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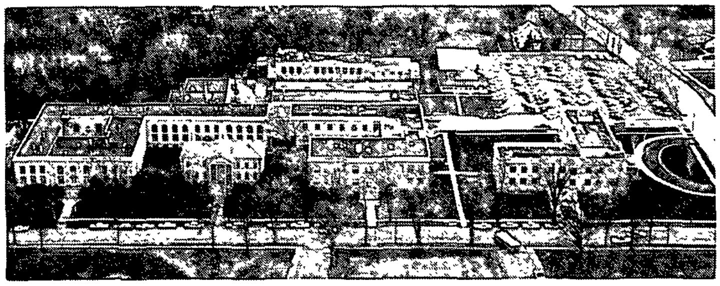

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PULPING TO LOW RESIDUAL LIGNIN CONTENTS IN THE KRAFT-ANTHRAQUINONE AND KRAFT PROCESSES

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ABSTRACT

Experiments have been done to determine the extent to which the kraft-anthraquinone and kraft processes can be used to pulp to very low lignin contents without detrimental effects on yield or pulp quality. Response surface methodology was used, together with direct search optimization, to minimize kappa number at several viscosity levels. The results show that the kraft-anthraquinone process can be operated in such a way as to effect substantial reductions in unbleached kappa number relative to current commercial practice, and the kraft process is capable of smaller reductions. For the kraft-anthraquinone process, operating conditions have been identified which may allow a 60% reduction in ubleached kappa number. The low-lignin pulps were more readily delignified by chlorination and caustic extraction than were conventional pulps, but were slightly more difficult to bleach to high brightness. Pulps produced at kappa numbers as low as 14 were similar in yield to conventional kraft control pulps but had marginally lower tear strengths.

INTRODUCTION

Conventional kraft pulping of softwoods for bleachable grades is normally terminated at kappa numbers of 30 to 35. Production of unbleached pulps having lower lignin contents ("low-lignin pulping") would reduce the amount of lignin which has to be removed in the first two bleaching stages. This would have the twofold benefit of reducing both bleachery effluent pollution potential and bleaching chemical cost. In these respects low-lignin pulping would be analogous to oxygen bleaching if comparable kappa number reductions could be achieved.

Low lignin pulping may also have other advantages. These include an improved overall mill energy balance as a result of increased recycle of organic materials, a reduction in the amount of screen rejects produced, and improved bleachability in short bleaching sequences. Chlorine free bleaching sequences might also have an improved chance of being successful if there were less lignin to be removed from the unbleached pulp.

The primary constraints on the degree to which the unbleached pulp lignin content can be reduced are pulp strength and pulp yield. Recovery capacity and digester capacity may also become important factors limiting the degree of delignification in the pulping step. The former must be considered since pulping to lower lignin contents will result in a greater load of organic material to the recovery system and the inorganic load may also increase, depending on the method chosen for reducing the unbleached lignin content. Digester capacity must be considered if the proposed strategy involves the use of longer cooking time. Bleachability may be another constraint if the ease of removal of the residual lignin is adversely affected by the means chosen for reducing unbleached lignin content.

In view of the magnitude of these potential benefits, a project was initiated at The Institute of Paper Chemistry to investigate means of achieving them without unduly impairing pulp strength, yield or bleachability. Early in the study it was recognized that anthraquinone may be a useful means to this end by virtue of the improved selectivity its addition imparts to the kraft process. Accordingly, the potential of the kraft-anthraquinone process was investigated by optimizing it for the production of low lignin pulps. Optimum conditions for similarly using the kraft process were also established, both to provide a basis for comparison and to investigate the extent to which kraft conditions can be varied to produce low lignin pulps in an otherwise conventional process.

Low-lignin pulping has also been the subject of recent research in Sweden by Hartler, Teder, and their coworkers (1-4). Their approach has involved modification of the time profiles of the concentration of alkali, hydrosulfide ion and dissolved lignin during a kraft cook. This was achieved by additions of alkali and withdrawal of liquor during the course of the cook. Our work, on the other hand, has been concentrated on evaluating smaller modifications to existing technology and has emphasized the application of anthraquinone.

KRAFT-ANTHRAQUINONE PULPING

A series of laboratory bomb cooks of loblolly pine chips was carried out with conditions varied to form a central composite rotatable experimental design (5). Regression analysis and deletion of nonsignificant terms gave the equations shown in Table I. These equations adequately described the behavior of the process throughout the region investigated.

One way of interpreting the equations is to calculate values of kappa number, yield, and viscosity for various sets of values of independent variables (process conditions). Plots of viscosity vs. kappa number and yield vs. kappa number may then be prepared with liquor-to-wood ratio, effective alkali and sulfidity as parameters. Figures 1 through 4 were obtained in this way.

It is apparent from Fig. 1 that anthraquinone addition is a promising route to lower kappa numbers since it allows a reduction in kappa number with no corresponding reduction in pulp viscosity or, by implication, in pulp strength. This comes about because at a given cooking time anthraquinone lowers the kappa number but has no effect on pulp viscosity. Substantial lowering of the kappa number by anthraquinone addition is similarly without effect on pulp yield, as shown in Fig. 2.

TABLE I

REGRESSION EQUATIONS FOR KRAFT-ANTHRAQUINONE PULPING

	R^2
Total yield, % = $45.0 - 2.2X_1 - 1.5X_2 - 0.6X_5 + 0.3X_2X_3 + 0.5X_1^2 + 0.2X_2^2 + 0.2X_5^2$	0.97
Screened yield, % = $45.0 - 2.2X_1 - 1.4X_2 - 0.6X_5 + 0.3X_2X_3 + 0.5X_1^2 + 0.2X_5^2$	0.97
ln (Kappa no.) = $2.85 - 0.39X_1 - 0.21X_2 - 0.07X_3 - 0.14X_5 + 0.03X_1X_3 + 0.04X_1X_5 + 0.06X_2X_3 + 0.11X_1^2 + 0.03X_2^2 + 0.04X_5^2$	0.99
ln (Viscosity, cp.) = $3.18 - 0.29X_1 - 0.25X_2 - 0.09X_1X_5 - 0.09X_2X_5$	0.89

Notes: 1. The independent variables in the above equations are defined as follows:

$$X_1 = \frac{(\text{Time at } 173^\circ\text{C, min}) - 120}{60}$$

$$X_2 = \frac{(\text{Effective alkali, \%}) - 18}{2}$$

$$X_3 = \frac{\log\,(\text{AQ charge, \%}) + 1}{\log 2}$$

$$X_5 = \frac{(\text{Sulfidity}) - 25}{10}$$

2. The equations are valid only within the region bounded by $X_1^2 + X_2^2 + X_3^2 + X_5^2 = 4$.
3. Constant conditions: 90 min rise to a maximum temperature of 173°C, liquor-to-wood ratio 4.0.

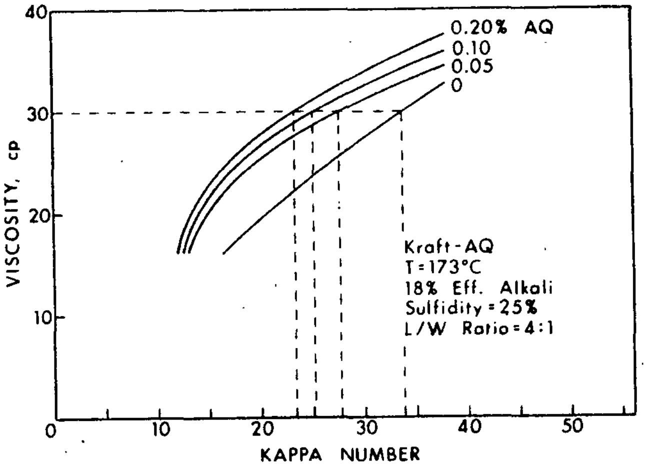

Figure 1. Effect of Anthraquinone Charge on the Viscosity-Kappa Number Relationship

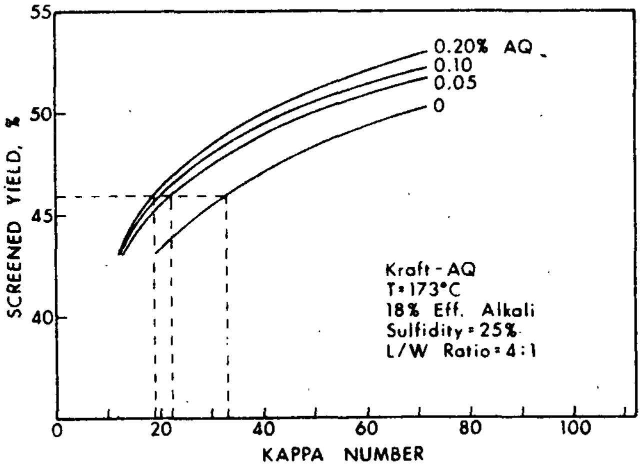

Figure 2. Effect of Anthraquinone Charge on the Yield-Kappa Number Relationship

Figure 3 shows that increasing the sulfidity has a beneficial effect on selectivity and lowers the achievable kappa number at fixed viscosity level, even in the presence of anthraquinone. There is, however, no corresponding effect of sulfidity on yield, that is, the yield-kappa number relationship is unaffected by sulfidity over the range investigated.

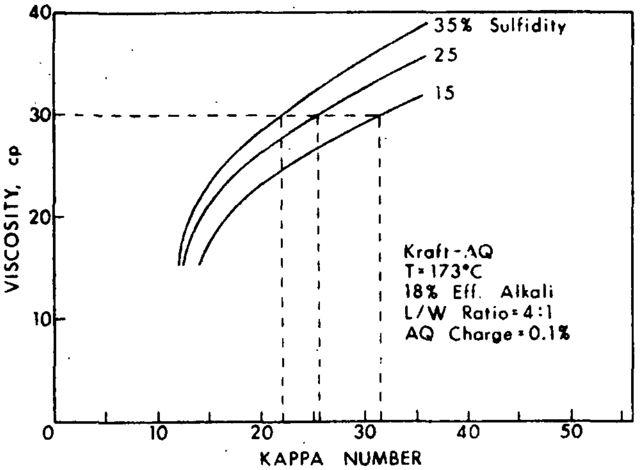

Figure 3. Effect of Sulfidity on the Viscosity-Kappa-Number Relationship

Increasing the effective alkali charge raises rather than lowers the minimum kappa number achievable at a fixed viscosity level, as shown in Fig. 4. The yield-kappa number relationship is, however, not affected by the level of effective alkali.

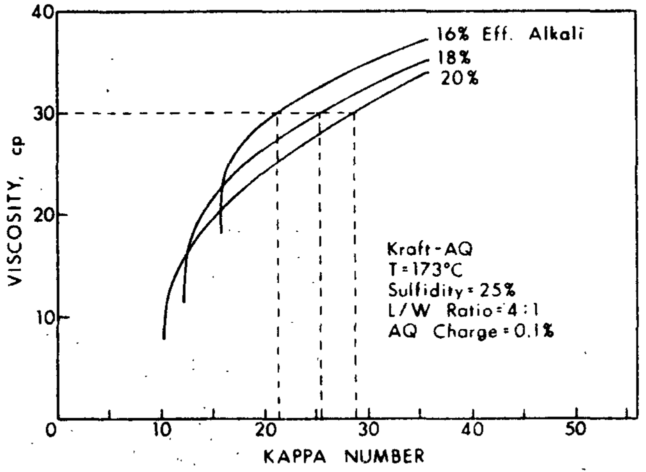

Figure 4. Effect of Effective Alkali Charge on the Viscosity-Kappa Number Relationship

These graphical illustrations are incomplete since they do not illustrate the fact that the effects of some of the variables depend on the levels of the others owing to the presence of interaction terms in the regression equations. On the other hand, the mathematical model comprised of the regression equations in Table I contains all of this information since it is a distillation of all of the significant results of the experimental program. It was therefore used as the basis for choosing optimum conditions.

Optimization analysis was done using the constrained direct search algorithm of Luus and Jaakola (6). The algorithm was used with the equations of Table I to find process conditions which would minimize kappa number at various levels of viscosity, subject to a constraint on the cooking time (H factor). These were termed "minimum-kappa" pulping conditions and are shown in Table II for two different pulp viscosity levels, 30 and 20 cp together with the expected kappa numbers and carbohydrate yields.

TABLE II

MINIMUM KAPPA (MK)
KRAFT-ANTHRAQUINONE PROCESS CONDITIONS

Type of Cook	H-Factor	Viscosity, cp.	Effective Alkali, %	AQ, %	Sulfidity, %	Kappa Number	Carbohydrate Yield,[a] %
Conventional kraft	2200	30	16	0	25	32	43.8
	4300	20	16	0	25	18	41.2
MK kraft-AQ	2000	30	18	0.30	38	17	44.9
		20	20	0.20	38	15	43.8

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[a] Carbohydrate yield = pulp yield after screening x (1 - 0.0015 x Kappa no.).

The first line of the table, labeled "conventional kraft," gives the results obtained when more or less normal operating conditions are used and the cook is terminated when the pulp viscosity reaches a value of 30. The kappa number of the resulting pulp is 32. As shown in the second line of the table, it is possible to reduce the kappa number to 18 simply by extending the cook, but it is necessary to nearly double the cooking time and significant losses in viscosity and yield are incurred. The third line gives the process conditions necessary to minimize the kappa number subject to the constraints that the viscosity not be allowed to drop below 30 cp and the H factor be no greater than 2000. It is apparent that combined use of anthraquinone and high sulfidity allows the kappa number to be reduced by nearly 50% with no increase in cooking time and no loss in viscosity or carbohydrate yield. If the viscosity constraint is relaxed to 20 cp the effective alkali charge may be increased to 20% allowing reductions in both anthraquinone charge and kappa number.

The relationship between the minimum achievable kappa number as defined above and the corresponding viscosity constraint may be thought of as an optimized viscosity-kappa number relationship, the various points on the curve being arrived at by holding the cooking time constant and varying the initial liquor composition. Two such curves for different H factors are shown in Fig. 5. Also included in the figure for comparison is the viscosity-kappa number relationship for a conventional kraft cook in which the cooking time is varied for constant initial liquor composition. It is apparent that kraft-anthraquinone pulping under suitable conditions gives, at a given viscosity level, kappa numbers which are much lower than can be obtained by conventional kraft pulping.

Verification of these results was sought by cooking a new wood sample under the conditions indicated in Table II. As seen in Table III the viscosities of the pulps cooked with anthraquinone were slightly lower than expected. The kappa numbers were in the expected range. These data confirm that anthraquinone can be used to prepare softwood pulps of kappa number 13 to 17 by judicious manipulation of the liquor composition in an otherwise conventional kraft process.

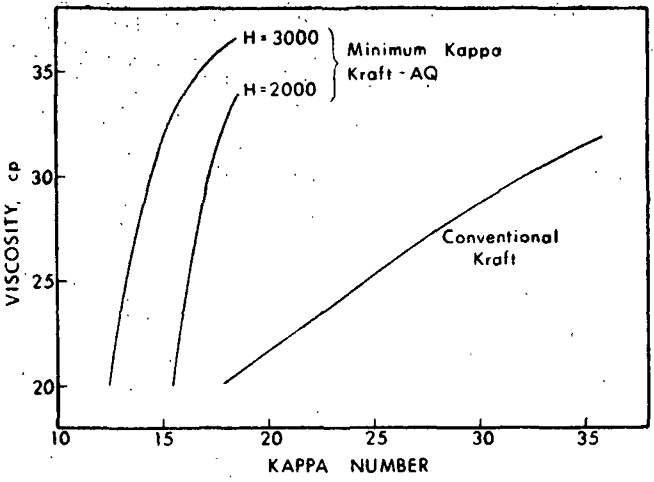

Figure 5. Conventional Kraft (H-factor Varied) and Optimized Kraft-Anthraquinone (H-factor 2000 or 4000) Viscosity-Kappa Number Relationship

TABLE III

MINIMUM KAPPA (MK)
KRAFT-ANTHRAQUINONE COOKS

Type of Cook	H-Factor	Viscosity, cp.	Kappa Number	Carbohydrate Yield, %
Conventional kraft	2200	36	31	46.4
	4300	22	17	44.0
MK kraft-AQ	2000	26	17	46.2
		19	13	45.0

KRAFT PULPING

An experimental program of kraft cooks similar to the anthraquinone series was carried out and the data treated in a similar fashion. The resulting regression equations are collected in Table IV. An optimization analysis similar to that described above for the kraft-anthraquinone case produced the results shown in Table V and Fig. 6. Confirmatory cooks of a different wood sample gave the results shown in Table VI. Agreement with the predictions was generally good.

TABLE IV

REGRESSION EQUATIONS FOR KRAFT PULPING

	R^2
Total yield, % = $43.6 - 2.8X_1 - 1.4X_2 - 0.9X_5 + 1.7X_6 - 0.4X_1X_6 + 0.6X_1^2 + 0.6X_6^2$	0.95
Screened yield, % = $43.6 - 2.6X_1 - 1.4X_2 - 0.8X_5 + 1.7X_6 - 0.4X_1X_6 + 0.5X_1^2 + 0.4X_6^2$	0.94
ln (Kappa no.) = $3.08 - 0.46X_1 - 0.22X_2 - 0.24X_5 + 0.19X_6 + 0.05X_1X_5 - 0.06X_1X_6 - 0.04X_5X_6 + 0.11X_1^2 + 0.09X_5^2$	0.99
ln (Viscosity, cp.) = $3.06 - 0.38X_1 - 0.23X_2 + 0.29X_6 - 0.08X_1X_2 + 0.06X_1^2 - 0.05X_6^2$	0.97

Notes: 1. The independent variables in the above equations are defined as follows:

$$X_1 = \frac{(\text{Time at } 173^\circ\text{C, min}) - 120}{60}$$

$$X_2 = \frac{(\text{Effective alkali, \%}) - 18}{2}$$

$$X_5 = \frac{(\text{Sulfidity, \%}) - 25}{10}$$

$$X_6 = (\text{Liquor-to-wood ratio, cc/g}) - 4$$

2. The equations are valid only within the region bounded by $X_1^2 + X_2^2 + X_5^2 + X_6^2 = 4$.
3. Constant conditions: 90 min rise to a maximum temperature of 173°C.

TABLE V

MINIMUM KAPPA (MK)
KRAFT PROCESS CONDITIONS

Type of Cook	H-Factor	Viscosity, cp.	Effective Alkali, %	Sulfidity, %	Liquor-to-wood Ratio, cc/gm	Kappa Number	Carbohydrate Yield, %
Conventional kraft	2200	30	16	25	4.0	32	43.8
	4300	20	16	25	4.0	18	41.2
MK kraft	2000	30	19	40	5.0	24	44.0
		20	21	37	4.1	17	41.0

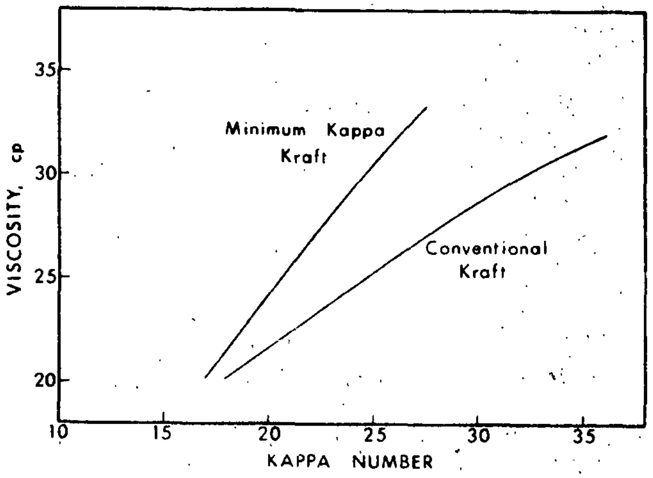

Figure 6. Conventional Kraft (H-factor Varied) and Optimized Kraft (H-factor 2000) Viscosity-Kappa Number Relationship

TABLE VI

MINIMUM KAPPA (MK)
KRAFT COOKS

Type of Cook	H-Factor	Viscosity, cp.	Kappa Number	Carbohydrate Yield, %
Conventional kraft	2200	36	31	46.4
	4300	22	17	44.0
Short MK kraft	2000	32	22	44.9
		18	15	43.6

These results show that the kraft process can be modified, without anthraquinone addition, to give pulps of much lower kappa number than are conventionally obtained, without serious losses in yield or viscosity. At a given viscosity level, however, the available reductions in kappa number are lower than in the kraft-anthraquinone process, and to maintain a viscosity level of 30 it is necessary to increase the liquor-to-wood ratio, a measure which may not be feasible in many mills.

BLEACHABILITY

To verify that low lignin pulping would result in the anticipated bleaching chemical cost saving, low-lignin pulps were prepared according to the strategies outlined above and their bleachabilities studied. Table VII shows partial results of a preliminary series of experiments designed to study the behavior of these pulps in chlorination and caustic extraction stages. It is apparent that the use of kappa number minimizing conditions in both the kraft and kraft anthraquinone systems makes the residual lignin easier to remove with chlorine and caustic.

TABLE VII

PREBLEACHING OF MINIMUM KAPPA (MK) PULPS

Type of Cook	Unbleached Kappa No.	Unbleached Viscosity, cp.	Extracted Pulp $KMnO_4$ No.
Conventional kraft	31	36	6.0
	17	22	5.6
MK kraft-AQ	17	26	3.6
	13	19	3.6
MK kraft	22	32	4.0
	15	18	4.2

Conditions: Chlorination — % Cl_2 = 0.2 x kappa no., 45 min, 25°C, 3% consistency.
Extraction — % NaOH = 0.5 x % Cl_2, 60 min, 60°C, 10% consistency.

Bleachability in the latter stages of the CEDED sequence was studied in experiments in which the amounts of chlorine dioxide in both the third and fifth stages were varied. The results were used to estimate the maximum final brightness achievable and the total amount of chlorine dioxide required to reach a final brightness of 87.5. As shown in Table VIII, it appears that reducing the unbleached kappa number causes a reduction in the brightness ceiling and an increase in the chlorine dioxide requirement. Thus, although the low lignin pulps are easier to delignify in the first two stages of the bleaching sequence, they are more difficult to brighten in the final stages.

TABLE VIII

BLEACHABILITY OF MINIMUM KAPPA (MK) PULPS IN
A CEDED SEQUENCE

Type of Cook	Unbleached Kappa No.	Brightness Ceiling	ClO_2 Requirement for 87.5 Brightness, % on pulp
Conventional kraft	31	90	1.2
	17	89	1.4
MK kraft-AQ	17	88	1.6
	13	89	1.2
MK kraft	22	89	1.6
	15	88	1.6

Conditions:
1. Chlorination — % Cl_2 = minimum required to give extracted $KMnO_4$ no. of 4.5 or lower, 45 min, 25°C, 3% consistency.
2. Extraction — % NaOH = 0.5 x % Cl_2, 60 min, 60°C, 10% consistency.
3. Chlorine dioxide — % ClO_2 varied, 3 hr, 70°C, 10% consistency.
4. Extraction — % NaOH = 0.5 x % ClO_2 in preceding stage, 60 min, 60°C, 10% consistency.
5. Chlorine dioxide — % ClO_2 varied, 3 hr, 70°C, 10% consistency.

A possible exception to this statement is the minimum kappa kraft-anthraquinone pulp of kappa number 13, which required no more chlorine dioxide than the conventional pulp.

PULP STRENGTH

Samples of both unbleached and bleached low-lignin pulps and conventional kraft controls were tested to determine their strength properties. As seen in Table IX an apparent loss in tear strength of approximately 10% was observed for all low-lignin pulps except the high viscosity minimum kappa kraft. It may be significant that this was the only one produced with a liquor-to-wood ratio higher than 4.

TABLE IX

STRENGTHS OF MINIMUM KAPPA (MK) PULPS

Pulp Type	Kappa No.	Viscosity		Tear Factor at 9.0 km Breaking Length	
		Unbleached	Bleached	Unbleached	Bleached
Conventional kraft	30	35	24	152	147
	17	23	16	145	130
MK kraft-AQ	17	28	21	138	132
	14	21	17	138	132
MK kraft	19	29	21	150	150
	16	17	15	141	124

EXPERIMENTAL

All pulping was done in bombs of approximately 500 mL capacity with loblolly pine chips as raw material. The bombs were heated by rotating them in an oil bath. Further details of the apparatus are given elsewhere (7).

Bleaching was done in sealed Mylar bags. The conditions are included as footnotes to the appropriate tables.

For evaluation of strength properties, Tappi Standard Methods were used and handsheets were prepared after processing in a PFI mill.

SUMMARY AND CONCLUSIONS

1. A significant reduction in the kappa number of unbleached alkaline pulps would be beneficial in terms of reduced bleachery effluent loadings, lower bleaching chemical cost, and better energy efficiency. In these respects, reducing the kappa number by changing pulping conditions would be analogous to the use of oxygen bleaching.
2. Relative to conventional practice, kappa number reductions of 40-50% are accessible in the kraft-anthraquinone and kraft systems by changing pulping conditions. These reductions are attained without serious losses in pulp viscosity or yield.
3. Low-lignin pulps produced by the method suggested in either the kraft-anthraquinone or kraft systems are no more difficult to delignify by chlorination and caustic extraction than are conventional kraft pulps.
4. Low-lignin pulps are slightly more difficult to brighten in the final stages of the bleaching sequence. However, the increased requirement for chlorine dioxide would be more than offset by the savings in chlorine and caustic associated with the lower unbleached kappa numbers.
5. Low-lignin pulps prepared according to the methods developed here had tear strengths which were approximately 10% lower than those of conventional kraft controls.

ACKNOWLEDGMENT

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