under neutral or alkaline conditions.[3-7] In general, the strength properties of sulfite chemimechanical pulps (SCMP) from softwood depend primarily on their content of sulfonate groups.[8-12] In the case of aspen SCMP, carboxyl groups also play an important role.[13] It appears that the saponification of ester groups is a reaction especially important to the strength development of hardwood CMP fibers.[14]

Although sulfite-based treatments are the most widely used in the commercial production of high-yield pulps, it is still not an ideal process, and suffers from a number of disadvantages such as potential pollution problems and brightness loss. Besides sulfite and alkali, a variety of oxidizing agents such as peracetic acid,[15,16] peroxide[17-20] and sodium percarbonate (P)[21] have also been shown to be effective as pretreatment agents for hardwoods. Recently, the use of peroxide in connection with the TMP production has received much attention[18-20] as evidenced in a commercial installation.[22] However, very little is known about the chemical role of these oxidants, and its relative effectiveness as compared to sulfites. To what extent the strength properties of these CMP can be ascribed to lignin oxidation is of particular interest.

This paper reports on the chemical characterization of aspen SCMP and PCMP and their sheet properties. The relationship between the strength improvement and total acidic groups of these high-yield pulps resulting from lignin oxidation (carboxyls) or sulfonation (sulfonate) is also discussed.

EXPERIMENTAL

Chip Pretreatment

Treatments of aspen (Populus tremuloides) chips with sodium percarbonate (sodium carbonate-hydrogen peroxyhydrate) or sodium sulfite were performed in an M & K digester. Both treatments were conducted at two different levels by varying either the chemical charge or reaction temperature. The percarbonate treatment employed a chemical charge of 10 (Sample 2) or 30 (Sample 3) % and the addition of 0.05% $MgSO_4$ using a liquor-to-wood ratio of 5:1 at 110°C for 60 min. while the sulfite treatment used a 6% sodium sulfite solution at a liquor-to-wood ratio of 6:1 at 135 (Sample 4) or 165 (Sample 5) °C for 30 min.

Fiberization and Refining

After chemical treatments, the chips were drained and refined under atmospheric conditions in an 8-in Bauer disc refiner at 2-3% consistency. The refining process consisted of three steps, with the disc clearance set at 0.040, 0.020, and 0.005 in, respectively. The coarse pulp was washed with water and the pulp yield was then determined in the usual fashion. The data for pulp yield and CS freeness of five unbeaten high-yield samples are summarized in Table 1. Second-stage refining of coarse pulps was conducted in a PFI mill using 30 g OD pulp at 10% consistency.

Analytical Methods

Klason and acid-soluble lignin, CED viscosity of pulps, and handsheet preparation and testing were determined by TAPPI standard methods. Unbeaten pulps were delignified with sodium chlorite[23] prior to the viscosity determination. Sulfonate and carboxyl group contents were determined by a conductometric method described by Katz et al.[24] Pulp fractionation was done in a Bauer McNett classifier.

RESULTS AND DISCUSSION

Table 1 illustrates some physical and chemical properties of five high-yield pulps from aspen. The two PCMP (Nos. 2 and 3) and two SCMP (Nos. 4 and 5) samples were obtained by varying the chemical charge and reaction temperature, respectively.

The chemical effect of percarbonate and sulfite treatments are discussed in terms of how they affect the characteristics of unbeaten pulps, rate of beating, and handsheet properties.

TABLE 1

Physical and Chemical Properties of Refiner and Chemimechanical Pulps from Aspen

Pulp Property	Sample 1 (RMP)	 2 (PCMP)	 3 (PCMP)	 4 (SCMP)	 5 (SCMP)
Yield, %	95	91.4	86.9	89.5	81.4
CS freeness, mL	510	570	570	680	680
Fiber Classification, %					
R 28-mesh	41.6	43.5	52.2	46.3	55.2
R 48-mesh	16.1	25.2	25.4	24.0	20.5
R100-mesh	8.9	8.7	8.5	9.3	7.9
R150-mesh	3.0	2.1	2.1	2.5	1.2
Pass 150-mesh	30.4	20.5	11.8	17.9	15.2
Lignin Content, % on Pulp					
Klason Lignin	19.3	18.2	16.7	14.8	12.4
Acid-Soluble Lignin	3.6	4.2	4.3	6.4	5.9
Total	22.9	22.4	21.0	21.2	18.3
Acidic groups, mmol/100g pulp					
Carboxylate	9.6	15.6	20.7	12.7	14.4
Sulfonate	-	-	-	7.9	12.3
Total	9.6	15.6	20.7	20.6	26.7
Viscosity, mPa.s	30.3	40.6	43.0	59.5	47.3

Fiber Separation

The data in Table 1 indicate that both percarbonate and sulfite treatments facilitate the mechanical fiber separation, resulting in an increase of the long-fiber fraction, a decrease of the fines fraction, and an increase in the freeness level and viscosity of the unbeaten pulps.

It appears that sulfite treatment is less degrading to the fiber than percarbonate at a molecular level. The chemical degradation and physical damage of fibers could occur during the chip-treatment and -refining stage, respectively. It is evident that both PCMP (No. 2) and SCMP (No. 4) samples are similar in pulp yield and fiber-length distribution. However, the SCMP sample has a 47.9% higher viscosity than the PCMP.

Lignin Content

As indicated in Table 1, the apparent lignin content of high-yield pulps is only slightly decreased by the chemical treatments. This is attributed mainly to a simultaneous dissolution of both lignin and carbohydrate components. The SCMP sample (No. 5), which was obtained in a relatively low yield (81.4%), however has a significant lower lignin content (18.3%) as compared to the control RMP (22.9%).

The data in Figure 1 show that the sulfite treatment removed slightly more lignin but less carbohydrates as compared to the percarbonate treatment at the same pulp yield. However, the difference between these two treatments is small, being less than 1% based on the wood.

On the other hand, the amount of acid-soluble lignin is significantly increased by chemical pretreatments (Table 1). An increase from 16% (expressed as percent of total lignin) to 20 and 30% was observed for the PCMP and SCMP fibers, respectively.

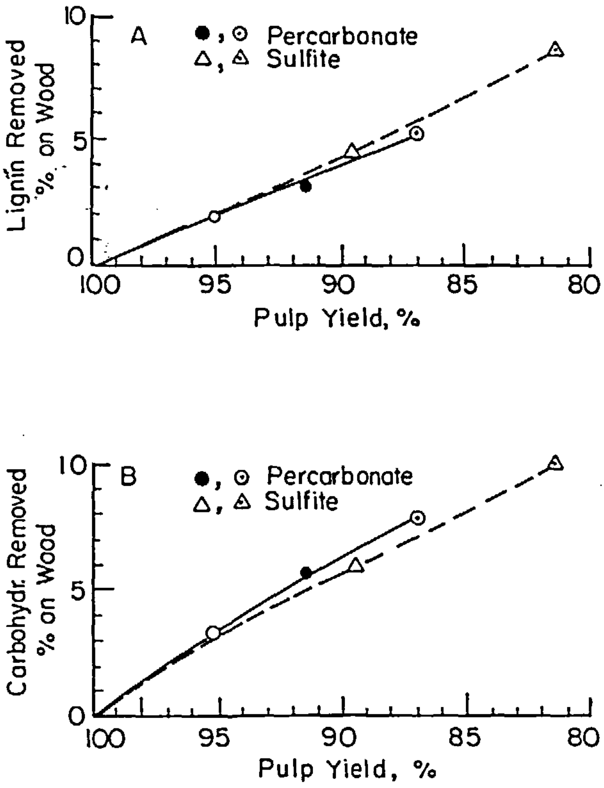

FIGURE 1. Effect of percarbonate and sulfite treatments of Aspen on lignin (A) and carbohydrate (B) removal as related to pulp yield.

<u>Sulfonate Group Content</u>

A comparison of samples 4 and 5 (Table 1) indicate that temperature has a profound influence on the extent of lignin sulfonation. Under otherwise identical conditions, an increase of temperature from 135 to 165°C resulted in an 80% increase in sulfonation based on lignin. The sulfonate content of sample 5 (obtained at 165°C), is only about half that of Norway spruce[25] under comparable treatment conditions.

The sulfonation under neutral or slightly alkaline conditions is generally thought of being limited to phenolic units of lignin.[26] Interestingly, by assuming that the unit mass of a C_9 unit is 230,[11] the sulfonate content of sample 5 is equivalent to 0.15 per C_9 unit, which is slightly higher than the phenolic hydroxyl content of a similar sulfonated aspen sample.[27]

Carboxyl Group Content

The major source of carboxylic groups in high-yield pulps is derived from the glucuronic acid content of xylan, which in the case of aspen is equivalent to 14.8 mmol/100g wood.[28] The carboxyl group content of the control RMP sample (No. 1) was 9.6 mmol/100g indicating that about 35% of the carboxylic groups were still esterified.

Both percarbonate and sulfite treatments significantly enhance the formation of carboxylate groups. A large effect was obtained with the percarbonate treatment, which produces additional carboxylate groups presumably from the oxidation of wood components. It is anticipated that such oxidation reactions would occur predominantly at the lignin components, notably the oxidative degradation of phenolic units and carbonyl groups present in side chains.[29] Preliminary data indicate that the phenolic hydroxyl content of the PCMP sample (No. 3) is at least 20% lower than that of the untreated RMP sample.

To what extent the oxidation of carbohydrates would contribute to the carboxylate formation remains to be determined. However, it was shown previously[30] that treatments of alpha cellulose with oxidative reagents such as peracetic acid and acid chlorite resulted in very little formation of carboxyl groups (less than 1 mmol/100g pulps).

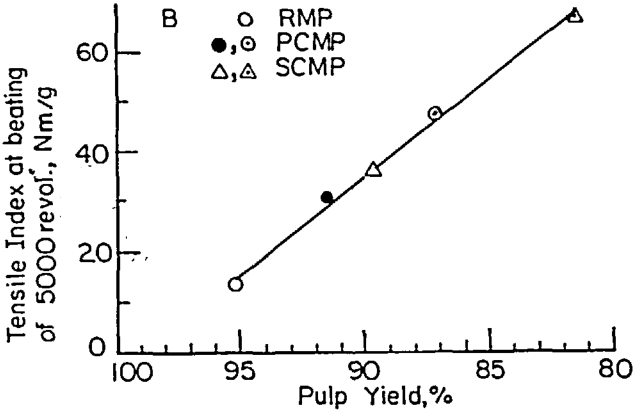

FIGURE 2. Beatability of aspen PCMP and SCMP in terms of tensile index development as related to pulp yield.

Rate of Beating

It was noted that the rate of beating, as indicated by the development of tensile strength, improves significantly with increasing level of percarbonate or sulfite treatments. The untreated RMP fibers develop little improvements even on extended refining.

Interestingly, the variation of beatability among the five high-yield samples can be directly related to the pulp yield as illustrated in Figure 2, where the tensile indexes of the pulps after beating in a PFI mill for 5000 revolutions are compared. Thus, the tensile strength development of the PCMP and SCMP fibers is essentially identical, when the same yield pulps are compared.

Handsheet Properties

The relationship of tensile or tear index and pulp yield is illustrated in Figure 3 for the five high-yield pulps at the same CS freeness (300 mL). The data indicate that compared with the

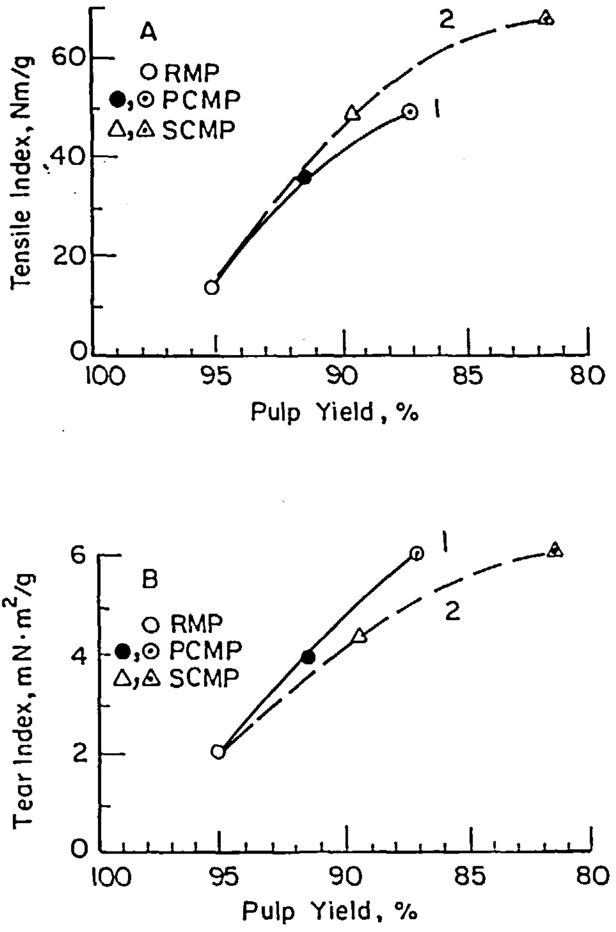

FIGURE 3. Effect of percarbonate (curve 1) and sulfite (curve 2) treatments on the tensile index (A) and tear Index (B) at 300 CS freeness of aspen CMP.

sulfite treatment at the same pulp yield, the percarbonate is superior in tear development but inferior in tensile improvement.

Similarly, compared at the same tensile index (40 Nm/g), and the same pulp yield, the PCMP fiber has a slightly higher tear index than the SCMP sample, notably in the low yield region. A difference of about 7% was found at an 85% yield.

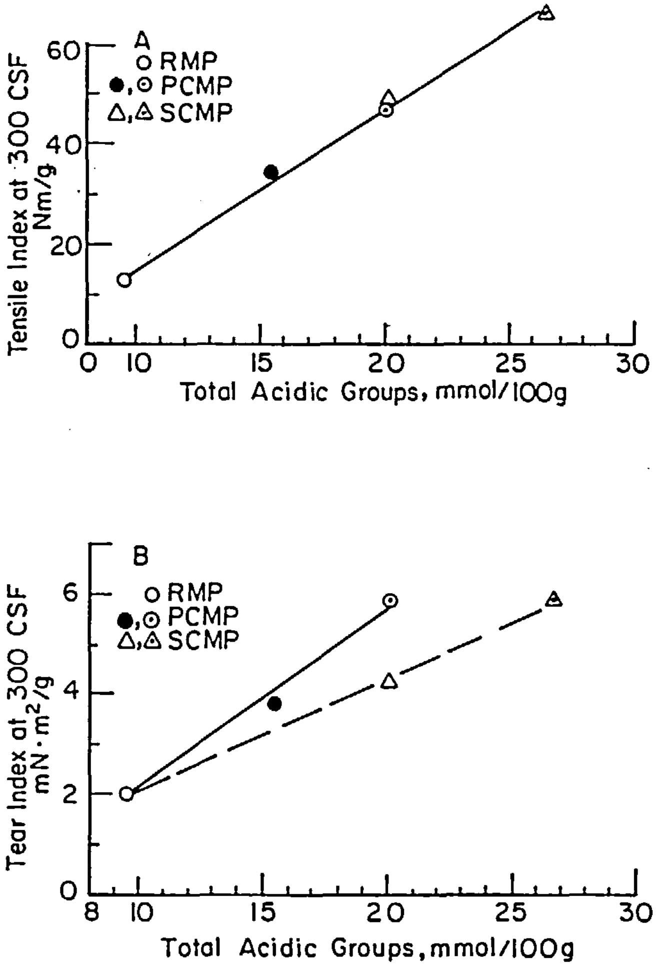

FIGURE 4. Effect of total acidic group content on the tensile (A) and tear (B) index of aspen PCMP and SCMP at 300 CS freeness.

Interestingly, both the tensile and tear improvements of PCMP and SCMP fibers can be linearly correlated with their total content of acidic (carboxyl and sulfonate) groups (Figure 4). Also, both PCMP and SCMP fibers follow the same tensile index-acidic groups relationship; this behavior indicates that the

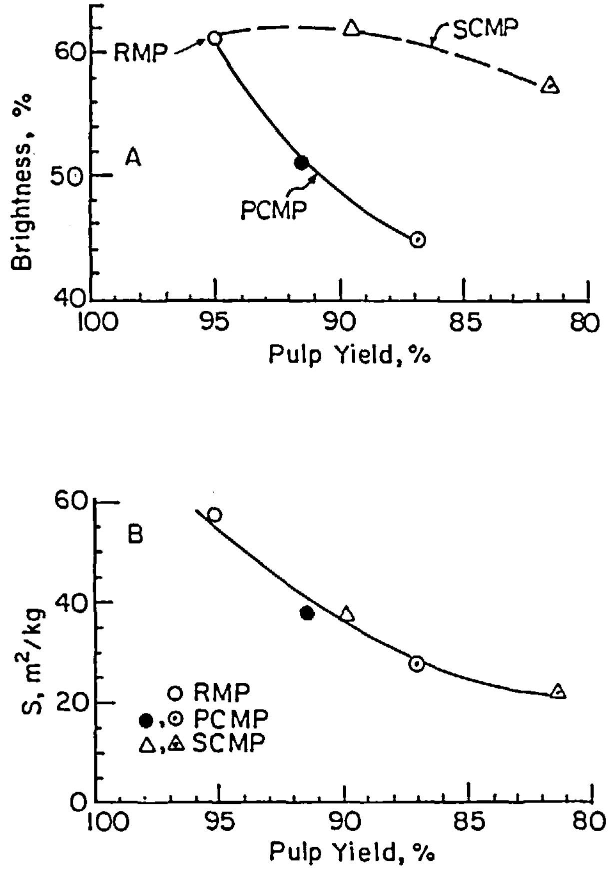

FIGURE 5. Effect of percarbonate and sulfite treatments on the brightness (A) and scattering coefficient (B) of aspen CMP.

sulfonation and the oxidation of lignin are equally effective with respect to tensile strength development. Lignin oxidation is superior to sulfonation in the case of the tear property.

Optical Properties

As shown in Figure 5A, the brightness of unbeaten PCMP is substantially lower than that of SCMP. A difference of 14 points in brightness unit was observed at a 90% pulp yield. However, there is little difference between these two CMP fibers in scattering coefficient, when compared at the same tensile index and yield (Figure 5B).

CONCLUSIONS

The chemical and strength properties of PCMP and SCMP fibers from aspen are quite comparable, but with some discernible differences. The PCMP when compared with SCMP of the same yield, has a slightly higher tear index, the same beatability and light scattering coefficient, but a lower tensile index and brightness.

Both the tensile and tear strength of RMP, PCMP, and SCMP fibers are closely related to their total acidic group contents. The data show that the sulfonation and the oxidation of lignin are equally effective in enhancing the tensile property while lignin oxidation has a larger effect in tear improvement.

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