Rate determining step and kinetics of oxygen delignification

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Abstract: A differentially operated, continuous stirred tank reactor (CSTR) was used to study the kinetics of oxygen delignification. The delignification kinetics and reaction rate were determined at different temperatures, oxygen pressures and caustic concentrations on softwood kraft pulps. The kinetics are first order in residual lignin content (HexA corrected). The kinetics of phenolic delignification can be described by assuming that the decomposition of the hydroperoxide anion at carbon 3 of the aromatic ring is the rate determining step. The cellulose degradation kinetics were described by two contributions: one due to radicals produced by phenolic delignification, and the other due to alkaline hydrolysis.

Any studies have been performed to determine the kinetics of oxygen delignification. Almost all kinetic equations were derived using experiments performed in laboratory batch reactors. However it is difficult to determine the reaction orders in alkali concentration and residual lignin content when operating a batch reactor at medium consistency (MC) because these variables are continuously changing with time. Also mass transfer of oxygen from the gas to the liquid phase must be efficient enough so that the oxygen concentration in the liquid phase is close to saturation throughout the experiment. Another difficulty is that pulp properties can only be determined after an experiment so that many experiments at different reaction times must be run, thereby increasing experimental error.

In the present study, a constant flow of an oxygenated caustic solution is fed to a MC pulp bed. The pulp bed is retained inside a basket placed inside a pressured reactor. The caustic solution circulates rapidly through the pulp, while fresh oxygenated caustic solution is added to the reactor and spent liquor is removed simultaneously at the same rate. In other words, the device is a differentially operated continuous stirred tank reactor (CSTR) in which the concentrations of the dissolved oxygen and NaOH are close to that of the feed.

Oxygen delignification kinetics previously reported have mathematical forms which were mostly chosen to obtain a good fit with the experimental data rather than derived based on fundamental chemical mechanisms. This leads to kinetic equations with high reaction orders in residual lignin content or to arbitrary identification of so called “fast reacting” and “slow reacting” lignin. Another aspect of the reported delignification equations is that the lignin content is generally derived from the kappa number, i.e. they do not distinguish between real lignin, hexenuronic acids (HexA) and non-lignin based oxidizable structures as identified by Li and Gellerstedt. Since it is known that hexenuronic acids are stable during oxygen delignification, the lignin content in the present study is corrected for the presence of HexA. The delignification data are then fitted to kinetics which are derived based on elementary reactions identified in a chemical mechanism of oxygen delignification. The cellulose degradation kinetics are described by two contributions: one due to radicals produced by phenolic delignification, and the other due to alkaline hydrolysis.

EXPERIMENTAL

Reactor setup

A flow diagram of the CSTR system is shown in Figure 1. Oxygen is bubbled overnight into a caustic solution in a pressurized (0.9 MPa maximum) heated stainless steel container of 11 liter. A 280 mL Berty reactor (Autoclave Engineers) with a 100 mL stationary basket holds the pulp bed. A rotor underneath the basket induces flow through the pulp mat. Any gas inside the reactor is vented at the top of the reactor so that the entire reactor is filled with liquid during operation. The reaction is started by feeding the oxygenated caustic solution at constant flow rate and oxygen pressure. The reactor pressure and temperature, and flow rate and UV-VIS absorption of the outflow stream are continuously recorded.

Pulps and analyses

Unbleached southern pine kraft pulps were used. The dissolved lignin concentration was determined from UV absorption at 280 nm using Indulin AT lignin (MeadWestvaco) for calibration. The HexA content of pulp was determined by the
method of Tenkanen et al. scaled down to 200 mg pulp. The residual lignin content in pulp, \( L_c \), was calculated as

\[
L_c = \left( \frac{\text{Kappa}}{10} \right) \times 1.5 \left( \frac{\text{mg lignin}}{\text{g pulp}} \right)
\]

where the kappa number is calculated as the initial pulp kappa number minus the amount of lignin dissolved as measured by UV. The kappa number is corrected for the HexA content (in \( \mu \text{mol/g} \) pulp). Since 10 \( \mu \text{mol/g} \) of HexA is equivalent to one kappa unit, the HexA content is divided by 10. The factor 1.5 is the standard conversion of kappa to mg lignin per gram of pulp. Ji has shown that the HexA content of pulp does not change during oxygen delignification except when a severe yield loss occurs so that HexA groups are removed together with the carbohydrates. To avoid lignin precipitation, 100 \( \mu \text{l} \) of dioxane was added to the samples.

Data analysis procedure

Details about the data analysis procedure can be found in earlier publications.

Development of rate expression and determination of rate constants

It is well accepted that the first step involving oxygen delignification is dissociation of phenolic groups forming an active lignin anion site, \( L^\sim \), as:

\[ L^\sim + O_2 = L^\sim + O_2^- \quad (2) \]

forming a superoxide anion radical, \( O_2^- \), and a lignin radical \( L^\sim \). Therefore the rate expression of oxygen delignification may be written as:

\[ -\frac{dL_c}{dt} = k [L^\sim] [O_2]_{\text{ads}} \quad (3) \]

where \([L^\sim]\) is the reactive lignin site concentration and \([O_2]_{\text{ads}}\) is the adsorbed oxygen concentration on the reactive lignin site. The equilibrium constant \( K_{HL} \), of the protonation of the lignin active site is:

\[ K_{HL} = \frac{[L^\sim^-] [H^+]}{[HL]} \quad (4) \]

When the total number of active lignin sites is defined as \( HL_{\text{total}} = L^\sim + HL^\sim \), it can be derived that:

\[ -\frac{dL_c}{dt} = k \cdot K_{HL} [HL_{\text{total}}] [OH^-] [O_2]_{\text{ads}} \quad (5) \]

where \([HL_{\text{total}}] = C \cdot L_c\), where \( C \) is a proportionality constant. Thus, equation (5) becomes:

\[ -\frac{dL_c}{dt} / L_c = k = \frac{[OH^-] [O_2]_{\text{ads}}}{K_{water} + K_{HL} [OH^-]} \quad (6) \]

where the constant \( K = K_{HL} [HL_{\text{total}}] C \). The reaction rate constant, \( k \), is obtained from the slope of the delignification rate versus \( L_c \) curve shown in Figure 2 for a commercial unbleached southern pine kraft pulp (Kappa 26). The linear decrease in delignification rate with HexA-free residual lignin content, \( L_c \), can be interpreted as a first order reaction in lignin.

The wavy character of the data is caused by slow small temperature fluctuations (\( \pm 1^\circ \text{C} \)) in the CSTR due to imperfect control.

Equation 6 predicts that when \([OH^-]\) is very high, the reaction order in \([OH^-]\) approaches zero, and that the reaction order in \([OH^-]\) should approach first order when \([OH^-]\) is close to zero. By taking the inverse of equation 6, we obtain

\[ \frac{1}{k} = \frac{K_{HL}}{K_{water}} + \frac{K_{water} [O_2]_{\text{ads}}}{[OH^-]} \quad (7) \]

The terms \( K_{HL} / K_{water} \) and \( K_{water} / K_{HL} [O_2]_{\text{ads}} \) are constant when the temperature and oxygen pressure are kept constant. Thus, by plotting \( 1/k \) versus \( 1/[OH^-] \) at constant temperature and oxygen pressure, but at variable \([OH^-]\), a linear relationship should obtained. This is indeed the case as shown in Figure 3. From the abscissa and slope of Figure 3 one obtains that \( K_{HL} / K_{water} [O_2]_{\text{ads}} = 29.54 \) and \( K_{water} / K_{HL} [O_2]_{\text{ads}} = 3.28 \) or \( K_{HL} = 9.01 \cdot K_{water} \). Since the \( pK_w \) of water, \(-log(K_{water})\), at 90°C is 12.40 (Palmer et al. 2004), the pKa of the active lignin sites at 90°C is calculated as 11.5. This value is almost two units higher than 9.8 measured for Indulin AT at this temperature, indicating that the lignin active site is not a phenolic group.

To include the effect of oxygen pressure in equation 6, a relationship was derived between \([O_2]_{\text{ads}}\) and \( P_{O_2} \) based on the following assumptions:

1. Oxygen adsorption follows a Langmuir type adsorption isotherm,
2. The total number of adsorption sites is constant,
3. The adsorption/desorption equilibrium can be described by equation 8.

\[ L^* - \text{O}_2,\text{ads} \equiv \text{O}_2,\text{ds} \]  

(8)

where \( \text{O}_2,\text{ds} \) is oxygen dissolved in the caustic solution.

As the adsorption and desorption of oxygen from the active lignin sites is fast, [\( \text{O}_2 \)] is at quasi-equilibrium, and the adsorption rate, \( r_\text{ads} = k[L^*][\text{O}_2,\text{ads}] \), is equal to the desorption rate, \( r_\text{ds} = k[L^*][\text{O}_2,\text{ds}] \). The total number of active sites is constant, i.e. \([\text{HL}^*] + [\text{O}_2,\text{ads}] = C_\text{t}\), thus it may be derived that

\[ [\text{O}_2,\text{ads}] = \frac{K_\text{e}[\text{O}_2,\text{ds}]}{1 + K[\text{O}_2,\text{ds}]} \]

(9)

where \( K_\text{e} = \frac{k_\text{ads}}{k_\text{ds}} \).

Equation 9 shows that when \([\text{O}_2,\text{ds}]\) is very large, the reaction is zero order in dissolved oxygen concentration, while it is first order in dissolved oxygen concentration at very low oxygen concentration. The dependence of \([\text{O}_2,\text{ds}]\) in water on the NaOH concentration and temperature has been reported by Tromans14. The data in the quoted paper show that for the present experimental conditions (0.5M NaOH), 0.55 MPa, and 110°C) the saturated oxygen concentration at oxygen delignification conditions is:

\[ [\text{O}_2,\text{ds}] = 6.4 \times 10^{-3} \times P_{\text{O}_2} \]

(10)

where \([\text{O}_2,\text{ds}]\) is expressed in mol/l and \( P_{\text{O}_2} \) in MPa.

Table 1 shows the saturated oxygen concentration at different oxygen partial pressures for the present experiments performed at 90°C. \( P_{\text{O}_2} \) is the saturated steam pressure at 90°C.

Inserting equations 9 and 10 into equation 6 gives

\[ \frac{-dL_{\text{LC}}}{dt} = C_1 \frac{[\text{O}_2]}{K_{\text{water}} + K_{\text{HL}}[\text{OH}]} \cdot \frac{P_{\text{O}_2}}{1 + 3.39P_{\text{O}_2}} \cdot L_{\text{LC}} \]

(11)

where \( C_1 = k \cdot K_{\text{HL}} \cdot C \cdot K_{\text{e}} \).

At constant temperature and \([\text{O}_2]/[\text{OH}]\), equation 11 can be rearranged as

\[ \frac{1}{(-dL_{\text{LC}}/dt)/L_{\text{LC}}}_\text{dis} = \frac{1}{k} = \frac{K_{\text{e}}}{C_2} \cdot \frac{1}{C_2P_{\text{O}_2}} \]

(12)

where \( C_2 \) is a constant. For the four conditions listed in Table 1, the slope of plots of \(-dL_{\text{LC}}/dt\) versus \(L_{\text{LC}}\) is equal to \( k\). A plot of the inverse of the slope (or \(1/k\)) versus \(1/P_{\text{O}_2}\) is presented in Figure 4. It can be seen that a relative straight line behavior is obtained, supporting the assumption that \([\text{O}_2,\text{ads}]\) is governed by a Langmuir-type adsorption. The value of \( K_\text{e} \) obtained from Figure 4 is \( K = 47.91/14.13 = 3.39 \) (1/MPa).

The constant \( C_1 \) in equation 11 was calculated using all the CSTR experiments performed at 90°C. The value of \( C_1 \) is 0.175 with a standard derivation of 0.0127. Thus, the final oxygen delignification kinetic equation at 90°C is:

\[ \frac{-dL_{\text{LC}}}{dt} = \frac{[\text{O}_2]}{1 + 3.39P_{\text{O}_2}} \cdot \frac{L_{\text{LC}}}{P_{\text{O}_2}} \]

(13)

with \(-dL_{\text{LC}}/dt\) expressed in mg lignin/g pulp/min, \([\text{O}_2]/[\text{OH}]\) in mol/l and \( P_{\text{O}_2} \) in MPa.

Based on equation 13, the first order reaction rate constant, \( k\), can be defined as

\[ k = 0.175 \cdot \frac{[\text{O}_2]}{1 + 3.39P_{\text{O}_2}} \cdot \frac{L_{\text{LC}}}{P_{\text{O}_2}} \]

(14)

Figure 5 illustrates that \( k \) calculated with equation (14) compares well with the measured reaction rate constant (slope of the experimental curves of \(-dL_{\text{LC}}/dt\) versus \(L_{\text{LC}}\)).

Finally, the activation energy was determined from the temperature dependence of the rate constant, \( k\), in the present study as 53 kJ/mol15. This value is in agreement with that of a reaction of the form \( \text{O}_2 + \text{O}_2 \rightarrow 2\text{O}_2 \rightarrow \text{O}_2 \text{H}_2\text{O}_2 \text{H}_2\text{O}_2 \) with a standard derivation of 0.0127.

To confirm the first order behavior in \( L_{\text{LC}} \), \(-dL_{\text{LC}}/dt\) was measured for three Loblolly Pine kraft pulps of different initial kappa numbers; 23, 26, and 34 (see Figure 6)16. The initial higher faster delignification may be due to additional peeling delignification
Oxygen delignification

As has been discussed by van Heiningen et al.17, the first order behavior in $L*$ can be interpreted that the lignin active sites, $L^*$, are uniformly distributed throughout the lignin, and have the same reactivity during the entire oxygen delignification process. It is generally accepted that the first step during oxygen delignification is the dissociation of the phenolic groups. This is the reason why the phenolic group content of residual lignin was measured before and after oxygen delignification. In agreement with literature data17 we obtained values for the phenolic fraction of lignin in the original pulp of around 0.41 and after 60 min at 90°C, 0.52 MPa oxygen pressure and 3.3 g/l of NaOH of around 0.27. After 3 h of oxygen delignification, the phenolic fraction of the residual lignin in pulp decreases further to 0.22, i.e. to half the initial value. Based on this and on the high pKa value of the lignin active sites, $L^*$ we suggest that the rate determining step of oxygen delignification is not a direct attack of oxygen on the dissociated phenolic groups.

The phenolic lignin content of the liquor was also measured. Figure 7 shows these values and that of the pulps at different reaction times as well as the sum of the phenolic group content in the pulp and liquor based on original pulp. As can be seen, the reduction in the amount of phenolic groups in the pulp is nearly equal to the amount of phenolic groups removed with the liquor since the sum of phenolic groups does not change significantly during oxygen delignification. This suggests that the dissolved lignin is still mostly aromatic in nature.

Finally, we found that the ratio (MeOH formation rate/32) / (delignification rate/185), as determined from the methanol and lignin content of the liquor samples, remains mostly constant during delignification at about 0.9 ± 0.2. This means that methanol is released essentially quantitatively from lignin monomer units when they are solubilized11.

The delignification rate versus residual lignin of three brown stock pulps cooked to different kappa numbers from the same Loblolly Pine (Figure 6) shows an initial fast rate. However, after oxygen delignification of the fresh 24.4 kappa brownstock pulp for different times (20 and 60 minutes) in a batch reactor, continued delignification in the CSTR does not display the initial fast rate (Figure 8). The absence of the initial fast rate for the latter two pulps has been explained by the absence of hemicelluloses with reducing ends and attached lignin fragments in these pulps17.

Figure 8 also shows that the oxygen delignified pulp obtained in a batch reactor has a similar delignification rate as the original pulp. This implies that lignin condensation is insignificant in a batch reactor since the pulps are exposed to high concentrations of dissolved lignin at the end of the delignification process.

Delignification mechanism

Based on the presented data we propose that the active lignin site is not the phenolic group, but another less acidic site which is uniformly distributed throughout the residual lignin to satisfy the first order in lignin rate behavior. Because hydroperoxides have a pKa of 12 – 13 compared to about 10.5 for Indulin AT at room
temperature, a mechanism proposed by Chang and Gratzl was adopted to explain the present kinetics. Figure 9 shows the formation of cyclohexadienone hydroperoxide by attack of oxygen at alkaline conditions on phenolic lignin.

As illustrated, a hydroperoxide anion is formed by reaction of superoxide radical anion with the phenolate radical located at the carbon 3 position. Chemical computational modeling to calculate the enthalpies of reactions of lignin model shows that the reaction pathway in Figure 9a is possible. Other phenolate radical intermediates have been proposed (McDonough 1996) where the radical is located on carbon 1 and the beta carbon in addition to the carbon 3 shown in Figure a. All these three structures are part of the same resonance structure in which the odd electron formally resides at each of the three carbon positions. The explanation, why the coupling of the superoxide anion radical with the radical at the carbon 1 and beta carbon is not effective for delignification, is that the formation of the respective oxirane and carbonyl structures is much more difficult than the formation of the muconic acid and quinone structures shown in Figure 9b when the hydroperoxide anion is located at the carbon 3 position.

Figure 9b shows that the hydroperoxide anion forms either a muconic acid structure and MeOH or an orthoquinone structure and MeOH. Since the hydroperoxide anion is the dominant species at pH > 12-13, based on the present kinetics is probable that the carbon at the 3 position of the lignin aromatic ring is the active site for oxygen delignification. Thus the present kinetics may be interpreted that the rate determining step is the unimolecular decomposition of the formed hydroperoxide anion, i.e. the rate is determined by the dissociated hydroperoxide concentration. The latter is determined by the concentration of adsorbed oxygen on methoxyl groups at the carbon 3 (the lignin active site, $I^*$), as well as by the pKa of the hydroperoxide. Further support that the carbon 3 with a methoxyl group is the lignin active site, $I^*$, is that almost all residual softwood lignin monomer units contain this moiety, thus explaining the uniform reactivity and first order kinetics in residual lignin for oxygen delignification.

The pH dependence of the kinetics implies that the protonated hydroperoxide does not fragment into muconic acid or quinone structures. Also, the fact that dissolved lignin mostly retains its aromatic nature, and that MeOH is released essentially quantitatively during delignification, further support the hypothesis that quinone formation is the dominant pathway.

**Kinetics of cellulose degradation**

The cleavage of cellulose was modeled by Iribarne and Schroeder 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 calculate 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=τ, as 1/DP_{t-1}/DP_{0}. DP can be obtained from the intrinsic viscosity ($\eta$) by equation (15). 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.

$$DP_{\text{Cellulose}} = \left(\frac{1.65[\eta] - 116H}{G}\right)^{\frac{1}{111}}$$

where $[\eta]$ is intrinsic viscosity of the pulp in cm²/g, and $G$ and $H$ are the mass fractions of cellulose and hemicellulose in the pulp (see Table 2). This formula considers the actual weight of cellulose rather than the pulp weight being responsible for the pulp viscosity, and makes a correction for the small contribution of the hemicelluloses to the intrinsic viscosity.

The number of moles of cellulose per gram of pulp, $m_n$, can be calculated by equation (16) as follows:

$$m_n = \frac{1}{162DP_n+18} \equiv \frac{1}{162DP_n} \left(\frac{\text{Moles}}{\text{Gram Pulp}}\right)$$

The content of cellulose (G) and hemicellulose (H) in the pulp was measured by high pressure anion exchange chromatography (HPAEC) on double hydrolyzed pulp samples. The results for the pulp samples are listed in Table 2.
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. The model can be described as equation (17):

\[
\frac{dm_c}{dt} = -k_c \frac{dK}{dt} + k_H [OH^-] \tag{17}
\]

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 (17) gives:

\[
m_c = m_c^0 + k_L (K - K_0) + k_H [OH^-] t \tag{18}
\]

Comparable results for the same brown stock pulp oxygen delignified in a batch reactor samples are given in Table 3. Since NaOH is rapidly consumed during the initial phase of oxygen delignification in a batch reactor, the influence of the term \( k_c [OH^-] \) in equation (18) may be neglected for \( t \geq 20 \) minutes. This allows calculation of \( k_c \) by fitting the batch reactor as \( 3.60 \times 10^8 \) (moles/g pulp·kappa). Using this value in the analysis of the CSTR data gives a value for \( k_H \) of 1.07 \times 10^9 (liter·mol cellulose/g pulp·g NaOH·minute). These two values provide a good fit of the cellulose degradation in the CSTR and batch reactor as can be seen in Figure 10.

**Conclusions**

The kinetics of oxygen delignification are first order in residual lignin content (HexA corrected), and follow a Langmuir-type behavior for adsorption of oxygen on the active aromatic lignin sites. The reaction order in NaOH of the kinetics implies that the rate determining step involves an acidic lignin active site with a pKa almost 2 units higher than that of phenol in lignin. Based on these results it is proposed that the lignin active site is the 3 carbon of the aromatic ring where oxygen reacts to form a hydroperoxide. The rate determining step is identified as the unimolecular decomposition of the formed hydroperoxide anion. The almost uniform presence of aromatic methoxyl groups in residual lignin further supports the first order in lignin kinetics. Further supporting evidence is the close relationship between delignification and demethoxylation. The significant reduction in phenolic group content of the lignin during oxygen delignification is consistent with the hypothesis that the rate determining step of oxygen delignification is not a direct attack of oxygen on the dissociated phenolic groups. The cellulose degradation during oxygen delignification was modeled by two contributions: one due to radicals produced by phenolic delignification, and the other due to alkaline hydrolysis.

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