EXTENDED OXYGEN DELIGNIFICATION OF ALKALINE PULPS FROM PINUS RADIATA

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ABSTRACT

Extended oxygen delignification of three types of alkaline pulps from **Pinus radiata** D.Don was investigated. Kraft, kraft-anthraquinone (kraft-AQ), and soda-anthraquinone (soda-AQ) pulps at 40 and 60 Kappa number were treated with oxygen to remove about 60, 70, and 75% of their residual lignin. Extended oxygen treatments resulted in less selective delignification, higher brightness at a given Kappa number, and generally less strength degradation in 60 Kappa than in 40 Kappa pulps; and in less selective delignification, lower brightness at a given Kappa number, and lower strength in soda-AQ pulps than in kraft and kraft-AQ pulps. The yields of kraft-AQ and soda-AQ pulps remained higher than those of kraft pulps after extended oxygen delignification. At 25 Kappa number use of extended oxygen treatments increased total yields by 3% over those attainable through continued pulping. With careful control, oxygen delignification of alkaline pulps could be extended to at least 60% lignin removal before significant strength losses occurred.

INTRODUCTION

Oxygen delignification of kraft pulps has become established world-wide (installed capacity over 2.5 million tonnes/year) as a selective method for lignin removal (Styan 1977). For softwood kraft pulps, it has become accepted practice to employ oxygen delignification as a pre-bleach treatment in order to lower pulp Kappa numbers by about 50% from 30 to 15 before full bleaching with conventional chlorine sequences (Almberg *et al.* 1979).

Though operating costs can be lessened by using oxygen delignification, the most common incentive for its use has been the ability of oxygen stages to reduce the total effluent load (Jamieson & Smedman 1973). Since oxygen stages are chloride-free and can be incorporated into brown stock washing systems, the dissolved organics generated by oxygen delignification can pass back through the kraft recovery cycle and be burned in the recovery boiler. This extra organic material will also contribute to the total energy generation of the recovery cycle.

Another option has been the use of oxygen to delignify high-Kappa pulps to bleachable Kappa levels in order to realise a yield advantage over conventional methods

(Jamieson & Fossum 1976). Previous studies (G. D. Crosby, unpubl. data) on *P. radiata* pulps showed that terminating of kraft pulping at high Kappa levels, followed by further delignification with oxygen, can result in total yield increases of 1% of more; this is because oxygen delignification is more selective than residual kraft delignification. To realise greater benefits in pulp yield, pollution abatement, operating costs, and energy recovery, oxygen treatments must be extended past the accepted limits of 50% lignin removal or 50 Δ Kappa % where:

$$\Delta \text{ Kappa } \% = \frac{\text{initial Kappa} - \text{final Kappa}}{\text{initial Kappa}} \times 100\%$$

Excessive oxygen treatments are known to severely degrade pulp carbohydrate components and result in lower pulp strengths (Singh 1979). However, Crosby's work on fully bleached kraft-oxygen pulps from *P. radiata* indicated that, when sufficient magnesium protector was present, oxygen delignification could be extended to 70 Δ Kappa % before tear and burst indices at a given sheet density began to decrease. Lower levels of oxygen delignification are used industrially to provide a safety margin against fluctuations which occur during continuous operations. However, as improved control systems are developed, industrial use of oxygen delignification should more closely approach maximum safe limits as determined in the laboratory (Almberg *et al.* 1979).

In the present study, several alkaline pulps from *P. radiata* were oxygen delignified to various extents and analysed. Kraft, kraft-anthraquinone (kraft-AQ), and soda-anthraquinone (soda-AQ) pulps at 40 and 60 Kappa number were oxygen delignified to approximately 60, 70, and 75 Δ Kappa %. Yield, brightness, viscosity, and handsheet properties were monitored to investigate the effects of extended oxygen delignification and to determine more accurately the maximum Δ Kappa % achievable before pulp strength properties begin to diminish significantly.

EXPERIMENTAL

Commercial *P. radiata* chips were screened in the laboratory and pulped in a 10-*l* Weverk rotary digester with a liquor-to-wood ratio of 4 : 1 and a 90-min rise to a maximum pulping temperature of 177°C. Kraft, kraft-AQ, and soda-AQ pulps were prepared at both 40 and 60 Kappa number (see Table 1) by employing optimum applications of active alkali and AQ additions as determined previously (Fullerton & Kerr 1981). Care was taken to exclude air from the digester prior to pulping. Pulps were screened on a 0.25-mm slotted Packer flat screen prior to analysis.

For oxygen delignification, screened pulps were soaked in appropriate amounts of sodium hydroxide and magnesium oxide/EDTA complex (1 : 5 weight ratio) at 10% consistency for 30 min, then pressed-out to 25% consistency and fluffed. Actual alkali uptake was determined by acid titration of the expressed liquor. Fluffed pulps were placed in a heated vapour-phase reactor and evacuated for 15 min. After steam heating of the pulp to about 105°C in 4–6 min, oxygen (20°C) was injected at 650 kPa and temperature rises were monitored as the exothermic reaction proceeded. Maximum temperatures after 5 min were normally about 116°–120°C (Table 2). After 30 min of reaction the oxygen pressure was relieved and the reaction chamber was purged with

TABLE 1—Pulping conditions and results for kraft, kraft-AQ, and soda-AQ pulps from **P. radiata**

Pulp	AQ charge (%)*	Active alkali (% Na_2O)*	H factor	Sulphidity (%)	Kappa number	Total pulp yield (%)*	Brightness (%)	Viscosity (mPa.s)
Kraft	0	15.8	1820	27.5	40.9	48.8	26.3	45.3
Kraft	0	13.6	1580	27.8	61.1	52.8	24.0	55.2
Kraft-AQ	0.05	13.9	1850	27.8	40.3	50.7	26.0	44.1
Kraft-AQ	0.05	14.4	1020	27.8	59.0	53.1	24.9	51.3
Soda-AQ	0.16	14.9	1850	0	40.2	49.7	26.0	28.0
Soda-AQ	0.14	13.2	1850	0	61.2	54.5	22.8	32.9

* Based on o.d. wood

TABLE 2—Extended oxygen delignification of kraft, kraft-AQ, and soda-AQ pulps from **P. radiata**

Pulp (initial Kappa)	Applied NaOH (% on pulp)		Temperature (°C)		Yield (%)		Kappa No.		Brightness (%)	Viscosity (mPa.s)
	Calculated	Actual	Initial	Max.	On pulp	On wood	Final	Δ %		
Kraft	3.0	—	107	117	94.8	46.3	13.8	66.3	43.5	25.2
(41)	5.0	6.5	107	118	91.4	44.6	10.8	73.6	50.0	20.1
	7.0	8.9	106	117	91.5	44.7	8.4	79.5	56.4	15.8
Kraft	3.0	4.4	105	116	93.6	49.4	25.0	59.1	33.5	28.7
(61)	5.0	6.7	105	116	89.7	47.4	18.6	69.6	40.8	24.5
	7.0	8.8	106	118	89.1	47.0	13.8	77.4	47.7	22.4
Kraft-AQ	3.0	4.3	105	116	93.9	47.6	14.5	64.0	42.6	27.6
(40)	5.0	—	105	118	92.5	46.9	11.5	71.4	48.9	22.6
	7.0	—	104	117	89.9	45.6	9.5	76.4	53.8	—
Kraft-AQ	3.0	4.1	105	116	92.0	48.9	26.8	54.6	35.5	25.7
(59)	5.0	6.7	104	116	90.4	48.0	20.0	66.1	41.2	21.6
	7.0	8.8	105	117	89.1	47.3	15.3	74.0	46.8	19.5
Soda-AQ	3.0	—	105	116	93.7	46.6	15.7	60.9	38.7	18.2
(40)	5.0	—	106	120	92.9	46.2	11.7	70.9	46.0	16.2
	7.0	8.6	105	119	91.5	45.5	9.5	76.4	50.3	13.6
Soda-AQ	3.0	3.6	105	120	92.1	50.2	23.8	61.1	33.0	22.4
(61)	5.0	6.7	105	120	89.4	48.7	17.9	70.9	38.9	19.4
	7.0	8.8	105	120	88.1	48.0	15.4	74.8	43.2	15.7

Standard conditions: 25% consistency, 30-min reaction time, 0.1% MgO on pulp.

nitrogen while the reactor was disassembled. Treated pulps were washed thoroughly with tap water.

Kappa number was determined by a half-scale modification of Appita Standard Method P201 M-59 and viscosity was measured according to TAPPI Standard T-230 os-76. Brightness was determined on brightness samples formed according to Tappi Standard T-218 os-75 and measured at 457 nm with a Zeiss "Elrepho" reflectometer on an absolute basis. Handsheet properties were determined according to Appita Standard Methods on pulps beaten in the PFI mill at 10% consistency with an applied load of 1.8 N/mm.

RESULTS AND DISCUSSION

Yield-Kappa Relationships

The yield advantages reported previously for kraft-AQ and soda-AQ pulps over kraft pulps are shown in Fig. 1 for a number of laboratory-produced pulps from *P. radiata* (Fullerton & Kerr 1981; Fossum *et al.* 1980). Total yields of kraft-AQ pulps (0.05% AQ on wood) were about 1% greater than those of kraft pulps at similar Kappa number. Soda-AQ pulps (0.1–0.2% AQ on wood) approached this degree of yield advantage at Kappa levels greater than 50.

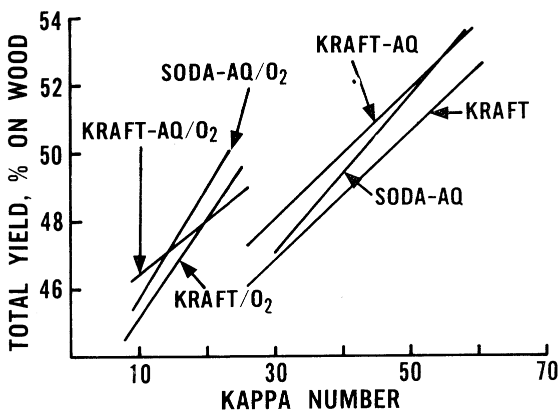

FIG. 1—Yield-Kappa relationships for untreated and oxygen-delignified alkaline pulps (correlation coefficients are 0.93 or better).

The yield-Kappa trends shown by the parent pulps were also present after extended oxygen delignification (Fig. 1). The anomalous slope of the kraft-AQ/O_2 regression was caused by the unusually low pulping yield of the 60 Kappa kraft-AQ pulp prepared for this study. Though the experimental data do not completely overlap, extrapolations of yield-Kappa plots show that at 25 Kappa number, use of extended oxygen delignification increased total yield by 3% over continued alkaline pulping.

Brightness

At a given Kappa number, the brightnesses of kraft, kraft-AQ, and soda-AQ pulps from *P. radiata* were generally similar (Table 1). However, after oxygen delignification kraft and kraft-AQ pulps were brighter than soda-AQ pulps (Fig. 2). Soda-AQ pulp brightness was consistently 2.0 to 2.5 points less after oxygen delignification to a given Kappa number. Andrews & Yethon (1979) reported that kraft and soda-AQ pulps from black spruce responded similarly to oxygen delignification but brightness-Kappa relationships were not determined. *Pinus radiata* soda-AQ pulps in this study were more difficult to bleach with oxygen to a given brightness level than corresponding kraft pulps.

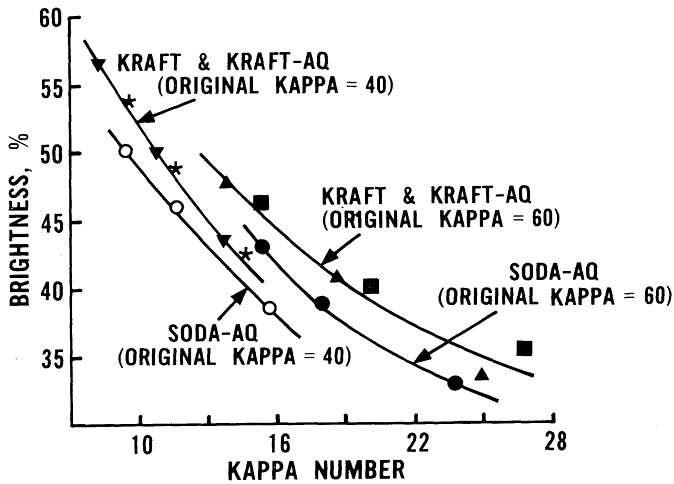

FIG. 2—Pulp brightness v. Kappa number after oxygen delignification.

Oxygen-treated alkaline pulps from 60 Kappa parent pulps were brighter at a given final Kappa number than were pulps delignified with oxygen from 40 Kappa parent pulps (Fig. 2). For example, at 15 Kappa number, pulps from 60 Kappa parent pulps were about 5.0 points brighter than pulps from 40 Kappa parent pulps. This trend seems to reflect the effect of greater extents of oxygen delignification needed for 60 Kappa parent pulps to reach the final Kappa number. If this brightness advantage is maintained through further bleaching, then the use of high-Kappa parent pulps and extended oxygen delignification should result in reduced demand for bleach chemicals.

Effectiveness

The effectiveness of oxygen treatments can be defined as the extent of oxygen delignification (Δ Kappa %) at a given level of applied alkali, all other reaction variables being constant. Unfortunately, the laboratory equipment employed in this study was not capable of tight control of reaction temperature (Table 2). However, there generally appeared to be no major differences in effectiveness for the three types of alkaline pulps and indeed others have found the effectiveness of oxygen delignification to be similar for kraft and soda-AQ pulps from black spruce (Table 2) (Andrews & Yethon 1979).

Beating Requirements

In agreement with previous studies (Chang *et al.* 1976), extended oxygen delignification of alkaline pulps significantly reduced beating requirements, measured here as revolutions in the PFI mill required to develop a given handsheet density (Fig. 3). Though 40 Kappa parent pulps were easier to beat than 60 Kappa parent pulps, after oxygen delignification their beating requirements were reduced to a common level. To reach 625 kg/m^3 sheet density, for example, 40 and 60 Kappa alkaline pulps required about 4000 and 8000 PFI revs, respectively, while all pulps after oxygen delignification required only about 2000 PFI revs. Similar beating trends were observed for the development of freeness with PFI mill beating.

As indicated by the slopes of the regressions in Fig. 3, the rate of sheet density development was similar before and after oxygen delignification. Thus oxygen treatments reduced beating requirements by making the unbeaten fibres more flexible and collapsible, and able to form denser unbeaten handsheets.

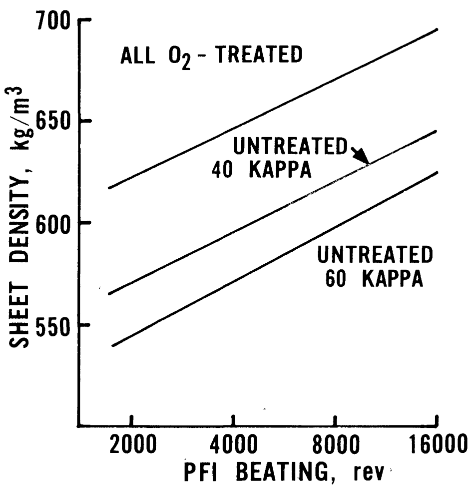

FIG. 3—Sheet density development with PFI beating for untreated and oxygen-delignified alkaline pulps (correlation coefficients are 0.95 or better).

Strength Properties

Tear-burst (or tear-tensile) relationships have been proposed by Rydholm (1965) and McLeod (1980) as a good basis for comparing overall levels of pulp strength. These trends for untreated and oxygen-treated alkaline pulps in the present study are presented in Figs 4, 5, and 6. For untreated parent pulps, plots of tear-burst relationships combined both the 40 and 60 Kappa pulps, and the order of pulp strengths was kraft > kraft-AQ >> soda-AQ. A similar ordering has been cited for alkaline pulps from black spruce (McLeod *et al.* 1980).

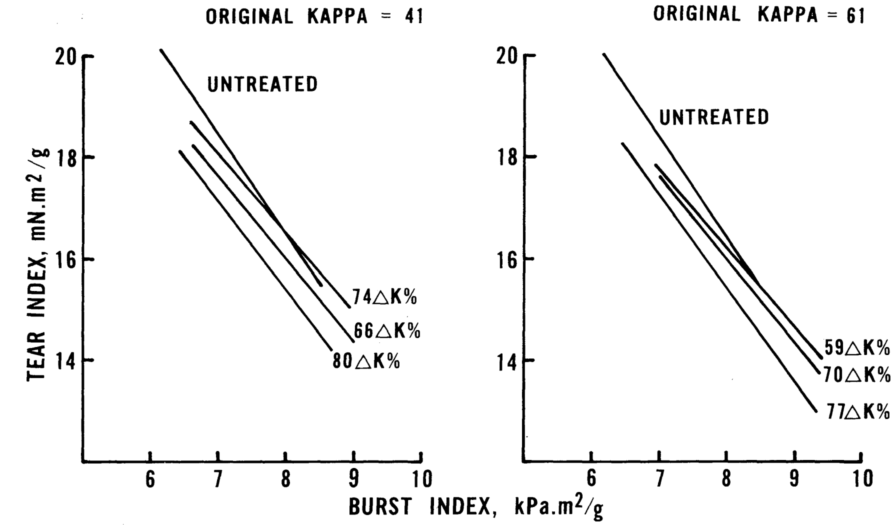

FIG. 4—Tear-burst relationships for untreated and oxygen-delignified kraft pulps (correlation coefficients are -0.91 or better).

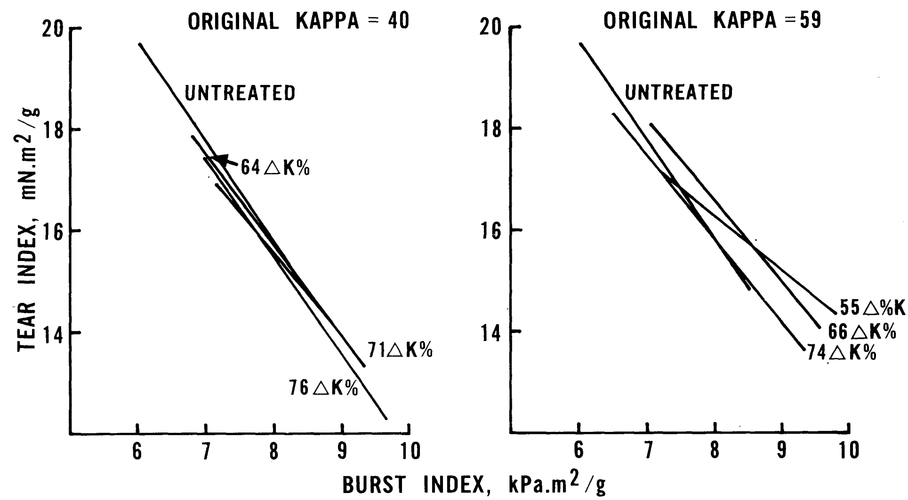

FIG. 5—Tear-burst relationships for untreated and oxygen-delignified kraft-AQ pulps (correlation coefficients are -0.88 or better).

Since alkaline pulps after oxygen delignification were faster beating, their tear-burst regressions included data points from the region where tear-burst relationships deviate from linearity (Figs 4, 5, and 6) (Kibblewhite 1973). Thus these regressions are somewhat flatter than those of the untreated parent pulps. Nevertheless, comparisons of tear-burst relationships are useful for the three types of alkaline pulps at the two levels of initial Kappa number and three levels of extended oxygen delignification.

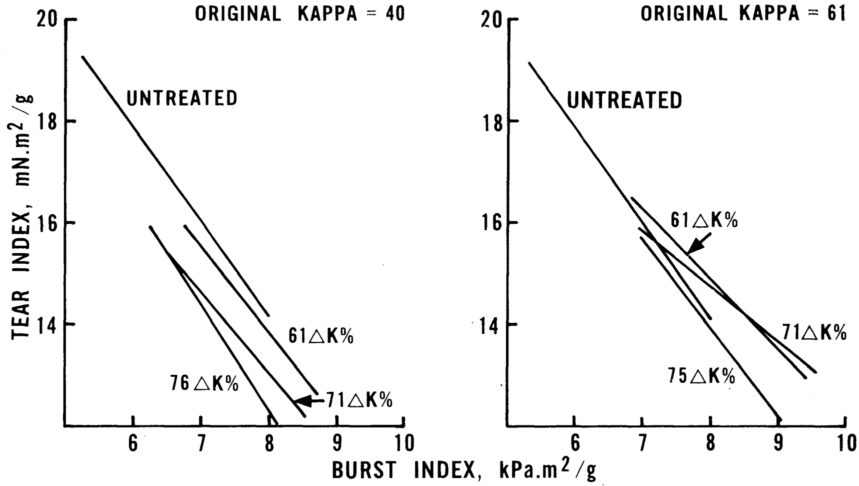

FIG. 6—Tear burst relationships for untreated and oxygen-delignified soda-AQ pulps (correlation coefficients are -0.91 or better).

For kraft pulps, oxygen delignification to about 70 Δ Kappa % was possible before significant losses in pulp strength occurred (Fig. 4). Kraft pulps at the 40 and 60 Kappa level appeared equally sensitive to extended oxygen delignification. Surprisingly, the kraft-AQ pulps in this study displayed a marked resistance to strength loss after extended delignification (Fig. 5). Apparently delignification up to 75 Δ Kappa % could be tolerated by kraft-AQ pulps at both the 40 and 60 Kappa levels. Soda-AQ pulps at the 40 Kappa level appeared especially sensitive to extended oxygen delignification and the maximum safe limit for pulp strength seemed to be about 60 Δ Kappa % (Fig. 6). At the 60 Kappa level, soda-AQ pulps were more resistant to oxygen treatments and showed drops in tear-burst levels only after delignification to more than about 70 Δ Kappa %.

For all alkaline pulps, oxygen delignification lowered burst indices at a given sheet density while having little effect on tear indices. As an example, these trends are shown for the 60 Kappa kraft pulp in Fig. 7. Burst-density plots uniformly decreased with increasing extents of oxygen delignification. Though tear-density regressions were less ordered, they generally showed little systematic effect from oxygen treatments. The relative effects of oxygen delignification on burst-density and tear-density relationships were rather surprising but have been confirmed in further studies to be published (Allison, in prep.).

Selectivity

Selectivity of oxygen treatments is normally defined as pulp viscosity at a given Kappa number (Olm & Teder 1979). According to this definition the selectivity of oxygen-delignified soda-AQ pulps was consistently less than that of kraft and kraft-AQ pulps (Fig. 8). However, the low initial viscosity levels of the untreated soda-AQ pulps were decreased much less by extended oxygen delignification than were the higher

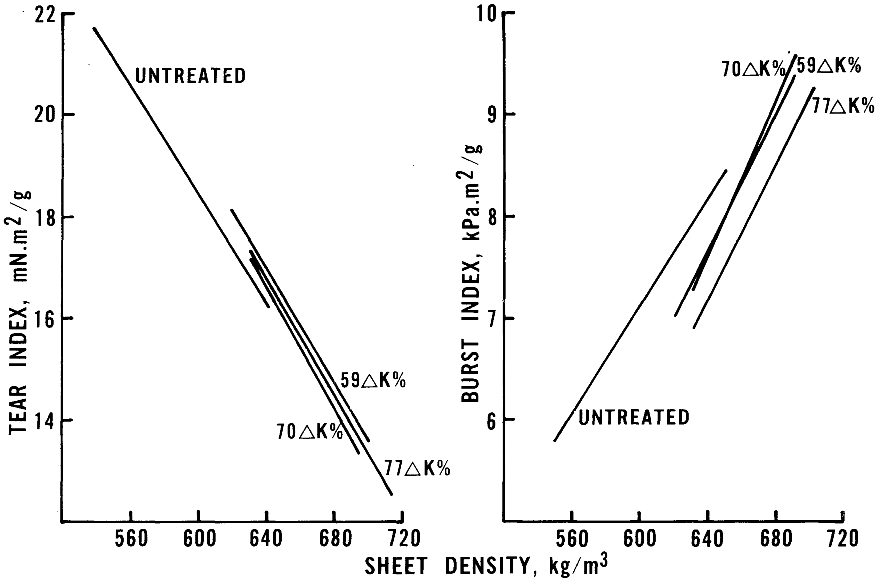

FIG. 7—Tear and burst indices v. sheet density for untreated and oxygen-delignified kraft pulp (original Kappa = 61; correlation coefficients are 0.84 or better).

viscosity levels of the untreated kraft and kraft-AQ pulps. Results also showed that extended oxygen delignification of 40 Kappa parent pulps was somewhat more selective on a viscosity basis than extended oxygen delignification of 60 Kappa parent pulps (Fig. 8).

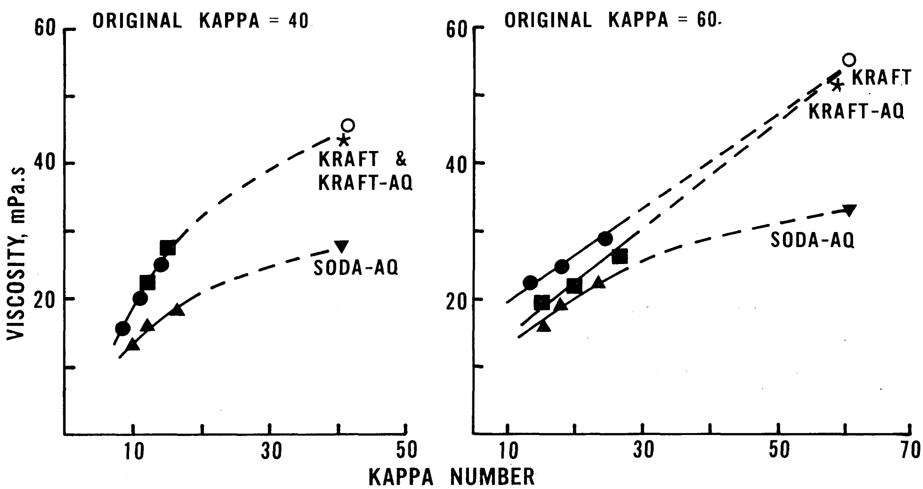

FIG. 8—Selectivity of oxygen delignification of alkaline pulps.

For *P. radiata* pulps in this study, plots of tear index (at 7.0 kPa.m^2/g burst index) *v. v*iscosity show that oxygen-delignified soda-AQ pulps give lower tear values at a given viscosity than oxygen-delignified kraft and kraft-AQ pulps (Fig. 9). For example, at 20 MPa.s viscosity, oxygen-delignified soda-AQ pulp had a tear index of 15.8 mN.m^2/g while oxygen-delignified kraft and kraft-AQ pulps had a tear index of 17.5 mN.m^2/g. Thus care must be taken when using viscosity as a comparative indicator of pulp strength for different alkaline pulps from *P. radiata,* especially after oxygen treatments.

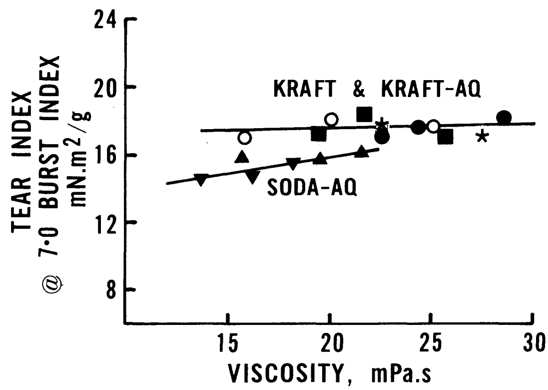

FIG. 9—Tear index at 7.0 kPa.m^2/g burst index as a function of viscosity for oxygen-delignified alkaline pulps.

CONCLUSIONS

Extended oxygen delignification (60–75 Δ Kappa %) of alkaline pulps from *P. radiata* enhanced yield-Kappa relationships and gave total yield increases at the 25 Kappa level of about 3% over yields achievable with continued pulping. Extended oxygen delignification also reduced the beating requirements of alkaline pulps.

Kraft and kraft-AQ pulps were about 5.0 points brighter than soda-AQ pulps after oxygen delignification to similar Kappa number. Also, all oxygen-delignified alkaline pulps from 60 Kappa parent pulps were brighter than those from 40 Kappa parent pulps at a given Kappa level.

Though pulp viscosities were significantly lowered by extended oxygen delignification, pulp strength levels could be maintained if treatments were carefully controlled to optimum limits. Tear-burst relationships suggested that: (a) kraft pulps could be oxygen delignified to about 70 Δ Kappa % without significant strength loss; (b) kraft-AQ pulps were surprisingly resistant and could be safely delignified to about 75 Δ Kappa %; (c) maximum safe limits for 40 and 60 Kappa soda-AQ pulps were about 60 and 70 Δ Kappa %, respectively.

Extended oxygen treatments tended to reduce burst-sheet density relationships while having little effect on tear-sheet density relationships. The use of viscosity to indicate relative pulp strengths for various alkaline pulps after oxygen delignification could not be recommended.

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REFERENCES

ALLISON, R. W.: Bleaching alkaline pulp from **Pinus radiata** (in prep.).

ALMBERG, L.; CROON, I.; JAMIESON, A. 1979: Oxygen delignification as part of future mill systems. **Tappi 62(6):** 33–5.

ANDREWS, D. H.; YETHON, A. E. 1979: Delignification and bleaching of soda-anthraquinone pulps with oxygen. **Tappi 62(6):** 29–32.

CHANG, H-M.; GRATZL, J.; McKEAN, W.; REEVES, R. H.; STOCKMAN, V. 1976: Some sheet properties of soda-oxygen pulps. **Tappi 59(8):** 72–5.

FOSSUM, G.; HAGGLUND, S.; LINDQVIST, B. 1980: Alkaline pulping of pine and birch with antraquinone as additive. **Svensk Papperstidning 83(16):** 455–60.

FULLERTON, T. J.; KERR, A. J. 1981: Practical aspects of kraft-AQ pulping of **Pinus radiata**. **Appita 35(2):** 135–9.

JAMIESON, A.; FOSSUM, G. 1976: Inflence of oxygen delignification on pulp yields. **Appita 29(4):** 253–6.

JAMIESON, A.; SMEDMAN, L. 1973: Integration of oxygen bleaching in the brown stock washing system. **Svensk Papperstidning 76(5):** 187–91.

KIBBLEWHITE, R. P. 1973: Effects of beating and wood quality on radiata pine kraft paper properties. **New Zealand Journal of Forestry Science 3(2):** 220–5.

McLEOD, M. 1980: Comparing pulp strengths: do's and don'ts. Paper presented at 66th Annual Meeting of Canadian Pulp and Paper Association, Montreal.

McLEOD, M.; FLEMING, B.; KUBES, G.; BOLKER, H. 1980: The strengths of kraft-AQ and soda-AQ pulps. **Tappi 63(1):** 57–60.

OLM, L.; TEDER, A. 1979: The kinetics of oxygen bleaching. **Tappi 62(12):** 43–6.

RYDHOLM, S. A. 1965: "Pulping Processes". Interscience, New York.

SINGH, R. (Ed.) 1979: "The Bleaching of Pulp". TAPPI Press, Atlanta, pp. 159–209.

STYAN, G. 1977: Exploitation of technology by the Canadian pulp and paper industry. **Pulp and Paper Magazine of Canada 78(6):** 87–94.