Development and verification of a predictive oxygen delignification model for hardwood and softwood kraft pulp

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ABSTRACT *General, predictive oxygen delignification kinetic equations for both softwood and hardwood kraft pulps are presented. The same kinetic equations apply for initial kappa numbers from 11 to 128 and for all consistencies up to 30%. The kinetic parameters (such as activation energy) and stoichiometric parameters in the model are determined by using a nonlinear, least-squares analysis on data from several different literature sources. The kinetics have been imbedded into a complete model that can be used to design and troubleshoot oxygen delignification stages in both high-consistency and medium-consistency mill systems.*

KEYWORDS
Kinetics
Mathematical models
Oxygen delignification
Process simulation
Pulping

Under environmental constraints, many mills are now being considered for possible retrofits with oxygen delignification. In the design stage, the size of the oxygen delignification tower, the temperature, and the chemical charges need to be optimized. System variables such as the optimum amount of washing and the location of the washers should be optimized, and a control strategy must be developed. These decisions could be made more easily using a predictive model.

We have developed and tested new kinetic equations and have incorporated these into an oxygen-delignification-stage model that applies to all reactor configurations. For example, the model can be used to evaluate and summarize batch laboratory data collected at constant oxygen pressure. The laboratory kinetic equations can then be used in the complete oxygen-stage model to design and evaluate alternative medium-consistency and high-consistency mill systems.

Previous kinetic models

The first oxygen-delignification kinetic model for high consistency was proposed in 1973 by Edwards and Norberg (*1*). In the kinetic model, Eq. 1, they used a dimensionless lignin concentration and proposed the idea of a lignin "floor level," meaning lignin that will not react in any reasonable length of time.

$$dK'/dt = k\,K'^{a}\,[OH]^{b} \qquad (1)$$

Teder and Olm (*2*) published the following kinetic rate equation:

$$dK/dt = k\exp(-E/RT)P^{0.5}_{oxygen}\,[OH]^{0.6}K^{3.2} \qquad (2)$$

This equation is over third order with respect to the kappa number and is not applicable to widely varying inlet kappa numbers because of the falsely large dependence on the kappa number.

Hsu and Hsieh (*3*) proposed a reaction rate for the first 2 min of the reaction and a second rate for times greater than 2 min. For the first 2 min:

$$dK/dt = k\exp(-E/RT)\,[OH]^{0.78}P^{0.35}_{oxygen}K^{3.07} \qquad (3)$$

For reaction times greater than 2 min:

$$dK/dt = k_2\exp(-E_2/RT)\,[OH]^{0.70}P^{0.74}_{oxygen}K^{3.07} \qquad (4)$$

This kinetic model fits some experimental data well, but if the initial kappa number is raised slightly, the reaction rate increases too much (i.e., to the third power). Hsu and Hsieh used only one initial kappa number in their experiments.

I. Experimental data for batch oxygen delignification compared with "best fit" model predictions of final kappa number

Data no.	Actual kappa no. Initial	Actual kappa no. Final	Predicted kappa no.	Error, %	Reaction time, min	Fraction caustic charge on pulp	Temp., °C	Oxygen pressure, psig	Wood species	Lit. ref.
1	29.5	25.0	23.0	-8.1	2	0.2	75	144.8	A	3
2	29.5	24.3	22.6	-6.8	5	0.2	75	144.8	A	3
3	29.5	23.1	22.2	-3.9	15	0.2	75	144.8	A	3
4	29.5	22.1	21.6	-2.5	30	0.2	75	144.8	A	3
5	29.5	20.7	20.7	0.2	50	0.2	75	144.8	A	3
6	29.5	20.0	20.0	-0.2	70	0.2	75	144.8	A	3
7	29.5	23.5	22.8	-2.9	2	0.6	75	144.8	A	3
8	29.5	21.9	22.3	1.7	5	0.6	75	144.8	A	3
9	29.5	20.6	21.1	2.6	15	0.6	75	144.8	A	3
10	29.5	19.1	19.6	2.4	30	0.6	75	144.8	A	3
11	29.5	18.6	17.7	-5.0	50	0.6	75	144.8	A	3
12	29.5	16.8	16.0	-4.7	70	0.6	75	144.8	A	3
13	29.5	20.5	21.9	7.0	5	1	75	144.8	A	3
14	29.5	20.0	20.2	1.1	15	1	75	144.8	A	3
15	29.5	17.5	17.9	2.5	30	1	75	144.8	A	3
16	29.5	16.3	15.3	-5.8	50	1	75	144.8	A	3
17	29.5	15.0	13.2	-11.9	70	1	75	144.8	A	3
18	29.5	18.8	20.7	10.4	3	1	100	144.8	A	3
19	29.5	17.0	19.4	14.1	5	1	100	144.8	A	3
20	29.5	15.0	16.5	10.2	10	1	100	144.8	A	3
21	29.5	12.5	14.2	13.4	15	1	100	144.8	A	3
22	29.5	12.0	12.2	1.9	20	1	100	144.8	A	3
23	29.5	16.5	19.9	20.5	1.2	1	125	144.8	A	3
24	29.5	14.0	16.4	17.2	2.9	1	125	144.8	A	3
25	29.5	11.3	13.5	20.1	4.7	1	125	144.8	A	3
26	29.5	9.0	10.0	11.3	7.7	1	125	144.8	A	3
27	29.5	6.8	7.7	13.9	10.6	1	125	144.8	A	3
28	29.5	21.5	21.7	0.7	3.6	0.6	100	50.6	A	3
29	29.5	20.0	20.9	4.6	5.9	0.6	100	50.6	A	3
30	29.5	17.0	18.3	7.6	15	0.6	100	50.6	A	3
31	29.5	15.0	14.8	-1.4	30	0.6	100	50.6	A	3
32	29.5	13.8	12.1	-12.3	45	0.6	100	50.6	A	3
33	29.5	20.0	21.4	6.9	3.6	0.6	100	99.9	A	3
34	29.5	17.5	20.2	15.2	6.8	0.6	100	99.9	A	3
35	29.5	15.0	17.4	16.0	15	0.6	100	99.9	A	3

A = Southern pine, B = Northern softwood, C = hardwood.
*Caustic charge was not given, so it was estimated to be 0.025.

Improved kinetic model

In 1975, Ackert, Koch, and Edwards (*4*) published a kinetic delignification model for chlorination that separated lignin into three categories: fast, slow, and nonreacting (floor level). This model makes the kinetics first order in each lignin type. Teder and Olm (*2*) applied this same model to oxygen delignification but tested it with data that did not specifically eliminate mixing effects.

We have improved this fast-slow lignin kinetic model by:

1. Expanding coverage to literature data from various sources in which mixing effects have been eliminated. The database includes hardwood and softwood, all consistencies up to 30%, and initial kappa numbers from 11 to 128.
2. Using the dissolved oxygen concentration rather than partial pressure, since oxygen solubility depends on temperature as well as pressure.
3. Including nonlinear caustic consumption (*6*).

The form of the kinetic model is then:

$$dK_f/dt = k_f \exp(-E_f/RT)\,[O_2]_{liq}^{r} K_f \quad (5)$$

$$dK_s/dt = k_s \exp(-E_s/RT)\,[O_2]_{liq}^{r} K_s\,[OH]^{s} \quad (6)$$

with

$$K = K_f + K_s + K_b$$

with initial conditions of

$$K_f = w_f K_i \quad (7)$$

$$K_s = w_s K_i \quad (8)$$

The oxygen consumption is linear:

$$\alpha = \text{kg } O_2/\text{kg of lignin reacted} \quad (9)$$

The consumption of caustic (*6*) is not linear:

$$\%\ \text{NaOH/pulp} = K_i\,(K_i\ /K_{out} - 1)/19.6 \quad (10)$$

With the oxygen delignification kinetics and stoichiometry described in terms of Eqs. 5–10, the parameters r, s, k_f, k_s, E_f, E_s, w_s, w_f, and α must be determined. All of the constants except α are determined from laboratory oxygen delignification data in the literature.

Estimation of kinetic parameters

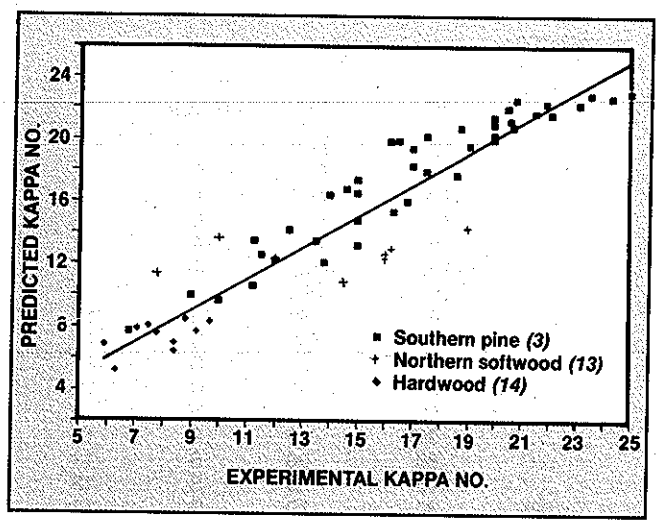
We conducted an extensive literature search to obtain a database for deter-

Data no.	Actual kappa no. Initial	Final	Predicted kappa no.	Error, %	Reaction time, min	Fraction caustic charge on pulp	Temp., °C	Oxygen pressure, psig	Wood species	Lit. ref.
36	29.5	13.5	13.5	-0.3	30	0.6	100	99.9	A	3
37	29.5	11.2	10.6	-5.3	45	0.6	100	99.9	A	3
38	29.5	20.8	22.5	8.2	1	0.6	100	144.8	A	3
39	29.5	16.2	19.8	22.3	6.8	0.6	100	144.8	A	3
40	29.5	14.6	16.8	14.9	15	0.6	100	144.8	A	3
41	29.5	11.5	12.6	9.4	30	0.6	100	144.8	A	3
42	29.5	10.0	9.7	-3.3	45	0.6	100	144.8	A	3
43	22.0	19.0	14.3	-24.6	20	...*	90	80	B	13
44	22.0	16.0	12.3	-22.8	40	...*	90	80	B	13
45	22.0	14.5	10.9	-25.2	60	...*	90	80	B	13
46	22.0	16.0	12.6	-21.1	40	...*	90	60	B	13
47	22.0	16.2	13.0	-19.9	40	...*	90	40	B	13
48	22.0	12.0	12.3	2.9	40	...*	90	80	B	13
49	22.0	10.0	13.7	36.7	40	...*	80	80	B	13
50	22.0	7.8	11.4	45.9	40	...*	95	80	B	13
51	12.3	8.8	8.5	-3.5	20	0.025	80	80	C	13
52	12.3	7.8	7.6	-2.3	40	0.025	80	80	C	13
53	12.3	5.9	6.9	16.5	60	0.025	80	80	C	13
54	12.3	7.8	7.6	-2.3	40	0.025	80	80	C	13
55	12.3	6.3	5.2	-17.0	40	0.025	100	80	C	13
56	12.3	7.5	8.1	7.8	40	0.025	80	20	C	13
57	12.3	7.1	7.9	11.2	40	0.025	80	40	C	13
58	12.3	9.2	7.7	-15.8	40	0.025	80	60	C	13
59	12.3	7.8	7.6	-2.3	40	0.025	80	80	C	13
60	12.3	9.7	8.3	-13.9	40	0.015	80	80	C	13
61	12.3	7.8	7.6	-2.3	40	0.025	80	80	C	13
62	12.3	8.4	7.0	-16.7	40	0.035	80	80	C	13
63	12.3	8.4	6.5	-23.2	40	0.045	80	80	C	13
64	11.0	9.8	5.5	-43.9	40	0.025	80	80	C	13
65	11.0	9.4	2.9	-69.4	40	0.025	100	80	C	13
66	128.9	90.0	83.4	-7.3	10	0.05	105	150	A	14
67	101.0	50.9	58.5	14.9	10	0.05	105	150	A	14
68	44.2	16.0	17.8	11.3	10	0.05	105	150	A	14
69	56.8	24.5	25.1	2.4	10	0.05	105	150	A	14

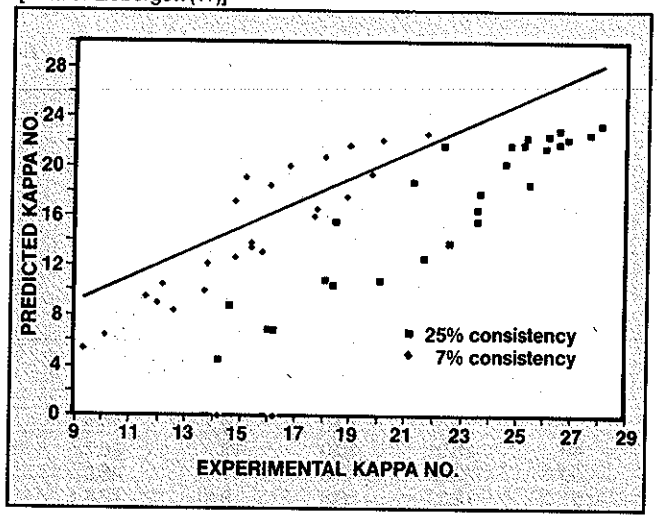
mining the constants in Eqs. 5-10. During the literature search, it became apparent that many laboratory systems for oxygen delignification studies had inadequate mixing and that pilot-scale and plant systems had more adequate mixing. Sources of laboratory oxygen delignification data for kraft pulps are:

1. Olm and Teder (*9*) whose experiments were shown by Hsu and Hsieh (*3*) to have insufficient mixing. Olm and Teder obtained different delignification rates for different consistencies with constant chemical concentrations, which reflects bad mixing.
2. Evans *et al.* (*10*) conducted experimental oxygen delignification at 1.57% consistency and obtained reaction rates much slower than those obtained by Hsu and Hsieh (*3*). The conclusion again is that there was insufficient mixing.
3. Liebergott *et al.* (*11*) obtained, at high consistency, delignification rates that are not as rapid as others reported in literature; this is because the reaction time included a heat-up period.
4. Hartler *et al.* (*12*) do not discuss mixing and collected delignification data in a manner which makes it difficult to estimate the starting time on the reaction.
5. Näsman and Annergren (*5*) obtained faster delignification rates in their pilot plant than they measured in the laboratory. This discrepancy was credited to poor mixing in the laboratory.
6. Hsu and Hsieh used low-consistency oxygen delignification with mixing (*3*). Since the consistency was shown to have no effect on the experimental delignification rates, the data are assumed to have "good" mixing. From Hsu and Hsieh, we used 42 data points (Southern pine) for estimating the kinetic parameters (**Table I**).
7. Duff *et al.* (*13*) designed a laboratory reactor specifically to determine mixing effects on oxygen delignification. From these data, we used 8 data points for two unspecified types of Northern softwood kraft pulps and 15 data points for two types of hardwood (Table I) to estimate the kinetic parameters.
8. Southern pine data from North Carolina State University (*14*) for a variety of initial kappa numbers at high consistency are also in-

1. Predicted vs. actual kappa numbers for batch oxygen delignification



2. Predicted vs. actual kappa numbers for batch oxygen delignification [data of Liebergott (11)]



II. Experimental data for medium-consistency plug flow oxygen delignification compared with predictions of final kappa number

Actual kappa no.		Predicted kappa no.	Reaction time, min	Caustic, %	Temp., °C	Oxygen, %	Top pressure, psig
Initial	Final						
30	18	21.5	80	3.0	100	1.0	72.8
30	21	22.7	80	1.5	90	0.9	72.8

cluded in the database for estimating the kinetic parameters.

All of the data used to determine the kinetic constants are listed in Table I along with the predicted kappa numbers from the final kinetic expressions. Since the model is nonlinear, we used a nonlinear least-squares technique (*8*).

The resulting kinetic equations for the fast and slow lignin are:

$$dK_f/dt = 1.51 \times 10^5 \exp(-31.6/RT)\,[O_2]_{liq}^{0.43} K_f \quad (11)$$

$$dK_s/dt = 1.68 \times 10^7 \exp(-61.4/RT)\,[O_2]_{liq}^{0.43} K_s\,[OH]^{0.875} \quad (12)$$

where the oxygen concentration in the liquid is expressed as kg/m³.

The initial conditions are:

$$K_f = 0.225K_i \quad (13)$$

$$K_s = 0.675K_i \quad (14)$$

The final kinetic model accounts for 96% of the variation in the data (i.e., $R^2 = 0.96$), which is reasonable since the same model was fit to data from three different sources including hardwoods, northern softwoods, and southern pine for consistencies up to 30% and initial kappa numbers from 11 to 128. A plot of predicted kappa numbers against actual kappa numbers shows that the points are clustered around the 45° line (**Fig. 1**).

However, some particular data points do not fit the model well at all. Consider Data Points 64 and 65 from Table I. These are a "different" hardwood compared to the other hardwood data. Compared with Data Points 61 and 55, respectively, the experimental final kappa values for Points 64 and 65 are much too high and are omitted from Fig. 1.

In the Northern softwood data from Duff (*13*), no caustic charge was given, so a 2.5% caustic charge was assumed. This is probably the reason for the apparent systematic error in the model for Northern softwood shown in Fig. 1.

The average error of the model predictions is 10% or 1.6 kappa units (omitting Data Points 64 and 65). In an actual industrial application, the model would be tuned for a specific pulp, and the prediction would be better.

Activation energies reported for data with poor mixing are 10,000 J/(mol°K) and 45,000 J/(mol°K), respectively, for the fast and slow lignin (*2*). The activation energies for Eqs. 3 and 4 with good mixing are reported to be 36,000 J/(mol°K) and 71,000 J/(mol°K), respectively, for lignin reacting in first 2 min and after 2 min. These latter activation energies are relatively close to the values determined in this work, especially considering the difference in the kinetic models.

The model was used to check the oxygen delignification rates measured by Liebergott *et al.* (*11*) for black spruce. We used only a portion of the data, since there are several hundred data points. **Figure 2** shows that the final kappa numbers predicted by the model are generally lower than Liebergott's experimental kappa numbers, although some of the low-consistency data are in close agreement. This discrepancy is because the reaction time included a heat-up period.

Mass transfer or mixing

Chemical reactions are the rate-

Notation

Primary notation is as follows:

E = activation energy of lignin reactions, kJ/kmol

K = kappa number

K' = dimensionless lignin concentration in pulp

k = pre-exponential rate constant for lignin reactions

$[O_2]$ = dissolved oxygen concentration, kg O_2/m^3 liquor

[OH] = hydroxide concentration, kg/m^3 liquor

P = pressure, MPa

R = gas constant, 8.314 kJ/(kmol°K)

T = temperature, °K

t = time, min

w = weighting factor

α = oxygen consumption, kg O_2/kg lignin reacted.

Subscripts are:

b = "floor" kappa no.

f = fast lignin

i = initial condition

liq = liquor

out = final condition

s = slow lignin.

Superscripts are:

a, b = reaction order

r = exponent for oxygen dependency

s = exponent for hydroxide dependency.

controlling steps that take place in oxygen delignification. For batch oxygen delignification with good mixing, the reaction rate has been shown to be much smaller than any mass transfer effects (*3*). With well-mixed gas, liquor, and pulp, there will be no mass-transfer limitations in the initial fast-delignification phase if the chemical supply surrounding the fibers is present in sufficient quantity. In the second part of the oxygen delignification reaction, which takes place slowly, mass transfer is much more rapid than the delignification.

Complete oxygen-stage model

Equations 5–10 describe oxygen delignification in isothermal batch reactors at constant oxygen pressure but are not directly applicable to mill-scale reactors. These equations have been incorporated into a complete oxygen stage model using the technique described by Kovasin *et al.* (*7*) to account for pressure changes as the pulp rises in a medium-consistency, upflow tower. The reactor model goes beyond Kovasin's by including temperature changes caused as heat is released during oxygen delignification. This change is especially important at higher consistencies.

To test the complete oxygen-stage model, we used data obtained on an industrial scale for delignification of 65% Japanese hardwood, 30% West Australian eucalyptus, and 5% New Zealand beech (*15*). The average inlet kappa number was 19.8, with an average discharge kappa number of 9.8. When the model was used with an oxygen consumption α of 0.8 kg O_2/kg lignin, the predicted outlet kappa number was 8.9, without any tuning.

The complete reactor model was also checked against data from pilot-plant, medium-consistency oxygen delignification of a Scandinavian pine kraft pulp (*5*). **Table II** shows a comparison of the actual and predicted kappa numbers for two pilot plant cases.

Conclusions

Oxygen delignification kinetic equations for kraft pulps have been developed that give reasonable predictions of outlet kappa numbers both for hardwood and softwood kraft pulp. The kinetic model overcomes some of the problems with previous oxygen delignification models, such as unrealistically high order on lignin.

The kinetic model has been successfully incorporated into a complete oxygen-stage model to predict mill-scale performance.□

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