OXYGEN DELIGNIFICATION

High-pressure oxygen delignification of kraft pulps

Part 1: kinetics

JOSÉ IRIBARNE AND LELAND R. SCHROEDER

ABSTRACT

Previous studies of oxygen delignification cover oxygen concentrations up to 0.012 mole/L in the aqueous alkaline media. This range was increased eight times through the application of very high oxygen pressure in the gas phase. The experimental results were generalized through apparent kinetics models. Delignification could be modeled in two phases, each first order on lignin content. One phase showed little dependence on alkali and oxygen, while the other phase was close to first order on both alkali and oxygen. The relative importance of the two phases depends on the operating conditions. Polysaccharide cleavage could be modeled in one phase, 0.3- and 0.4-order on alkali and oxygen concentration, respectively.

Application:

The use of high pressure could potentially improve the selectivity of alkaline oxygen stages, enabling higher delignification while maintaining pulp strength.

OLM AND TEDER *(1)* SHOWED that almost all the lignin in kraft pulp can be removed with an oxygen stage. However, the practical extent of delignification is limited by the degradation of carbohydrates in the pulp. If allowed to proceed far enough, the degradation will result in loss of pulp strength. This nonselectivity currently limits the oxygen stages to 40–50% delignification *(2, 3)*.

Almost all of the proposed TCF (totally chlorine free) bleaching sequences utilize an initial oxygen delignification stage carried to the farthest extent compatible with carbohydrate protection *(4–7)*. Therefore, improvements in the oxygen delignification process could have a significant impact on the economic feasibility of TCF bleaching.

Limitations in alkaline oxygen delignification

The presence of many reactive species makes the reaction of oxygen with lignin and carbohydrates very complicated. Oxygen can be reduced to water through four one-electron transfers, as illustrated in **Fig. 1**. The sequence is: oxygen → peroxy radicals → hydrogen peroxide → hydroxyl radicals → water. At high pH, the intermediate oxidants exist primarily as their conjugate bases.

Hydroxyl radicals react not only with lignin but also with the pulp polysaccharides, resulting in random chain cleavage. The reduction in the cellulose average degree of polymerization ultimately affects the pulp strength properties. Oxygen is the least reactive of the oxidants. To react, oxygen requires high temperatures, and/or the ionization of functional groups in the substrate, to facilitate the release of electrons. Thus, oxygen delignification is carried out in strongly alkaline media at relatively high temperatures. The increase in temperature is limited by a sharp increase in carbohydrate degradation above 120°C *(8)*.

Mass-transfer limitations are also a serious consideration for oxygen delignification *(2, 9, 10)*. Gas-to-liquid and liquid-to-solid transfers of oxygen are necessary to initiate the oxidation of lignin, as seen in **Fig. 2**. Increasing the mass-transfer areas A_1 and A_2 is only partially effective because of (a) the inherent slowness of the diffusion phenomena involved and (b) the low solubility of oxygen in aqueous media (e.g., 1% of the solubility of chlorine) *(11)*.

Motivation of the study

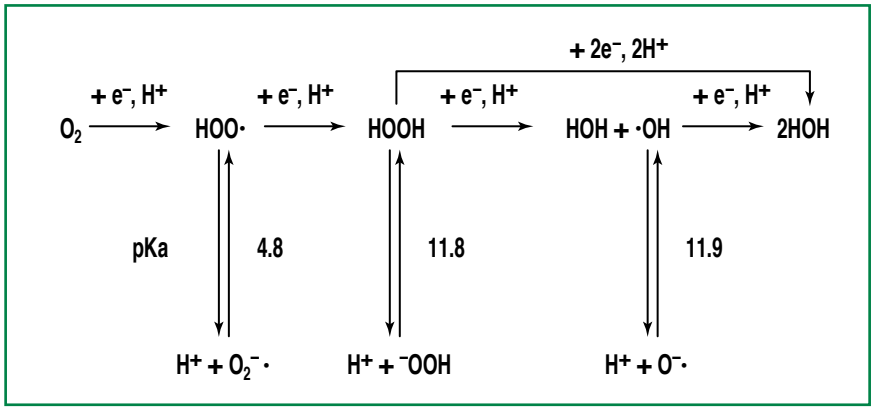
Previously reported oxygen-delignification studies have covered a range of oxygen pressures up to 1.5 MPa *(12)*, which implies a maximum possible concentration of 0.012 mole O_2/L in the aqueous media *(13)*. The maximum alkali concentration in the same experiments *(12)* was approximately 30 times the maximum oxygen concentration. It was decided to extend the range of oxygen concentrations through the application of high oxygen pressure in the gas phase. The main hypothesis was that higher concentrations of oxygen might increase delignification rates and change the relative importance of the oxygen species present in the delignification. Both effects could potentially improve the selectivity of the process.

EXPERIMENTAL

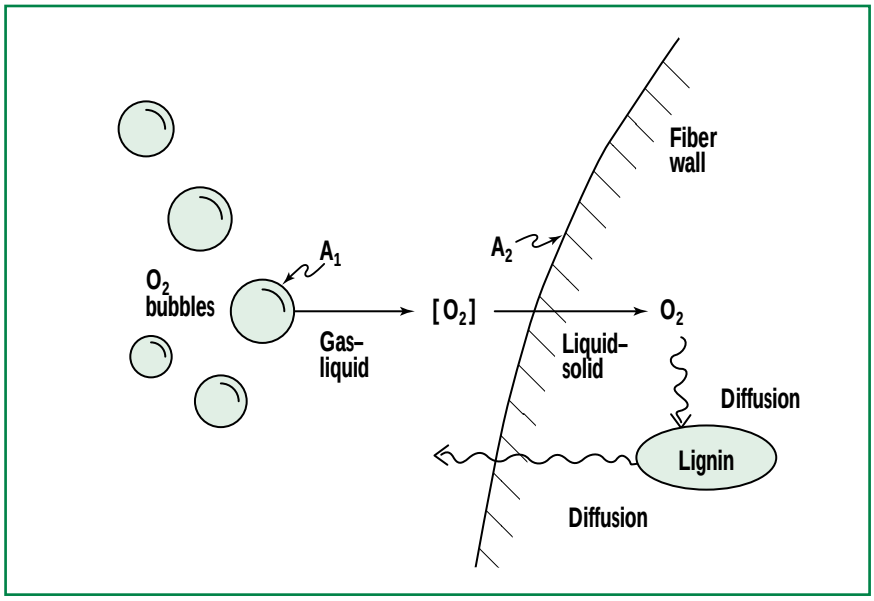
Experiment design

Alkaline oxygen delignification at high pressure was studied using a uniform-precision, central-composite, rotatable design that required 32 trials to test five factors at five levels *(14)*. The factors investigated were:

- Initial lignin content of the pulp, κ_0
- Reaction time, Δt
- Reaction temperature, T



1. Species in the reduction of oxygen to water [adapted from Gratzl (8)]



2. Mass transfer in oxygen delignification

- Oxygen partial pressure, p_{ox}
- Alkali concentration, [OH^-].

The minimum and maximum levels of each variable in this investigation are indicated in **Table I**. The table also includes the range of values used in previous studies *(1, 12, 15)*. Other process variables were explored in preliminary trials to find appropriate settings for the set of experiments.

The response parameters in the experiment were:

- Mass yield, *Y*
- Final kappa number, κ_t
- Final CED (cupriethylene diamine) viscosity, η_t
- Brightness, R_∞
- Zero-span breaking length, ZBL.

Kraft pulping

Green chips of loblolly pine (*Pinus taeda* L.) were cooked in batch digesters with indirect heating. Only the cooking time was varied. All other parameters were held constant as follows:

- Active alkali = 21% on o.d. (ovendry) wood
- Effective alkali = 18% on o.d. wood
- Sulfidity = 30%
- Liquor-to-wood ratio = 4:1
- Maximum temperature = 175°C.

The cooked chips were dispersed in a hydrapulper. Then the pulps were thoroughly washed, screened, centrifuged to 30–40% consistency, crumbed, and stored at 5°C. Before their use, the pulps were redispersed and prepared into pads at 10% consistency.

Alkaline oxygen delignification

The oxygen delignification trials were done in a 500-mL, high-pressure, stirred reaction vessel (Pressure Products Industries, Inc., Warminster, PA). The setup is sketched in **Fig. 3**. All major parts and piping are made of stainless steel type 316, with silicone rubber seals, and are protected from overpressure by rupture discs (not shown). Caustic is fed with a metal-diaphragm metering pump (American Lewa, Inc., Holliston, MA). The fluid exits the vessel through a sintered filter and is depressurized in a back-pressure regulator (Tescom Corp., Elk River, MN). The gas–liquid separation is effected in a vessel that drains by gravity.

The time constant of the reactor, τ, and the delay due to the inlet piping, θ, were estimated from the system's response to a step change in the incoming NaOH concentration *(16)*. There was an excellent correlation between the test data and an analytical model with θ = 4 min and τ = 11 min (r = 0.9998).

In preliminary trials, it was found that the reaction rates changed little below 2% pulp consistency, provided sufficient mixing. Carbohydrate protection improved marginally with doses of magnesium salt over 0.5% on o.d. pulp. The delignification rates did not increase when the mass-transfer areas of oxygen (A_1 and A_2 in Fig. 2) were enlarged by addition of a sintered bubbler (dotted lines in Fig. 3) and refining of the pulp. These results suggest that oxygen availabil-

ity was not a limiting factor in the trials.

The conditions used in subsequent experiments were as follows:

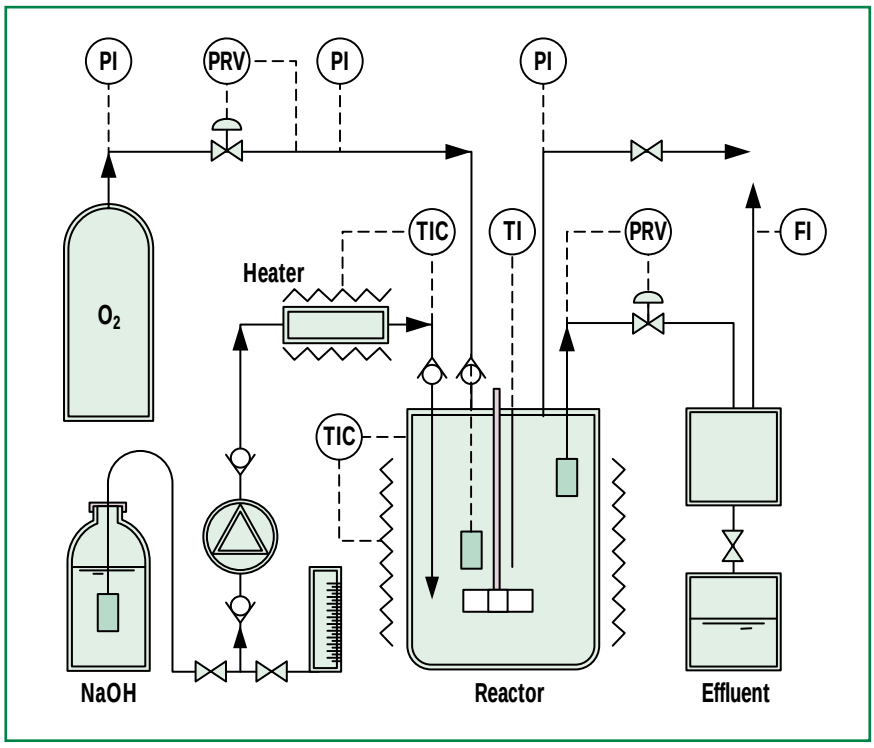
- Pulp load = 10 g o.d. unrefined pulp
- Mixing = flat-blade impeller at 900 rpm
- Oxygen bubbler not installed
- $MgSO_4 \cdot 7H_2O$ addition = 0.5% on o.d. pulp.

The pulp suspension at mild agitation was heated with a continuous flow of hot distilled water. After the heat-up time, a predetermined volume of 2.8*M* NaOH solution was pumped into the reactor from the measuring cylinder. Then the source was shifted to a solution at the desired NaOH concentration. This combination of pulse and step in the alkali supply results in a fast rise to the desired concentration after the piping delay. A small, continuous flow of oxygen was established through the reactor. After the desired reaction times, the flows were stopped, and the reactor depressurized. The pulps were quenched and washed by displacement with distilled water.

Seven "zero-time" control runs were done according to the same procedures, except that no NaOH was used. As a partial test of an optimization strategy, two additional trials were done adding only the NaOH pulse, hot distilled water thereafter, and depressurizing the reactor after 7 min of reaction. The average temperature in the last two trials was 78°C.

Pulp analysis

Kappa numbers were determined according to TAPPI UM 246 (micro kappa number). The same relationship between kappa number and acid-insoluble (Klason) lignin content was found for kraft pulps before and after alkaline oxygen delignification. This was previously observed by Hartler *et al. (12)*.



3. Experimental setup for high-pressure alkaline oxygen delignification

Variable	Previous studies	This study
κ_0, mL/g	30–40	20–60
Δt, min	0–360	1–21
T, °C	75–130	50–150
p_{ox}, MPa	0–1.5	0–18.4
$[OH^-]$, mole/L	0.005–0.4	0–0.4

I. Range of process variables in the alkaline oxygen delignification of kraft pulp

Holocellulose viscosities were determined according to TAPPI T 230 om-89 (capillary viscometer method) using the closed-bottle procedure. Holocelluloses were prepared using a mild acid chlorite treatment. The conditions used maximize the degree of polymerization and yield of carbohydrates.

- Sodium chlorite = 0.5 g/o.d. g pulp
- Acetic acid = 0.1 mL/o.d. g pulp
- Consistency = 10%
- Storage = 24 h at 25°C in the dark.

One handsheet of each pulp sample was made according to TAPPI T 205 om-88. On each handsheet, four replicate measurements were used to determine brightness and zero-span breaking length according to TAPPI T 452 om-92 and T 231 cm-85, respectively.

Kinetic calculations

The SAS/STAT software package (SAS Institute, Inc., Cary, NC) was used to compute least-square-error estimates of the parameters of the nonlinear kinetic equations. To pro-

Trial	Δt, min	T, °C	p_{ox}, MPa	[OH^-], mole/L	[O_2], mole/L	D-factor, h	G-factor, h	κ_0, mL/g	η_0, mPa·s	Y, %	κ_t, mL/g	η_t, mPa·s	R_∞, %GE	ZBL, km
	AVERAGE PROCESS CONDITIONS					HEAT-UP TIME		STARTING KRAFT PULP		ALKALINE OXYGEN-DELIGNIFIED PULP				
1	6	72	4.2	0.30	0.023	0.2	0.1	51.5	32.1	95	32.5	19.4	25	14.8
2	16	75	4.6	0.10	0.030	0.0	0.0	51.5	32.1	94	31.0	22.8	24	14.9
3	16	129	4.3	0.29	0.025	1.6	8.7	51.5	32.1	79	4.8	4.1	61	6.5
4	11	100	9.0	0.20	0.049	0.3	0.2	20.3	12.4	95	3.9	5.3	48	11.1
5	11	101	9.4	0.19	0.052	0.1	0.1	58.0	33.1	81	13.4	10.0	40	13.0
6	1	102	9.4	0.20	0.052	0.2	0.2	39.1	27.3	93	20.0	15.9	27	14.7
7	11	105	9.4	0.19	0.052	0.2	0.2	39.1	27.3	n.a.	9.1	9.3	41	11.6
8	16	127	13.8	0.09	0.089	4.1	92.1	51.5	32.1	80	2.0	4.1	71	7.7
9	16	128	13.8	0.29	0.076	1.0	5.5	31.4	22.6	75	3.8	3.2	57	6.4
10	6	123	13.8	0.29	0.072	2.9	34.4	51.5	32.1	87	12.5	7.7	38	11.2
11	16	77	14.0	0.10	0.083	0.0	0.0	31.4	22.6	94	11.6	16.9	34	15.4
12	6	126	4.4	0.09	0.030	1.2	5.0	51.5	32.1	77	15.5	6.3	33	10.0
13	21	103	9.0	0.19	0.050	0.2	0.2	39.1	27.3	88	7.2	9.1	52	12.1
14	11	50	9.1	0.20	0.067	0.0	0.0	39.1	27.3	91	28.0	26.3	25	15.4
15	11	100	9.0	0.19	0.049	0.2	0.2	39.1	27.3	87	10.9	9.1	37	12.1
16	11	104	9.0	0.19	0.050	0.1	0.1	39.1	27.3	91	9.1	10.2	44	12.7
17	16	76	14.0	0.29	0.065	0.0	0.0	51.5	32.1	90	18.2	13.8	33	15.2
18	16	127	3.9	0.09	0.028	1.6	8.0	31.4	22.6	81	7.3	5.0	41	10.0
19	6	128	13.8	0.09	0.090	1.0	4.7	31.4	22.6	90	5.6	5.5	49	10.2
20	6	77	14.0	0.10	0.083	0.0	0.0	51.5	32.1	93	28.9	18.8	25	14.7
21	11	157	8.5	0.18	0.075	4.3	173.2	39.1	27.3	51	2.5	2.2	61	5.2
22	11	103	0.02	0.20	≈0.0005	0.1	0.1	39.1	27.3	94	29.6	23.8	22	14.9
23	11	102	18.4	0.19	0.085	0.5	0.3	39.1	27.3	86	9.3	6.9	39	10.5
24	11	105	9.0	0.19	0.050	0.5	0.3	39.1	27.3	89	7.6	5.0	43	8.4
25	16	77	4.1	0.30	0.022	0.0	0.0	31.4	22.6	98	11.2	8.6	34	12.4
26	6	126	3.9	0.29	0.023	1.1	3.9	31.4	22.6	84	6.0	4.4	46	7.2
27	6	76	14.0	0.30	0.065	0.0	0.0	31.4	22.6	85	13.4	14.3	33	14.6
28	6	74	4.2	0.10	0.028	0.0	0.0	31.4	22.6	91	21.1	18.3	25	15.1
29	11	101	9.0	≈0.0003	0.065	0.3	0.3	39.1	27.3	91	33.2	22.1	22	14.3
30	11	101	9.0	0.39	0.038	0.2	0.1	39.1	27.3	75	8.4	5.6	45	9.7
31	11	105	9.0	0.19	0.050	0.4	0.3	39.1	27.3	86	8.6	5.9	43	10.4
32	11	102	9.0	0.19	0.049	0.4	0.4	39.1	27.3	84	7.3	6.4	47	10.9
Center trials														
Average										87	8.8	7.6	43	11.0
Standard deviation										3	1.3	2.2	3	1.5

II. Summary of high-pressure alkaline oxygen delignification trials

vide the required analytical expressions of the models' results, average values of temperature and of alkali and oxygen concentrations in each trial were used. The derivatives were calculated numerically.

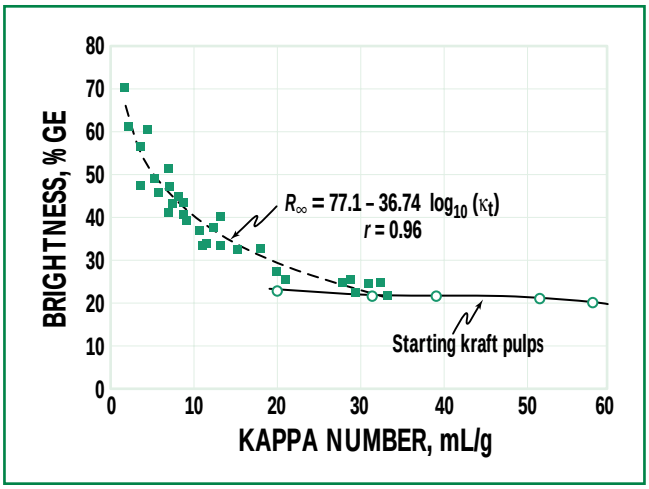
RESULTS AND DISCUSSION

General

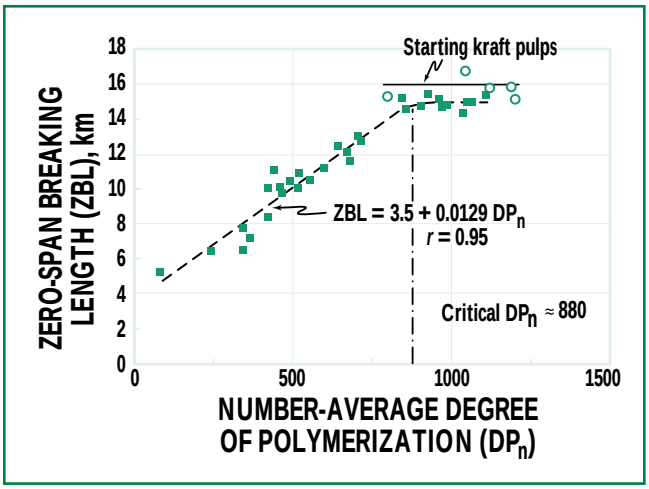
The results of the experiment are presented in **Table II**. All the response parameters (Y, κ_t, η_t, R_∞, ZBL) varied over relatively wide ranges. In particular, the final kappa numbers varied between 2 mL/g and 33 mL/g, and the final CED viscosities ranged from 2 mPa·s to 26 mPa·s. This is remarkable, considering that the maximum reaction time was only 21 min. The repeatability, as indicated by the standard deviation of six trials at the same target conditions, was reasonable. Yield was repeatable to ±3 yield percentage points, kappa number to ±1 mL/g, CED viscosity to ±2 mPa·s, brightness to ±3 GE percentage points, and zero-span breaking length to ±2 km. However, these figures imply a low resolution for the low-kappa-number, low-viscosity trials.

Internal associations

Significant internal associations were found among the response parameters. **Figure 4** shows the relationship between kappa number and



4. Relationship between brightness and kappa number



5. Relationship between number-average degree of polymerization and zero-span breaking length

brightness. Similar trends have been reported previously for oxygen delignification at conventional pressures *(12, 17, 18)*.

A nonlinear relationship between ZBL and CED viscosities was transformed into a fairly linear form when the latter were replaced by the corresponding number-average degree of polymerization (DP_n). **Figure 5** shows that ZBL increases in direct proportion to the average polysaccharide chain length and reaches a plateau over a critical DP_n value, around 880. This behavior is typical of polymeric materials, but it is generally difficult to observe when decreasing the DP_n of polysaccharides by pulping or bleaching, because other phenomena occur simultaneously *(19)*. The critical DP_n found in this work corresponds to a CED viscosity of 15 mPa·s (TAPPI T 230 om-89) and to an intrinsic viscosity of 800 dm^3/kg (SCAN C15–16:62). These figures are somewhat lower than typical values 20 mPa·s or 900 dm^3/kg reported elsewhere *(20, 21)*, probably because of the relatively low starting viscosity of loblolly pine kraft pulps in comparison with other softwood pulps.

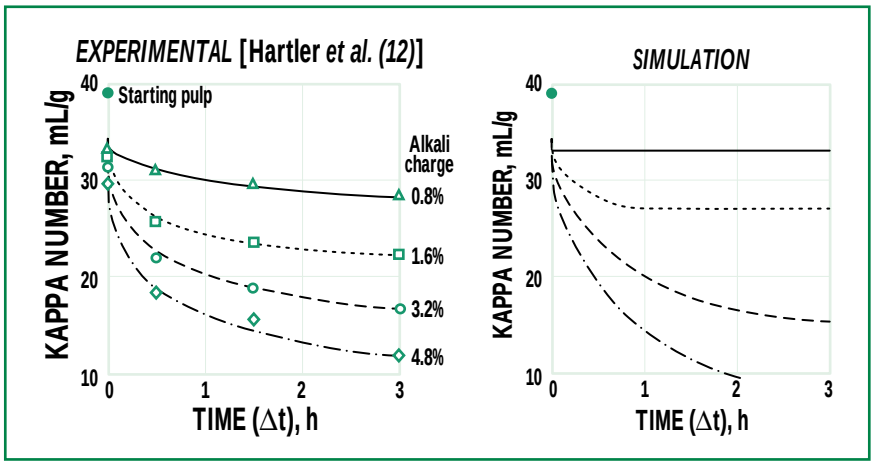
Reference	REACTION ORDER χ	ß[a]	α	Activation energy (*E*), kJ/mole
Hartler *et al. (12)*	n.a.	n.a.	n.a.	69
Edwards and Norberg *(26)*	2	n.a.	1[b]	48.6
Järrehult and Samuelson *(27)*	1	n.a.	n.a.	n.a.
Evans *et al. (28)*	1	1.23	1[b]	49.1
Olm and Teder *(1)*				
Initial (fast) phase	0.1	0.1	1	10
Final (slow) phase	0.3	0.2	1	45
Teder and Olm *(25)*	0.6	0.5	3.2	70
Kovasin *et al. (29)*	0.13	0.5	1	18.6
Hsu and Hsieh *(15)*				
Initial (fast) phase	0.78	0.35	3.07	36
Final (slow) phase	0.70	0.74	3.07	71
Myers and Edwards *(23)*				
Initial (fast) phase	0	0.43	1[b]	31.6
Final (slow) phase	0.875	0.43	1[b]	61.4
Vincent *et al. (24)*				
Initial (fast) phase	0	0.4	1[b]	24.2
Final (slow) phase	0.39	0.38	1[b]	46.3
Perng and Oloman *(18)*	0.4	0.5	4.8	60
This study	0.7	0.7	2.0	51
Initial phase	1.2	1.3	1	67
Final phase	0.3	0.2	1	40

[a]On concentration or pressure, according to the reference
[b]Over a "floor level" of lignin

III. Parameters of the apparent kinetic expression for alkaline oxygen delignification

Apparent delignification kinetics

As in other bleaching processes, alkaline oxygen delignification is characterized by a fast initial rate and a considerable slowdown as the reactions proceed. Abbot and Ginting *(22)* showed that these processes can be described with several different models, resulting in divergent interpretations. In this study, the high-pressure delignification data were



6. Effect of alkali charge on the batch oxygen delignification of kraft pulp (20% consistency, T = 100°C, p_{ox} = 0.5 MPa)

used to calculate the best parameters in two models: a single equation (high order) on lignin and two parallel equations (first order) on lignin. The general form of the rate expressions is:

$$-d\kappa_i/dt = k_i\, e^{-E/RT}[OH^-]^{\chi}[O_2]^{ß}\kappa_i^{\alpha} \quad (1)$$

where

E = activation energy
R = ideal gas constant
χ,ß,α = reaction orders.

In Eq. 1, a yield-weighted kappa number is used in place of lignin mass, kappa number being proportional to the lignin content of the remaining pulp. The calculated reaction orders are included in **Table III**, along with the corresponding values found in previous studies. For t expressed in min, κ in mL/g, and $[OH^-]$ and $[O_2]$ in mole/L, the rate constants of this study are

- single equation:

$$k = 3 \times 10^6 \ (r^2 = 0.92)$$

- parallel equations:

$$k_i = 6 \times 10^{11}$$

$$k_f = 6 \times 10^4 \ (r^2 = 0.97)$$

The initial condition for the parallel-equation model is:

$$\kappa_i(0) = 0.57\ \kappa_0$$

$$\kappa_f(0) = 0.43\ \kappa_0$$

The high-pressure single-equation delignification model is similar to the single-equation model proposed by Teder and Olm *(25)* for conventional oxygen pressure. The main differences are their higher reaction order with respect to lignin, 3.2, and their higher activation energy. Myers and Edwards *(22)* pointed out that high reaction orders on lignin reflect the use of only one initial lignin content and give abnormal reaction rates for high initial kappa numbers. The lower order in the present equation gives normal rates throughout. The higher activation energy is probably a consequence of the shorter range of temperatures that was studied.

The two equations in the present parallel model are:

$$-d\kappa_i/dt = 6 \times 10^{11}\, e^{-67/RT}[OH^-]^{1.2}[O_2]^{1.3}\kappa_i \quad (2)$$

$$-d\kappa_f/dt = 6 \times 10^4\, e^{-40/RT}[OH^-]^{0.3}[O_2]^{0.2}\kappa_f \quad (3)$$

At the average alkali and oxygen concentrations of this study, the model predicts that the initial delignification (Eq. 2) would be essentially complete in about 7 min. The final delignification (Eq. 3) would be much slower. However, at conventional oxygen pressure and decreasing alkali concentration, the relative importance of the rate expressions would be reversed, i.e., the second delignification rate (Eq. 3) would be higher than the first (Eq. 2). This is consistent with the models in previous studies, in that the rate expression with lower dependence with respect to alkali and oxygen corresponds to the "fast" delignification *(1, 23, 24)*.

Figure 6 shows the application of the parallel-equation model to simulate results of batch oxygen delignifications. The simulation assumes a stoichiometric coefficient of 1.33 x 10^{-3} g of NaOH per g of softwood pulp and per unit drop in kappa number, derived from experimental data *(17)* and industrial experience *(3)*.

An important characteristic of the present model is the high reaction orders with respect to alkali and oxygen in one delignification phase. Previous models *(1, 23, 24)* had smaller reaction orders with respect to alkali concentration and oxygen partial pressure or concentration. The differences can be attributed in part to the "salting-out" effect. The presence of alkali reduces the dissolved oxygen concentration at a given partial pressure and temperature, eventually decreasing the delignification rate. If the "salting-out" effect was not expressly accounted for, the apparent reaction orders with respect to alkali and oxygen would be lower. Additional evidence in support of the present rate expres-

sion includes the first order on alkali concentration found in the specific experiment of Järrehult and Samuelson *(27)* and the similar activation energies in the lignin-model studies of Ljunggren *et al. (30)*.

Apparent polysaccharide cleavage kinetics

The cleavage of polysaccharide chains was monitored by the increase in the number-average moles of cellulose per metric ton of pulp (m_n). To estimate the various m_n, the number-average degrees of polymerization (DP_n) were calculated using an equation by Godsay and Pearce *(31)*:

$$DP_n = 961.38 \log_{10}(\eta) - 245.3 \quad (4)$$

where

η = CED viscosity (T 230 om-89), mPa·s.

and the various m_n were inferred using the known molecular weight of the anhydro glucose unit:

$$m_n = 10^6/(162\ DP_n)\ \text{mole/Mg} \quad (5)$$

Kinetic calculations, using a single-equation model, showed that the reaction order with respect to the number of chains was essentially equal to zero (0.0 ± 0.7). The coefficient of determination did not change when zero-order dependence was forced in the model (r^2 = 0.96 in both cases). The equation is of the following general form:

$$dm_n/dt = k\ e^{-E/RT}[OH^-]^{\chi}[O_2]^{\beta} m_n^{\alpha} \quad (6)$$

The calculated reaction orders are included in **Table IV**, along with the corresponding values found in previous studies. For t expressed in min, m_n in mole/Mg, $[OH^-]$ and $[O_2]$ in mole/L, the rate constant, k, is 7 x 10^{10}. Thus, the present rate expression is:

$$dm_n/dt = 7 \times 10^{10}\ e^{-78/RT}[OH^-]^{0.3}[O_2]^{0.4} \quad (7)$$

The fact that it was not necessary to use two parallel equations to obtain zero-order apparent kinetics, as in Olm and Teder's work *(1)*, may be due to the different method of evaluating the various m_n or to a relatively low resolution in the present experiment.

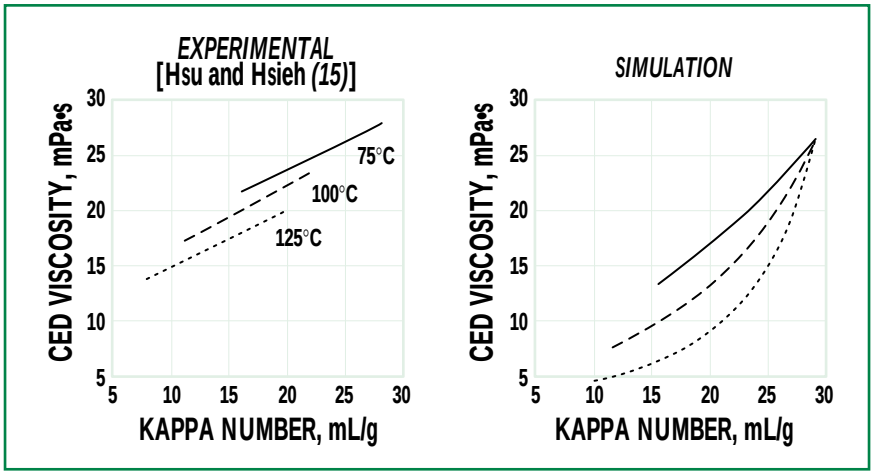
A simulation of Hsu and Hsieh's experiments *(15)*, using the present models, is presented in **Fig. 7**. A comparison with the experimental data indicates that, although the CED viscosities drop faster in the simulation, the change in selectivity with temperature follows a similar trend. The difference may be related to the use of 12% magnesium salt (as $MgSO_4 \cdot 7H_2O$ on o.d. pulp) by Hsu and Hsieh *(15)*, much more than used in this study.

Selectivity model

The delignification and polysaccharide cleavage models allow for direct evaluation of the oxygen delignification chemical selectivity, defined as the ratio of the delignification rate to the cleavage rate:

$$-d\kappa/dm_n = [-(d\kappa_i/dt)-(d\kappa_f/dt)]/(dm_n/dt) \quad (8)$$

Substitution of Eqs. 2, 3, and 7 into Eq. 8 gives:



7. Effect of temperature on the selectivity of oxygen delignification ([OH⁻] = 0.1 mole/L, p_{ox} = 0.34 MPa, [O_2] ≈ 0.003 mole/L, κ_0 = 29.5 mL/g, η_0 = 26 mPa · s)

Reference	REACTION ORDER χ	ß*	α	Activation energy (E), kJ/mole
Hartler et al. *(12)*	n.a.	n.a.	n.a.	86
Olm and Teder *(1)*				
Initial (fast) phase	0.2	0.8	0	40
Final (slow) phase	0.6	0.1	0	53
Perng and Oloman *(18)*	0.7	2.1	–5.3	94
This study	0.3	0.4	0	78

*On concentration or pressure, according to the reference

IV. Parameters of the apparent kinetic expression for polysaccharide cleavage during oxygen delignification

	H_2O	0.01*M* NaOH	0.1*M* NaOH
α_1	5.351	3.236	9.582
α_2	-1.252×10^{-2}	-7.466×10^{-3}	-2.436×10^{-2}
α_3	-7.954×10^{1}	-5.602×10^{1}	-9.477×10^{1}
α_4	2.135×10^{-4}	1.558×10^{-4}	2.517×10^{-4}
α_5	2.125×10^{4}	1.542×10^{4}	2.460×10^{4}

***V. Coefficients for estimating oxygen concentration in Eq. 10* (13)**

$$-d\kappa/dm_n = (9\ e^{11/RT}\ [OH^-]^{0.9}\ [O_2]^{0.9}\ \kappa_i) + (9 \times 10^{-7}\ e^{38/RT}\ [O_2]^{-0.2}\ \kappa_f) \quad (9)$$

Initially, before the exhaustion of κ_i lignin, the chemical selectivity would be maximized by high alkali and oxygen concentrations. In the second phase, the concentration of alkali would be unimportant, and a high oxygen concentration would be detrimental. This suggests that oxygen concentration should be reduced as much as possible after the first phase, e.g., by depressurization to atmospheric pressure. Additionally, both phases should be run at the minimum temperature compatible with the desired delignification.

The predicted effect of temperature on selectivity is consistent with the results of previous studies *(12, 15, 24)*. As a preliminary test of the other strategies proposed, two trial runs were done in two stages. The first stage consisted of 7 min of reaction at high oxygen pressure (16.4 MPa) and high initial alkali concentration (0.4 mole/L). The second stage was at atmospheric pressure with a lower alkali concentration, through exhaustion. Delignifications of 52% and 62% were achieved in total reaction times of 15 min and 30 min, respectively, while maintaining the CED viscosity over the critical value of 15 mPa·s. These promising results suggest that the use of higher pressures in the alkaline oxygen delignification of kraft pulps is a possibility worth considering.

KEYWORDS
Alkaline pulps, alkalinity, bibliographies, bond cleavage, carbohydrates, chemical properties, chemical pulps, chemical reactions, delignification, equations, high pressure, kraft pulps, nonmetals, oxygen, polysaccharides, pressure, reaction kinetics, sugars, vapor phase.

CONCLUSIONS

There was a strong association between the brightness and kappa number of high-pressure oxygen-delignified kraft pulps. The relationship is similar to that observed at conventional pressures.

There also was a strong association between zero-span breaking length (ZBL) and number-average degree of polymerization (DP_n) of the delignified pulps. The ZBL decreased under a critical DP_n value of 880.

The apparent delignification kinetics could be modeled in two phases, each first order on lignin content:

- One phase showed little dependence with respect to alkali and oxygen concentrations.
- The other phase was close to first order with respect to alkali and oxygen concentrations.
- The relative importance of the phases depends on the operating conditions. At high oxygen and alkali concentrations, the higher-order delignification rate would be faster.

The apparent polysaccharide cleavage kinetics during alkaline oxygen delignification could be modeled in one phase, 0.3- and 0.4-order with respect to alkali and oxygen concentration, respectively.

The delignification and polysaccharide cleavage models suggest that the selectivity can be maximized by:

- Low reaction temperatures
- A short first stage at high oxygen pressure and high alkali concentration
- A second stage at atmospheric pressure.

This strategy was shown to be beneficial in trial runs. **TJ**

Iribarne is a Ph.D. candidate and Schroeder is professor and chair of Paper Science and Engineering. Both are affiliated with the State University of New York, College of Environmental Science and Forestry, One Forestry Drive, Syracuse, NY 13210.

The authors thank Jon F. Myers of P.H. Glatfelter Co. for providing the loblolly pine logs used in the study. J. Iribarne was supported by an Amcham–Fulbright scholarship during the research.

Received for review June 22, 1995.
Accepted Sept. 19, 1996.
Presented at the TAPPI 1995 Pulping Conference.

APPENDIX

Estimation of oxygen concentrations

The estimation of the oxygen concentrations in the aqueous alkaline media was based on the equations of Brodén and Simonson *(13)*:

$$[O_2], \text{ mmole/L} = \alpha_1 + \alpha_2 T + \alpha_3 p_{ox} + \alpha_4 p_{ox} T^2 + \alpha_5 (p_{ox}/T) \quad (10)$$

where

T = saturation temperature, K

p_{ox} = partial pressure of oxygen, MPa

α = coefficients, which depend on the sodium hydroxide concentration, as indicated in **Table V**.

The equations are valid for T = 50–150°C and p_{ox} = 1–5 MPa. To extend their applicability to higher pressures, the predictions for pure water were compared with the high-pressure experimental results of Stephan *et al. (32)*. The comparisons indicate that Brodén and Simonson's equation is accurate to p_{ox} = 12 MPa and overestimates the concentrations at higher pressures. The ratio of predicted-to-actual concentrations increases fairly linearly with pressure and, therefore, the predictions can be corrected through the use of a factor:

$$f = 1.183 - 0.0184 p_{ox} \quad (11)$$

for p_{ox} > 12 MPa.

After the correction, the experimental results of Stephan *et al. (32)* could be predicted with a standard error of ±5 mmole/L (r = 0.993).

To estimate the oxygen concentration at any particular alkali concentration, including extrapolations to [OH^-] = 0.4 mole/L, a modified Stechenow equation was used:

$$[O_2] = f \cdot 10^{k[OH-]+c} \quad (12)$$

where k and c are coefficients obtained through regression of Brodén and Simonson's predictions at zero, 0.01M, and 0.1M NaOH, each calculated at the same temperature and oxygen partial pressure.

Effect of heat-up time

Seven "zero-time" control trials were performed to determine the effect of the heat-up time in the pulp samples. The different initial kappa numbers and target temperatures that were used in these trials covered the range of heat-up conditions in the main experiment. Although no alkali was added in these trials, the pH and conductivities of the effluents indicate that some residual alkali was present in the pulp and could be extracted with hot water. This should have resulted in the diffusion of lignin fragments, matching the "leaching" of kraft pulps reported by Favis *et al. (33)* and Li and MacLeod *(34)*. The heat-up with a continuous flow of water can also be associated with an enhanced pulp washing, which should result in additional delignification *(35)*. As oxygen was added at the end of the heat-up time, significant delignification reactions should also have occurred, particularly at high temperatures.

Delignifications ranged from 13% to 49% in the control trials. Delignification increased with both time and temperature, with an activation energy similar to that reported by Favis *et al*. for the "leaching" of kraft pulps: E = 75 kJ/mole *(33)*. The existence of similar phenomena in the control trials was further verified by a kinetic calculation. D-factors were defined as a relative measure of the reaction rate, with D = 1 at 100°C, using an activation energy of 75 kJ/mole. A good correlation was found between the logarithm of the D-factors and the delignifications in the control trials (r = 0.93). Therefore, the delignification during the heat-up time of the main experiment trials could be estimated with an equation of the type proposed by Hatton *(36)*:

$$\Delta(Y\kappa)/\kappa_0 = 0.346 + 0.05216 \log_{10}(D) \quad (13)$$

The cleavage of polysaccharides was monitored through the increase in the moles of cellulose per metric ton of pulp, Δm_n. In the control trials, Δm_n ranged from 0.03 mole/Mg to 3.65 mole/Mg. The values increased with time and temperature, with an activation energy similar to that reported by Kubes *et al.* for the alkaline hydrolysis of native cellulose: E = 179 kJ/mole *(37)*. Kubes *et al.* used this activation energy to define a time- and temperature-dependent kinetic coefficient, the G-factor. There was a good correlation between the logarithm of the G-factors and the logarithm of Δm_n in the control trials (r = 0.92). Thus, the increase in the moles of cellulose during the heat-up time of the main experiment trials could be estimated with a power function:

$$\Delta m_n = 0.479\, G^{0.2966} \quad (14)$$

LITERATURE CITED

1. Olm, L. and Teder, A., *Tappi* 62(12): 43(1979).
2. McDonough, T. J., *TAPPI 1992 Bleach Plant Operations Short Course Notes*, TAPPI PRESS, Atlanta, p. 99.
3. Tench, L. and Harper, S., *Tappi J.* 70(11): 55(1987).
4. Forbes, D. R., *Pulp Paper* 66(9): 79(1992).
5. Perala, J. and Germgård, U., *79th Annual Meeting Technical Section Preprints,* CPPA, Montréal, 1993, pp. A281–85.
6. Lachenal, D. and Nguyen-Thi, N. B., *ATIP* 48(2): 49(1994).
7. Malinen, R., Rantanen, T., Rautonen, R., *et al., International Pulp Bleaching Conference Papers,* CPPA, Montréal, 1994, pp. 187–94.
8. Gratzl, J. S., *Papier* 46(10A): V1(1992).
9. Hillström, R., Jamieson, A., Lindqvist, B., *et al., Svensk Papperstid.* 80(6): 167(1977).
10. Hsu, C. L. and Hsieh, J. S., *Tappi J.* 68(11): 126(1985).
11. Reeve, D. W., *Pulp and Paper Manufacture,* Vol. 5, "Alkaline Pulping," 3rd edn., Joint Textbook Committee TAPPI–CPPA, Atlanta–Montreal, 1989, pp. 389–469.
12. Hartler, N., Norrström, H., and Rydin, S., *Svensk Papperstid.* 73(21): 696(1970).
13. Brodén, A. and Simonson, R., *Svensk Papperstid.* 82(16): 487(1979).
14. Diamond, W. J., *Practical Experiment Designs for Engineers and Scientists*, 2nd edn., Van Nostrand Reinhold, New York, 1989, pp. 269–75.
15. Hsu, C. L. and Hsieh, J. S., *Tappi J.* 70(12): 107(1987).
16. Sundaresan, K. R. and Krishnaswamy, P. R., *Can. J. Chem. Eng.* 56(2): 257(1977).
17. Singh, R. P. and Dillner, B. C., "Oxygen bleaching," Chap. 7 in *The Bleaching of Pulp*, 3rd edn. (rev.), TAPPI PRESS, Atlanta, 1979, pp. 159–209.
18. Perng, Y.-S. and Oloman, C. W., *Tappi J.* 77(7): 115(1994).
19. Rydholm, S. A., *Pulping Processes,* Wiley (Interscience), New York, 1965, p. 1160.
20. Gustavsson, R. and Swan, B., *Tappi* 58(3): 120(1975).
21. Liebergott, N., van Lierop, B., Teodorescu, G., *et al., TAPPI 1987 International Oxygen Delignification Conference Proceedings,* TAPPI PRESS, Atlanta, p. 231.
22. Abbot, J. and Ginting, Y. A., *J. Pulp Paper Sci.* 18(3): J85(1992).
23. Myers, M. R. and Edwards, L. L., *Tappi J.* 72(9): 215(1989).
24. Vincent, A. H. D., Nguyen, K. L., and Mathews, J. F., *Appita* 47(3): 217(1994).
25. Teder, A. and Olm, L., *Paperi Puu* 63(4a): 315(1981).
26. Edwards, L. and Norberg, S., *Tappi* 56(11): 108(1973).
27. Järrehult, B. and Samuelson, O., *Svensk Papperstid.* 81(17): 533(1978).
28. Evans, J. E., Venkatesh, V., Gratzl, J. S., *et al., Tappi* 62(6): 37(1979).
29. Kovasin, K., Uusitalo, P., and Viilo, M., *TAPPI 1987 International Oxygen Delignification Conference Proceedings,* TAPPI PRESS, Atlanta, p. 223.
30. Ljunggren, S., Gellerstedt, G., and Pettersson, M., *Proceedings of 6th International Symposium on Wood and Pulping Chemistry,* Vol. 1, Appita, Melbourne, 1991, pp. 229–36.
31. Godsay, M. P. and Pearce, E. M., *TAPPI 1984 Oxygen Delignification Symposium Proceedings*, TAPPI PRESS, Atlanta, p. 55.
32. *IUPAC Solubility Data Series* (R. Battino, Ed.), Vol. 7, "Oxygen and Ozone," Pergamon, Oxford, 1981, pp. 462–63.
33. Favis, B. D., Willis, J. M., and Goring, D. A. I., *J. Wood Chem. Technol.* 3(1): 1(1983).
34. Li, J. and MacLeod, J. M., *J. Pulp Paper Sci.* 19(2): J85(1993).
35. Mao, B. and Hartler, N., *Nordic Pulp Paper Res. J.* 9(2): 134(1994).
36. Hatton, J. V., *Tappi* 56(7): 97(1973).
37. Kubes, G. J., Fleming, J. M., MacLeod, J. M., *et al., TAPPI 1981 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 423.