Influence of kraft pulping on the kinetics of oxygen delignification

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ABSTRACT

Conventional kraft pulping was performed on mixed northeastern hardwood chips in a laboratory digester. Four pulps of kappa no. 15–16 were produced with the sulfidity held constant while the effective alkali charge and H-factor were varied. The pulps were used in oxygen delignification experiments performed under industrially relevant conditions. Response variables were: kappa number, viscosity, COD, residual alkali, and final pH. Values were found to depend on the effective alkali concentration used in pulping. The results suggest that more refractory lignin moieties occur during kraft pulping at low alkali levels and high H-factors. An alternative explanation is that pulps with high xylan content are more difficult to delignify in an oxygen stage.

Application:

A high concentration of effective alkali in kraft pulping makes an oxygen delignification stage more efficient, leading to savings in bleaching chemicals.

OXYGEN DELIGNIFICATION IS A proven approach for extending delignification after kraft pulping. Decreases in kappa number in an oxygen delignification stage lead to savings in chlorine dioxide and other chemicals used to reach the target brightness. Furthermore, effluents from an oxygen delignification stage can be recycled to the chemical recovery system, which reduces the environmental impact from color, COD, AOX, and BOD in bleach plant effluents (*1*).

Oxygen delignification kinetics are complex, and reaction rates vary for different wood species and pulping processes. Delignification proceeds rapidly during the first 5–10 min of the oxygen stage and then proceeds more slowly in the remaining delignification time. The kinetics of delignification are thought to be controlled by the transfer of oxygen and alkali into the cell wall and by refractory residual lignin moieties formed during kraft pulping.

A major area left unexplored in oxygen bleaching is the relationship between delignification kinetics in the oxygen stage and conditions that exist during kraft pulping and other unit operations in the fiber line. Here we look at how kraft pulping conditions affect reaction kinetics in the oxygen delignification stage.

BACKGROUND

Kinetics of oxygen delignification

Oxygen delignification kinetics have been described with different kinetic models (*2*). Guven and co-workers have summarized several proposed kinetic models (*3*). They concluded that data for the first and second delignification phases correlated well with kraft pulping conditions and the response variables of the brownstock pulp. Data for the initial rate period correlated in terms of *H*-factor, residual effective alkali, kappa number, and fiber coarseness. Data for the second rate period could be fitted to the initial effective alkali used in kraft digestion and to the kappa number, fiber coarseness, and pulp yield.

Agarwal and co-workers performed a detailed investigation of the oxygen delignification kinetics for mixed southern hardwoods for a one-stage process (*4*). They found that the three primary process variables that affect the decrease in kappa number are, in decreasing order of importance:

- Temperature
- Alkali concentration
- Oxygen pressure.

They found that the delignification process is hindered in the second reaction period, for which the most likely causes are: (a) restricted solid state mass transfer of oxygen and alkali into the cell wall, (b) lignin condensation reactions, and (c) the presence of carbohydrates such as xylans that are bound to lignin groups and which resist delignification under alkaline conditions.

High apparent reaction orders have been observed with respect to the lignin content in kinetic studies of various bleaching processes. Schoon showed that a power-law equation applies when polymer degradation occurs by an infinite number of first-order reactions proceeding in parallel with various moieties in the polymer (*5*).

The data for kappa number vs. time can be fitted to a power-law rate equation of apparent order *q*:

$$-r_a = -dK/dt = k K^q \qquad (1)$$

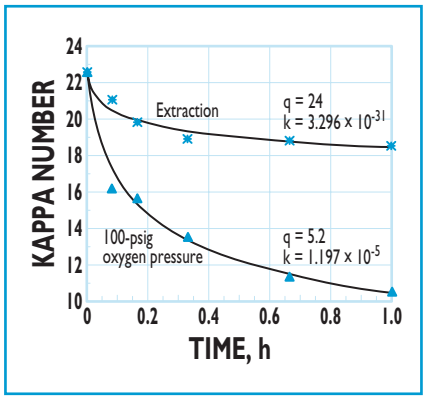
The reaction rate constant, k, is correlated to the initial alkali concentration (OH^-, g/L), temperature (K), activation energy (kJ/mole), and oxygen pressure (psig) (*4*).

Refractory lignin groups would have low first-order reaction rate

Effective alkali, %	Cooking time, min	*H*-factor	Kappa no.	Viscosity, cp	Brightness, % ISO	Yield, %	Black liquor pH	Black liquor Residual AA,* g/L
12	180	3051	16.3	44.6	27.0	48.9	11.3	4.1
15	62	1100	16.2	34.1	32.2	47.3	12.9	10.2
18	35	654	15.5	29.6	34.4	45.7	13.1	18.2
21	18	409	15.0	29.5	34.7	45.2	13.3	27.4

*Residual active alkali in the black liquor.

I. Results of kraft pulping experiments



1. Delignification of a softwood in a pure extraction stage and an oxygen stage, each at 100°C with 2.5% alkali (6).

coefficients and could account for the slow rate in the second period. **Figure 1** illustrates hindered delignification for a pure extraction stage and an oxygen stage, each for softwood pulp at 100°C with 2.5% alkali (*6*). The lower apparent order (q = 5.2) results because the lignin structure is more susceptible to alkali under the oxygen-stage conditions.

Effect of pulping conditions

Pulping conditions would be expected to affect response variables in oxygen bleaching in a subsequent stage. Fundamental process variables in kraft pulping are: wood species; chip thickness; the concentrations of hydroxyl (OH^-), sulfide ($S^=$), and bisulfide (HS^-) ions; and time and temperature (*H*-factor).

In the mill, numerous industrial variables will also affect the outcome of the pulping process. These mill variables include wood aging, moisture content, and the effectiveness of steaming and chip impregnation. These variables are likely to affect response variables in oxygen delignification, including the kappa number decrease, viscosity, alkali consumption, and COD.

OBJECTIVE AND SCOPE

Our goal in this work was to investigate the influence of conventional kraft pulping on the kinetics of oxygen delignification. All pulps were delignified in a medium-consistency oxygen reactor according to the techniques described by Guven *et al*. (*3*) and Agarwal and co-workers (*4*). Details of the experimental program are summarized elsewhere (*7*).

Mixed northeastern hardwood chips were used. Kraft pulps were prepared with the same target kappa number (15–16), starting at four different initial alkali concentrations. To obtain these four pulps, we varied the effective alkali charge and changed the *H*-factor by adjusting the pulping time to meet the kappa number target while keeping the temperature constant (170°C).

Mild pulping was performed at 12% and 15% EA (effective alkali) with high *H*-factors. These pulps were compared with pulps of similar kappa numbers prepared at 18% and 21% EA at low *H*-factors to represent harsh conditions. These four pulps were washed well and were subjected to oxygen delignification in a single-stage medium-consistency reactor.

Carbohydrate and lignin analyses were performed to determine the component sugars and the soluble and insoluble lignin. The data for kappa number were plotted against time and were fitted to the kinetic model given by Eq. 1.

RESULTS

Results of pulping experiments

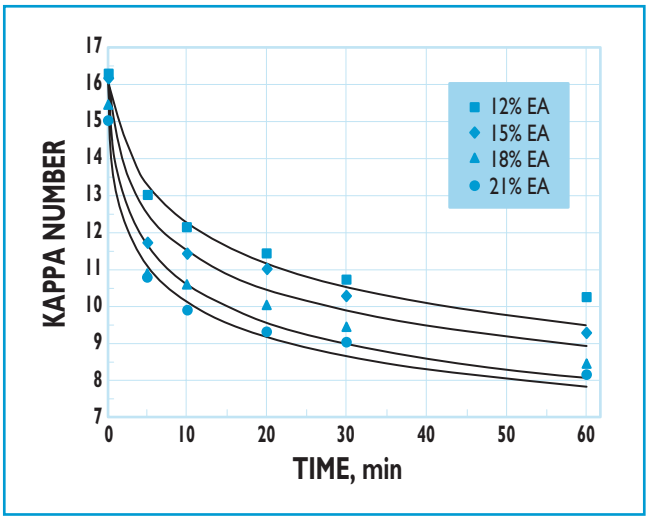
The results of the kraft pulping experiments are summarized in **Table I**. Pulp yield varied systematically between 48.9% and 45.2% when the effective alkali was increased from 12% to 21%. The highest viscosity was obtained at the lowest effective alkali level: 44.6 cp at 12% EA, as compared to 29.5 cp at 21% EA.

Pulping at high alkali concentration for short periods of time leads to lower hemicellulose content. Pulping for long periods of time at low alkali concentration would be expected to produce pulps with increased hemicellulose content as well as condensed and refractory lignin structures (*8*). Pulp brightness was the lowest for the pulp prepared at 12% EA (27% ISO) and highest for the pulp processed at 21% (34.7% ISO).

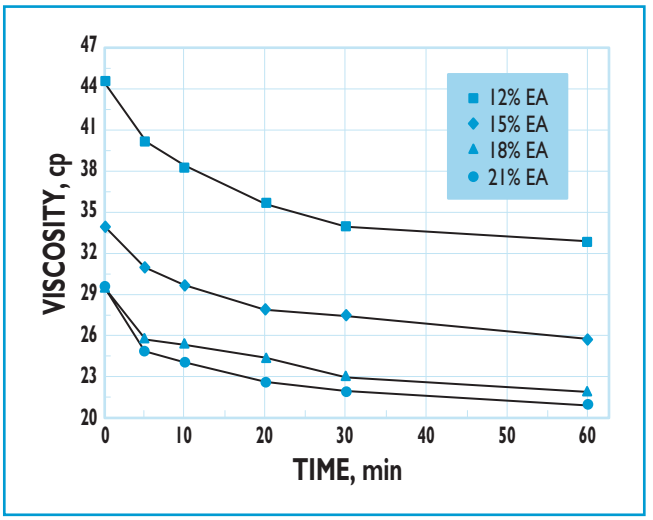
Oxygen delignification experiments

Kappa number. **Figure 2** shows curves for kappa number decreases over an hour for the four pulps produced. All experiments were conducted at 90°C at 1.5% alkali and an oxygen pressure of 100 psig in a single-stage medium-consistency oxygen reactor.

The figure illustrates that the delignification rate curve increases systematically with increasing effective alkali in the digester up to about 18% EA. The difference between the rates for 18% EA and 21% EA was small. These results suggest either that more oxygen-refractory lignin groups are formed when the pulping is carried out with less alkali or that



2. Influence of effective alkali concentration in kraft pulping on the relationship between kappa number and oxygen delignification time.

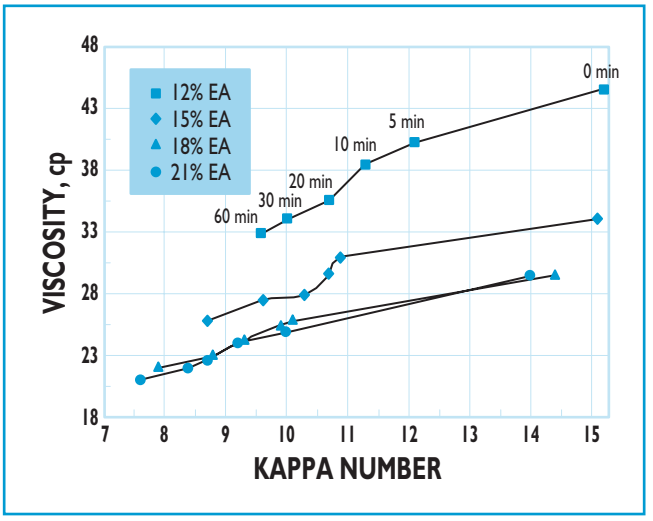


3. Influence of effective alkali concentration in kraft pulping on the rate of viscosity loss in the oxygen delignification stage.

Sample	q	k	R^2
12% EA	7.57	9.07×10^{-10}	0.968
15% EA	7.91	6.19×10^{-10}	0.867
18% EA	7.27	5.44×10^{-9}	0.912
21% EA	7.86	1.74×10^{-9}	0.992
Avg.	7.65	n.a.	0.930

n.a. = not applicable.

II. Kinetic parameters for Schoon's model, showing the effective alkali concentrations



4. Pulp selectivity as indicated by the relationship between viscosity and kappa number.

the stability of the hemicellulose polymers in the pulps may be a factor.

We fit the data for kappa number vs. time to Eq. 1 by making log–log graphs of the rate data [$-dK/dt$] plotted against the kappa number, as explained by Agarwal and co-workers (*4*):

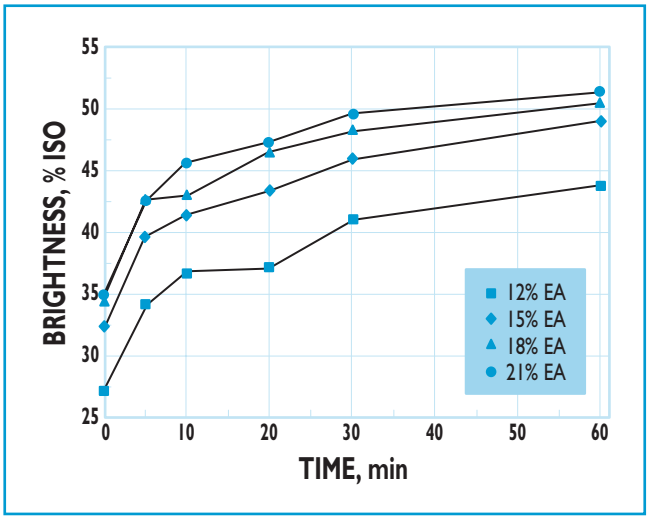
$$\log[-dK/dt] = \log k + q \log K \qquad (2)$$

The values of q and K are estimated from the slope and intercept of the regression line through the data.

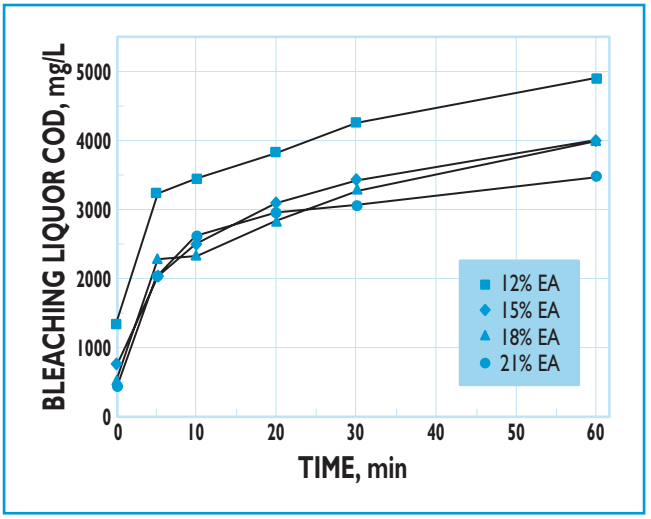
The results of this calculation are summarized in **Table II**. The Schoon model (*5*) fits the data well, with an average R^2 value of 0.93. (The smooth curves in Fig. 2 represent the model equation.) The apparent reaction order, q, had an average value of 7.65. The reaction rate coefficient k increases with increasing effective alkali. The increase in k indicates that pulping the northeastern hardwood at a higher effective alkali charge leads to a larger decrease in kappa number during oxygen delignification.

Viscosity and selectivity. **Figure 3** shows how the effective alkali concentration in kraft pulping affects the rate of viscosity loss in the oxygen delignification stage after pulping. **Figure 4** presents the corresponding selectivity curves. The shapes of the viscosity–time curves (Fig. 3) are similar for all four of the kraft pulps tested, and the curves vary systematically with the addition level of effective alkali.

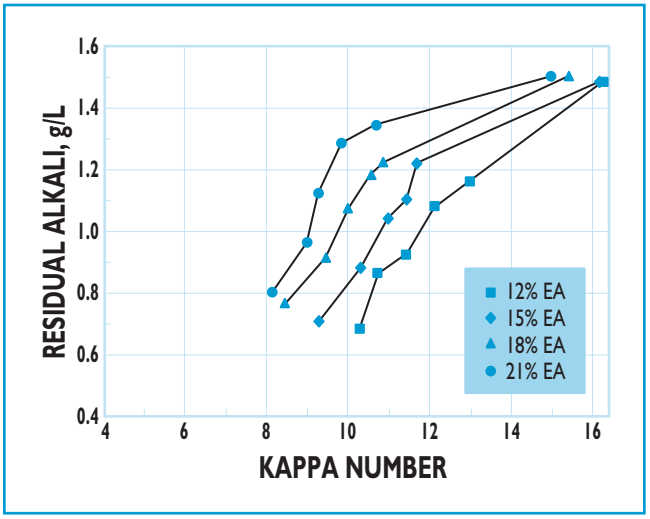
As these results also show, the final pulp viscosity after oxygen delignification parallels the viscosity of the pulp leaving the digester. (Presumably, the intrinsic fiber strength should follow a similar pattern.) This pattern is clearly seen in the selectivity data in Fig. 4. Interestingly, similar selectivity curves were obtained for the pulps produced at 18% and 21% EA, but differences were obtained with alkali additions of 12% and 18% EA.



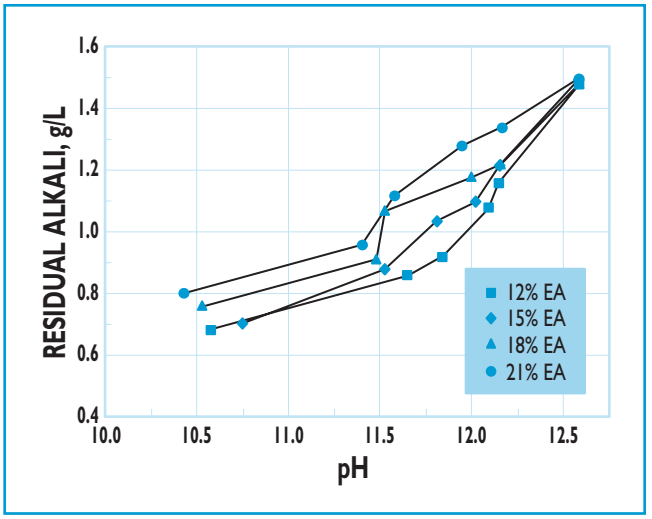
5. Influence of effective alkali concentration in kraft pulping on the delignification rate in the oxygen stage.



6. Influence of effective alkali concentration on the rate of COD formation in the subsequent oxygen delignification stage.



7. Influence of effective alkali concentration on the relationship between residual alkali and kappa number in the oxygen delignification stage.



8. Influence of effective alkali concentration on the relationship between residual alkali and bleaching liquor pH in the oxygen delignification stage.

Brightness. Brightness data are presented in **Fig. 5**. As this figure shows for the oxygen delignification stage, the pulps bear the same relationship to each other on exiting as they do on entering. The lowest initial brightness occurred for the pulp produced at 12% EA (Table I).

These results suggest that longer exposure time at the pulping temperature results in the formation of more chromophoric groups. The additional chromophoric groups must be removed in the oxygen stage and later bleaching stages. These results further suggest that the brightness for a pulp exiting a commercial oxygen stage will be determined by the incoming kappa number and the exposure time in the digester once the oxygen-stage conditions are fixed.

Chemical oxygen demand. As **Fig. 6** shows, additional COD was formed with increasing reaction time in the oxygen stage for all four well-washed pulps. The COD curves have approximately the same shape, but the pulp produced with 12% EA had considerably higher COD concentrations at equivalent reaction times.

The data shown at time zero in Fig. 6 are the COD values contained in liquor squeezed from the pulp after the alkali and magnesium sulfate were added but before the reaction mass was heated and the oxygen was added. These data indicate that the higher-yield pulp produced at

12% EA lost more material of low molecular weight than did the pulps produced at the higher effective alkali concentrations. Thus, the pulp at 12% EA had a higher COD.

Oxygen and alkali react with organic material removed from the cell wall and any carryover black liquor from the digester. Because competitive COD formation and elimination reactions are involved, the COD curves increase with time in Fig. 6. These curves increase for well-washed pulp because oxygen and alkali do not react extensively with dissolved cell wall material. For high amounts of carryover, the COD curves actually decrease with time (*9*, *10*) because the oxygen reacts with the organic solids in the carryover.

Alkali consumption. Figure 7 reports the residual alkali values of the reaction liquor squeezed from the pulp samples after they have been exposed to oxygen.

At equivalent kappa numbers, less alkali was consumed during oxygen delignification by the brownstock pulps produced under the higher concentrations of effective alkali. Alkali consumption decreased systematically with increasing concentrations of effective alkali used in pulping (*7*). This outcome is interpreted to mean that the pulp with the highest hemicellulose content loses more carbohydrates during oxygen delignification and thus consumes more alkali than the other pulps at equivalent kappa numbers.

Figure 8 illustrates the relationship between the residual alkali content and the pH of the spent liquor. There is some scatter in the data. However, at a given pH, the residual alkali is higher in the pulps prepared using the highest values of effective alkali, or 21% and 18% EA. The shapes of the curves in Fig. 8 most likely are attributable to the complex relationship between the liberation of organic acids and carbon dioxide during oxygen delignification. The levels of the curves depend on the hemicellulose content of the incoming pulps.

Sample (% EA)	Glucan, %	Xylan, %	Mannan, %	Arabinan, %	Galactan, %	Total carbohydrates, %
			Kraft pulp			
12	72.4	21.1	0.45	0.10	0.07	94
15	74.0	20.6	0.35	0.00	0.00	95
18	76.4	20.0	0.47	0.03	0.07	97
21	78.3	17.9	0.72	0.10	0.10	97
			Oxygen-stage pulp			
12	74.9	21.5	0.37	0.05	0.05	97
15	76.9	20.9	0.41	0.00	0.00	98
18	78.5	19.3	0.42	0.09	0.06	98
21	80.1	17.4	0.48	0.05	0.05	98
			Quality control history*			
Mean	45.2	15.9	1.75	0.40	0.54	64
Std. dev.	0.75	0.30	0.08	0.03	0.04	n.a.

Rhamnan was not detectable.
*Aspen wood quality control standard.

III. Carbohydrate content of kraft pulps and oxygen-delignified kraft pulps

Sample (% EA)	Kappa no.	Extractives, %	Soluble lignin, %	Klason lignin, %	Total lignin, %
			Kraft pulp		
12	16.3	0.18	0.80	1.30	2.10
15	16.2	0.18	0.92	1.11	2.13
18	15.5	0.19	0.85	1.20	2.05
21	15.0	0.16	0.84	1.29	2.13
			Oxygen-stage pulp		
12	10.3	0.13	0.63	0.64	1.27
15	9.3	0.13	0.69	0.22	0.91
18	8.4	0.20	0.66	0.29	0.95
21	8.2	0.14	0.69	0.28	0.97

IV. Lignin and extractives contents of kraft pulps and oxygen-delignified kraft pulps

Pulp composition. The carbohydrate composition and lignin content were determined for the kraft pulps and the 60-min samples after oxygen delignification (Tables III and IV). Component sugars were detected with high-pressure liquid chromatography after acid hydrolysis (*7*). As the results show, increasing the alkali concentration during kraft pulping successively reduced the xylan content of the pulps. There did not appear to be significant changes in the xylan concentration across the oxygen stage, which was operated at 90°C with 1.5% NaOH.

The glucan concentration in the brownstock pulp increased from 72.4% to 78.3% when the alkali was increased from 12% to 21% in the kraft pulping (Table III), while the yield decreased from 48.9% to 45.2%

(Table I). In the oxygen stage, the glucan content increased as a result of decreases in lignin content. Few statistical differences could be detected in the concentrations of mannan, arabinan, and galactan with increasing effective alkali in the digester, nor were differences manifested as changes in content across the oxygen stage.

The methylene chloride extractives content and the soluble and insoluble lignin values shown in Table IV do not indicate significant differences among the four pulps tested. The notable exception is the Klason lignin value of 0.64% and a total lignin content of 1.27% after oxygen delignification for the sample processed at 12% EA.

DISCUSSION

In the laboratory experiments, the effective alkali, sulfidity, *H*-factor, and liquor-to-wood ratio were carefully controlled. The three factors determine the concentrations of the $S^{=}$, OH^{-}, and SH^{-} ions. The time at temperature determines the *H*-factor and greatly influences the reaction kinetics.

In a mill situation, many other variables are involved in determining the quality of the final pulp. Such variables include chip thickness, moisture content, the extent of air removal through steaming, the degree of chemical penetration, liquor profiling, and black liquor recirculation. These variables, together with the primary process variables, would affect the final kappa number and the carbohydrate composition of the kraft pulp. In a mill, variability in the wood, changes in the pulping liquor, and numerous secondary variables also affect pulp quality.

For oxygen delignification, the high reaction order can be explained by assuming that delignification proceeds through a large number of parallel, first-order reactions which take place simultaneously and in which the different lignin moieties react at different rates, as suggested by Schoon (*5*). Such a mechanism is supported by the work of Johansson and Ljunggren (*11*), who conducted oxygen delignification experiments in alkaline media using various lignin model compounds. Axegard, Moldenius, and Olm (*12*) reported that high reaction orders occur in prebleaching, final bleaching, oxygen bleaching, and even in hydrogen peroxide bleaching of mechanical pulps.

Hemicelluloses exhibit significantly different responses toward the hydroxyl ion during kraft pulping (*8*, *13*, *14*). The glucomannan polymers are unstable, and they undergo extensive reactions during conventional kraft pulping of hardwoods. The xylan polymer content of hardwoods is very high, approaching 30% (*15*). In contrast to the glucomannan polymers, the O-acetyl-4-O-methylglucuronxylan polymers in hardwoods are much more stable. Although altered by loss of acetyl groups and changes in the α-D-4-O-methylglucuronic acid side groups, the xylan polymers are retained to a large degree during alkaline pulping (*16*).

Because xylans are stable in alkaline pulping, their content is high in the resulting hardwood pulp. Pulping at high effective alkali levels (18% and 21%) for short periods of time (35 and 18 min) should lead to lower hemicellulose concentrations in the pulps because of the high alkalinity. Pulping for longer periods (180 and 62 min) at low alkali (12% and 15%) would be expected to lead to more condensed and refractory lignin structures because of the long exposure times and decreased alkali concentration. The presence of refractory lignin linkages would decrease the delignification rate in a following oxygen stage.

Additionally, the lignin polymer is bonded to the xylan hemicellulose polymer through benzyl ester linkages and benzyl ether linkages (*16*). These lignin-to-hemicellulose linkages and the stability of the hexenuronic acid side groups on the xylose polymers formed during kraft pulping could also influence the results of oxygen delignification (*17*).

CONCLUSIONS

Mixed northeastern hardwood chips were pulped to the same brownstock kappa number under high and low concentrations of effective alkali. The concentration greatly affected the rate of a subsequent oxygen delignification stage, in which well-washed pulp was used.

Conventional kraft pulping with a low effective alkali concentration and a high *H*-factor produced pulps at higher yields. However, the pulps were more difficult to delignify in the oxygen stage. The oxygen stage easily delignified pulps produced under a low *H*-factor but with high concentrations of effective alkali. Higher-yield pulps had a higher xylan content.

The power law model for hindered chemical reactions (*5*) adequately describes the kinetic rate data for oxygen delignification. The experimental results can be explained if one assumes that delignification in the oxygen stage is hindered by refractory lignin moieties formed in the pulping process, by high xylan content (*17*) , or a combination of these effects. **TJ**

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