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Oxygen Delignification Kinetics: CSTR and Batch Reactor Comparison

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In the past, oxygen delignification studies were mostly performed in batch reactors, whereby the caustic and dissolved oxygen concentrations are changing during the reaction. Also the lignin content and cellulose degradation of the pulp are only established at the end of an experiment when the sample is removed from the reactor. To overcome these deficiencies, a differential reactor system (called Berty reactor) has been adopted. In this continuous stirred-tank reactor (CSTR), the dissolved oxygen concentration and the alkali concentration in the feed are kept constant, and the rate of lignin removal is determined from the dissolved lignin concentration in the outflow stream measured by UV–vis spectroscopy. The delignification rate is found to be first-order in HexA-free residual lignin content. The delignification rate reaction order in [NaOH] and oxygen pressure are 0.412 ± 0.060 and 0.305 ± 0.260 respectively. The activation energy is 54.5 ± 6.8 kJ/mol. *AIChE J,* 53: 2681–2687, 2007
Keywords: oxygen delignification, kinetics, model

Introduction

Oxygen delignification is widely used for lignin removal before bleaching pulp. The well known advantages of oxygen delignification over extended cooking are chemical cost savings, yield retention and improved environmental.[1] Since oxygen delignification is accompanied by undesirable cellulose degradation, better understanding of oxygen delignification kinetics and its relation to cellulose degradation may point to improved operation in industrial practice. Therefore, a kinetic study of oxygen delignification should include the kinetics of both delignification and cellulose degradation. Normally, delignification is measured by the decrease of Kappa number, which is an indirect method to measure lignin content of pulps. Cellulose degradation is monitored by the decrease in intrinsic viscosity [η] of pulps. However, it is now well known that the kappa number does not correctly represent the amount of residual lignin in the pulp, since hexenuronic acid (HexA) and other nonlignin structures also consume $KMnO_4$ in the kappa number measurement.[2] In this study, the HexA content was considered in the reaction modeling. A new and significant aspect of this approach is that the experimental technique allows determination of the reaction rate dependence on lignin content in the pulp at constant dissolved oxygen and alkali concentrations. Delignification rates are measured using a differential continuous stirred-tank reactor (CSTR), where the dissolved oxygen concentration and the alkali concentration in the feed are kept constant, and the rate of lignin removal is determined from the dissolved lignin concentration in the outflow stream measured by UV–vis spectroscopy.[3]

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Kinetic modeling

The kinetics of oxygen delignification are usually presented by a power-law equation which includes the influence of the process variables, such as reaction temperature, oxygen pressure and caustic concentration[4]

$$-r_L = -\frac{dK}{dt} = k[OH^-]^m P_{O2}{}^n K^q \tag{1}$$

where K is the kappa number; $[OH^-]$ is the caustic concentration and P_{O2} is the absolute oxygen pressure. The constants m,

Table 1. Summary of Kinetics Equations Using the Power-Law Model

Reference	$[OH^-]$ Exponent (m)	$[O_2]$ or Po_2 Exponent (n)	Kappa Number Exponent (q)	Activation Energy (kJ/mol)	Frequency Factor (A)
Agarwal(1998)	–	–	7.7	–	–
Perng (1997)	0.4	0.5	4.8	60	1.8
Teder (1981)	0.6	0.5	3.2	70	–
Kovasin (1987)	0.13	0.5	1	18.6	–
Iribarne (1997)	0.7	0.7	2.0	51	3×10^6
Evans (1979)	1	1.23	1	49.1	10^5

n, and q are obtained by fitting of the experimental data. The reaction-rate coefficient k depends on the temperature, and is assumed to follow the Arrhenius form

$$k = A \exp\left(-\frac{E_A}{RT}\right) \tag{2}$$

where E_A is the activation energy (J/mol), R is the ideal gas constant (8.314 J/mol·K), T is the absolute temperature (K) and A is a preexponential factor $(\text{min}^{-1})(\text{g/L})^{-\text{m}}(\text{psia})^{-\text{n}}$.

A summary of the different power-law equations reported in the literature for oxygen delignification is given in Table 1.

The reaction orders m, n and the activation energy in Table 1 are difficult to compare, because the experiments were done with different pulps. It can also be seen that reaction order in kappa number varies from 1 to 7.7, and the activation energies range from less than 20 to 70 kJ/mol. The results in Table 1 were obtained from batch reactors, where [NaOH] was changing during the reaction and influenced the rate calculation.

Cellulose degradation

The cleavage of cellulose polymers was modeled by Iribarne and Schroeder[4] as the increase in number-average moles of cellulose per gram of pulp (m_n). Similarly, cellulose degradation can be described by the number of cellulose chain scissions during oxygen delignification. Violette and van Heiningen[10] calculated the number of cellulose chain scissions from the average degree of polymerization of cellulose (DP) in the pulp at time $t = 0$, and time $t = t$, that is, as $1/\text{DP}_\text{t} - 1/\text{DP}_0$.

DP can be obtained from the intrinsic viscosity $[\eta]$ by

$$DP = \left(\frac{1.65[\eta] - 116H}{G}\right)^{1.111} \tag{3}$$

where $[\eta]$ is intrinsic viscosity of the pulp in cm^3/g, and G and H are the mass fractions of cellulose and hemicelulose in the pulp.[11] This formula assumes the viscosity depends on the mass of cellulose rather than the total pulp mass, and corrects for the small contribution of the hemicelluloses to the pulp's intrinsic viscosity.

The number of moles of cellulose per gram of pulp m_n, can be calculated by

$$m_n = \frac{1}{162DP_n + 18} \cong \frac{1}{162DP_n}\left(\frac{Moles\ Cellulose}{Gram\ Pulp}\right) \tag{4}$$

where the factor of 162 is the molecular weight of the anhydroglucose unit, and 18 is the molecular weight of water.[4]

Experimental

Oxygen delignification experiments were performed both in a CSTR, and a batch Parr reactor. The Parr reactor is a 2 L horizontal stainless steel reactor obtained from Parr Instruments, with an anchor rotating device that wipes the inside of the reactor with Teflon blades. Figure 1 shows the Parr reactor system.

The flow diagram of the CSTR system is shown in Figure 2. Oxygen from a gas cylinder is bubbled into a NaOH solution contained in a pressurized (maximum 130 psig) 12 L stainless steel container. The container is kept at a controlled temperature by an external heating blanket. The CSTR reactor is a 280 mL Berty style reactor (Autoclave Engineers) with a 100 mL stationary basket which holds the pulp bed. A rotor underneath the basket induces flow through the pulp bed. The entire reactor is filled with liquid, and any gas inside the reactor is vented at the top of the reactor. For each experiment, oxygen was bubbled overnight through the NaOH solution to obtain a saturated oxygen concentration. Then the reaction was started by feeding the oxygenated caustic solution at constant flow rate and oxygen pressure. The reactor pressure, temperature and outflow rate were recorded every 5 s, and the UV–vis absorption of the outflow stream was recorded every 15 s.

Commercial unbleached softwood pulp sheets were homogenized. Oxygen delignification was done at 90°C, 75 psig, 3.0% NaOH (on oven dry pulp), and 10% consistency (g of pulp/100 g pulp suspension) in the batch reactor. In the CSTR, the reaction conditions were 90°C, 75 psig, 3.3 g/L NaOH and 4.0 g pulp in the reactor basket. The volume of the CSTR basket is 100 mL. The pulp consistency in the basket was about 10%, which is close to the batch reactor experiment. The reaction times for batch reactor and CSTR experiments were 10, 20, 40, 60 and 180 min. Because we used large excess alkali and oxygen, the concentrations in the feed and the exit of the CSTR

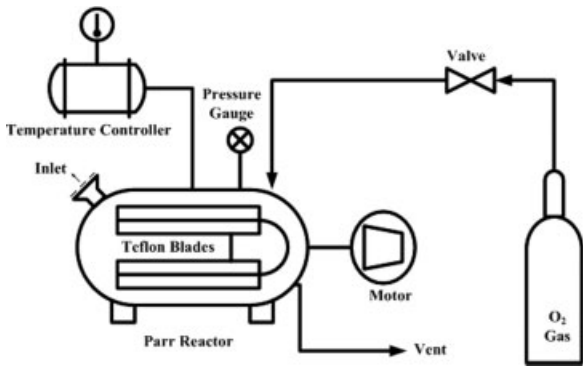

Figure 1. Horizontal Parr reactor system.

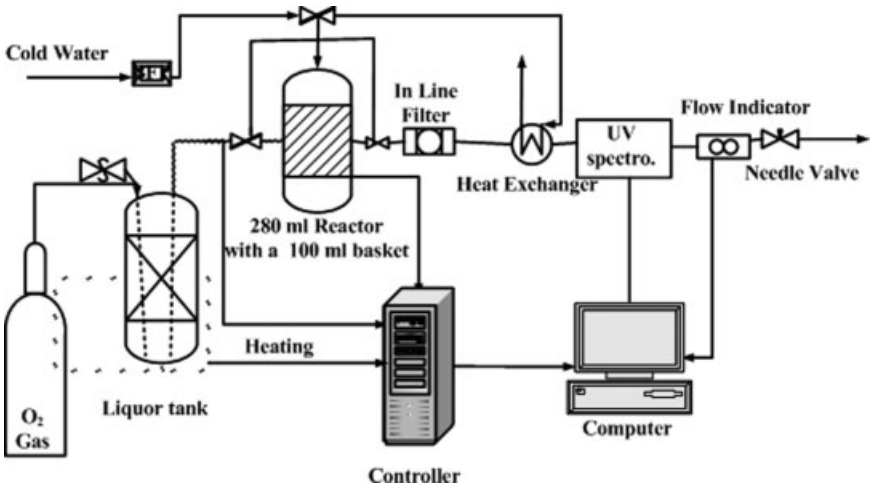

Figure 2. CSTR reactor system.

were approximately the same. This was verified for the alkali by comparing the pH of the feed and product streams. The 3.3 g/L NaOH concentration used in the CSTR was calculated based on the 3.0% NaOH charge in the batch reactor, so that the NaOH concentration in the CSTR would be essentially identical to the initial concentration in the batch reactor. The following calculation shows how the concentration in the CSTR was determined:

Batch reactor conditions: 10% consistency, 4.0 g pulp, 3% NaOH

Total NaOH = $4.0/0.10 \times 0.03 = 1.2$ g

Total liquid = $4/0.10 - 4.0 = 36$ g

CSTR Equivalent: NaOH concentration = $1.2/36 = 0.033 = 3.3\%$.

Raw Materials

The oxygen delignification rate was studied using a commercial unbleached southern pine kraft pulp with an initial Kappa number of 24.4, and intrinsic viscosity of 1,189 mL/g.

Measurements

The dissolved lignin concentration was measured using a flow cell, and a HP8453 UV–vis spectrophotometer from Agilent. The absorption at 280 nm was converted to lignin concentration using a calibration curve prepared from purified lignin-Indulin AT from Mead-Westvaco. It is found that the extinction coefficient of the purified lignin is 24.8 L g^{-1} cm^{-1}. Since lignin structures may change during oxygen delignification, the lignin extinction coefficient may be different over the reaction time. However, we closed the lignin mass balance using klason lignin and UV absorption at 280 nm for the samples at five different reaction times using the calibration curve.[3] This shows that the lignin extinction coefficient does not change significantly during oxygen delignification. The work of Camilla Roost et al. also shows that lignin structure does not change much before and after oxygen delignification.[12] Additionally, some other chemicals formed during oxygen delignification may have an absorption at 280 nm, which interferes with the calculation of total removed lignin amount. However, the amount is negligible at regular experiment conditions. It should be pointed out that the influence of other chemicals' absorption at 280 nm can be obvious when the experiment is done at very long time, high alkali concentration, high-temperature and high-pressure. Yun Ji's PhD thesis shows that the experiment at 6 h, 115°C and 90 psig, the calculated lignin is more than the lignin present in the original pulp.[13] The kappa numbers of the pulps were measured using the TAPPI standard method T236-cm-85. We also tested the kappa number and viscosity from different locations inside the pulp bed. The results show that the pulp is uniformly treated. However, since the amount of pulp in the basket is rather small, the kappa test method was modified such that all of the chemical dosages were reduced to one tenth of the amount in the TAPPI method. Intrinsic viscosities of the pulps were determined following the A.S.T.M. designation D1795-62 (reapproved 1985). The HexA group content was determined after acid hydrolysis of the pulps, and UV measurement of the hydrolysis products (2-furoic acid and 5-carboxy-2-furaldehyde), which have a clear absorption peak at 245 nm. The HexA content of the final pulp samples generated at 90°C, 3.3 g/L NaOH and 75 psig in the CSTR reactor were measured. The HexA content of all the samples was between 21 and 23 μmol/g pulp, confirming that HexA is stable during oxygen delignification. Because HexA contributes to the kappa number, the residual lignin content in the pulp was corrected for the HexA content in the pulp. Typically, 10 μmole HexA corresponds to between 0.86−1.1 kappa units.[14,15] In this study, 10 μmol HexA is considered as 1 kappa unit, thus, the residual lignin content in pulp was calculated by

$$L_c = \left(Kappa - \frac{HexA}{10}\right) \times 1.5 \quad \left(\frac{\text{mg lignin}}{\text{g pulp}}\right) \tag{5}$$

The pulp in this study contained an average of 22 μmol HexA/g pulp, which is equivalent to 2.2 kappa units or 3.3 mg ($22/10 \times 1.5 = 3.3$ mg) lignin/g pulp.

The monosugars were measured by HPAEC with two-stage hydrolysis. (The first stage is performed in 72% H_2SO_4 at 30°C, while the second stage is performed in 4% H_2SO_4 at 121°C.)

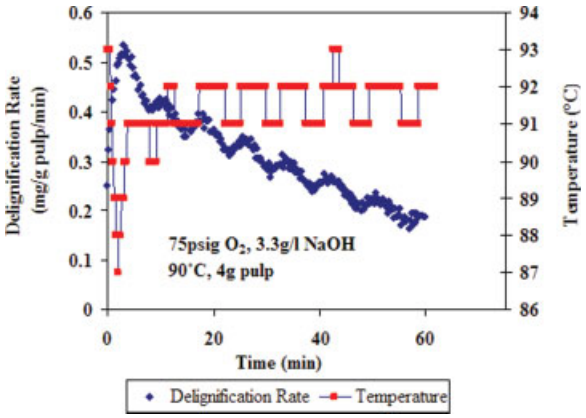

Figure 3. Delignification rate and reaction temperature vs. time.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Data Analysis Procedure

The CSTR methodology was validated by showing that the oxygen delignification kinetics are not influenced by the amount of pulp in the reactor, the feed flow rate, and rotor speed (over 400 rpm).[3] Most experiments were performed with 4 g (oven dry basis) of pulp, because of the volume of the basket and analysis requirements. The dissolved lignin mass balance for the well mixed reactor during time interval dt, is:

$$\text{Inflow-Outflow} + \text{Dissolved by Reaction} = \text{Accumulated in Reactor}$$

or

$$0 - \phi_v C(t)dt + r(t)m_p dt = V_r dC(t) \tag{6}$$

or

$$r(t) = \left[\phi_v C(t) + V_r \frac{dC(t)}{dt}\right]\frac{1}{m_p} \tag{7}$$

where $r(t)$ is the rate of delignification (mg lignin/g pulp/min); Φv is the liquid-flow rate (mL/min); $C(t)$ is the dissolved lignin concentration (mg lignin/mL); Vr is the reactor volume (mL), and mp is the pulp weight (o.d pulp).

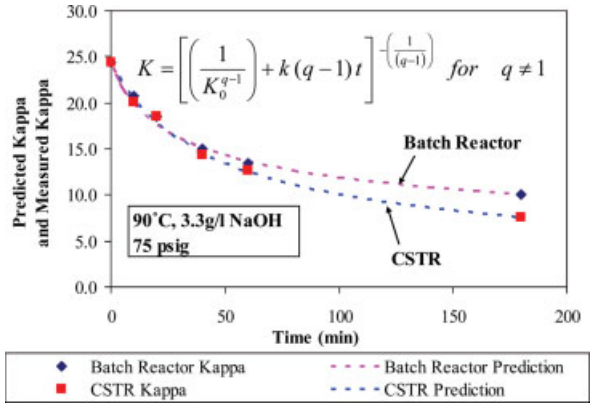

Figure 4. Kappa number model and experimental CSTR and batch reactor data.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The reactor volume Vr, was determined by a residence-time distribution (RTD) experiment using a step-input with methyl red tracer. Analysis of the RTD determined that the Berty reactor and piping up to the UV–vis detector could be described by a CSTR of 265 mL, and a plug-flow volume of 96 mL. This closely agrees with our estimate of the free volume in the reactor and piping, respectively. Therefore, $V_r = 265$ mL, and the residence time between the Berty reactor and UV detector t_d is

$$t_d = \frac{96}{\phi_v} \tag{8}$$

Thus, the dissolved lignin concentration inside the Berty reactor at time t, $C(t)$, is equal to the concentration measured by UV at time $t + t_d$, $C_L\,(t + t_d)$

$$C(t) = C_L(t + t_d) \tag{9}$$

and

$$r(t) = \frac{\phi_v}{m_p} C_L(t + t_d) + \frac{V_r}{m_p}\frac{dC_L}{dt}\Big|_{t+t_d} \tag{10}$$

The amount of lignin removed from the pulp at time t is

$$\phi_v \int_0^{t+t_d} C_L(t)dt + V_r C_L(t + t_d) \tag{11}$$

A typical delignification rate calculated from the UV–vis results using Eq. 10 is plotted, along with reactor temperature vs. time in Figure 3. The delignification rate initially increases rapidly from 0.25 to about 0.5 mg·g pulp^{-1}·min^{-1}, during the time in which the water in the reactor is replaced by the oxygenated caustic solution. The time scale of the initial increase is consistent with the average residence time of 4.5 min for the liquid in the reactor system in this experiment. Because of limitations in the temperature control (± 1°C), the data show correlated fluctuations over the reaction time.

Results and Discussion

Comparison of delignification rates

Figure 4 presents a comparison of delignification experiments using the batch and CSTR reactors. The CSTR and batch kappa numbers are almost the same during the first 30 min. However, the CSTR kappa numbers are lower than the batch reactor kappa numbers after 40 min, which indicates a higher rate of delignification in the CSTR. After 3 h reaction, the CSTR kappa number is five points lower. This is because the CSTR is continuously fed with a fresh oxygenated caustic solution, while the caustic concentration decreases continuously with time in the batch reactor due to consumption by acid

Table 2. Summary of Batch Reactor and CSTR Kappa Number Power-law Model

90°C, 3.3 g/l NaOH, 75 psig (0,10, 20, 40, 60 and 180 min)		
Parameter	Reaction Order q	Reaction Constant k (min^{-1})
CSTR	2.70	9.0327×10^{-5}
Batch	4.25	8.918×10^{-7}

Table 3. Cellulose and Hemicelulose Content, Intrinsic Viscosity and Cellulose DP

O_2 Delig Time, t (min)	Cellulose, G (g/g od pulp)		Hemicellulose, H (g/g od pulp)		Intrinsic Viscosity, η (ml/g)		Polymerization Degree, DP	
	Batch	CSTR	Batch	CSTR	Batch	CSTR	Batch	CSTR
0	0.714	0.714	0.142	0.142	1189	1189	6561	6561
10	0.723	0.732	0.139	0.139	1058	1079	5674	5724
20	0.723	0.734	0.138	0.142	1011	1033	5394	5435
40	0.729	0.746	0.139	0.140	924	877	4831	4445
60	0.736	0.750	0.140	0.138	898	828	4629	4144
180	0.736	0.763	0.141	0.135	829	592	4230	2784

products, such as carboxylic acid[16] released from the pulp. The kinetic data obtained in both reactors were analyzed using the power-law equation. Figure 4 shows that the data obtained in both the CSTR and batch reactor are well presented by the power-law Eq. 1.

Table 2 presents the power-law model parameters for delignification in the CSTR and batch reactor calculated using Eq. 1. The reaction order for lignin is higher in the batch reactor to describe a stronger decrease in delignification rate at lower kappa numbers, but the reaction constant k, is lower. The calculated reaction rate is a combination of reaction order and reaction constant. However, the order obtained in the CSTR is more accurate because the caustic concentration and dissolved oxygen concentration remain constant in the CSTR. In the batch reactor, the order of the rate dependence on lignin concentration cannot be separated from the effect of decreasing caustic concentration as the reaction proceeds.

Selectivity comparison

It is well known that hydroxyl radicals generated in the oxygen delignification reaction attack both lignin and cellulose. We conducted experiments using the batch and CSTR reactors at the same operating conditions to compare the pulp properties and selectivity. To calculate the DP of cellulose in the pulps using Eq. 3, we measured the content of cellulose (G) and hemicellulose (H) in the pulp by high-pressure anion exchange chromatography (HPAEC) on the two-stage acid hydrolyzed pulp samples.[17] The results for the pulp samples in the CSTR and batch reactor are listed in Table 3.

The delignification-cellulose degradation selectivity remains constant during batch delignification, but decreases during delignification in the CSTR. We have plotted the kappa number change vs. cellulose cleavages per glucose unit (calculated as $1/DP_t$-$1/DP_0$) in Figure 5. Note that the relationship is linear for the batch reactor data, while the change in kappa number decreases with increasing number of cellulose cleavages for the pulps in the CSTR. The explanation for the linear behavior in the batch reactor data is that cellulose degradation is caused by radical species, the formation of which is proportional to the degree of delignification.[18] The alkali hydrolysis influence on batch reactor data is relatively small after 30 min of reaction.

However, the decrease in delignification-cellulose degradation selectivity in the CSTR suggests there is an additional cellulose degradation mechanism, which becomes important when the caustic concentration remains high throughout the process. For instance, the alkaline hydrolysis of cellulose may be significant in the CSTR, where the fibers are continuously exposed to a constantly high-alkaline concentration.

Because of the differences in selectivity observed in the batch and CSTR reactions, the cellulose degradation was modeled by two contributions: one due to radicals produced by phenolic delignification, and the other due to alkaline hydrolysis. The model containing both rates is

$$\frac{dm_n}{dt} = -k_c \frac{dK}{dt} + k_h[OH^-] \tag{12}$$

where m_n is the number of moles of cellulose per gram of pulp (mole/g pulp); is the rate constant for radical attack (moles/g pulp · kappa); and k_h is the alkaline hydrolysis rate constant

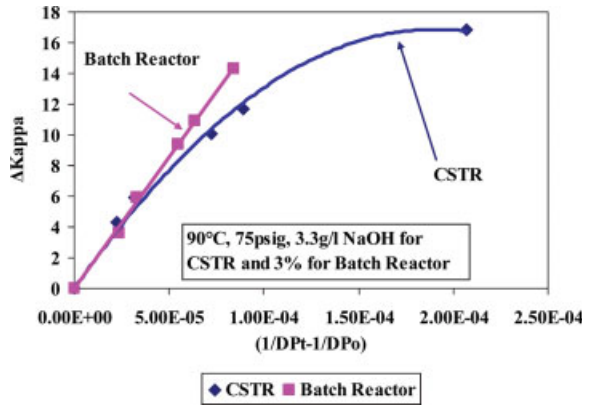

Figure 5. ΔKappa vs. (1/DP−1/DP$_0$) of CSTR and batch reactor.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

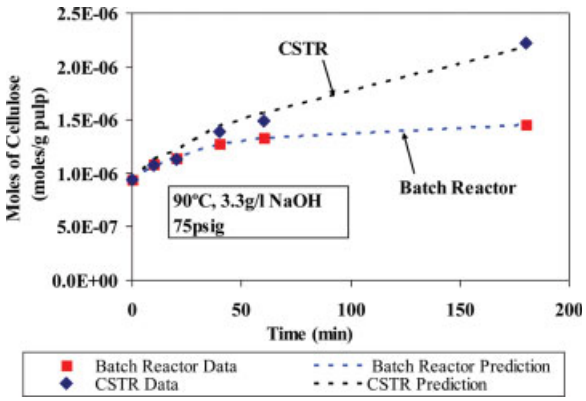

Figure 6. Degradation of cellulose in CSTR and batch reactors; experimental and predicted data.

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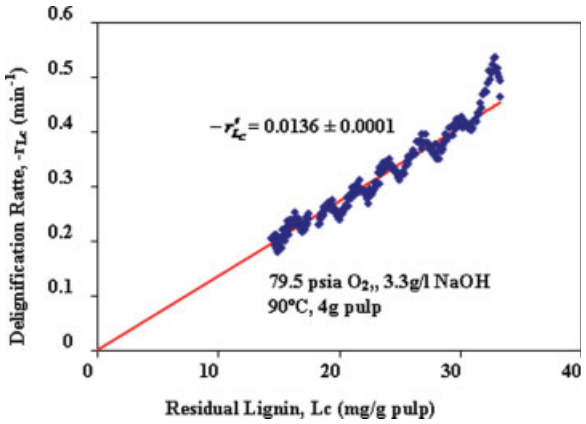

Figure 7. Delignification rate vs. residual lignin for the data in Figure 3.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

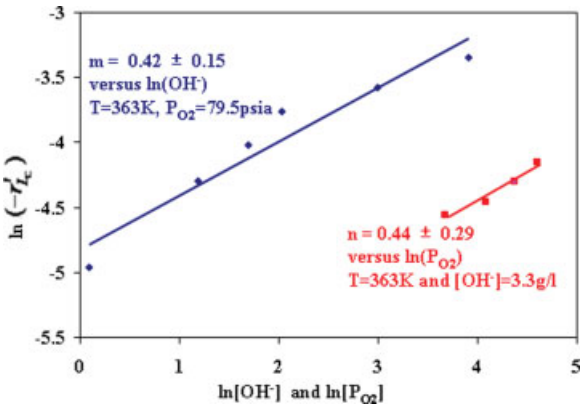

Figure 8. $\ln(-r'_{Lc})$ vs. $\ln([OH^-])$ and vs. $\ln(P_{O2})$.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(L · mol cellulose/g pulp · g NaOH · min); $[OH^-]$ is the alkali concentration in g/L.

Integration of Eq. 12 gives

$$m_n = m_0 + k_c(K - K_0) + k_h[OH^-]t \tag{13}$$

Since NaOH is rapidly consumed during the initial phase of oxygen delignification in the batch reactor, the influence of the term $k_h[OH^-]t$ was neglected for $t \geq 20$ min in the calculation. This allows the calculation of k_c by fitting the data for the batch reactor at t $\geq$ 20 min as 3.60×10^{-8} (moles/g pulp · kappa). Using this value for the analysis of the CSTR data gives a value for k_h of 1.07×10^{-9} (L · mol cellulose/g pulp· g NaOH· min). These values provide a reasonable fit to the cellulose degradation in the CSTR as illustrated in Figure 6. The Batch reactor data were best represented by k_h = zero.

Kinetic Model for Oxygen Delignification

The CSTR was used to independently determine the oxygen pressure and caustic concentration influence on the delignification rate since these concentrations do not vary during a single experiment. The residual lignin in the pulp was calculated using Eq. 5, so that the time-dependent data could be plotted vs. residual lignin. As an example, the data from Figure 3 are plotted in Figure 7. The data for other operating conditions also show a generally linear relationship between delignification rate, and residual lignin content if the first few minutes of reaction are ignored when water in the CSTR is replaced by the oxygenated caustic solution. Therefore, we have assumed the reaction is first-order in residual lignin in our model.

Table 4. Rate Constants of Different Experiments

Temperature (°C)	Total Pressure (psig)	Oxygen Pressure (psia)	NaOH (g/liter)	$-r'_{L_c} \times 1000$ (min^{-1})
81	75	82.8	3.3	9.77 ± 0.17
91	75	79.5	3.3	13.6 ± 0.1
100	75	75.0	3.3	19.3 ± 0.1
112	75	68.9	3.3	37.5 ± 0.4
117	75	65.2	3.3	43.3 ± 0.9
90	35	39.5	3.3	10.4 ± 0.1
90	55	59.5	3.3	11.5 ± 0.01
93	95	99.5	3.3	15.6 ± 0.1
89	75	79.5	1.1	6.97 ± 0.08
93	75	79.5	5.5	17.9 ± 0.01
93	75	79.5	7.7	23.1 ± 0.1
90	75	79.5	20	27.8 ± 0.1
89	75	79.5	50	35.0 ± 0.5

The delignification rate model in terms of residual lignin content is

$$-r_{L_C} = Ae^{-\frac{E}{RXT}}[OH^-]^m {P_{O2}}^n L_C \tag{14}$$

where $-r_{L_C}$ is the delignification rate (mg/g pulp/min); T is the reaction temperature (K); $[OH^-]$ is the initial sodium hydroxide concentration (g/L); P_{O2} is the oxygen pressure (psia), and L_c is the residual lignin corrected for HexA content (mg/g pulp).

The derivative of $-r_{L_C}$ with respect to L_c, $-r'_{L_C}$, is a pseudo-first-order rate constant with units of min^{-1}, and is calculated from the slope of the data in Figure 7. The linearized form of the model is then

$$\ln(-r'_{L_C}) = \ln(A) - \frac{E}{RT} + m\ln[OH^-] + n\ln\left(P_{O_2}\right) \tag{15}$$

Experiments were performed at different temperatures, oxygen pressures and alkali concentrations, and the results are

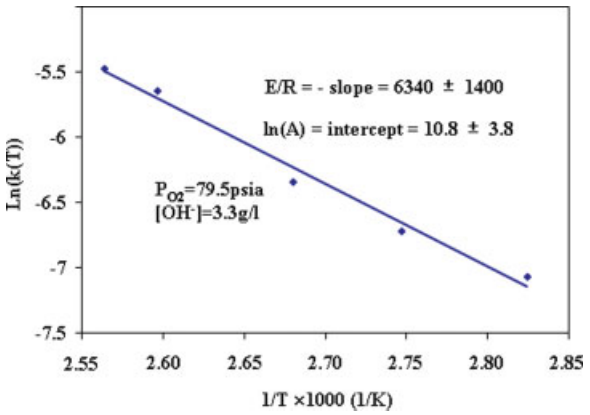

Figure 9. Arrhenius construction to determine activation energy and preexponential factor.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

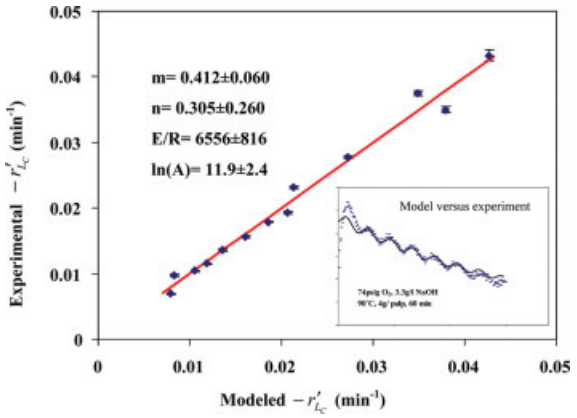

Figure 10. Experimental $-r'_{Lc}$ vs. modeled $-r'_{Lc}$ for data in Table 4.

The straight line represents a perfect fit. Inset shows model fit for data in Figure 3, including oscillatory temperature control. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

summarized in Table 4. Note that the partial pressure of oxygen was calculated by the total pressure minus the vapor pressure of water for a given temperature. The uncertainties in the values of $-r'_{Lc}$ (and all reported uncertainties) represent 95% confidence intervals, based on the linear regressions.

Data for experiments at 90°C were used to independently determine m and n by plotting ln $(-r'_{Lc})$ vs. ln($[OH^-]$) and vs. ln(P_{O2}) in Figure 8. Linear regression of the two sets of data determined m = 0.42 ± 0.15 and n = 0.44 ± 0.29. Then, the temperature-dependent data were used to calculate the preexponential factor and activation energy for P_{O2} = 75 psia, and $[OH^-]$ = 3.3 g/L. First, values of k(T) were calculated using $-r'_{Lc}$, $[OH^-]$, and P_{O2}, and then the kinetic parameters were determined from the Arrhenius construction in Figure 9. This analysis determined E = 53 ± 12 kJ/mol, and ln(A) = 10.8 ± 3.8, so A = 4.9×10^4 min^{-1}(g/L)$^{-0.42}$ (psia)$^{-0.44}$.

In addition to independently determining the parameters of the rate expression, a statistical software package was used to perform a multivariate analysis of all of the data simultaneously. The parameters determined by this analysis are consistent with the ones determined independently, but this analysis improved the uncertainties. From the analysis, m = 0.412 ± 0.060, n = 0.305 ± 0.260, E = 54.5 ± 6.8 kJ/mol, and ln(A) = 11.9 ± 2.4. The experimental values of $-r'_{Lc}$ are plotted in Figure 10 vs. the values of $-r'_{Lc}$ calculated from the model. Note that the model provides a reasonable estimate of the delignification rate over the entire range of experimental conditions. Finally, the inset of Figure 10 demonstrates that the model also accurately predicts the effect of the temperature oscillations for the data in Figure 3.

Conclusions

Oxygen delignification kinetics were studied using a CSTR to separate the dependence on caustic concentration from the dependence on lignin concentration. Using this technique, it was found unambiguously that the rate of delignification is first-order in HexA-free residual lignin content of the pulp. The activation energy of 54.5 kJ/mol is consistent with a reaction controlled process. Furthermore, it is proposed that the cellulose degradation during oxygen delignification can be described by two contributions: one due to radicals produced by phenolic delignification, and a much smaller contribution due to alkaline hydrolysis. Periodic addition of smaller charges of caustic during industrial delignification is recommended to improve the overall selectivity at the same degree of delignification.

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