Reaction Kinetics in Oxygen Bleaching

The oxygen bleaching of wood pulp takes place in a heterogeneous system involving oxygen (gas), water (liquid), and fiber (solid). Inconsistent effects of process variables (reaction temperature, alkali concentration, and oxygen pressure) on the overall oxygen delignification rate of wood pulp in various reacting systems have been reported in the literature.

An apparent intrinsic reaction rate model, excluding the interphase mass transfer effects, has been developed based on oxygen bleaching experiments in an agitated and ultralow-consistency (solids content) reactor. The apparent intrinsic reaction rate model shows a faster delignification rate than those reported in the literature. The degree of inadequate delignification observed in the literature data is likely to be caused by insufficient mass transfer of bleaching chemicals to fibers.

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Introduction

To comply with more stringent environmental regulations, oxygen was introduced as a possible first bleaching stage in pulp mills in 1970. The use of oxygen before chlorination in the pulp bleaching plant can reduce the wastewater effluent chemical oxygen demand (COD) by 50% and biological oxygen demand (BOD) by 25–50% while saving chemical costs by more than 25% through decrease use of chlorine, chlorine dioxide, and hypochlorite (Waldestam et al., 1980; Croon and Larsson, 1983).

Oxygen bleaching is a heterogeneous reaction which occurs in a system comprising fiber (solid), water (liquid), and oxygen (gas). The reaction kinetics depends on reaction temperature, oxygen pressure, and alkali concentration as well as adequate mixing of oxygen and alkali with fibers. Most kinetic studies on oxygen bleaching have been focused on overall delignification rates. The effects of process variables on the overall delignification rate, as reported by various authors and shown in Table 1, have been inconsistent.

Although different reactors at high (30–22%), medium (16–8%) and low (4–2%) consistencies have been developed in the industry, the fundamental mass transfer and kinetic problem in oxygen bleaching is not well understood (Elton et al., 1980; Kirk et al., 1978; Kleppe et al., 1981; Nasman and Annergren, 1980). This may be attributed to the limited knowledge of lignin chemistry in fibers and the complex characteristics of pulp slurries with irregular and flexible fiber structures.

To simplify the system, oxygen bleaching experiments were performed in an agitated reactor at ultralow consistency. The interphase mass transfer rates were found to have no effect on the overall delignification rate. The intrafiber mass transfer resistance was likely to be insignificant if the prediction by the Weisz-Prater criterion is valid (Froment and Bischoff, 1979).

However, the intrafiber mass transfer and the intrinsic reaction rates were considered together here as an apparent intrinsic reaction rate to include the possible effect of the intrafiber mass transfer on the overall delignification rate. An apparent intrinsic reaction rate model was developed based on the experimental data at 0.4% consistency. The degree of inadequate delignification observed in the literature data as compared to this study is likely to be caused by insufficient mass transfer of bleaching chemicals to fibers.

Background

The effect of process variables on oxygen delignification rates without mixing was first investigated by Hartler et al. (1970) in Sweden. They claimed that oxygen pressure, ranging from 3.1×10^5 to 1.7×10^6 N/m^2 and pulp consistency, ranging from 5 to 30%, had no effect on the reduction of Kappa number. (The estimated percent lignin content is equal to $0.147 \times$ Kappa number for Kraft pulp [Casey, 1980].)

These results were inconsistent with later studies by Hsu and Hsieh (1985a, b, 1986). For a medium consistency pulp (10 and 14%), both oxygen pressure and consistency did affect the delignification rate.

Evans et al. (1979) also studied the kinetics of low-consistency oxygen delignification. Based on the order of magnitude for activation energy predicted by their model, they concluded that diffusion might be important. This was contrary to

Table 1. Effect of Process Variables on Delignification Rate

Ref.	Alkali Conc.	O_2 Partial Press.	Activation Energy × 10^{-3} J/kmol
Hartler et al. (1970)	No numerical values reported	Insignificant in O_2 partial press. range 3.1×10^5 to 1.7×10^6 N/m^2	68,970
Edwards & Norberg (1973)	Reaction order of 2	No effect at excess O_2 conc.	48,590
Evans et al. (1979)	Reaction order of 1 or 2	Reaction order of 1.23–1/24	46,600–49,000
Olm & Teder* (1979)	Reaction orders of 0.1 and 0.3	Reaction order of 0.1–0.3	44,700 & 9,900

*With two stages of kinetics

Hartler's conclusion that oxygen bleaching was chemical-reaction rate limited.

Edwards and Norberg (1973) developed a general kinetic model applied to oxygen bleaching at a constant oxygen pressure. They assumed that the oxygen delignification rate was controlled by the chemical reaction rate, without experimental verification.

Jarrehult and Samuelson (1978) used a very low consistency (0.2 and 1.0%) pulp to eliminate the effect of alkali charge depletion on the delignification rate. In their experiments, the delignification of pulp was observed during a preheating period with alkali in solution. Thus the true initial delignification rate could not be obtained from their data.

Olm and Teder (1979) developed oxygen bleaching kinetic data with two pseudofirst-order reactions. However, fiber overlapping in the pulp bed of their studies could interfere with the mass transfer of bleaching chemicals to individual fibers.

Theory

A diagram of the microscopic bleaching process for a single fiber in an agitated reactor at ultralow consistency is shown in Figure 1. The bleaching process is described as follows:

1. Oxygen transfer from the gas phase through a gas film into the gas-liquid interfacial boundary
2. Oxygen transfer from the interfacial boundary through a liquid film into the bulk liquid phase
3. Diffusion and convection of oxygen molecules from the bulk phase into the liquid layer surrounding the fiber
4. Diffusion of OH^- ions and oxygen molecules through the liquid layer to the fiber
5. Interfiber mass transfer for the multifiber structure
6. Intrafiber mass transfer with fiber delignification at reaction sites in the fiber

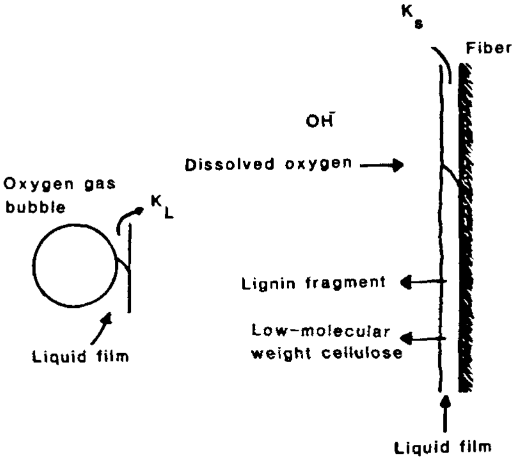

Figure 1. Microscopic oxygen bleaching process of a single fiber.

The following assumptions were made for the proposed model:

1. The liquid-to-fiber ratio is high enough that the fibers are completely dispersed and suspended in the liquid phase.
2. The NaOH solution is well mixed before injection of oxygen gas.
3. With oxygen bleaching carried out in a highly agitated pressurized tank, the oxygen concentration in the bulk phase is assumed to be uniform.
4. The resistance of transfer of oxygen molecules from the gas phase into the liquid phase is mainly in the thin film near the gas-liquid interfacial boundary.
5. The interfiber mass transfer is greatly reduced for a well-dispersed and agitated system.
6. The dissolved lignin does not affect the transfer of oxygen molecules and OH ions due to its very low concentration in the liquid phase.

The overall delignification rate can therefore be formulated as

$$F = F(k_L a_L, k_S a_S, k, [OH^-], P_0, K, T). \qquad (1)$$

For oxygen-liquid mass transfer in an agitated reactor with fibers suspended in the liquid phase, the following equation can be used to determine the $k_L a_L$:

$$\frac{dC_L}{dt} = k_L a_L (C_L^* - C_L) \qquad (2)$$

Since fibers are circulated in an agitated reactor, the liquid-solid mass transfer is considered to be carried out by the diffusion mechanism (Satterfeld, 1970). Thus the Sherwood number, $k_S \cdot dp/D = 2$, is used in this study.

Experimental Method

Pulp preparation and experimental setup

A southern pine Kraft pulp (Kappa number = 29.5, viscosity = 26 cp [0.026 Pa · s]) was used in these experiments. As shown in Figure 2, the apparatus consisted mainly of 1 L pressurized reactor equipped with a stirrer. The reactor temperature was computer-controlled. In the gas-absorption experiments, the regulating valve for the NaOH solution was removed and the open port was used for liquid sampling.

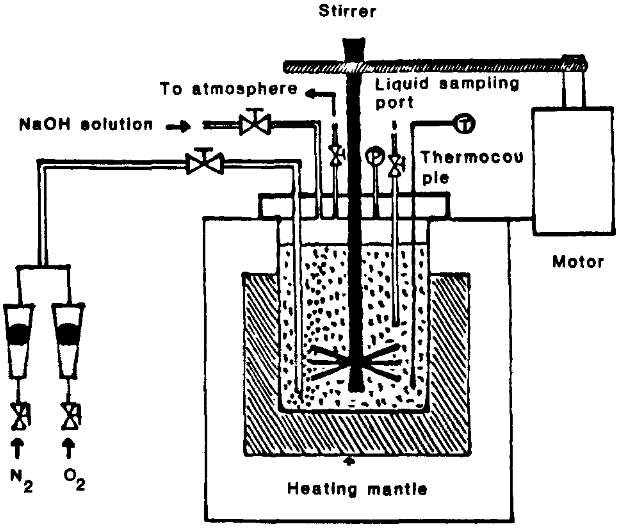

Figure 2. Experimental setup for oxygen bleaching experiments.

Gas-liquid mass transfer

The diffusivity of carbon dioxide in water is very close to that of oxygen in water (Jhaveri and Sharma, 1967). The gas-side resistances of these two gases are negligible in comparison with the liquid-side resistance. Therefore, carbon dioxide was used here to determine the gas-liquid volumetric mass transfer coefficients because its concentration in water could be more accurately measured by the wet chemistry method.

Initially, 850 mL distilled water, 3.4 g unbleached pulp, and 0.38 g $MgSo \cdot 7H_2O$ (a protector for carbohydrates in oxygen bleaching) were introduced into the reactor. The stirrer was set at the desired speed. Then the reactor was heated to 55°C under a nitrogen atmosphere. Liquid samples were withdrawn with a 20 mL syringe to avoid absorption and desorption of gas. The first sample was withdrawn before injection of carbon dioxide. The partial pressure of carbon dioxide was maintained at 1 atm thereafter. Each sample was added to a solution of sodium hydroxide and barium chloride to transform the absorbed carbon dioxide into barium carbonate according to the reaction

$$2\,NaOH_{(aq)} + BaCl_{2(aq)} + CO_{2(g)} \longrightarrow 2\,NaCl_{(aq)} + BaCO_{3(s)} + H_2O \quad (3)$$

The excess sodium hydroxide was titrated with hydrochloric acid.

Oxygen bleaching

In the oxygen bleaching experiments, the same amounts of materials were used as in the gas-liquid mass transfer experiments. Initially, nitrogen was bubbled through the solution for 5 min to purge the system. Then the reactor was heated under agitation to the reaction temperature at 3.8×10^5 N/m^2 nitrogen atmosphere. During the heating period, the prepared NaOH solution was placed inside a feeding tube. High-pressure nitrogen forced the NaOH solution into the reactor when the temperature reached the set point.

After feeding the NaOH solution, oxygen was injected and bubbled through the solution very quickly to reach the desired oxygen pressure above the liquid phase. The oxygen gas flow rate was then regulated to maintain the normal operating conditions. The oxygen pressure was held constant by an outlet flow valve located on top of the reactor.

At the end of each experiment, the reactor was opened quickly and the solution inside was poured into cold water. The pulp slurry was filtered through a Buchner funnel and washed completely. The washed pulp was dried in air for one day before testing. The Kappa number and viscosity tests were performed according to TAPPI standard testing methods (TAPPI, 1980).

Results and Discussion

Mass transfer effect

The volumetric mass transfer coefficients at the operating conditions were obtained by correcting the values from the carbon dioxide absorption experiments, Figure 3, with the surface renewal theory

$$K_L = C\sqrt{D} \tag{4}$$

where C is a constant and independent of pressure (Sherwood et al., 1975).

The effect of reaction conditions on the Kappa number reduction vs. the volumetric mass transfer coefficients is shown in Figure 4. It is interesting to note that even when the mass transfer rate was increased up to seven times, Kappa number reduction did not show any significant change. Therefore, it was concluded that the gas-liquid mass transfer resistance was negligible in comparison to the apparent intrinsic reaction rate during the 30 min reaction time.

The liquid-fiber volumetric mass transfer coefficient was estimated to be about 7 by the equation

$$k_S a_S = 2.0\left(\frac{D}{d_p}\right) a_s \tag{5}$$

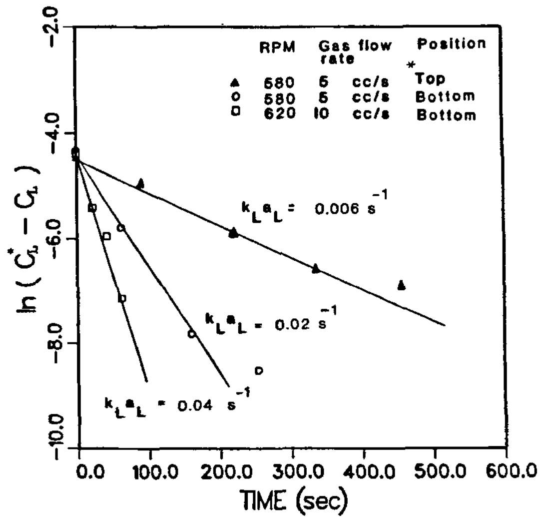

Figure 3. Gas-liquid mass transfer coefficients determined by gas absorption method.

*Position: Top, O_2 injected above solution surface; Bottom, O_2 injected below solution surface

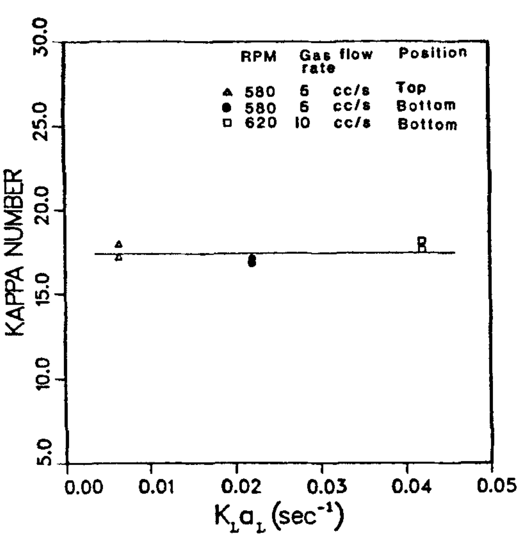

Figure 4. Effect of mass transfer on Kappa number reduction.

$T = 100°C$; $[OH^-] = 0.02$ kmol/m^3; $P_0 = 7.9 \times 10^5$ N/m^2
Reaction time, 30 min; pulp consistency, 0.4%; initial Kappa no., 28.5

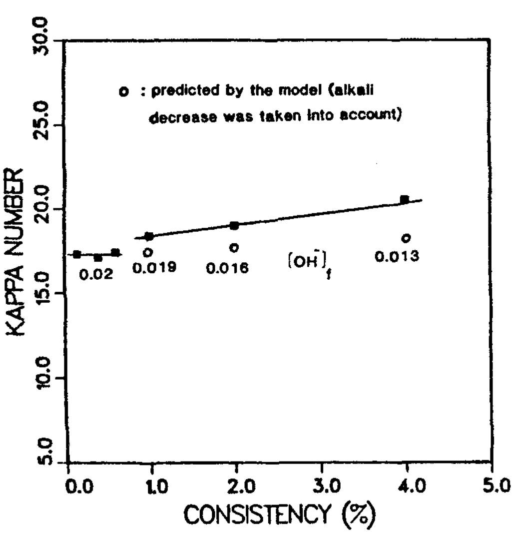

Figure 5. Effect of consistency on Kappa number reduction.

Data as in Figure 4.

where the numerical values of D, d_p, a_S are estimated to be respectively 2.6×10^{-9} m^2/s, 4.4×10^{-5} m, and 5.8×10^4 m^{-1} (Sherwood et al., 1975; Casey, 1980; Reeve, 1985).

Since the liquid-fiber mass transfer rate is roughly 150 times faster than the gas-liquid mass transfer, due to a much larger liquid-fiber surface area, it is assumed that the liquid-fiber transfer resistance is negligible in comparison with the apparent intrinsic reaction rate. Therefore, under the agitated and low-consistency conditions, it is concluded that interphase mass transfer resistance is negligible.

The effect of intrafiber diffusion was estimated by the Weisz-Prater criterion (Froment and Bischoff, 1979)

$$\Phi = \frac{r_{obs}L^2}{D_e C_s} \tag{6}$$

The consumption of oxygen in the reaction with the lignin was experimentally found to be of the order of 10^{-5} (kmol O_2/Kappa number kg oven-dry fiber) by Thompson and Corbelt (1975). The r_{obs} value was estimated to be in the order of 10^{-2} C_{O_2} (kmol O_2/s · m^3) by taking the fiber density (Britt, 1970) and the Kappa number reduction rate into account. The cylindrical fiber characteristic length was found to be 10^{-6} m (Casey, 1980). Since there were no reported data for oxygen diffusivity inside the fibers, this factor was estimated using a bulk oxygen diffusivity in the liquid phase divided by a tortuosity conservatively estimated to be on the order of 10^2.

The Weisz-Prater criterion thus calculated was of the order 10^{-3}. With its value being much less than 1, it is likely that the intrafiber mass transfer resistance was insignificant in comparison to the intrinsic reaction rate if the prediction of the Weisz-Prater criterion is valid.

Consistency effect

As consistency increases in the ultralow-consistency reactor, fibers start to tangle, lowering the delignification rate. The effect of consistency on Kappa number reduction is shown in Figure 5. When consistency was gradually increased from 0.6 to 4%, alkali concentration in the liquid phase could not be maintained constant. Open data points represent those obtained at 0.4% consistency, taking the alkali concentration decrease into account by the model developed below.

When the consistency was decreased from 0.6 to 0.15%, the Kappa number reduction did not change. It was concluded that the effect of fiber entanglement on the overall delignification rate has been eliminated at this ultralow-consistency range. Therefore, we concluded that the apparent intrinsic reaction kinetics can be obtained using data at 0.4% consistency.

Apparent intrinsic kinetic model development

The oxygen bleaching experiments were conducted at 0.4% consistency with three levels of process variables—reaction temperature, alkali concentration, and oxygen partial pressure—to obtain the apparent intrinsic reaction rate. Reaction conditions were chosen to be 75, 100, and 125°C reaction temperature; 0.02, 0.06, and 0.1 kmol/m^3 NaOH concentration; and 4.4×10^5, 7.9×10^5, and 1.1×10^6 N/m^2 oxygen partial pressure. To obtain more reliable conclusions and better model development, more than 150 runs were conducted.

Figures 6 to 8 show that increases in any of the three process variables can increase the Kappa number reduction at either the initial or the later stage. The kinetic data were fitted with the least-square error method by an empirical model.

$$-\frac{dK}{dt} = k \exp\left(-\frac{E}{RT}\right)[OH^-]^m P_o^n K^o \tag{7}$$

A nonlinear least-square Gauss-Newton method (Dennis and Schnabel, 1983) was used to obtain the optimal values of m, n, o, k, and E. The fitted equation was obtained as

$$-\frac{dK}{dt} = 0.24 \exp\left(-\frac{8.3 \times 10^7}{RT}\right)[OH^-]^{1.0} P_o^{0.89} K^{6.27} \tag{8}$$

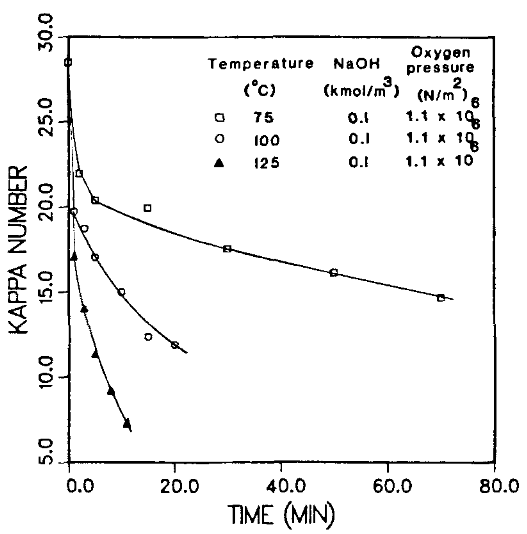

Figure 6. Effect of temperature on delignification rate.

with a correlation coefficient of 0.92.

The high reaction order on the Kappa number resulted from a sharp decrease of the delignification rate during the run. This suggested that the following two-stage model might better describe the experimental data:

$$-\frac{dK}{dt} = 2.46 \exp\left(-\frac{3.6 \times 10^7}{RT}\right) [\mathrm{OH}^-]^{0.78} P_o^{0.35} K^{3.07} [u(t) - u(t-2)] + 143.49 \exp\left(-\frac{7.1 \times 10^7}{RT}\right) [\mathrm{OH}^-]^{0.70} P_o^{0.74} K^{3.07} u(t-2) \quad (9)$$

with a correlation coefficient of 0.97. The unit step function, $u(t)$, was used to imply that in the first 2 min of reaction time, the kinetic equation was described by the first term and during the rest of the reaction time was described by the second term.

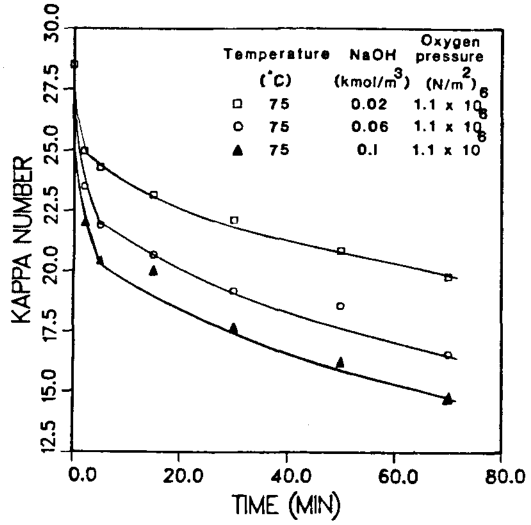

Figure 7. Effect of alkali on delignification rate.

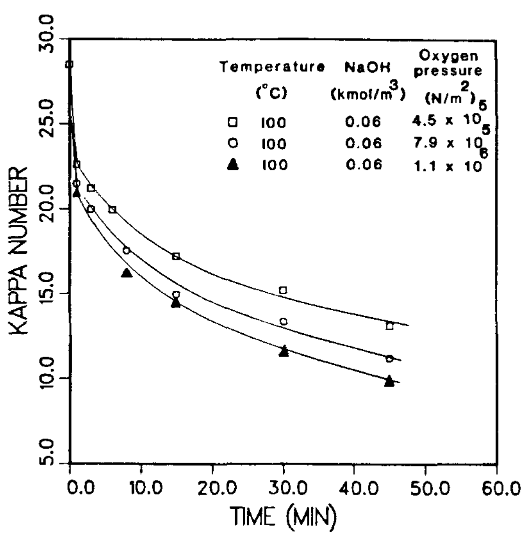

Figure 8. Effect of oxygen pressure on delignification rate.

Comparison with literature data

The kinetic data obtained in this ultralow-consistency reactor were compared with those in the literature. Figure 9 compares the kinetics at ultralow consistency with that at medium consistency (Hsu and Hsieh, 1985a, b). The mixing of NaOH with pulp was done manually for the runs at medium consistency. At the beginning of the run, both had the same alkali concentrations. Figure 9 shows that at 10% consistency, Kappa number reduction was much slower than that at 0.4% consistency in both the initial and later stages.

Figure 10 shows the same comparison with the data of Olm and Teder (1979). Both sets of data had constant alkali concentration; the slow Kappa number reduction in these studies mainly resulted from inadequate mixing of pulp and bleaching chemicals.

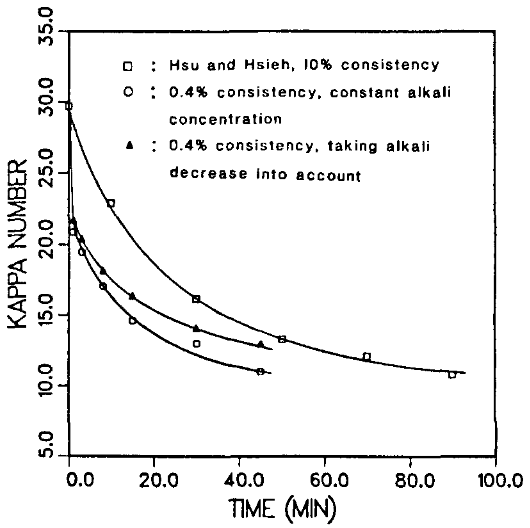

Figure 9. Kinetics comparison, data of Hsu and Hsieh (1985) and this work.

T = 100°C; $P_0 = 7.9 \times 10^5$ N/m²
□ Initial $[\mathrm{OH}^-]$ = 0.1 kmol/m³
○ $[\mathrm{OH}^-]$ = 0.1 kmol/m³

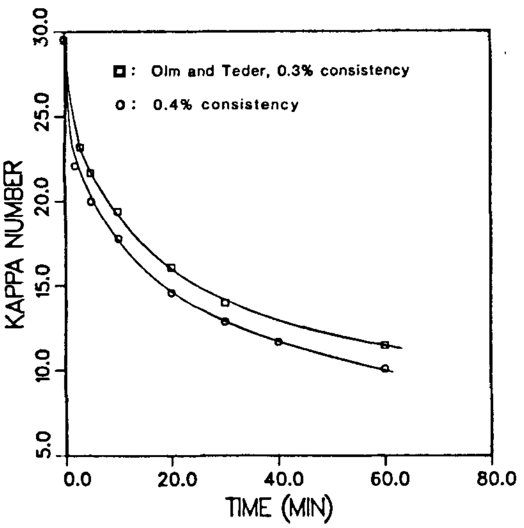

Figure 10. Kinetics comparison, data of Olm and Teder (1979) and this work.
$T = 110°C$; $[OH^-] = 0.02$ kmol/m^3; $P_0 = 1.1 \times 10^6$ N/m^2

Figure 11 compares the kinetics of the present study with that of Evans et al. (1979). The decreasing alkali concentration was incorporated into our study by the two-stage model. Figure 12 compares the kinetic data with those obtained from an industrial type high-shear mixer (Nasman and Annergren, 1980) at 10% pulp consistency. It shows that Kappa number reductions at ultralow consistency were faster in both the initial and later stages. However, when the alkali decrease is taken into account, the ultralow-consistency kinetics approach those of the industrial high-shear mixer.

Conclusions

1. In an agitated and ultralow-consistency (0.4%) reactor, no significant effects of oxygen mass transfer on the delignification rate were observed either from experimental or theoretical approaches.

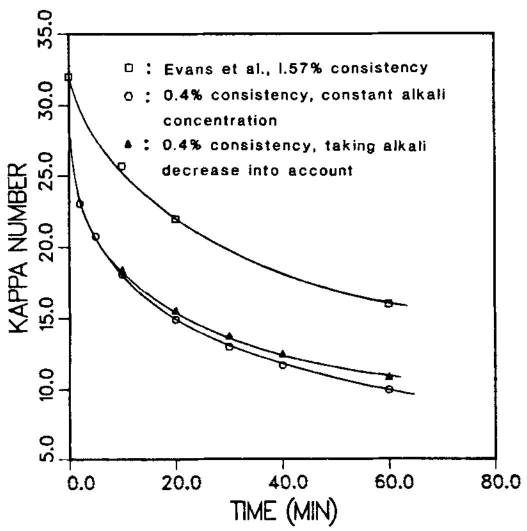

Figure 11. Kinetics comparison, data of Evans et al. (1979) and this work.
$T = 110°C$; $P_0 = 1.1 \times 10^6$ N/m^2
□ Initial $[OH^-] = 0.02$ kmol/m^3
O $[OH^-] = 0.02$ kmol/m^3

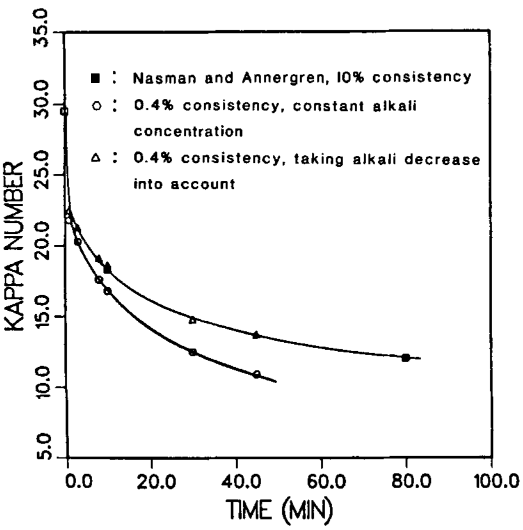

Figure 12. Kinetics comparison, data of Nasman and Annergran (1980) and this work.
$T = 100°C$; $P_0 = 6.0 \times 10^5$ N/m^2
■ Initial $[OH^-] = 0.1$ kmol/m^3
O $[OH^-] = 0.1$ kmol/m^3

2. When the consistency of pulp in this system was increased from 0.4 to 4%, a decrease in Kappa number reduction was observed. This was attributed to the inadequate mixing of the higher consistency slurry and decreasing of alkali concentration in the liquid phase.

3. When the consistency dropped from 0.4 to 0.3 or 0.2%, the Kappa number reduction change was insignificant. This led to the conclusion that the effect of other fiber entanglements on the overall delignification rates was eliminated in this range of consistency.

4. An apparent intrinsic reaction rate model in oxygen bleaching has been developed based on the experimental data at 0.4% consistency. The result predicted by this model has a faster delignification rate than those reported in the literature because of improved mass transfer of bleaching chemicals to the individual fibers. The reduction of the delignification rate caused by inadequate mass transfer of the bleaching chemicals to fibers could be quantified by comparing the experimental data with those obtained from the apparent intrinsic reaction rate model.

Acknowledgment

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Notation

a_S = fiber surface area, m^{-1}
C = solute concentration, kmol/m^3
C_S = solute concentration at liquid-solid interface, kmol/m^3
C^* = equilibrium solute concentration, kmol/m^3
d_p = fiber diameter, m
D = solute diffusivity in liquid phase, m^2/s
D_e = effective solute diffusivity in fiber, m^2/s
E = activation energy, N · m/kmol
k = apparent reaction rate constant, including intrafiber mass transfer phenomena and intrinsic raction rate, Kappa no./min/(kmol/m^3)^m/(N/m^2)^n/(Kappa no.)^o

k_La_L = volumetric gas-liquid mass transfer coefficient, s^{-1}
k_Sa_S = volumetric liquid-solid mass transfer coefficient, s^{-1}
K = Kappa number
L = fiber characteristic length in Weisz-Prater criterion, m
m = reaction order of Kappa no. in apparent reaction rate
n = reaction order of alkali concentration in apparent reaction rate
$[OH^-]$ = alkali concentration in solution, kmol/m^3
P_o = oxygen partial pressure, N/m^2
r = observed oxygen reaction rate, kmol O_2/s · m^3
R = gas constant, 8,314 J/kmol · K
t = reaction time, min
T = temperature, K
$u(t)$ = unit step function

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