O₂ delignification Kinetics from CSTR and Batch Reactor Data

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ABSTRACT

Many kinetic studies of oxygen delignification have been reported in literature. In the past these studies were mostly performed in batch reactors whereby the caustic and dissolved oxygen concentrations are changing during the reaction. This makes it difficult to determine the reaction order of the different reactants in the rate expressions. 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, we have adopted a differential reactor system (called Berty reactor) which is used frequently for fluid-solid reaction rate studies. 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. Experiments were performed at different temperatures (80ºC, 90ºC, 100ºC and 110ºC), oxygen pressures (35psig, 55psig, 75psig and 95psig) and caustic concentrations (1.1g/l, 3.3g/l, 5.5g/l and 7.7g/l). 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 0.6 and 0.5 respectively. The activation energy is 47 kJ/mol. The rate of cellulose degradation is described by two terms: one due to radicals produced by phenolic delignification, and the other due to alkaline hydrolysis

INTRODUCTION

Oxygen delignification is widely used for lignin removal before bleaching pulp. The well known advantages of oxygen delignification are chemical cost savings, yield retention and improved environmental performance. Better understanding of oxygen delignification kinetics and its relation to cellulose degradation may point to improved operation in industrial practice. Lignin and cellulose degradation occur simultaneously during oxygen delignification. 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 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 non-lignin structures also consume $KMnO_4$ in the kappa number measurement (Li, 1999). In this study, the HexA content will be considered in the kinetics modeling. Another aspect of the present approach is that the kinetics are determined in 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 (Ji and van Heiningen, 2006).

Kinetic Modeling

The kinetics of oxygen delignification is usually presented by a power law equation which includes the influence of the process variables such as reaction temperature, oxygen pressure and caustic concentration (Iribarne and Schroeder, 1997):

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

In equation (1), K is the Kappa number; $[OH^-]$ is the caustic concentration and $[P_{O2}]$ is the absolute oxygen pressure. The constants m, n, and q are obtained by fitting of the experimental data. The reaction rate coefficient k depends on the temperature and is given by the Arrhenius equation:

$$k = A\exp(-\frac{E_A}{RT}) \quad (2)$$

In equation (2), E_A is the activation energy, R is the gas constant, T is the absolute temperature and A is the frequency factor.

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

Table 1 Summary of Kinetics Equations using the Power Law Model

Reference	$[OH^-]$ exponent (m)	$[O_2]$ or P_{O2} 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	-
Iribane (1997)	0.7	0.7	2.0	51	3×10^6
Evans (1979)	1	1.23	1	49.1	10^5

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.

Cellulose Degradation

The cleavage of cellulose polymers was modeled by Iribarne and Schroeder (1997) as the increase in number-average moles of cellulose per gram of pulp (m_n). Similarly one can describe the cellulose degradation by the number of cellulose chain scissions during oxygen delignification. Violette and van Heiningen (2003) calculate the number of cellulose chain scissions from the average degree of depolymerization of cellulose (DP) in the pulp at time t=0 and time t=t, i.e. as $1/DP_t - 1/DP_0$

DP can be obtained from the intrinsic viscosity [η] by equation (3) (van Heiningen et al, 2003):

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

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. This formula considers the actual weight of cellulose rather than the pulp weight being responsible for the viscosity, and makes a correction for the small contribution of the hemicelluloses to the pulp intrinsic viscosity.

The number of moles of cellulose per gram of pulp, m_n, can be calculated by equation (4) (Iribane and Schroeder, 1997) as:

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

In equation (4), the factor of 162 is the molecular weight of the anhydrous glucose unit and 18 is the molecular weight of water.

EXPERIMENTAL
Oxygen delignification experiments were performed both in a CSTR and a batch Parr reactor. The Parr reactor is a 2-liter horizontal stainless steel reactor obtained from Parr Instruments with an anchor rotating device which wipes the inside of the reactor with Teflon blades. Figure 1 shows a schematic diagram of the Parr reactor set-up.
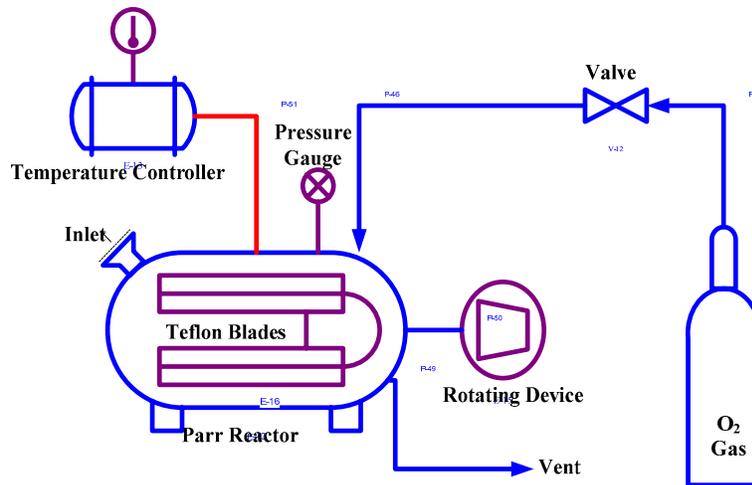

Figure 1 Schematic Diagram of the Horizontal Parr Reactor Set-up

The flow diagram of the CSTR setup is shown in Figure 2. Oxygen from a gas cylinder is bubbled into a caustic solution held in a pressurized (130 psig max.) 3 gallon stainless steel container. The container is kept at a desired temperature by an external heating blanket. The actual reactor is a Berty reactor (Autoclave Engineers) with a stationary basket which holds the pulp bed. The nominal volume of the reactor is a 280 ml. It contains a 100 ml basket with a rotor underneath which induces flow through the pulp

mat inside the basket. The entire reactor is filled with liquid at the operating pressure, and any gas inside the reactor is vented at the top of the reactor. Oxygen is bubbled overnight through a NaOH solution to obtain a saturated oxygen concentration. Then the reaction is started by feeding the oxygenated caustic solution at constant flow rate and oxygen pressure. The reactor pressure, temperature and outflow rate are recorded every 5 seconds. The UV-VIS absorption of the outflow stream is monitored every 15 seconds.
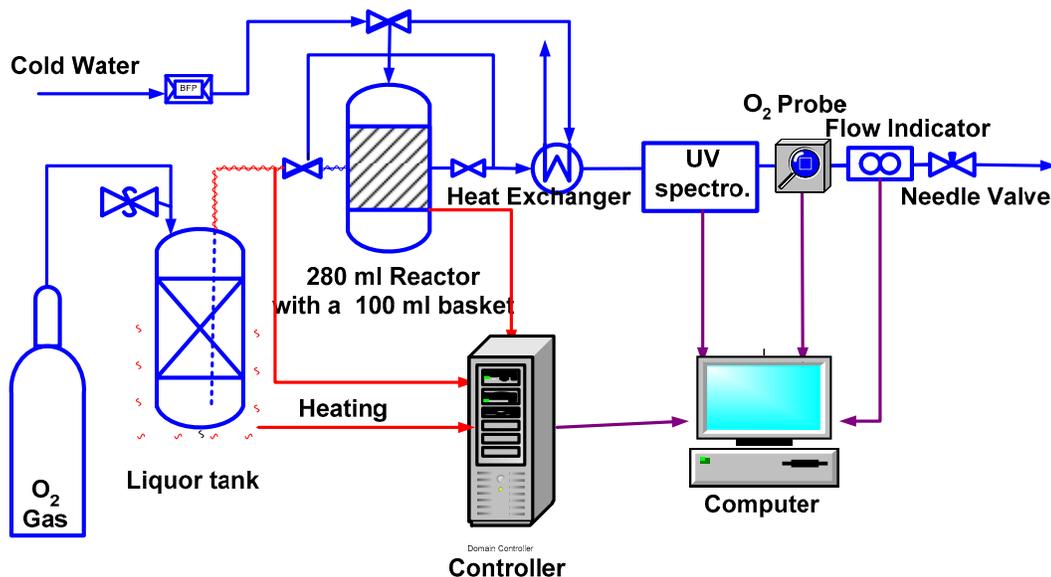

Figure 2. Diagram of CSTR Reactor Setup

Raw Materials
A commercial unbleached southern pine kraft pulp with an initial Kappa number of 24.4 and intrinsic viscosity of 1189 ml/g was used.

Measurements
The dissolved lignin concentration was measured using a flow cell and a HP8453 UV-VIS spectrophotometer from Agilent. The absorption at 280nm was converted to lignin concentration using the calibration curve made by purified lignin (Indulin AT from Mead-Westvaco, extinction coefficient of 24.8 liter$\cdot$g$^{-1}\cdot$cm^{-1}). The extinction coefficient does not change much during oxygen delignification was verified by mass balance (Ji and vanHeiningen, 2006). (The kappa number of the pulps was measured according to a modified method of the TAPPI standard T236-cm-85. All the chemical dosages were reduced to one tenth of the amount in TAPPI method due to the small amount of samples. Intrinsic viscosity of the pulps was determined following the A.S.T.M. designation D1795-62 (re-approved 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 245nm. The HexA content of the final pulp samples generated at 90ºC, 3.3g/l NaOH and 75 psig in the CSTR reactor were measured. The HexA content of all these samples falls between 21 and 23 mmol/kg pulp, confirming that HexA is stable during oxygen delignification.

Because HexA contributes to the kappa number, the residual lignin content in the pulp should be corrected for the HexA content in the pulp. Typically, 10mmole/kg HexA corresponds to 0.86-1.1 unit of kappa number (Li and Gellerstedt, 2002; Jääskeläinen et al, 2002). In the present study, 10mmol/kg HexA is considered as 1 kappa unit, thus, the residual lignin content in pulp is as:

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

The pulp in this study has an average value of 22mmol/kg HexA which is equivalent to 2.2 kappa units or 3.3 mg (2.2×1.5 =3.3 mg) lignin.

Data Reduction Procedure

The CSTR operation 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 400rpm) (Ji and vanHeiningen, 2006). Most experiments were performed with 4 grams (oven dry basis) of pulp because of the volume of the basket and analysis requirement.

The dissolved lignin mass balance for the well mixed reactor during time interval, dt, is:

Inflow - Outflow + Dissolved by Reaction = Accumulated in Reactor

or $$0 - \phi_v C(t)dt + r(t)m_p dt = V_r dC(t) \qquad (6)$$

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

where $r(t)$ is the rate of delignification (mg lignin/g pulp/min)
Φ_v is the liquid flow rate (ml/min)
$C(t)$ is the dissolved lignin concentration (mg lignin/ml)
V_r is the reactor volume (ml)
m_p is the pulp weight (o.d pulp)

The reactor volume, $V_{r,}$, was determined by a step tracer residence time distribution experiment. Methyl red was used as a tracer. Analysis of the residence time distribution curve showed 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 the free volume in the reactor and piping respectively. Therefore, V_r is taken as 265 ml, and the residence time between the Berty reactor and UV detector, t_d, is

$$t_d = \frac{96}{\phi_v} \qquad (8)$$

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

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 vs. time plot calculated from the UV-VIS results using equation (10) is shown in Figure 3. Using equation (5), the delignification rate vs. residual lignin in the pulp is shown in Figure 4.
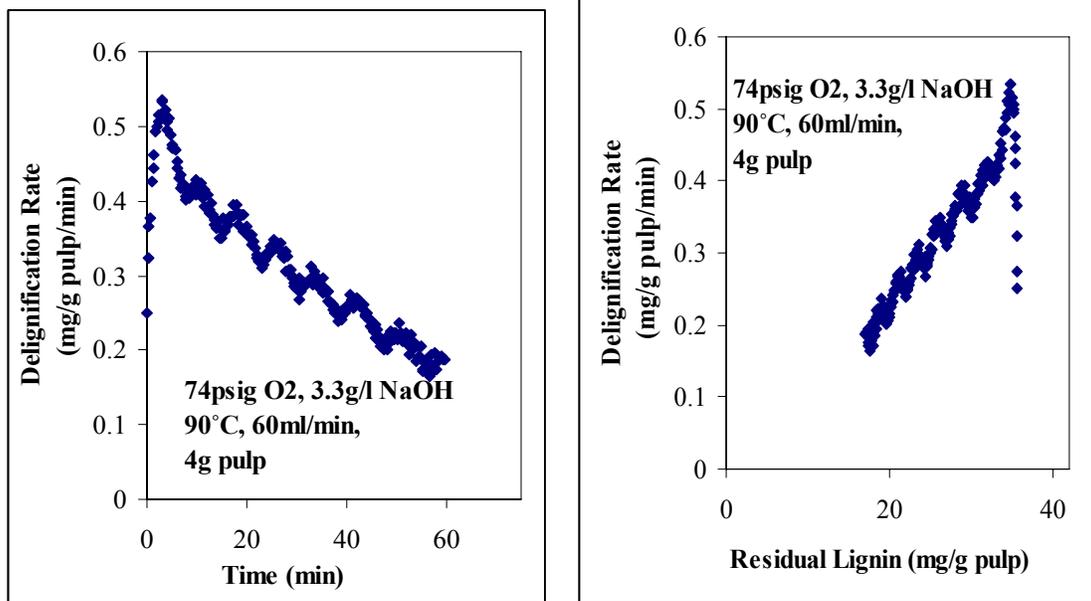

Figure 3 Delignification Rate vs. Time   **Figure 4 Delignification Rate vs. Residual Lignin amount**

The results in Figure 3 show a rapid initial increase in delignification rate due to the fact that it takes a few minutes before the water in the reactor is replaced by the oxygenated caustic solution. The average residence time of the liquid in the reactor system for this experiment is about 4.5 minutes. Figure 4 shows that the delignification rate decreases with the residual lignin amount in a linear fashion.

RESULTS AND DISCUSSION

Kappa Number Reduction in the CSTR and Batch Reactors

Figure 5 shows the experimental pulp kappa numbers in the CSTR and batch reactor. The CSTR and batch kappa numbers are almost the same during the first 30 minutes. However, the CSTR kappa numbers are lower than the batch reactor kappa numbers after 40 minutes. After 3 hours reaction, the CSTR kappa number is 5 points lower. This can be explained by the fact that 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 products released from the pulp. The kinetic data obtained in both reactors were also analyzed using the power law equation. Figure 5 shows that the data obtained in both the CSTR and batch reactor are well presented by the power law equation (1).

$$K = \left[\left(\frac{1}{K_0^{q-1}} \right) + k\,(q-1)\,t \right]^{-\left(\frac{1}{(q-1)} \right)} \quad for \quad q \neq 1$$

90°C, 3.3g/l NaOH
75 psig

- - - - Predicted Batch Reactor Kappa   ■   Measured Batch Reactor Kappa
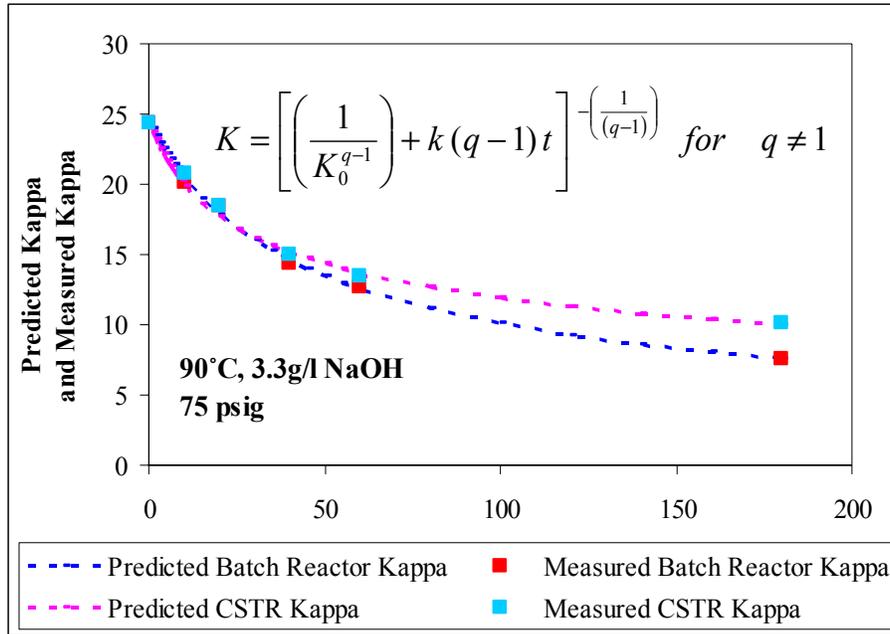- - - - Predicted CSTR Kappa   ■   Measured CSTR Kappa

Figure 5 Kappa Number Model and Experimental Data of CSTR and Batch Reactor

Table 2 summarizes the power law model parameters for delignification in the CSTR and batch reactor calculated from equation (1). The reaction order for lignin is higher in the batch reactor in order to describe a stronger decrease in delignification rate at lower kappa numbers, but the reaction constant k in the batch reactor is lower. However, because the caustic concentration and dissolved oxygen concentration remain constant in the CSTR, the order obtained in the CSTR gives the correct effect of kappa number on the delignification rate. In another words, the lignin reaction order obtained in the batch reactor contains the effect of the decreasing caustic concentration with time.

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

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

In order to calculate the DP of cellulose in the pulps using equation (3), it was necessary to measure the content of cellulose (G) and hemicellulose (H) in the pulp. This was done by high pressure anion exchange chromatography (HPAEC) on the double hydrolysed pulp samples (Davis, 1998). The results for the pulp samples in the CSTR and batch reactor are listed in Table 3.

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

Shown in Figure 6 is the kappa number change plotted versus cellulose cleavages per glucose unit calculated as $1/DP_t-1/DP_0$. It can be seen that a linear relationship is obtained for the batch reactor data, while the change in kappa number decreases with increasing number of cellulose cleavages for the pulps in the CSTR. This indicates that the delignification-cellulose selectivity remains constant in the batch reactor. The explanation for this behavior is that the cellulose degradation is caused by radical species, the formation of which in turn is proportional to the degree of delignification (Violette, 2003).
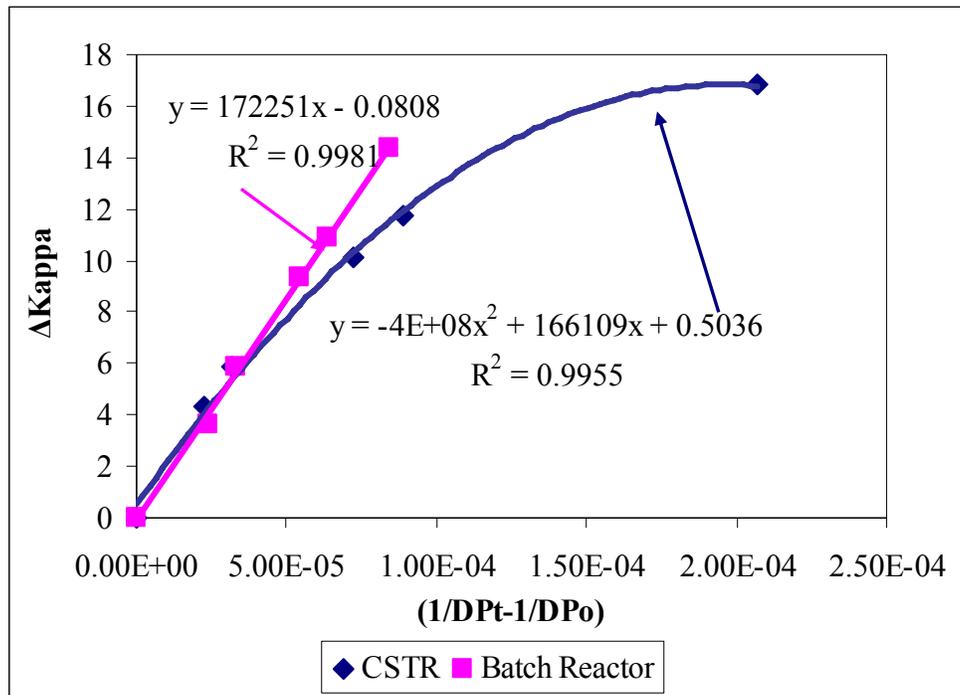

Figure 6 ΔKappa vs. ($1/DP-1/DP_0$) of CSTR and Batch Reactor

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

Based on these results the cellulose degradation was modeled by two contributions: one due to radicals produced by phenolic delignification, and the other due to alkaline hydrolysis. Therefore, the model can be described as equation (12):

$$\frac{dm_n}{dt} = -k_c \frac{dK}{dt} + k_h \left[OH^-\right] \qquad (12)$$

where k_c is the rate constant for radical attack, and k_h is the alkaline hydrolysis rate constant. [OH⁻] is the alkali concentration in g/L.

Integration of equation (12) gives:

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

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 $t \geq 20$ minutes. This allows the calculation of k_c by fitting the data for the batch reactor at $t \geq 20$ minutes 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} (liter·mol cellulose/g pulp·g NaOH·minute). These values provide a good fit of the cellulose degradation in the CSTR as can be seen in Figure 7. The good fit of the Batch reactor data was obtained by setting k_h to zero.
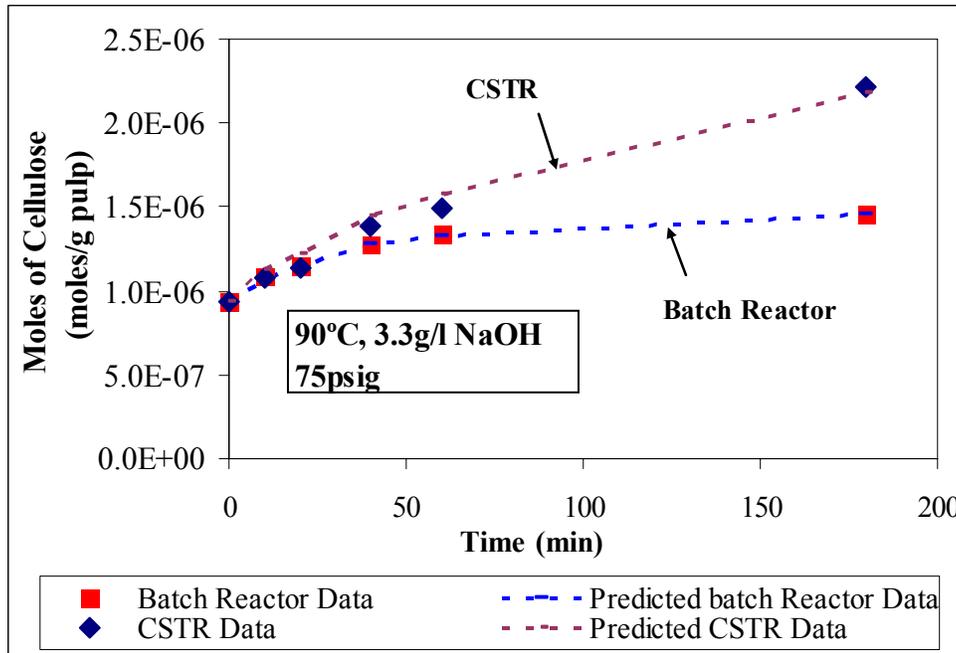

Figure 7. Degradation of Cellulose in CSTR and Batch Reactors; Experimental and Predicted Data

Modeling Oxygen Delignification in CSTR at Different Operating Conditions

To eliminate the effect of changing of caustic concentration, the effect of operating conditions on oxygen delignification was studied in the CSTR. Experiments were performed at different temperatures (80ºC, 90ºC, 100ºC and 110ºC), oxygen pressures (35psig, 55psig, 75psig and 95psig) and alkali concentrations (1.1g/l, 3.3g/l, 5.5g/l and 7.7g/l).

The effect of caustic concentration, oxygen pressure and temperature are shown in respectively Figures 8, 9 and 10. The data shows generally a linear decrease in delignification rate with residual lignin content if the first few minutes reaction are ignored when water in the CSTR is replaced by the oxygenated caustic solution. Therefore, a first order reaction in residual lignin is assumed for the delignification kinetics. The slopes of the straight line fits through the data in Figures 8 – 10 are listed in Table 4 as the rate constants.
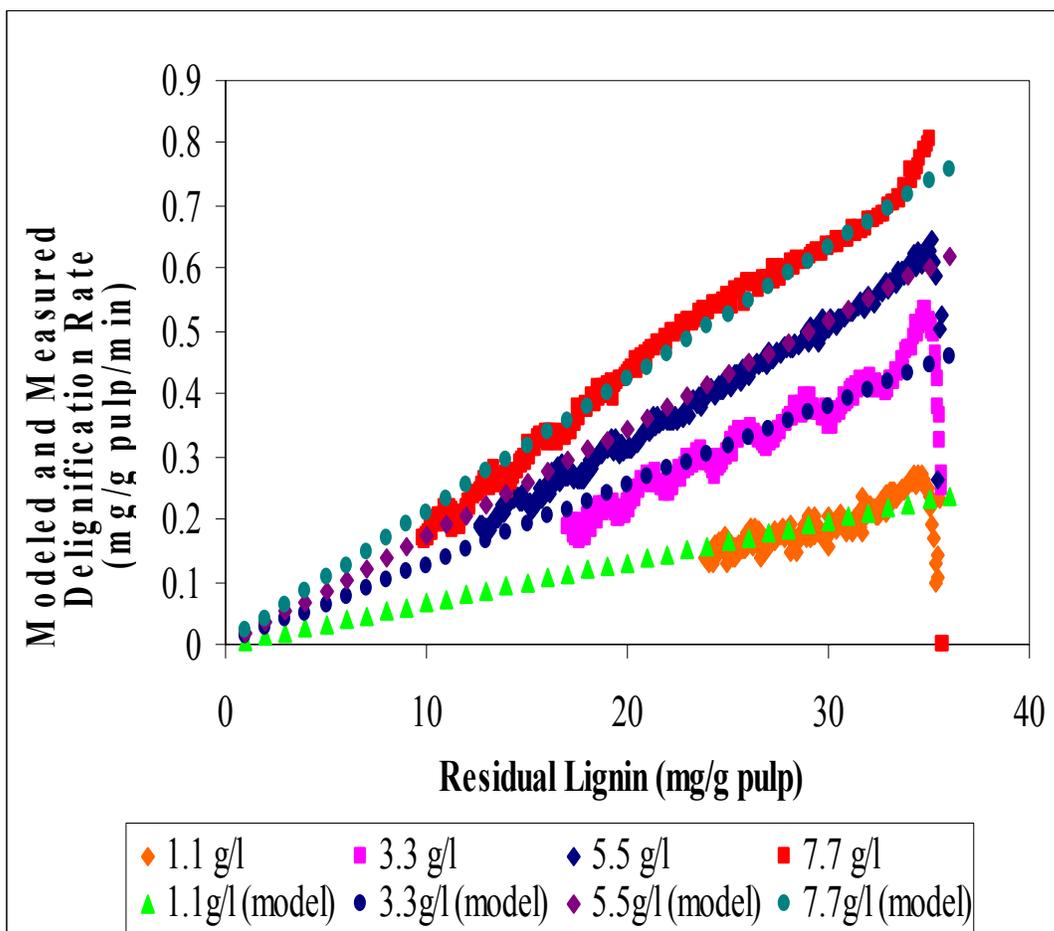

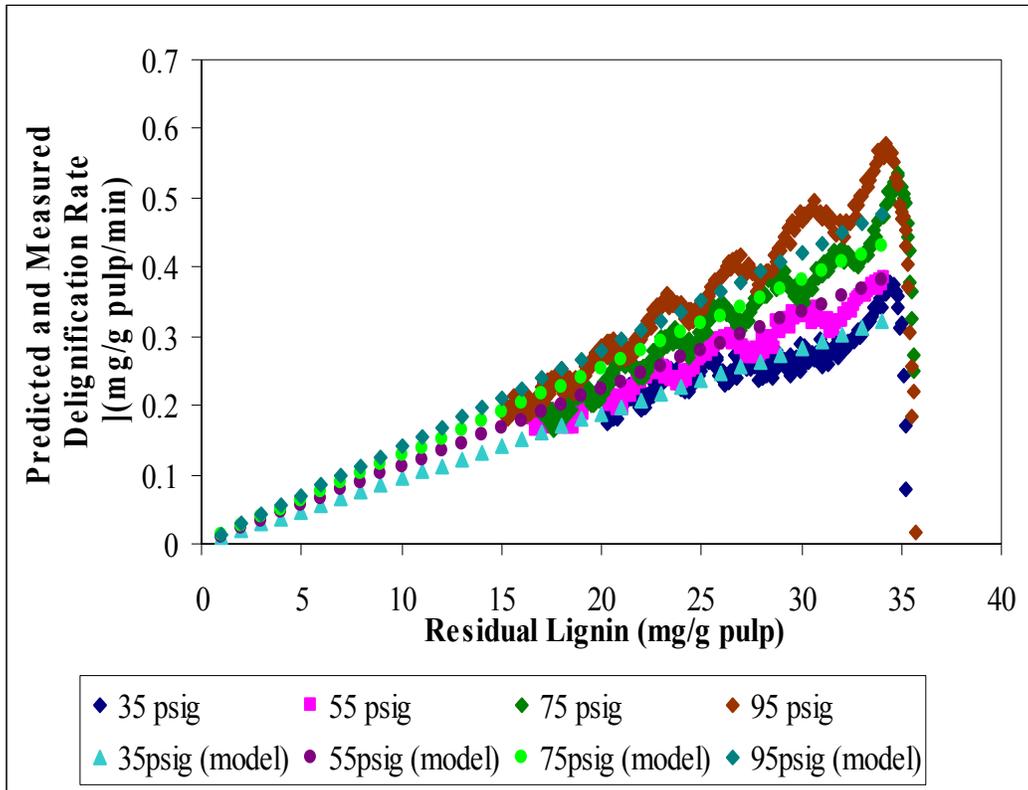Figure 8 Delignification Rate vs. Residual Lignin at Different Caustic Concentrations

Figure 9 Delignification Rate vs. Residual Lignin at Different Oxygen Pressures
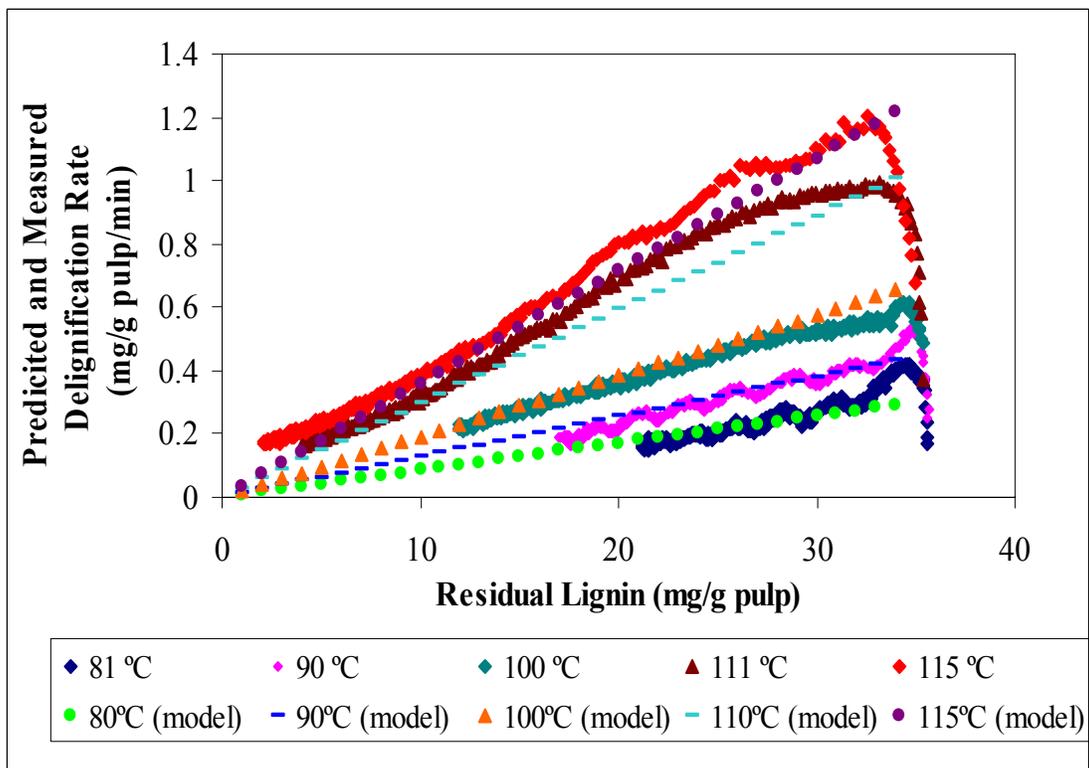

Figure 10 Delignification Rate vs. Residual Lignin at Different Temperatures

Table 4 Rate Constants of Different Experiments

Runs	Temperature (°C)	Pressure (psig)	NaOH (g/liter)	Rate Constant
1	80	75	3.3	0.0086
2	90	75	3.3	0.0124
3	100	75	3.3	0.0173
4	110	75	3.3	0.0305
5	115	75	3.3	0.0348
6	90	35	3.3	0.0094
7	90	55	3.3	0.0107
8	90	75	3.3	0.0124
9	90	95	3.3	0.01396
10	90	75	1.1	0.0064
11	90	75	3.3	0.0124
12	90	75	5.5	0.0166
13	90	75	7.7	0.0207

From equation (1) and (2) it follows that

$$\ln(k_L) = \ln(A) - \frac{E}{RT} + m\ln[OH^-] + n\ln[P_{O_2}] \qquad (14)$$

Use of this equation for the experiments with variable [OH⁻] at constant temperature T and oxygen pressure [P_{O₂}] yields as best fit the [OH⁻] reaction order m = 0.60. Similarly the application of equation (14) to the experiments with variable oxygen pressure [PO2] at constant temperature and [OH⁻] gives the [P_{O₂}] eaction order n = 0.50. The variable temperature data at constant [OH⁻] and oxygen pressure P_{O_2} results in an activation energy of 46.75 kJ/mol and a frequency factor A of 3.47×10^3 min^{-1}(g/l)$^{-m}$(psia)$^{-n}$

Thus, the model to fit all the data is equation (15).

$$r = 3.47 \times 10^3 e^{-\frac{4.675 \times 10^4}{R \times T}} [OH^-]^{0.60} [P_{O2}]^{0.50} L_C \qquad (15)$$

where r = delignification rate (mg/g pulp/min)

    T = reaction temperature (K)

    [OH⁻] = initial sodium hydroxide concentration (g/l)

    [P_{O₂}]= oxygen pressure (psia)

    L_c = residual lignin amount in pulp corrected for hexA content (mg/g pulp)

The predictions obtained with equation (15) are also shown in Figures 8 – 10. It can be seen that the predictions are quite good except for the highest temperatures of 110ºC and 115ºC in Figure 10 where equation (15) gives a slight under prediction. Further work is needed to develop a mechanistic model which would be in agreement with equation (15).

CONCLUSIONS

To eliminate the effect of changing of caustic concentration, the effect of operating conditions on oxygen delignification was studied in a CSTR. It was found that the rate of delignification is first order in HexA-free residual lignin content of the pulp. Similarly the reaction orders in hydroxide concentration and oxygen pressure are 0.6 and 0.5 respectively. The activation energy of 47kJ/mol is in agreement with a reaction controlled process. 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.

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