Extended delignification of southern pine with anthraquinone and polysulfide

Jian Er Jiang

ABSTRACT: Extended modified cooking of southern pine with polysulfide (PS) and anthraquinone (AQ) to a kappa number as low as 8 was conducted in the laboratory. The effects of adding AQ and PS on pulp yield and strength properties were investigated. In the range of kappa numbers studied, the addition of 0.1% AQ resulted in a marginal (≤ 0.5%) increase in pulp yield. Charging 2% PS to extended modified cooking increased pulp yield by about 1.5% on wood. A 3% PS charge increased the screened pulp yield by about 3%, from about 42% to 45% (on wood) at kappa no. 12. Applying both 0.1% AQ and 2% PS resulted in a yield increase of about 2.5%, considerably higher than additive. The addition of AQ to extended modified cooking decreased the pulp tear strength. In the presence of PS , there was no detrimental effect on tear. Up to 3% addition of pulysulfide showed no significant effect on pulp tear strength in cooking to a kappa number as low as 12.

KEYWORDS: Alkaline pulping, anthraquinone, chemical pulping, chemical reactions, continuous process, delignification, kappa number, ketones, kraft pulping, mechanical properties, modified kraft process, permanganate number, pinus, polysulfides, properties, pulps, quinones, softwoods, sulfides, yield.

Modified continuous cooking (MCC®) *(1–3)* and extended modified continuous cooking (EMCC®) *(4)* are well established industrial practices, producing pulps at kappa numbers near 25 and 18, respectively. Strength properties of modified pulps are comparable to or better than those of a conventional kraft (CK) pulp at about kappa no. 30. Results from our recent work indicate that a softwood pulp at kappa numbers as low as 12 can be produced both in the laboratory and in a mill-scale operation with comparable strength properties. These strong pulps with very low residual lignin contents decrease the use of bleaching chemicals and greatly facilitate bleaching effluent control.

Because significant yield loss ultimately occurs at low kappa numbers, the ability to cook down to a very low lignin content while preserving pulp strength makes the pulp yield issue even more pressing. Both polysulfide (PS) and anthraquinone (AQ) are effective pulping additives for yield improvement with CK cooking (> kappa no. 30) *(5–10)* and extended (kappa no. 15–30) cooking *(11–16)*. A synergistic effect on yield increase using both PS and AQ has also been observed at kappa numbers as low as 15 *(11–14)*.

It was shown in our earlier work *(15–16)* that adding 2% PS to extended modified cooking of southern pine resulted in about 2% pulp yield increase in the range of kappa no. 15–20. In addition, the strength of the PS pulps was not affected. Therefore, as a continued effort, it was desirable to extend pulping to kappa numbers less than 15 and to study the effect of AQ and PS in this range.

Experimental

Commercial southern pine chips from Georgia were used in this study. Prior to cooking, the chips were screened to remove fines and fractions thinner than 2 mm, thicker than 10 mm, and longer than 45 mm.

Jiang is manager, R&D Laboratory, Kamyr, Inc., Ridge Center, Glens Falls, NY 12801.

I. Summary of pulping data

Cook	PS, %	AQ, %	Kappa no.	Visc., mPa·s	S. yield, %	Reject, %	EA charge[a], % Impreg.	Cooking	Max. temp., °C	H factor
BC78	0	0	31.1	38.9	46.8	0.28	19.7	-	170	1590
BE106	0	0	17.6	31.8	43.9	0.02	12.0	5.0	165	3130
BE126	0	0	17.0	29.3	44.0	0.02	12.0	5.0	165	3130
BE139	0	0	17.0	31.4	44.0	0.03	12.0	5.0	165	3140
BE142[b]	0	0	14.9	30.9	43.3	0.02	12.0	5.0	165	3140
BE112	0	0	11.8	19.0	41.9	0.01	14.0	4.0	169	4110
BE111	0	0	10.4	15.7	40.9	0.01	14.0	4.0	171	4840
BE110	0	0	10.2	15.2	40.9	0.01	13.0	5.0	170	4750
BE109	0	0	9.8	12.9	40.5	0.01	13.0	5.0	170	4740
BM102	0	0	24.5	36.1	45.6	0.15	13.0	5.0	170	2196
BM104	0	0	23.9	37.5	45.4	0.09	13.0	5.0	170	2193
BM107	0	0.1	22.3	31.6	46.1	0.07	13.0	5.0	170	2196
BM122	0	0.1	19.3	30.7	45.7	0.04	13.0	5.0	170	2209
BE115	0	0.1	9.4	12.8	40.2	0.01	14.0	5.0	170	4750
BE125	0	0.1	16.0	27.4	44.3	0.02	12.0	5.0	165	3130
BE113	2	0	11.8	24.4	42.5	0.01	14.0	4.0	171	4840
BE116	2	0	10.7	22.8	42.7	0.01	14.0	5.0	170	4750
BE155	2	0	8.1	17.0	41.2	0.01	16.0	5.0	170	4750
BE154	2	0.1	10.6	24.2	43.7	0.01	14.0	5.0	170	4760
BE117	2	0.1	9.9	21.2	43.6	0.01	14.0	5.0	170	4750
BE156	2	0.1	8.7	19.7	42.7	0.03	16.0	5.0	170	4660

[a]EA charges (as NaOH) did not include EA consumed in the countercurrent simulation, which varied from 2.5 to 4.5% on wood depending on cooking temperature. WL sulfidity was 30% (based on AA) for all cooks.
[b]End of cook residual EA: 24 g/L as NaOH; all other modified cooks: 17–18 g/L as NaOH.

Polysulfide liquor was prepared by dissolving about 250 g sulfur powder into 2 L of sodium sulfide aqueous solution (120 g/L) at 60°C. When a PS charge was required in a cook, a mixture of white liquor, PS liquor, NaOH solution, and water was prepared as the cooking liquor, and the nominal [$Na_2S/(NaOH + Na_2S)$] sulfidity was 30% based on active alkali (AA). AQ (a 50% aqueous suspension, courtesy of Westvaco Corp. and ICI Canada Inc.) was added directly to the chips in the digester prior to liquor circulation and heating.

Cooking was carried out in a 24-L digester equipped with indirect heating and circulation. Detailed laboratory pulping and pulp processing procedures can be found elsewhere *(4, 15, 16)*. In the simulation of countercurrent cooking, the effective alkali (EA) concentration was controlled near 11 and 18 g/L (as NaOH) in the beginning and at the end of the stage, respectively. The concentration of dissolved organics was controlled at about 45 g/L at the end of all extended modified cooks. Other major pulping parameters are given in **Table I.**

Carbohydrate compositions of pulp samples were determined in duplicates by anion exchange high-performance liquid chromatograph (HPLC)*(17)*. Unless otherwise stated, TAPPI Test Methods were followed throughout this study.

Effect on brownstock yield

Screened pulp yields for various cooks are plotted against kappa number in **Fig. 1.** Note that the pulp yield decreased dramatically below kappa no. 18. The yield loss was approximately 3% on wood, for a decrease of 6–8 kappa units. This large yield loss demonstrates the importance of finding ways to increase pulp yields in extended delignification.

Addition of 0.1% AQ increased brownstock yield by about 1% near kappa no. 25. However, the yield increase became marginal (≤ 0.5% on wood) at about kappa no. 16 and was not measurable in the lower kappa range. Since no replicate cooks were conducted with AQ in the lower kappa range, there was some uncertainty about this decreasing AQ effect. However, the extremely high repeatability of the three control cooks at about kappa no. 17 (Table I) and results from carbohydrate analysis (**Table II**) suggest that the yield measurement was accurate and that this decreasing effect was most likely true. Furthermore, this is in general agreement with a previous study, where a similar but less profound trend was observed with SAQ (sodium salt of 1,4-dihydro-9, 10-dihydroxyanthracene) in a slightly higher kappa number range *(13, 14)*.

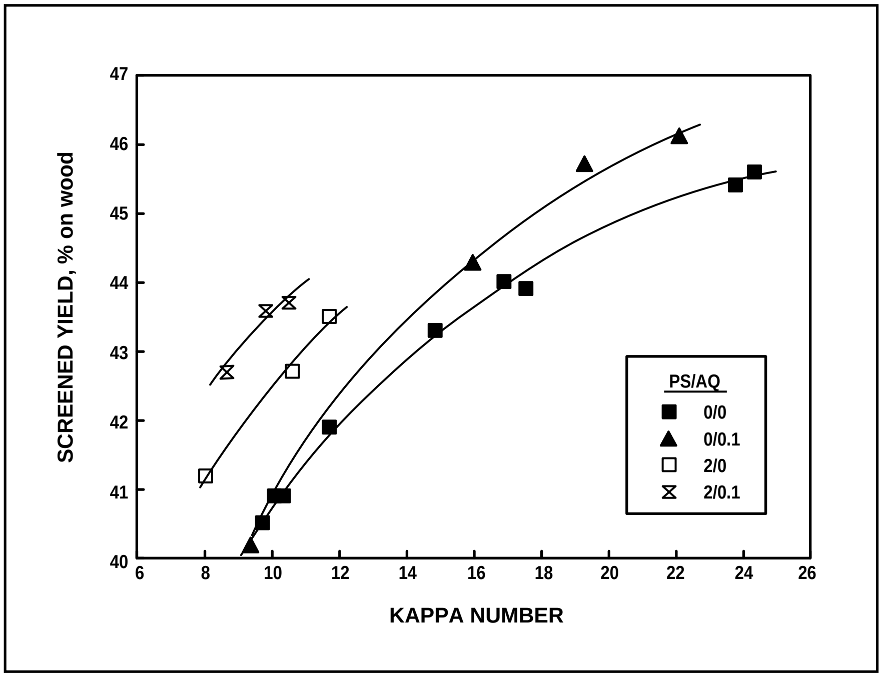
Addition of 2% PS gave an average yield increase of about 1.5% (on wood) within the range of kappa no. 8–12. This is somewhat less than the previously reported 2.0%, 2.5%, and

4.0% yield increases in the higher kappa ranges of 15–25, 25–30 *(13–16)*, and above 30 *(5–7)*, respectively. These results indicate that the yield improvement by PS addition decreases with an increasing degree of delignification.

The finding that AQ and PS are less effective for yield improvement in the lower kappa number range can probably be explained by the relative instability of hemicelluloses compared to that of cellulose. The yield increase by the addition of AQ or PS is mainly from an increased retention of hemicellulose, in particular glucomannans in pulp (Table II). Hemicelluloses are generally less stable than cellulose due to their amorphous structures. A higher cooking temperature, a longer time, and/or an increased total EA charge was required when pulping to a much lower lignin content (Table I). These more severe conditions decreased the retention of hemicelluloses more than that of cellulose (Table II), resulting in a greater yield loss for the AQ and PS pulps.

Another factor contributing to the less effective yield improvement is that, because it undergoes practically complete thermal decomposition at cooking temperatures *(7, 18)*, PS becomes ineffective in preventing yield loss from "secondary peeling" reactions. Although AQ is stable throughout a cook, only a small fraction of the AQ added is available in the cooking liquor *(19)* for carbohydrate stabilization when the maximum cooking temperature is reached. In addition, AQ can oxidize the C-2 and C-3 hydroxyl groups in sugar units to form carbonyl groups, promoting chain cleavage and secondary peeling reactions. As a result of the increased secondary peeling reactions, greater yield losses occur. The increased cellulose chain cleavage may also account for the lower viscosity values of AQ pulps observed in the present study (**Fig. 2**) as well as in the literature *(9–14)*.

1. Effect of AQ and PS addition on pulp yield. PS and AQ charges (% on wood) are indicated in the legends.



Synergistic effect of AQ and polysulfide on yield

The effect on yield increase from 0.1% AQ and 2% PS addition was profound. As seen in Fig. 1, within the kappa range of 8–12, simultaneous addition of 2% PS and 0.1% AQ resulted in about 2.5% yield increase compared to the sum of about 1.5% increase from applying PS and AQ individually. This is in good agreement with the "synergistic" effect reported in the literature *(13, 14, 20, 21)*. One possible mechanism may be that PS participates in the AHQ-lignin and AQ-carbohydrate redox system *(22)*, where partial regeneration of PS and/or stabilization of PS against disproportionation takes place.

The synergistic effect most likely occurs in the early stages of a cook, since PS readily undergoes thermal decomposition (disproportionation) above 140°C *(7, 18)*. Results given in Table II from carbohydrate analysis suggest that the yield increases from addition of AQ, PS, or AQ + PS were mainly attributable to an increased retention of glucomannans in pulp. In fact, it is impossible to determine from the results which additive was applied.

Effect on pulp strength properties

Results of pulp physical properties are summarized in **Table III**. The tear vs. tensile curves of three control pulps, with kappa numbers of 17.0, 11.8, and 10.2, are compared to those of a CK pulp at about kappa no. 31 in **Fig. 3**. Note that the EMCC pulp at kappa no. 17 gave tear results comparable to those of the CK reference pulp.

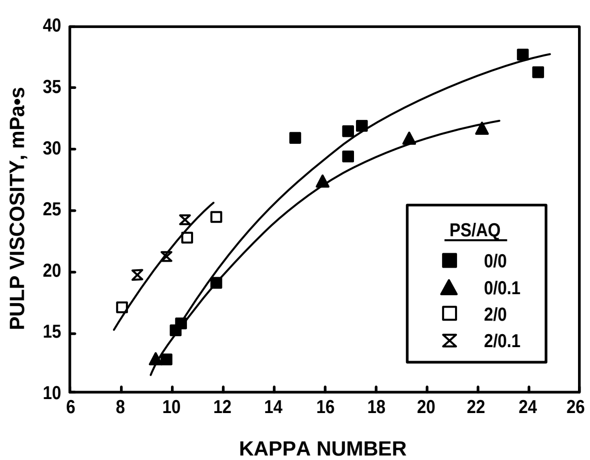
The other two pulps with lower kappa numbers gave a slightly lower (5–10%) tear strength at a constant tensile than both the CK reference pulp and the kappa no. 17 control pulp. A careful analysis of the strength data in Table III suggests that the strength loss was not due to a lower tear but rather a lower tensile at a given pulp freeness. This is illustrated in Fig. 3 by a horizontal shift of the data points for the lower-kappa pulps toward the lower tensile indexes. The loss in tensile was ap-

II. Effect of polysulfide and anthraquinone addition on carbohydrate yield[a] (% on wood)

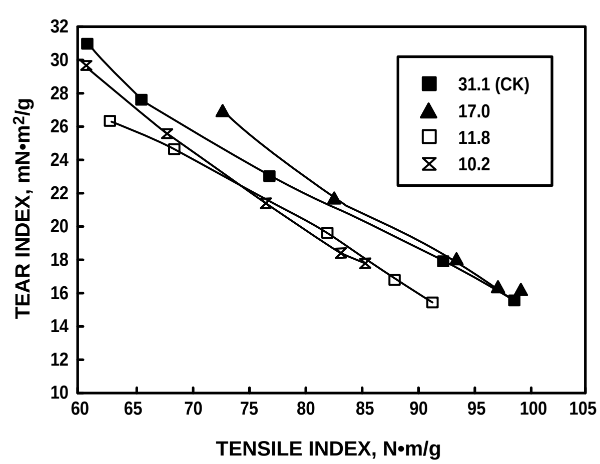
PS/AQ, % on wood	Kappa no.	Arab.	Galac.	Glucan	Mannan	Xylan	Total hemis[b]	Total hemis/ glucan
0/0	31.1	0.2	0.2	37.9	3.1	3.3	6.9	0.18
0/0	17.0	0.2	0.2	36.6	2.6	3.1	6.0	0.16
0/0	10.4	0.1	0.2	35.2	2.5	2.6	5.3	0.15
0/0.1	16.0	0.2	0.1	37.5	3.1	3.1	6.5	0.17
0/0.1	9.4	0.1	0.2	34.9	2.4	2.2	4.7	0.13
2/0	10.7	0.1	0.1	36.5	2.9	2.4	5.5	0.15
2/0.1	10.6	0.1	0.2	36.5	3.6	2.4	6.3	0.17

[a]Results are averages of duplicates.
[b]Total hemis = Total sugar - glucan

2. Effect of AQ and PS addition on pulp viscosity. PS and AQ charges (% on wood) are indicated in the legends.



3. Tear vs. tensile strength of a CK reference and three EMCC® control pulps. Kappa numbers are indicated in the legend.



parently due to a lower content of hemicelluloses, in particular xylan, in pulps (Table II) caused by more extensive pulping.

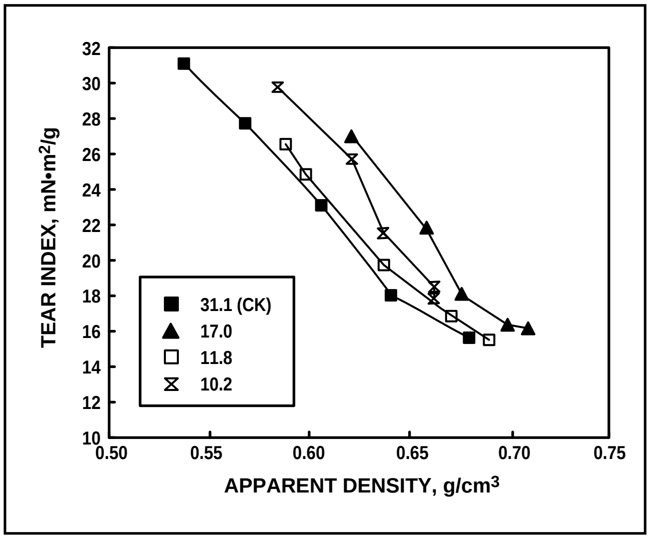
When the tear index is plotted against apparent handsheet density (or 1/bulk), these two pulps showed a similarly lower tear than the kappa no. 17 pulp but gave a comparable or slightly better tear than the CK reference pulp (**Fig. 4**). The difference in these two types of tear comparisons may be explained on the basis of fiber coarseness and flexibility. Fibers in the CK reference pulp, having a higher lignin content and yield, were more coarse and less flexible than the extended delignified fibers. They required more refining in order to improve interfiber bonding and give the same apparent density. It is well known that the tear strength of softwood pulps decreases with increasing refining after reaching an initial maximum.

Compared to the control pulps with similar kappa numbers, two AQ pulps gave a higher or comparable tensile but a lower tear index at a given freeness (Table III). Conse-

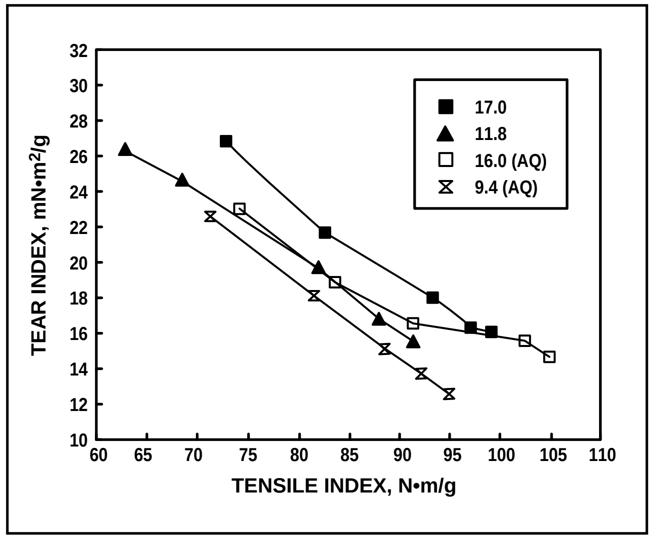
III. Summary of pulp PFI data

Cook	*PFI revs.*	*CSF, mL*	*Bulk, cm^3/g*	*Burst index*	*Tensile index*	*Tear index*
BC78	500	758	1.86	3.55	60.8	31.0
CK ref.	1,000	750	1.76	4.07	65.6	27.6
Kappa no. 31.1	2,000	717	1.65	5.14	76.8	23.0
	5,000	553	1.56	6.53	92.3	17.9
	10,000	212	1.47	7.32	98.6	15.4
BE126	1,000	723	1.61	5.25	72.8	26.8
EMCC ref.	2,000	691	1.52	6.11	82.5	21.6
Kappa no. 17.0	4,000	568	1.48	6.93	93.3	17.9
	6,000	422	1.43	7.24	97.0	16.2
	8,000	277	1.41	7.47	99.1	15.9
BE112	500	741	1.70	4.00	62.8	26.4
EMCC ref.	1,000	723	1.67	4.50	68.5	24.7
Kappa no. 11.8	2,000	695	1.57	5.43	81.9	19.6
	4,000	571	1.49	6.27	88.0	16.7
	7,000	343	1.45	6.60	91.2	15.4
BE110	500	733	1.71	3.88	60.6	29.7
EMCC ref.	1,000	725	1.61	4.69	67.8	25.5
Kappa no. 10.2	2,000	701	1.57	4.95	76.5	21.4
	4,000	600	1.51	6.07	83.2	18.3
	7,000	417	1.51	6.32	85.2	17.7
BE115	1,000	710	1.64	4.53	71.2	22.6
EMCC	2,000	676	1.55	5.33	81.4	17.9
AQ 0.1%	4,000	540	1.46	6.23	88.6	15.0
Kappa no. 9.4	6,000	364	1.42	6.31	92.2	13.5
	8,000	215	1.37	6.36	94.8	12.4
BE125	1,000	711	1.58	5.09	74.1	23.0
EMCC	2,000	673	1.52	6.04	83.7	18.8
AQ 0.1%	4,000	534	1.46	6.94	91.3	16.4
Kappa no. 16.0	6,000	367	1.41	7.35	102.0	15.4
	8,000	236	1.39	7.60	105.0	14.4
BE113	1,000	723	1.60	5.03	74.9	24.9
EMCC	2,000	703	1.54	5.99	84.0	19.4
PS 2%	4,000	577	1.47	6.74	93.7	16.7
Kappa no. 11.8	6,000	389	1.44	7.17	98.2	15.3
	8,000	267	1.43	7.02	100.4	14.5
BE116	1,000	740	1.61	4.48	71.9	26.1
EMCC	2,000	690	1.54	5.91	83.6	20.0
PS 2%	4,000	568	1.48	6.65	93.6	16.5
Kappa no. 10.7	6,000	375	1.41	6.84	99.4	14.5
	8,000	248	1.39	7.20	101.2	14.2
BE 154	1,000	729	1.59	4.89	71.8	21.8
EMCC	2,000	672	1.53	5.90	80.1	17.9
PS 2%	4,000	543	1.45	6.82	88.8	16.4
AQ 0.1%	6,000	336	1.42	7.13	97.4	14.6
Kappa no. 10.6	8,000	235	1.38	7.23	99.2	130.4
BE156	1,000	710	1.56	4.72	70.2	19.3
EMCC	2,000	662	1.51	5.51	79.5	15.7
PS 2%	4,000	492	1.44	6.40	85.0	13.8
AQ 0.1%	6,000	299	1.39	6.79	91.3	11.5
Kappa no. 8.7	8,000	204	1.34	7.14	92.7	11.1

4. Tear vs. apparent density of a CK reference and three EMCC control pulps



5. Effect of 0.1% AQ addition on pulp tear vs. tensile strength



quently, the AQ pulps showed a slightly lower (5–10%) tear-tensile strength relationship (**Fig. 5**). The finding that the AQ pulps were somewhat weaker than the control pulps is in general agreement with results reported in the literature *(9–14)*. The lower strength is probably caused by an increased cellulose chain cleavage promoted by AQ, as previously discussed.

The addition of 2% PS increased the tensile without lowering the tear strength. As a result, the tear-tensile curves for the PS pulps are about 5–10% higher than the control pulp at about the same kappa number (**Fig. 6**). The increase in tensile is apparently due to an improved interfiber bonding with a higher content of hemicelluloses (Table II).

Addition of both 2% PS and 0.1% AQ resulted in a higher tensile, a lower tear (Table III), and a tear-tensile strength comparable to or slightly lower than the control pulp (**Fig. 7**). The higher tensile from the PS addition appeared to compensate for the lower tear that was most likely caused by the AQ addition in the comparison of tear vs. tensile strength. The other AQ pulp at kappa no. 8.7 showed a considerably lower tear strength, probably due to more extensive carbohydrate degradation.

The finding that adding PS does not lower pulp strength appears to be contradictory to the literature *(5–7)*. A probable explanation is that, even though they have a higher retention of hemicelluloses than their controls, the low-kappa PS pulps are in fact lower in hemicelluloses than the CK pulps at kappa no. 31, either in absolute amounts (% on wood) or relative to cellulose, as shown in Table II. In other words, these low-kappa PS pulps do not possess an excessively high content of hemicelluloses to adversely affect the tear strength through excessive interfiber bonding, as believed in the case of higher-kappa PS pulps. On the contrary, the increased retention of hemicelluloses probably helped improve the pulp tensile strength (Fig. 6), which was considerably lowered when extending pulping to the kappa range of 8–12 (Table III).

Concluding remarks

The addition of 0.1% anthraquinone offers brownstock yield increases of about 1.0% and 0.5% at kappa nos. 24 and 16, respectively. No measurable yield improvement can be found at kappa no. 10 in extended cooking of southern pine. Addition of AQ in general results in a lower tear strength, probably as a result of increased cellulose chain cleavage.

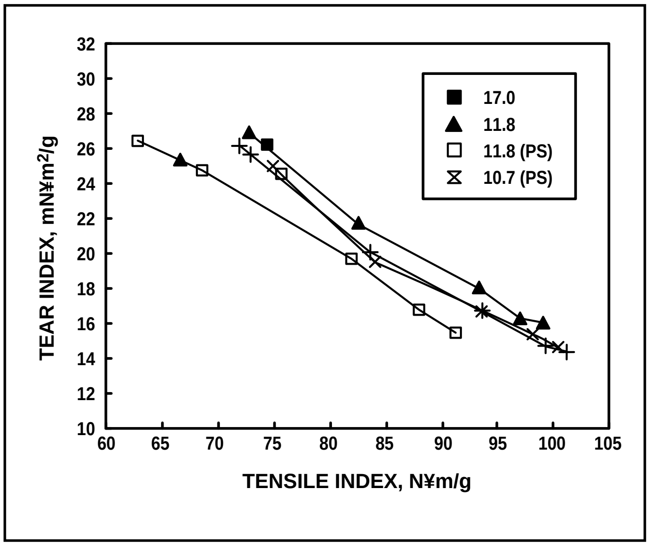
The addition of 2% polysulfide increases the yield by about 1.5% in the range of kappa no. 8–12. The PS pulps generally show a tensile index higher than, and a tear index comparable to, those of the control EMCC pulps within the kappa number range. Addition of 2% PS and 0.1% AQ increases pulp yield by about 2.5% in the range of kappa no. 8–12, suggesting a synergistic effect. Pulp strength properties are not significantly affected.

Both the improvement in pulp strength and pulp yield can be achieved with southern pine by combining modified cooking with AW and PS pulping. Southern pine pulps at kappa nos. 10–12 can be produced with a yield comparable to a pulp of at least kappa no. 20 and strength properties comparable to a conventional kraft pulp at kappa no. 30.

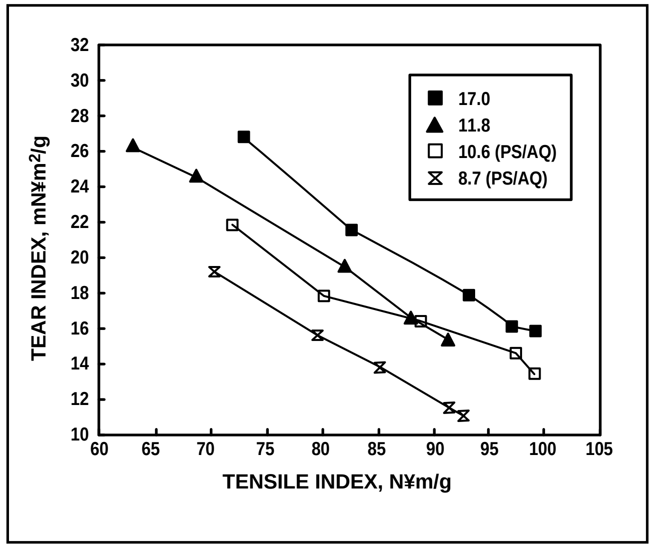
Literature cited

1. Sjoblom, K., Mjoberg, J., and Hartler, N., *Paperi ja Puu* 65(4): 227(1983).
2. Backlund, E. A., *Tappi J.* 67(11): 62(1984).
3. Sjoblom, K., Mjoberg, J., Söderqvist-Lindblad, M., *et al.*, *Paperi ja Puu* 70(5): 452(1988).
4. Jiang, J. E., Greenwood, B.F., Phillips, J. R.,*et al.*, *Appita* 45(1): 19(1992).
5. Kleppe, P. J., *Tappi* 58(8): 172(1975).

6. Effect of 2% PS addition on pulp tear vs. tensile strength



7. Effect of both 0.1% AQ and 2% PS addition on pulp tear vs. tensile strength



6. Green, R. P. and Prusas, Z. C., *Pulp Paper Can.* 76(9): T272(1975).
7. Ringley, M. B., *Southern Pulp and Paper Manufacturer* 39(1): 24(1976).
8. Holton, H. H., *63rd Annual Technical Section Meeting Proceedings,* CPPA, Montreal, 1977, p. A107.
9. Brown, G. W. and Knowles, S. E., *TAPPI 1981 Pulping Conference Proceedings,* TAPPI PRESS, Atlanta, p. 109.
10. Irvine, G. M. and Nelson, P. J., *Appita* 39(4): 289(1986).
11. Pekkala, O., *Paperi ja Puu* 64(11): 735(1982).
12. Pekkala, O., *Paperi ja Puu* 68(5): 385(1986).
13. Mayovsky, J., *Pan-Pacific Pulp and Paper Technology Conference Proceedings,* Japan TAPPI, Tokyo, 1992, p. 2.
14. Mayovsky, J., "Low Kappa Kraft, Kraft-SAQ, Polysulfide, and Polysulfide-SAQ Pulping and Physical Properties Comparison," M.S. thesis, University of Washington, Seattle, 1992.
15. Jiang, J. E., *TAPPI 1992 Pulping Conference Proceedings,* TAPPI PRESS, Atlanta, p. 683.
16. Jiang, J. E., *Tappi J.,* in press.
17. Worrall, J. J. and Anderson, K. M., *J. Wood Chem. Technol.* 13(3): 429(1993).
18. Teder, A., *Svensk Papperstid.* 72(9): 294(1969).
19. Surma-Slusarska, B. and Surewicz, W., *Paperi ja Puu* 65(11): 750(1983).
20. Kleppe, P. J., *Paperi ja Puu* 63(4): 204(1981).
21. Green, R. P. and Smith, G. C., *TAPPI 1983 Pulping Conference Proceedings,* TAPPI PRESS, Atlanta, p. 79.
22. Fleming, B. I., Kubes, G. J., MacLeod, J.M., *et al., Tappi* 61(6): 43(1978).

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