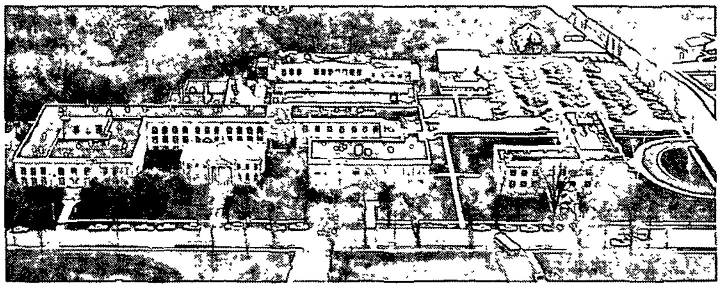


THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES

NUMBER 135

EFFECTS OF KRAFT PULPING CONDITIONS ON OXYGEN DELIGNIFICATION AND SUBSEQUENT C_DED BLEACHING

T. J. McDONOUGH, M. CUKIER, AND D. A. NELSON

AUGUST, 1983

EFFECTS OF KRAFT PULPING CONDITIONS ON OXYGEN DELIGNIFICATION AND SUBSEQUENT C_DED BLEACHING

T. J. McDonough
Group Leader
The Institute of Paper Chemistry
P. O. Box 1039
Appleton, WI 54912

M. Cukier*
Special Student
The Institute of Paper Chemistry
P. O. Box 1039
Appleton, WI 54912

D. A. Nelson**
Graduate Student
The Institute of Paper Chemistry
P. O. Box 1039
Appleton, WI 54912

ABSTRACT

Effects of kraft and kraft-anthraquinone pulping conditions on the response of southern pine pulp to oxygen delignification and subsequent C_DED bleaching were sought in a laboratory study. Lignin removal in the oxygen stage was facilitated by reducing the unbleached kappa number in the range 15-35, but was unaffected by changes in effective alkali charge, sulfidity, or anthraquinone addition during pulping. Rates of viscosity loss and carbohydrate dissolution were independent of both unbleached kappa number and the conditions used to prepare the pulp. Subsequent bleaching of the oxygen delignified pulp was similarly relatively unaffected by pulping conditions. Fully bleached brightness was determined by the ratio of chlorine dioxide charge to extracted kappa number, and not by pulping conditions. A mathematical model derived from the experimental data was used to illustrate interrelationships between the pulping and oxygen bleaching stages. Pulp viscosity and yield after the oxygen stage are maximized by terminating the kraft cook at some optimum value of kappa number which decreases as the post-oxygen kappa number target is decreased.

INTRODUCTION

In the manufacture of bleached kraft pulps, the selection of pulping conditions is guided by considerations of pulp yield and quality, pulping chemical costs, and costs for bleaching chemicals and effluent treatment. This implies the need for information concerning the effects of conditions in the digester on the bleachability of the resulting pulp. That such effects may be significant is suggested by the results of previous studies of these phenomena (1-3) and the observation of so-called lignin "memory" effects during kraft pulping (4).

Apart from the need to select appropriate conditions for making pulp of a predetermined kappa number, there is a need for information upon which to base selection of unbleached kappa number targets. If the lignin content of the pulp issuing from the digester is too high, excessive bleaching chemical costs, effluent loadings, and shive counts will result at the expense of incremental energy recovery. If it is too low, pulp yield and quality will suffer. Depending on the circumstances surrounding the operation of a given mill, it may be desirable to move away from the conventional kappa number norms in either direction. Severely recovery-limited mills will consider raising unbleached kappa number targets to increase yield and throughput; mills limited by bleaching chemical availability or cost or by their capacity for effluent treatment may want to lower it (5,6). In either case, one needs to be able to predict the effect of a given change upon all of the relevant dependent variables.

Some of these effects are so well-known as to be considered self-evident: increasing the unbleached kappa number will increase shive counts in the bleached pulp unless compensating changes are made in the bleach plant; the consumption of chlorine in the first bleaching stage is approximately proportional to unbleached kappa number. Others, however, are open to question. It has been pointed out, for example, that kraft pulping to lower kappa number increases the total active chlorine requirement for a given bleached brightness (3,7), but this says little about the character of the lignin in the unbleached pulp. Since the consumption of active chlorine in the chlorination stage is proportional to kappa number, it might mean that both the amount and nature of the lignin remaining after extraction are independent of the degree of pulping. Consequently, the chlorine dioxide requirement in succeeding stages would be independent of unbleached kappa, and the total active chlorine consumption per unit of unbleached kappa would increase if the degree of pulping were increased. Alternatively, it could mean that the amount of lignin remaining after extraction is proportional to unbleached kappa, and that it is more resistant to removal by chlorine dioxide at lower values of unbleached kappa. The two kinds of effects should be studied separately.

The objective of the present work was to study the implications of pulping conditions and unbleached kappa number level on the performance of the OC_DED sequence with regard to both delignification and brightening. (Effects on shives and dirt will be the subject of a separate study.) Southern pine was pulped in a laboratory digester under a variety of conditions of effective alkali (EA) charge, sulfidity (S), and anthraquinone (AQ) charge, to three different nominal kappa number levels. Each pulp was then further delignified in a high consistency oxygen stage at three different levels of applied caustic. Some of the oxygen-delignified pulps were bleached to a brightness in the 86-88 range by a C_DED sequence. The results were then analyzed by multiple linear regression techniques to determine the effects of pulping conditions and unbleached kappa number on H-factor requirement, unbleached viscosity and yield, ease of removal of lignin and resistance to viscosity loss in the oxygen stage, yield loss in the oxygen

* Presently Deputy Manufacturing Manager, Maryvale Pulping Project, Australian Paper Manufacturers Limited, South Melbourne, Victoria, Australia.
** Presently Process Engineer, Crown Zellerbach, St. Francisville, LA.

stage, response to chlorination and extraction, and response to chlorine dioxide.

RESULTS AND DISCUSSION

Pulping

The pulping data and unbleached pulp properties are contained in Table 1, and the corresponding regression equations (from which nonsignificant terms have been removed) are shown in Table 2. Both the H-factor required to reach a given kappa number and the yield showed the expected dependence on the experimental variables. A surprising aspect was the absence of any effect of AQ on viscosity at a given kappa number. A decidedly beneficial effect was observed in previous studies (1,6) and might be expected in view of the observation by Kubes et al. in high liquor-to-wood ratio cooks of black spruce that viscosity depends only on time, temperature, and EA concentration (8). Adding AQ decreases the cooking time to reach a given kappa number and might therefore be expected to give higher viscosity. An explanation is not yet available, but inter- and intraspecies differences in wood characteristics must be considered.

to obtain, for each property, a single number representing the response of that property to the bleaching process. The resulting values could then be related to the experimental variables.

Delignification

Delignification was well described by assuming a linear relationship between the reciprocal of the kappa number and the alkali charge. Figure 1 is typical of the plots obtained, and the correlation coefficients of all such plots were uniformly in the range 0.98-1.00, as can be seen in Table 1. It can be shown that this behavior is consistent with a kinetic model in which the rate of lignin removal is second-order in lignin and first-order in base, and the rate of base depletion is first-order in base and first-order overall. According to this model, the slope of a plot of reciprocal kappa versus alkali charge at fixed reaction time is proportional to the delignification rate constant. For the purposes of the present study, it suffices to regard this slope as an indicator of the ease with which a pulp's lignin can be removed in an oxygen stage. In what follows, it will be referred to as "delignifiability".

Table 1 Experimental pulping data[a]

Cook No.	Effective Alkali, Na_2O, % o.d. wood	Anthraquinone, % o.d. wood	Sulfidity, % active alk.	H Factor	Kappa Number	Viscosity, mPa • s	Yield, % o.d. wood	Screened Yield, % o.d. wood
8	16	0	25	5717	15.4	12.6	42.7	42.7
6			40	4328	15.4	12.7	43.0	43.0
10		0.1	25	4432	17.8	13.8	44.0	43.9
12			40	3793	15.1	14.6	43.6	43.6
15	22	0	25	2940	15.3	9.0	41.1	41.1
17			40	2240	14.1	(12.1)[c]	41.9	41.8
21		0.1	25	2362	15.0	10.2	42.9	42.8
23			40	1664	15.3	13.1	43.0	43.0
3	16	0	25	3586	22.8	21.3	46.4	46.4
4			40	2582	24.2	25.7	46.1	46.0
9		0.1	25	2741	21.2	20.7	45.8	45.7
13			40	1857	23.8	23.8	46.4	46.3
16	22	0	25	(1886)[b]	16.6	13.2	42.6	42.5
18			40	1158	20.3	17.2	44.6	44.5
22		0.1	25	1408	20.7	16.7	44.9	44.8
24			40	964	26.0	22.0	46.9	46.8
5	16	0	25	2358	28.0	26.1	46.9	46.7
7			40	(1600)[b]	21.7	26.9	45.6	45.4
11		0.1	25	1309	33.0	30.2	49.0	48.6
14			40	1170	35.0	33.9	48.3	47.9
2	22	0	25	1101	31.7	24.8	47.7	47.5
20			40	731	33.2	30.0	47.7	47.5
26		0.1	25	818	34.6	24.8	50.4	50.2
25			40	675	36.9	28.2	49.0	48.6

[a]Constant conditions: Liquor-to-wood ratio 4 mL/g; 90 min. rise to 173°C.
[b]Preliminary regression analysis indicated that this was an atypical observation. It was omitted from the subsequent analysis.
[c]This value was not available when the regression analysis was done.

Oxygen Bleaching

Oxygen bleaching gave the results shown in Table 3. Samples of each pulp were bleached with 1, 2, and 3% NaOH, and the resulting kappa number, viscosity, and yield data were treated in such a way as

In Fig. 2, delignifiability is shown as a function of kappa number for all pulping conditions used. It depends on unbleached kappa number but not on pulping conditions, as is apparent from this figure and from the corresponding regression equation in Table 2. Interestingly, the lignin of low-kappa pulps is more easily removed in an oxygen stage than that of pulps with more conventional kappa numbers.

Table 2 Results of regression analysis of pulping and oxygen bleaching data[a,b]

	H-Factor Required	Total Yield, % o.d. wood	Scr. Yield, % o.d. wood	Unbl. Visc., mPa•s	Delignifi-ability[c]	Vulner-ability[d]	Yield Loss Index[e]
Constant Term	1691	46.53	46.40	23.43	24.6	8.94	-0.216
Coefficients of:							
XK	-1203	+3.03	+2.88	+9.00	-15.9		
XEA	-722	-0.09	-0.07	-1.83			
XAQ	-252	+0.37	+0.36				
XS	-274	-0.11	-0.12	+1.32			
XK^2	+631	-0.84	-0.90	-2.63	+7.5		
XK•XEA	+500	+0.30	+0.35	-1.02			
XK•XAQ							
XK•XS	+228	-0.42	-0.43				
XEA•XAQ							
XEA•XS							
XAQ•XS							
Multiple correln. coeff. R^2	0.97	0.98	0.99	0.96	0.94	--[f]	--[f]
Standard error of estimate	282	0.42	0.43	1.54	3.3	1.29	0.169
95% confidence interval[g]	±124	±0.18	±0.18	±0.66	±1.4	±0.56	±0.073
Uncertainty[h], %	7	0.4	0.4	3	6	6	34

[a]Dependent variable = constant term + Σ (coefficient x independent variable). Blank entries represent coefficients not significantly different from zero.
[b]Independent variables defined as follows: XK = (Kappa No. -25)/10; XEA = (EA chge, % - 19)/3; XAQ = (AQ chge, % -0.05)/0.05; XS = (sulfidity -32.5)/7.5.
[c]Slope from plot of 1/kappa vs. % NaOH in oxygen stage, x 10^3.
[d]Slope from plot of 1/viscosity vs. % NaOH in oxygen stage, x 10^3.
[e]Slope from plot of lignin-free yield (% o.d. wood) vs. % NaOH in oxygen stage.
[f]No significant regression.
[g]Width of 95% confidence interval for true value of dependent variable at average values of all independent variables, i.e. at XK, XEA, XAQ, and XS, all approximately equal to zero.
[h]Confidence half-interval as percentage of calculated value when XK, XEA, XAQ, and XS are all approximately equal to zero. (Under these conditions the calculated value of the dependent variable is approximately equal to the constant term.)

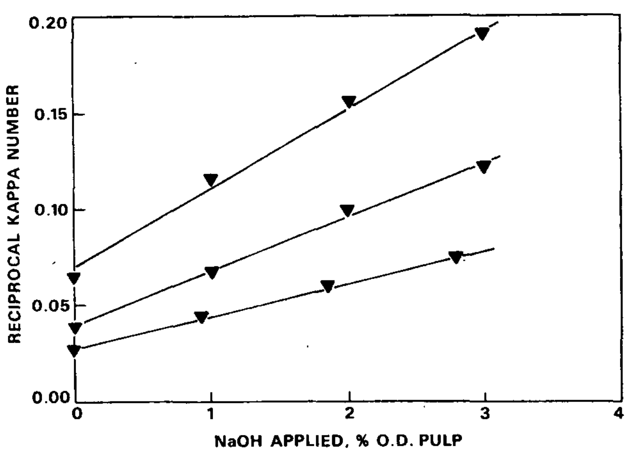


Fig. 1 The reciprocal of the kappa number is linearly related to caustic charge in the oxygen stage, regardless of pulping conditions. Data shown are for cooks with 0.1% AQ and 22% EA at 40% sulfidity.

Viscosity

Viscosity loss in the oxygen stage was characterized by a linear relationship between the reciprocal of the viscosity and the alkali charge. It can be shown by a development similar to that presented by Kubes et al. (8) that such a relationship is consistent with the assumptions that random chain cleavage occurs by a reaction which is effectively zero-order in both glycosidic bonds and that base depletion is first-order in base and first-order overall. Under these assumptions the slope of the reciprocal viscosity-alkali charge plot is proportional to the rate constant for chain cleavage. For the present purpose, it is regarded as an indicator of the sensitivity of a pulp to viscosity loss during oxygen bleaching and will be referred to as "vulnerability".

Typical plots of reciprocal viscosity versus alkali charge are shown in Fig. 3. The slopes are tabulated in Table 3, together with the corresponding correlation coefficients, most of which were in the upper third of the range 0.93-1.00. Figure 2 shows that the slope of such a plot, or the vulnerability of the pulp, is independent of both pulping conditions and unbleached kappa number. This was confirmed by regression analysis of the data (Table 3).

Table 3 Response of experimental pulps to oxygen bleaching[a]

Cook No.	Effective Alkali, Na_2O, % o.d. wood	Anthraquinone, % o.d. wood	Sulfidity, % active alk.	Kappa Number	Graph Symbol	Delignifiability[b] Slope x 10^3	Delignifiability[b] Corr. Coeff.	Vulnerability[c] Slope x 10^3	Vulnerability[c] Corr. Coeff.	Carbohydrate Yield Loss Intercept	Carbohydrate Yield Loss Slope	Carbohydrate Yield Loss Corr. Coeff.
8	16	0	25	15.4	○	47	0.99	8.14	0.96	42.36	-0.207	0.88
6			40	15.4	△	55	0.98	8.09	0.96	43.37	-0.542	1.00
10		0.1	25	17.8	●	42	1.00	10.4	0.99	44.41	-0.026	0.24
12			40	15.1	▲	47	0.99	7.42	0.93	43.52	-0.316	0.94
15	22	0	25	15.3	□	(64)[d]	0.98	7.83	0.99	40.56	-0.049	0.63
17			40	14.1	▽	50	1.00	(9.61)[e]	0.90	41.82	-0.196	0.89
21		0.1	25	15.0	■	46	1.00	8.92	0.93	43.84	-0.345	0.92
23			40	15.3	▼	41	1.00	9.38	0.99	42.40	-0.168	0.73
3	16	0	25	22.8	○	28	1.00	8.06	0.98	45.71	-0.224	0.82
4			40	24.2	△	25	1.00	9.19	1.00	46.00	-0.450	0.95
9		0.1	25	21.2	●	26	0.99	9.25	1.00	46.34	-0.477	0.96
13			40	23.8	▲	29	0.99	9.10	1.00	45.52	-0.167	0.99
16	22	0	25	16.6	□	46	1.00	12.8	1.00	41.97	-0.291	1.00
18			40	20.3	▽	35	0.99	7.48	0.98	43.07	0.116	0.60
22		0.1	25	20.7	■	34	1.00	8.73	0.97	44.95	-0.222	1.00
24			40	26.0	▼	28	1.00	8.41	0.98	44.05	0.102	0.98
5	16	0	25	28.0	○	22	1.00	9.04	0.98	46.17	-0.264	0.75
7			40	21.7	△	26	1.00	8.33	0.98	45.40	-0.334	0.93
11		0.1	25	33.0	●	16	1.00	9.74	1.00	47.85	-0.165	0.43
14			40	35.0	▲	18	1.00	6.53	0.94	46.59	-0.086	0.41
2	22	0	25	31.7	□	16	1.00	9.72	0.97	46.19	-0.360	0.81
20			40	33.2	▽	15	1.00	10.0	0.98	45.97	-0.218	0.52
26		0.1	25	34.6	■	15	0.99	10.2	0.99	47.68	(-0.822)[d]	0.84
25			40	36.9	▼	17	1.00	8.73	0.99	47.82	-0.134	0.97

[a]Constant conditions: 100 psig (0.79 mPa) O_2, 30 min. at 120°C, 1% $MgSO_4 \cdot 7H_2O$; 25-27% consistency.
[b]From plot of reciprocal of kappa number after bleaching vs. % NaOH applied.
[c]From plot of reciprocal of viscosity after bleaching vs. % NaOH applied.
[d]Preliminary regression analysis indicated that this was an atypical observation. It was omitted from the subsequent analysis.
[e]This value was not available when the regression analysis was done.

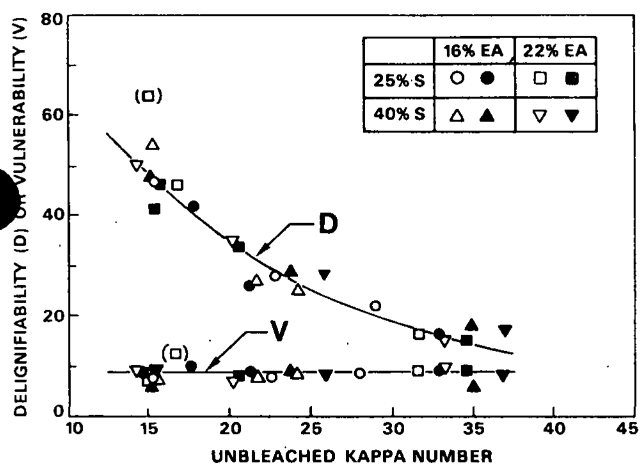


Fig. 2 The delignifiability (D) of a pulp in an oxygen stage depends on its unbleached kappa number but not on the conditions used to prepare it. It's vulnerability to depolymerization (V) depends on neither.

Yield

Yield loss in the oxygen stage was characterized by plotting the post-oxygen carbohydrate yield, based on wood, against the alkali charge. The slope of this plot, tabulated in Table 3 for all pulps, was taken as a measure of a pulp's sensitivity to yield loss in the oxygen stage. The measured yields were very high, often exceeding the theoretical values at low unbleached kappa and low alkalinity. This observation is consistent with the known high yield selectivity in oxygen bleaching of kraft pulps and the likely addition of measurable quantities of carboxylate oxygen and sodium. To separate the latter effect from the effect of actual carbohydrate dissolution, the unbleached carbohydrate yields were not included in the plots used to arrive at the slopes shown in Table 3.

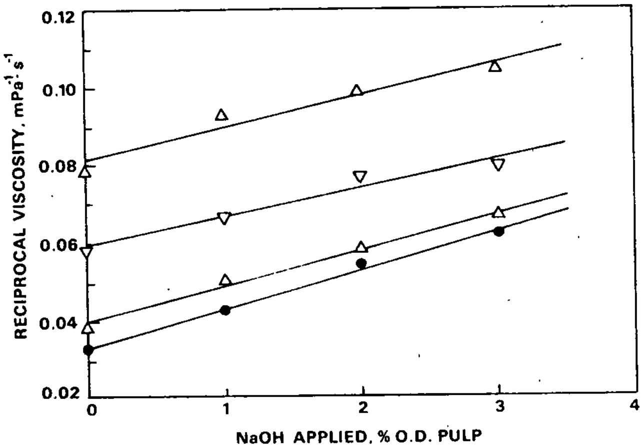


Fig. 3 The reciprocal of pulp viscosity is linearly related to caustic charge in the oxygen stage, regardless of pulping conditions. Symbols are as shown in Table 3.

Sensitivity to yield loss exhibited no systematic dependence on the experimental variables. An average slope value of 0.22 may be taken to represent the carbohydrate yield loss for each percent of sodium hydroxide applied (Table 2).

Final Bleaching

The pulps produced with an EA charge of 16% were fully bleached in the OC_DED sequence to determine the effects of the experimental variables on bleaching response after the oxygen stage, with respect to both delignification and brightening. Each pulp was delignified 40-50% in the oxygen stage before chlorination. The results are shown in Table 4. After chlorinating with a constant ratio of chlorine to oxygen bleached kappa number, the caustic-extracted kappa numbers exhibited a moderate upward trend as the unbleached kappa number (and therefore also the oxygen bleached appa number) increased. This somewhat undesirable ffect of increasing unbleached kappa number was offset by an increase in the kappa number reduction per unit of chlorine consumed. These findings suggest that chlorination of the higher-kappa pulps at higher temperature might remove the effect on extracted kappa number.

Model and Implications

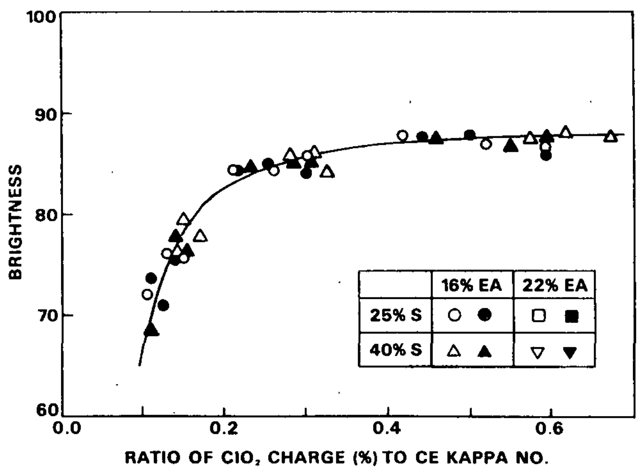
The regression equations and parameter values of Table 2 constitute a model for combined kraft pulping and oxygen bleaching which may be used to predict the consequences of various operating strategies. Figure 5, for example, shows the viscosity-kappa number relationships to be expected

Table 4 Experimental OC_DED bleaching data

Cook No.	Pulping: AQ, % o.d. wood	Pulping: Sulfidity, % act. alk.	Pulping: Kappa No.	Oxygen: Kappa No.	Oxygen: Visc.,[b] cp.	Chlorination: Cl_2, % pulp	Chlorination: Residual, % pulp	Chlorination: pH	Chlorination: Extracted Kappa No.	Δ Kappa / Cl_2 consumed	Chlorine Dioxide[a]: ClO_2, %	Chlorine Dioxide[a]: Residual, % pulp	Chlorine Dioxide[a]: Visc., cp.
8	0.0	25	15.4	8.4	9.8	2.0	0.33	2.4	3.1	3.1	1.2	0.17	9.3
3			22.8	12.7	12.0	3.0	0.57	2.1	2.7	4.2	0.9	0.15	12.4
5			28.0	17.6	16.2	4.2	0.43	1.9	3.8	3.7	1.0	0.11	16.0
6		40	15.4	8.5	10.8	2.0	0.47	2.2	2.4	4.0	1.1	0.18	10.6
7			21.7	12.3	13.3	3.0	0.24	2.1	2.6	3.6	0.8	0.10	14.6
4			24.2	13.0	15.8	3.1	0.71	2.1	2.8	4.3	0.8	0.10	15.6
10	0.1	25	17.6	8.8	10.3	2.1	0.22	2.4	2.7	3.2	1.7	0.35	9.4
9			21.2	11.5	14.9	2.8	0.31	2.1	3.6	3.1	1.2	0.16	14.9
11			33.0	18.3	19.9	4.4	0.34	1.8	3.2	3.7	1.0	0.10	18.9
12		40	15.1	8.3	8.1	2.0	0.18	2.4	2.9	2.9	1.0	0.19	10.2
13			23.8	12.4	13.7	3.0	0.71	2.0	2.7	4.2	1.0	0.17	15.7
14			35.0	20.2	17.2	4.9	0.80	1.8	3.5	4.2	1.0	0.07	22.0

[a]Interpolated to 86 brightness.
[b]Interpolated from earlier oxygen bleaching data.

Each of the extracted pulps was bleached with .4, 0.8, and 1.6% chlorine dioxide, and the charge equired to attain a brightness of 86 was obtained by interpolation. Table 4 shows that, with the exception of one apparently spurious observation, the chlorine dioxide requirement was not greatly affected by the experimental variables. This is even more apparent when the chlorine dioxide requirement is expressed on an extracted kappa number basis. Figure 4, in which brightness is plotted against this ratio for all 36 pulp samples, illustrates the point.



ig. 4 Fully bleached brightness depends on the ratio of the ClO_2 charge to the kappa number after caustic extraction but not on digester conditions.

for termination of the kraft cook at two different kappa numbers, 35 and 20. The higher unbleached kappa number gives higher viscosity for a given post-oxygen kappa, except for values of the latter which are lower than 12. Figure 6 generalizes this relationship to other values of unbleached kappa number for various values of bleached kappa. It is apparent that there exists an optimum unbleached kappa number for maximizing viscosity after the oxygen stage and that this optimum decreases as the post-oxygen kappa number target decreases. Increasing the sulfidity of the kraft cook lowers the optimum unbleached kappa and increases viscosity after the oxygen stage.

Similar relationships for yield are shown in Fig. 7 and 8. For maximizing yield after oxygen bleaching, the optimum unbleached kappa number for conventional cooking is near the upper end of the range studied, although a moderate reduction (e.g. to improve bleached viscosity) is possible without severe yield loss. Cooking at high sulfidity moves the optimum unbleached kappa number to lower values.

Relationships such as those shown in Fig. 5-8 are expressions of how the relative selectivities of kraft pulping and oxygen bleaching vary with kappa number. As such, they are very dependent on the relationship between pulping selectivity and pulping variables. For southern pine at least, the latter appears to be quite variable from one wood sample to another, presumably as a result of differences between growing localities. An example is the variation we have observed in the response of viscosity to AQ addition. Pending further investigation of the factors responsible for differences between wood samples, Fig. 5-8 can be considered to apply in a qualitative sense.

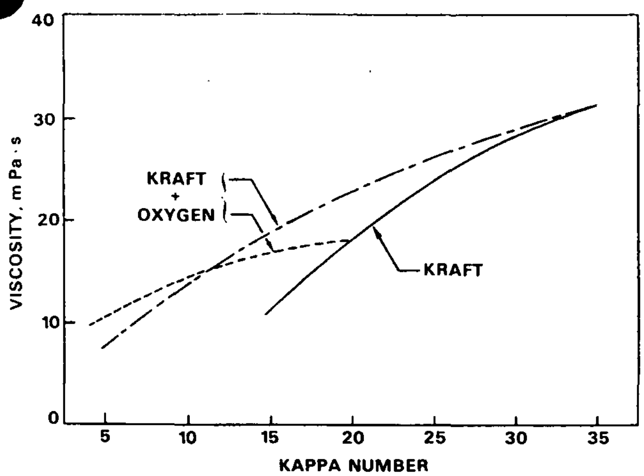


Fig. 5 For a kappa number of 12 or less after the oxygen stage, terminating the kraft cook at kappa number 35 gives lower viscosity than extending the cook to kappa number 20.

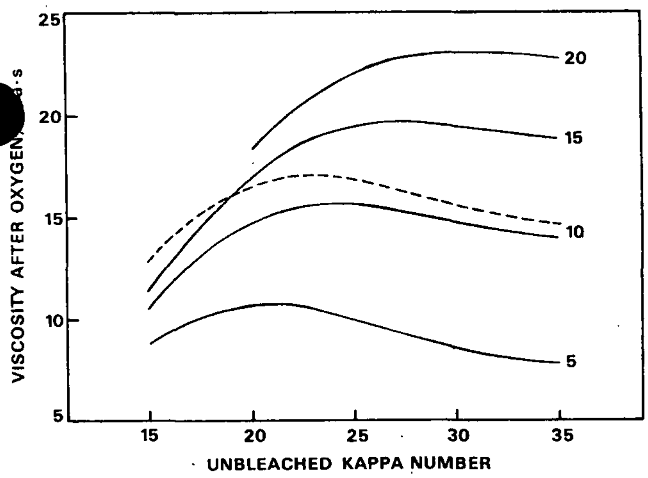


Fig. 6 At 25% sulfidity and 16% EA, the optimum unbleached kappa number depends on the post-oxygen-stage kappa number target, which is the parameter in the graph. Raising the sulfidity to 90% (dashed line) decreases the optimum unbleached kappa number.

CONCLUSIONS

1. Oxygen delignification of southern pine kraft and kraft-anthraquinone pulps is facilitated by reducing the unbleached kappa number over the range 15-35. The ease of lignin removal by oxygen is unaffected by the following changes in pulping conditions: EA charge from 16 to 22%; sulfidity from 25 to 40%; and AQ charge from 0 to 0.1%.

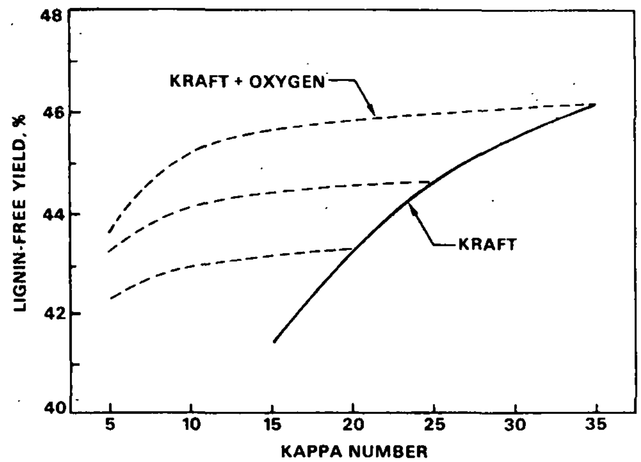


Fig. 7 Terminating the kraft cook at kappa number 35 gives higher yield after the oxygen stage than extending it to lower kappa numbers.

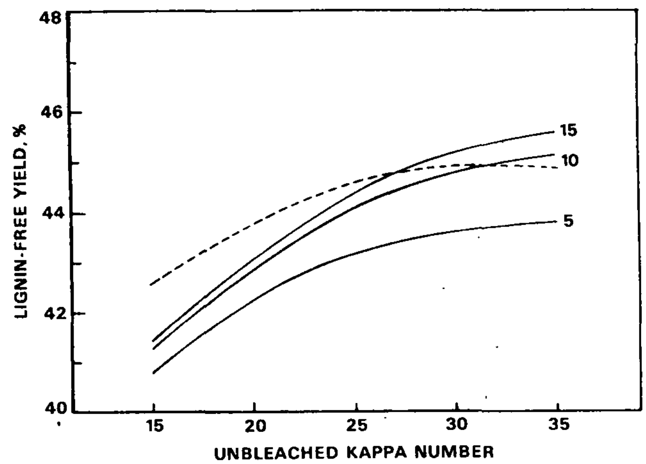


Fig. 8 At 25% sulfidity, 16% EA and with no AQ, terminating the cook at kappa number 35 gives the highest yield for all values of post-oxygen-stage kappa number, which is the parameter on the graph. Raising the sulfidity to 40% and adding 0.1% AQ (dashed line) decreases the optimum unbleached kappa number.

2. The rate of viscosity loss and the rate of carbohydrate dissolution during oxygen delignification are independent of both unbleached kappa number and the conditions used to prepare the pulp over the above ranges.

3. Pulp of a given unbleached kappa number which has been 40-50% delignified in an oxygen stage responds to subsequent C_DED bleaching in a manner which is nearly independent of the pulping conditions. For a fixed ratio of chlorine charge to post-oxygen kappa number, the kappa

number after caustic extraction increases, but chlorine consumption per unit of kappa number reduction decreases with increasing unbleached kappa number. Fully bleached brightness is determined by the ratio of chlorine dioxide charge to extracted kappa number and not by pulping conditions.

4. Pulp viscosity after the oxygen stage can be maximized by terminating the kraft cook at some optimum value of kappa number. This value decreases as the post-oxygen kappa number target is decreased. Increasing the sulfidity of the kraft cook increases the viscosity after the oxygen stage and decreases the optimum unbleached kappa number.

5. The optimum kappa number for yield preservation is higher than that for viscosity preservation. It is decreased by adding AQ and increasing the sulfidity of the kraft cook. Both optima depend on the relationship between pulping selectivity and pulping conditions, which appears somewhat variable in the case of southern pine.

EXPERIMENTAL

Materials

Southern yellow pine, thought to be Loblolly pine (pinus taeda), was chipped in a laboratory Carthage chipper and screened in a Dynoscreen vibrating screen. The fraction passing through a 3/4-inch screen and retained on a 1/4-inch screen was air-dried and stored at 4°C until required. Triplicate determinations of specific gravity gave the values 0.478, 0.498 and 0.497.

Cooking liquor was prepared as required from sodium hydroxide and sodium sulfide solutions of known concentrations. No sodium carbonate or black liquor was included.

Pulping

Three kg. of chips (o.d. basis) were charged to a 2-ft^3 digester equipped with forced external circulation and indirect steam heating. After charging the cooking liquor and sufficient dilution water to bring the total weight of water to 12 kg., the circulation pump was started and AQ, if required, was sprinkled into the circulating liquor stream. The digester was brought up to temperature in 90 min. and H-factor (9) was recorded from 100°C to temperature at 10-min. intervals. The digester was relieved when the temperature reached 100°C and again when the pressure reached 30 psig. Temperature was monitored by top and bottom thermocouples, which read within 1°C of each other, the bottom reading being lower. When the desired value of H-factor had been reached, the circulation pump was stopped, and the pressure was reduced by venting to 60 psig. before opening the blow valve to eject the free liquor. The chips were retained in a basket within the digester, where they were washed with fresh hot water before being removed and fiberized under a Williams disintegrator at approximately 4% consistency. The pulp was then further washed and dewatered in a centrifuge, weighed, stored to allow moisture equilibration, and sampled for consistency determination. Rejects were determined by screening a 200 g. subsample on a Valley flat screen with 0.008-inch slots. The screened pulp was centrifuged, fluffed, sampled for testing, and stored prior to oxygen bleaching.

Oxygen Bleaching

Oxygen bleaching was done at a consistency of 25-27% in a reactor equipped with stainless steel mesh trays and heated by direct steam. All bleaches were conducted in the presence of 0.1% magnesium ion based on o.d. pulp. The chemicals were added to the fluffed pulp in a Hobart mixer, and the pulp was then placed in the preheated reactor. The reactor was evacuated, pressurized to 40 psig with oxygen, quickly heated to 120°C, and immediately pressurized to 100 psig. After bleaching, the pulp was diluted to 4% consistency for pH determination and subsequently washed in a screen box.

Final Bleaching

The last three bleaching stages were done in sealed polyester bags. Chlorination was done at a chemical application rate of (0.24 x kappa)%, with 15% replacement by equivalent chlorine dioxide at 25°C and 3% consistency for 45 minutes. Caustic extraction was at 60°C and 10% consistency for 60 min. with a caustic charge of (0.55 x %chlorine)%. The sodium hydroxide was mixed with the chlorinated pulp in a Hobart mixer. The chlorine dioxide stage was done at 70°C and 10% consistency for 180 min. with chlorine dioxide containing a negligibly small amount of elemental chlorine and with addition of sodium hydroxide to achieve a terminal pH reading near 4.

Testing

Kappa number, viscosity and brightness were determined by TAPPI Standard Methods T236 os-76, T230-os76 and T452-0S77. An exception was the determination of the kappa numbers of the partially delignified pulps. In these cases the standard method was scaled down by a factor of 1/2 for oxygen bleached pulps and by a factor of 1/4 for chlorinated and extracted pulps.

ACKNOWLEDGMENTS

Thanks are due Mr. V. J. Van Drunen for his technical advice and assistance with the experiments.

Portions of this work were used by one of the authors (D.A.N.) as partial fulfillment of the requirements for the Master of Science degree at the Institute of Paper Chemistry.

LITERATURE CITED

1. T. J. McDonough and J. L. Herro, Tappi **65**(9):117-21(1982).

2. B. Carno, H. Norrstrom and L. A. Ohlson, Svensk Papperstid. **78**(4):127-9(1971).

3. P. Axegard, S. Norden and A. Teder, Svensk Papperstid. **81**(4):97-100(1978).

4. S. LeMon and A. Teder, Svensk Papperstid. **76** (11):407-14(1973).

5. N. Hartler, Svensk Papperstid. **83**(15):483-4 (1978).

6. T. J. McDonough and V. J. Van Drunen Tappi **63** (11):83-6(1980).

7. N. E. Virkola, O. Jarvela and V. Vartiainen, Paperi Puu **47**:575-xx(1965).

8. G. J. Kubes, B. I. Fleming, J. M. MacLeod, and H. I. Bolker, Proc. 1981 TAPPI Pulping Conf., p. 423-30, Tappi Press, Atlanta, 1981.

9. K. E. Vroom, Pulp Paper Mag. Can. **xx**:228-33 (1957).