Low-kappa pulping without capital investment: using anthraquinone for low-kappa pulping

Lynda G. Sturgeoff and Yvette Pitl

ABSTRACT: The reduction in kappa number obtainable with anthraquinone (AQ) compared to conventional kraft pulps of northern and southern softwoods and northern hardwood was measured at sulfidities of 15%, 25%, 30%, and 40%. At each sulfidity, the effective alkali was adjusted to give a kappa number of about 30 (softwoods) or 18 (hardwood) in the absence of AQ. In this way, sulfidity effects and overcooking effects on low-kappa AQ pulping could be distinguished. Cooks then were repeated under identical conditions but with AQ added (0.1% on wood for softwoods and 0.05% on wood for hardwood) to demonstrate the additional reduction in kappa number due to AQ. Reductions in kappa number of from 6% to 23%, depending on the wood furnish and the sulfidity, were found. These reductions were obtained with no significant yield penalty; in some cases, yield gains were observed.

KEYWORDS: Anthraquinone, hardwoods, kappa number, pulping, softwoods, sulfidity.

The days when kraft pulping was carried to a traditional brownstock kappa number of 30–35 for softwood or 18–22 for hardwood are ending. Growing concern over the use of chlorine for pulp bleaching and the associated production of organochlorine compounds in bleach plant effluents has prompted the pulp and paper industry to investigate ways of reducing the use of chlorinated bleaching chemicals. One approach is to extend delignification during pulping with extended delignification processes (MCC, EMCC, RDH, and Superbatch) or with post-pulping processes such as oxygen delignification. Anthraquinone (AQ) is an important noncapital method available to lower brownstock kappa numbers exiting the digester.

In 1977, Holton first reported that AQ reduces the kappa number obtained under otherwise identical pulping conditions in both kraft and soda pulping *(1)*. At that time, there was very little interest in low-kappa pulping. Therefore, this reduction in kappa was utilized to achieve other objectives such as relieving pulp mill bottlenecks or reducing sulfur emissions *(2)*. **Figure 1** illustrates these uses of AQ.

A series of papers in the early 1980s by McDonough and co-workers showed that it was possible to pulp to very low kappa numbers *(3–7)*. Using a high effective alkali (20%), a high sulfidity (38%), and a high charge of AQ (0.20% or 0.30% on wood), they were able to produce a softwood pulp of kappa number 15–17. In 1982, Pekkala reported similar results *(8)*. He also used a very high charge of AQ (from 0.1% to 0.8%) to reduce the kappa number from 33 for a conventional kraft cook to about 25.

This early work provided the basis for the recent interest in low-kappa pulping using AQ. The conditions, though, are not generally applicable to today's needs. The early results evaluated methods of achieving the lowest possible kappa numbers through multiple process changes in the kraft cook. However, mills can use AQ simply to lower the kappa number without changing any

Sturgeoff is senior research chemist and Pitl is a chemist for ICI Forest Products, Mississauga, ON, Canada L5K 2L3.

other cooking conditions.

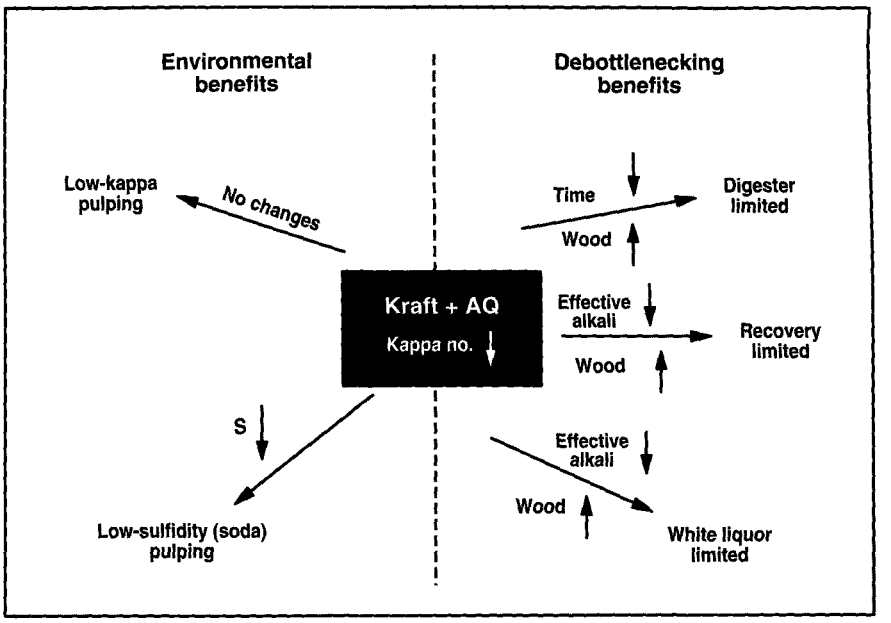
Within the last two years, interest in low-lignin pulping with anthraquinone has resurfaced. There have been several recent reports on the use of AQ for low-kappa pulping, both in the laboratory *(9–13)* and in mill trials. In a conventional softwood batch kraft cook, use of AQ generally resulted in a reduction of 3–7 kappa numbers (that is, a reduction of between 10% and 24%) *(9, 10)*. The application of AQ for low-kappa pulping goes beyond the conventional kraft process. A further lowering of kappa numbers by some 25–30% is achieved in extended cooking processes such as RDH pulping and modified batch pulping *(11, 12)*. Pulp quality was largely unaffected by AQ low-kappa pulping *(9–13)*.

As expected, the reduction in the lignin content of these pulps then can be employed to reduce the C-stage total available chlorine charge, which, in turn, results in a substantial reduction in the caustic requirements of the subsequent extraction stage. The net result of these bleaching chemical reductions is a reduced effluent color, reduced AOX and BOD loading, and, depending on the ClO_2 substitution level, reduced dioxin and furan levels.

Interestingly, there is very little information available on the use of AQ for low-kappa pulping of hardwoods. Some data can be extracted from the early literature. In 1979, Blain reported on the benefits of AQ in alkaline pulping of hardwoods. Data from that paper can be used to show that a 12% reduction in kappa is obtainable using 0.05% AQ in a kraft cook of a mixture of red maple and sugar maple at 25% sulfidity *(14)*. Data from a 1980 paper by Fossum and co-workers can be used to show a 25–33% reduction in kappa number in the kraft pulping of birch at constant yield *(15)*.

In the past two years, extended delignification has been one of the most popular applications for AQ in North America, with numerous mill trials planned or completed. To be practical, the low-lignin pulps must be produced without a reduction in yield or a degradation of fiber properties.

1. Potential benefits of kraft-AQ pulping



I. AQ-induced reductions in kappa number at constant percent effective alkali for southern softwood

S, %	*Effective alkali, %*	*AQ,* %*	*Kappa no.*	*Reduction in kappa, %*
0	14	...	111.8	...
0	14	0.1	58.9	47
12	14	...	48.6	...
12	14	0.1	35.6	27
25	14	...	28.7	...
25	14	0.1	24.2	16
40	14	...	21.2	...
40	14	0.1	20.6	3

* on o.d. wood

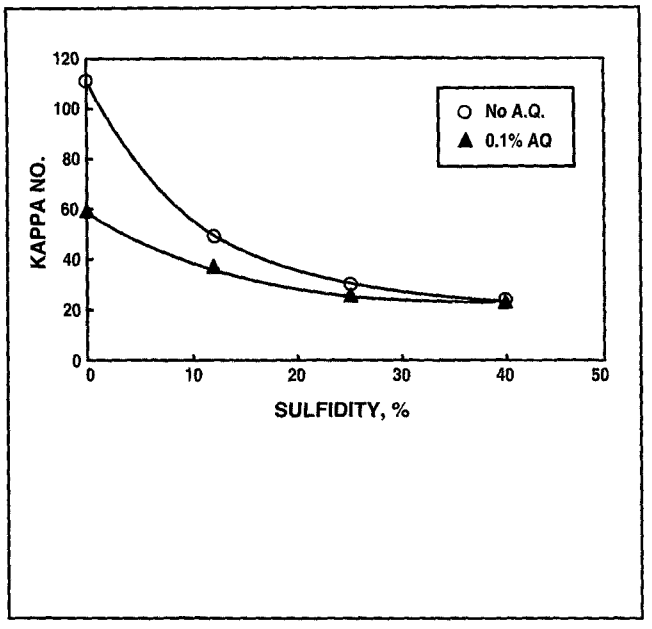
Results and discussion

Sulfidity and AQ

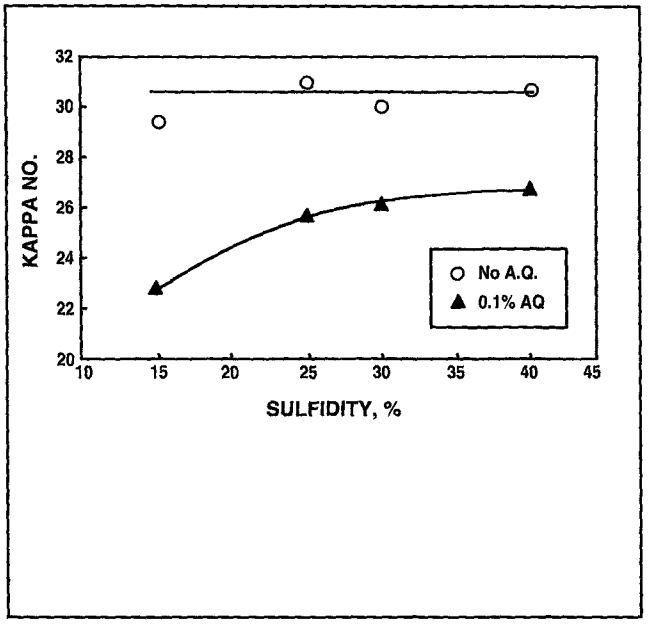
Holton first showed that AQ is highly effective in soda pulping and that its effectiveness decreases with increasing sulfidity in kraft pulping *(1)*. An equivalent reductive delignification mechanism for both AQ and sulfide was proposed in 1980 *(16, 17)*. Later studies have shown that sulfidity can be replaced by AQ to maintain a constant kappa number, without varying the effective alkali or *H* factor *(18)*.

Figure 2 and **Table I** show typical results of kappa number vs. sulfidity at constant effective alkali. These results were obtained with a mixture of southern softwoods. In the absence of AQ, the kappa numbers decreased

2. Kappa number vs. percent sulfidity at constant percent effective alkali for southern softwood



3. Influence of sulfidity on AQ for northern softwood



II. AQ-induced reductions in kappa number at constant no-additive kappa number for northern softwood

S, %	Effective alkali, %	AQ,[a] %	Kappa[b]	Reduction in kappa, %	Yield,[b] %
15	15.5	...	29.4	...	46.9
15	15.5	0.1	22.7	23	46.3
25	13.8	...	31.0	...	47.7
25	13.8	0.1	25.6	17.5	47.6
30	13.4	...	30.1	...	47.5
30	13.4	0.1	26.1	13.3	47.9
40	12.5	...	30.7	...	47.8
40	12.5	0.1	26.7	13.1	48.7

[a] on o.d. wood
[b] average of two cooks

with increasing sulfidity. At high sulfidity, the kappa numbers leveled off. With AQ, the kappa number reduction was greatest for a soda cook. By 40% sulfidity, almost no additional reduction in kappa number was obtained with AQ. Under these conditions, the wood was cooked to a kappa number of about 21. Since the wood was so overcooked due to the high sulfidity, one might not expect any further reduction in kappa number to be possible due to AQ. That is, it is not clear if the lack of kappa number reduction with AQ is due to a diminishing effectiveness of AQ at high sulfidity or to the already low kappa number.

In this paper, we have addressed this problem. A series of cooks were done over a range of sulfidity, adjusting the effective alkali to target a constant kappa number of either 30 or 18 (softwoods or hardwoods, respectively) in the absence of AQ. AQ was then used at these pulping conditions. In this way, we can clearly see the actual benefit of AQ for low-kappa pulping of equivalent pulps over a range of sulfidities from 15% to 40%.

The magnitude of the effect of AQ likely varies with wood type. Therefore, three different types of woods were used in this study: northern and southern softwoods and northern hardwoods.

For each wood furnish, several pulping runs were evaluated at 15%, 25%, 30%, and 40% sulfidity and at different effective alkalis until conditions that gave a 30 kappa number (softwoods) or an 18 kappa number (hardwood) were found for each sulfidity. These conditions then were used to evaluate the effect of AQ at each sulfidity.

Northern softwood

Table II shows the reduction in kappa number obtained at each sulfidity studied for a mixture of northern softwoods (primarily black spruce). At 15% sulfidity, a 23% reduction in kappa number was obtained. Even at 40% sulfidity, a significant reduction in kappa number of 13% was obtained (**Fig. 3**). No penalty in yield is paid for the lower kappa number; indeed, at the higher

sulfidities, there may still be some yield benefit due to AQ.

Southern softwood

Table III and **Fig. 4** present the results obtained with a mixture of southern softwoods. The reduction in kappa number obtainable with AQ drops smoothly with increasing sulfidity. Even at 40% sulfidity, a small reduction in kappa number of 6% is achievable. Again, the low-kappa AQ pulps were obtained at the same or slightly higher yield than the conventional kraft pulps.

Northern hardwood

To study hardwoods, the effective alkali used was adjusted over the same range of sulfidities to target a kappa number of 18. The northern hardwood, obtained from an eastern Canadian mill, was a mixture of several different species. Since cooks were done on a relatively small scale (see Experimental), the run-to-run variability was quite high, reflecting sampling variability. Single bombs could contain a disproportionate amount of one species at the expense of the others. Consequently, no clear trend in the percent reduction obtainable with AQ over the sulfidity range was established. Reductions in kappa number of 12–13% were obtained at the three lowest sulfidities studied. At 40% sulfidity, the run-to-run variability masks any kappa number reduction from AQ. As in previous cases, no penalty is paid in yield for the increased delignification. Results are given in **Table IV** and **Fig. 5**.

Pulp yields and wood furnishes

The yield of low-kappa-number pulp obtained is comparable to the yield of untreated pulp. At low sulfidity, where the reduction in kappa number is greatest, there may be a small total yield loss for the AQ pulps. However, the AQ pulp contains a greater percentage of cellulosic material than the conventional kraft pulp at higher kappa number. At high sulfidity, where AQ is less effective in reducing the kappa number, there is a small net yield gain. **Figure 6** illustrates the yields obtained for the various woods and sulfidities studied.

The wood furnish affects the additional amount of delignification obtainable with AQ. In general, northern softwood results in the greatest percent reduction of kappa number. The smaller reductions observed with the northern hardwood probably reflect the greater variability in wood furnish and the correspondingly greater experimental error. The results are summarized in **Fig. 7**, which shows the percent reduction in kappa number achievable for different types of wood at the four sulfidities studied.

III. AQ-induced reductions in kappa number at constant no-additive kappa number for southern softwood

S, %	Effective alkali, %	AQ,[a] %	Kappa[b]	Reduction in kappa, %	Yield,[b] %
15	16	...	33.1	...	46.4
15	16	0.1	26.1	21%	46.1
25	14	...	34.6	...	46.5
25	14	0.1	28.4	18%	47.1
30	13.5	...	33.7	...	46.9
30	13.5	0.1	29.3	13%	47.4
40	12.5	...	33.0	...	47.6
40	12.5	0.1	31.1	6%	48.0

[a] on o.d. wood
[b] average of three cooks

IV. AQ-induced reductions in kappa number at constant no-additive kappa number for northern hardwood

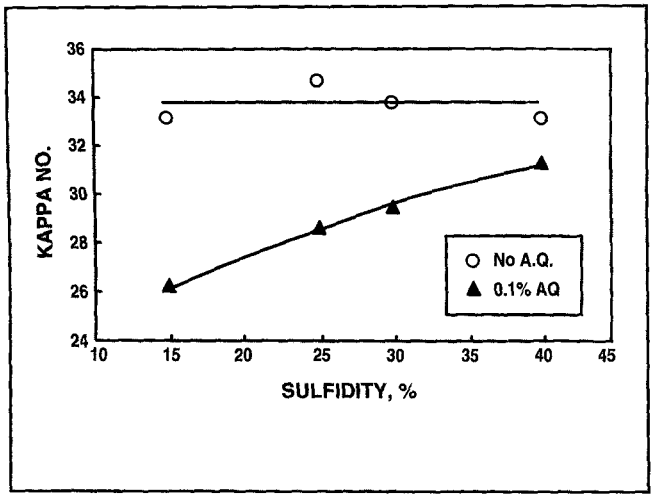
S, %	Effective alkali, %	AQ,[a] %	Kappa[b]	Reduction in kappa, %	Yield,[b] %
15	14.2	...	18.3	...	49.8
15	14.2	0.05	16.0	13	50.0
25	13.0	...	19.8	...	50.0
25	13.0	0.05	17.1	13.6	50.4
30	12.8	...	19.5	...	50.2
30	12.8	0.05	17.1	12.3	50.5
40	12.3	...	17.6	...	49.8
40	12.3	0.05	18.9	–7.4	50.2

[a] on o.d. wood
[b] average of four cooks

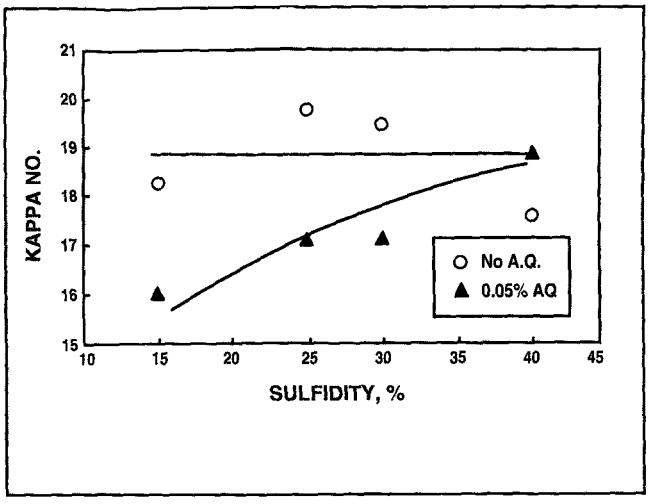
Conclusions

Anthraquinone is an effective method of reducing the kappa numbers obtained from the kraft pulping of both hardwoods and softwoods. The magnitude of the reduction obtainable for softwoods depends on the sulfidity and decreases with increasing sulfidity. For northern hardwood, any sulfidity effect is

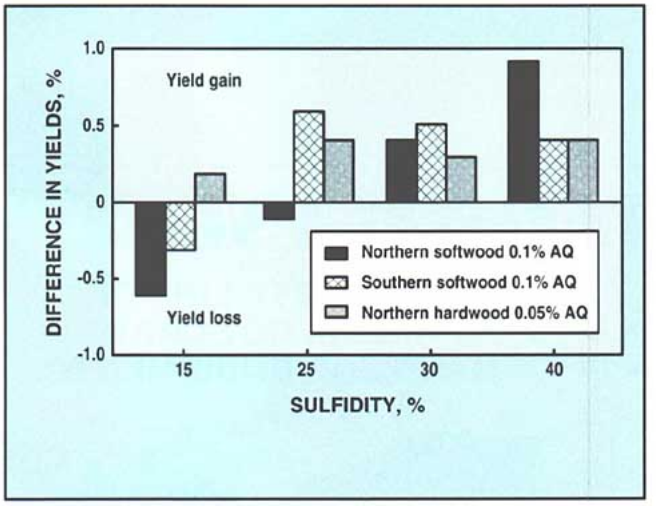
4. Influence of sulfidity on AQ for southern softwood



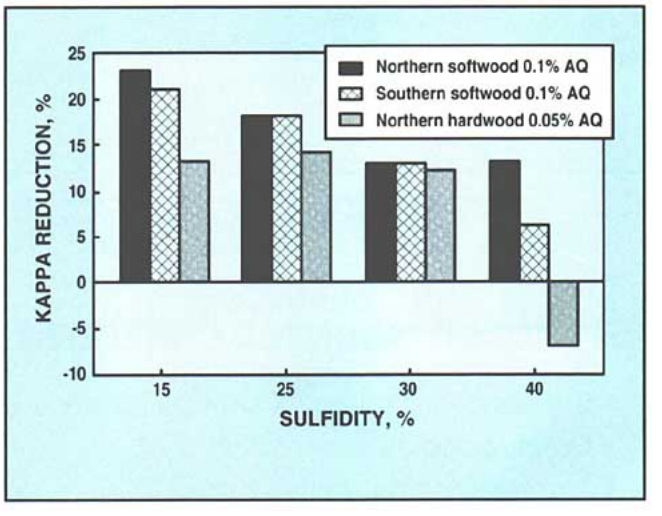
5. Influence of sulfidity on AQ for northern hardwood



6. Difference in yield between low-lignin kraft/AQ and standard kraft cooks



7. Effect of wood species on AQ kappa reductions



masked by the lower repeatability of the results.

In contrast to earlier studies, when the overcooking of wood at high sulfidity is avoided, it becomes clear that AQ continues to have an impact on pulping at high sulfidities. Even at 40% sulfidity, a significant reduction in kappa number can be achieved.

This reduction in kappa number is obtained with no penalty in yield. Indeed, in some cases, AQ still imparts a small yield advantage.

The wood furnish also affects the additional degree of delignification obtainable with AQ. In general, northern softwood results in the greatest percent reduction of kappa.

Experimental

Pulping experiments were carried out on a multiple bomb assembly consisting of eight 0.6-L bomb digesters of 75-g chip capacity. These were mounted on a rotating rack within a larger, horizontal-axis pressure vessel. The whole microdigester assembly was surrounded by a water bath, through which heat was transferred to the microdigesters from electric coils wrapped around the large pressure vessel.

Wood chips obtained from North American mills were dried at room temperature to at least 90% consistency and fractionated. Cooks were done on 75 g of a 50:50 mixture of 2–4-mm and 4–6-mm chips. Chip moisture was restored by soaking with dilution water in the bomb for 16 hours prior to the addition of cooking chemicals and additive. Cooking followed immediately using the conditions noted below. On completion of pulping, the entire bomb contents were diluted with water to 2 L and broken up in a disintegrator. The pulp was subsequently washed, and measurements of the total pulp yield

and kappa number were taken in the usual manner.

Data reported at each of the cook conditions are averages of at least duplicate runs. Typical run-to-run repeatability is about ± 1 kappa number for northern softwood, which is primarily black spruce. Run-to-run repeatability decreases to ± 2 kappa numbers for the southern softwood and the northern hardwood.

Cook conditions:

- Liquor-to-wood ratio: 4:1
- Rise time: 60 min
- Hold time: 90 min
- Maximum temperature: 170°C
- Sulfidity: as noted, calculated as percent of effective alkali
- Effective alkali: as noted
- AQ: as noted.

Literature cited

1. Holton, H. H., *Pulp Paper Can.* 78(10): T218(1977).
2. Blain, T. J. *Tappi J.* 76(3): 137(1993).
3. McDonough, T. J. and Van Drunen, V. J., *Tappi J.* 63(11): 83(1980).
4. McDonough, T. J. and Herro, J. L., *TAPPI 1981 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 371.
5. McDonough, T. J. and Herro, J. L., *TAPPI 1982 Annual Meeting Proceedings*, TAPPI PRESS, Atlanta, p. 373.
6. McDonough, T. J. and Van Drunen, V. J., *TAPPI 1982 International Pulp Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta, p. 59.
7. McDonough, T. J. and Herro, J. L., *Tappi J.* 65(9): 117(1982).
8. Pekkala, O., *Paperi ja Puu* 64(11): 735(1982).
9. Rajan, P. S., Griffin, C. W., Jameel, H., *et al.*, *TAPPI 1992 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 985.
10. Goyal, G. C., Powers, J., and Cronlund, M., *TAPPI 1992 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1047.
11. Watson, P. A., Gustafson, R. R., McKean, W. T., *et al.*, *TAPPI 1992 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 847.
12. Sezgi, U. S., Abuhasan, M. J., Jameel, H., *et al.*, *Appita* 45(3): 173(1992).
13. Pekkala, O., *Paperi ja Puu* 68(5): 385(1986).
14. Blain, T. J., *J. Pulp Paper Sci.* 5(1): TR3(1979).
15. Fossum, G., Hagglund, S., and Lindqvist, B., *Svensk Papperstid* 83(15): 430(1980).
16. Fleming, B. I., Bolker, H. I., Kubes, G. J., *et al.*, *Tappi* 63(11): 73(1980).
17. Clayton, D. W. and Fleming, B. I., *Paperi ja Puu* 63(4a): 275(1981).
18. Kutney, G. W., *TAPPI 1984 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 65.

Received for review July 22, 1993.

Accepted Feb. 22, 1994.

Presented at the TAPPI 1993 Pulping Conference.