A new CSTR for oxygen delignification mechanism and kinetics study

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Abstract: We have adopted a differential reactor system used frequently for fluid-solid rate studies (so-called Berty reactor) for oxygen delignification study. In this continuous stirred tank reactor (CSTR), the dissolved oxygen and the alkali concentration in the feed are kept constant, and the lignin removal rate is determined from the dissolved lignin concentration of the outflow stream measured by an online UVVIS. It is better suited for kinetics and mechanistic studies because the products formed during extraction are immediately removed from the reaction system.

Oxygen delignification is widely used for lignin removal before bleaching. The well-known advantages of oxygen delignification are chemical cost savings, yield retention and improved environmental performance. The disadvantages are the high capital cost and lower lignin-cellulose selectivity compared to chlorine dioxide bleaching. The lower selectivity has limited commercial single-stage delignification of softwoods to about 50% lignin removal. With improved selectivity, it may be possible to extend the delignification further. Therefore, a better understanding of the mechanism of delignification and its interaction with carbohydrate degradation may lead to identification of improved oxygen delignification conditions.

Many researchers [1,2,3] used model compounds to study the mechanism of oxygen delignification. Based on these studies, it is now well accepted that the initial step is the generation of a phenolate radical and a superoxide anion radical from the attack of oxygen on the phenolate anion formed from phenolic lignin at alkaline conditions. The resonance stabilized phenoxyl radical structures then undergo reaction with themselves (lignin condensation) or with oxygen species such as hydroxyl (HO·), hydroperoxy (HOO·) and superoxide (O2·–) radicals to form organic acids, carbon dioxide and other small molecular weight organic products via side chain elimination, ring opening and demethoxylation reactions [1].

Johansson and Ljunggren [3] found that phenolic structures with a conjugated side chain, like stilbene and enol ethers, react very rapidly, whereas diphenylmethane-type condensed structures are particularly resistant to oxygen bleaching. The p-hydroxyphenyl and 5,5′-biphenolic units in the residual lignin are quite stable and tend to accumulate during oxygen delignification [4,5]. During oxygen delignification, the number of phenolic hydroxyl groups in the pulp decrease and the number of carboxylic acid groups increase, which is expected since the degradation products from oxygen delignification are predominately organic acids and carbon dioxide [6].

There are many papers in the literature on the lignin structure after cooking and oxygen delignification. However, it is very difficult to isolate the residual lignin without changing the lignin chemically, especially when lignin is only a small portion of the pulp. Also, the yield of residual lignin is only 30-80% [7]. These studies generally suggest that the lignin structures, before and after oxygen delignification, are not very much different [8]. Many researchers have suggested [9,10] that the residual lignin is covalently bound to the hemicellulose through so-called LCC (lignin carbohydrate complexes) linkages. Backa et al. [9] proposed that, after cooking, the residual lignin consists mostly of oligolignin structures bound to hemicellulose through LCC bonds. Therefore, the decreasing efficiency of oxygen delignification at increased lignin removal may be explained by the lack of phenolic groups and by the presence of LCC bonds [11].

A modified oxygen delignification mechanism proposed by Backa et al. [9] is shown in Fig. 1. The chain represents a part of a hemicellulose chain with two end groups. The circle at one end in structure I represents a labile reducing end, while the bar at the other end is a non-reducing end. The reducing end of the chain is subject to endwise peeling and, finally, the stopping reaction, so that in structure II both ends of the chain are stable. The residual lignin (in the form of low molecular weight oligolignins) is bound to the hemicellulose chain through LCC bonds. The formation of structure II after the peeling leads to loss of lignin, and is called “endwise peeling delignification”. Also, the phenolic end of one of the oligolignins in structure II dissociates to phenolate (structure III), where it reacts with oxygen according to so called “phenolate delignification”.

Since the radical species, shown as hydroxyl radical in Fig. 1, is formed at a location close to the hemicellulose chain, it may cleave the chain and form two new end groups, one reducing and one non-reducing (structure IV). It should be noted that in a pulp mill, dissolved lignin and LCC fragments react with oxygen to form radicals, leading to lower selectivity and possibly poorer bleachability of the pulp. Our present study is performed to further test the validity of this proposed mechanism by using a new kinetic reactor which allows...
the analysis of dissolved delignification products as a function of time.

Many studies have been performed to determine the kinetics of the oxygen delignification equation [12,13,14]. The sodium hydroxide concentration [OH⁻] decreases significantly during kinetic studies performed in medium consistency laboratory batch reactors. The hydroxide concentration may be kept relatively constant by using consistencies which are at least an order of magnitude smaller than commonly used in industrial practice. In the present study, medium consistency conditions and a constant NaOH concentration are realized by continuous flow of an oxygenated caustic solution through a pulp bed. The whole bed is contained inside a reactor in which the caustic solution is rapidly circulated through the pulp bed, while fresh oxygenated caustic solution is added and spent liquor is removed simultaneously. Thus, this novel medium consistency kinetic system is that of a differential continuous stirred tank reactor (CSTR) with dissolved oxygen and sodium hydroxide concentrations close to that of the feed.

**EXPERIMENTAL**

**Reactor Setup**

The flow diagram of the reactor setup is shown in Fig. 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 the 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 280 ml. It contains a 100 ml basket with a rotor underneath which induces flow through the pulp mat inside the basket, Fig. 3. 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 the NaOH solution to obtain a saturated oxygen concentration at room temperature at desired pressure. The oxygenated solution is heated the second day to a desired temperature and pressure, and excess oxygen (due to the lower solubility of oxygen at higher temperature) is released through a gas valve. 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. The UV-VIS data are converted into dissolved lignin concentration using a calibration curve prepared with Indulin AT lignin of MeadWestvaco, Fig. 4.

**Raw Materials**

A commercial unbleached southern pine kraft pulp with an initial kappa number of 26 (Tappi Standard) and intrinsic viscosity of 1205 ml/g (A.ST.M designation D1795-62 reapproved in 1985) was used.

**Measurements**

The following measurements were performed on the oxygen delignification spent liquor: total organic carbon (TOC) and total inorganic carbon (TIC) were determined using a Shimadzu TOC-5000A Analyzer with autosampler at the Plant, Soil and Environment Science Department of the University of Maine. The dissolved lignin concentration was measured using a HP8453 UV-VIS spectrophotometer from Agilent. The absorption at 280 nm was converted to lignin concentration using the calibration in Fig. 4. The methanol concentration was determined using headspace gas chromatography (HS-GC) at the Georgia Institute of Technology [15].

**Data Reduction Procedure**

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

\[
\text{Inflow – Outflow + Dissolved by Reaction} = \text{Accumulated in Reactor}
\]

or

\[
0 - \phi_p C(t) \, dt + r(t) \, mp \, dt = V_d \frac{dC}{dt}
\]

where

- \( \phi_p \) is the liquid flow rate (ml/min)
- \( C(t)\) is the dissolved lignin concentration (mg lignin/ml)
- \( V_d \) is the reactor volume (ml)
- \( mp \) 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

\[
t_d = \frac{96}{\phi_p}
\]
Thus the dissolved lignin concentration inside the Berty reactor at time $t$, $C(t)$, is equal to the concentration measured by UV at time $t+t_d$, $CL(t+t_d)$:

$$C(t) = CL(t+t_d)$$  \(4\)

and

$$r(t) = \frac{\phi_p}{m_p} C_L(t+t_d)$$

$$+ \left. \frac{V_r}{m_p} \frac{dC_L}{dt} \right|_{t+t_d}$$  \(5\)

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

$$\phi_p \int_0^t \phi_p C_L(t) \, dt + V_r C(t+t_d)$$  \(6\)

A typical dissolved lignin concentration profile is displayed in Fig. 5. Application of equation 5 leads to the rate of delignification versus time, shown in Fig. 6.

Figure 5 shows a finite dissolved lignin concentration at time $t = 0$ because lignin is leached from the pulp by hot water extraction before the start of the experiment. The results in Fig. 6 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 (residence time in Berty reactor is $265/60 = 4$ minutes and 25 seconds).

**RESULTS AND DISCUSSION**

**Validation of Reactor System**

The reactor operation was validated by showing that the oxygen delignification kinetics were not influenced by the amount of pulp in the reactor, feed flow rate, and rotor speed under the basket. The results, in Fig. 7, show that at stirring speeds of 200 rpm or higher, the oxygen delignification profile is independent of rotor speed. A rotor speed of 400 rpm was adopted as the normal operating condition. The effect of flow rate is seen in Fig. 8. It shows that the delignification rate is not affected by the flow rate. Because of the size of the feed tank, a flow rate of 75 ml/min was adopted for the rest of the experiments. Figure 9 shows the effect of pulp weight on the delignification rate. The close agreement of the three results confirms that the experimental method and procedures are sound and reproducible. Because of analysis requirements, most experiments were performed with 4 grams (oven dry basis) of pulp.

**Lignin Mass Balance**

In Fig. 10, the amount of lignin removed, as calculated by equation 6, was compared with the difference in Klason lignin content between the original and delignified pulps obtained after different reaction times. The slope of the straight line in Fig. 10 is 0.91, which is slightly less than 1.0, probably due to experimental error. The small difference shows that the lignin mass balance is reasonably closed. The amount of removed lignin calculated by equation 6 versus change in kappa number is plotted in Fig. 11. This figure shows that the removed lignin expressed in % on pulp (od) is equal to 0.188 $\times$ Kappa.

**Effect of Different Initial Conditions**

If the reactor is initially filled with caustic of the same concentration as that of the feed, then there would be no initial transient in the NaOH concentration. However, some lignin would be extracted from
the pulp by NaOH during the heating period prior to starting the actual experiment. Therefore, how the delignification rate was affected by the initial conditions in the reactor, i.e. filled with pure water or NaOH solution, was tested.

Three experiments were performed with the reactor initially filled with non-oxygenated NaOH or filled with water. In two experiments, the heating time of the reactor to the desired temperature was about 2 hours. The third experiment was performed with water in the reactor, but the preheating time increased to 10 hours. It can be seen, in Fig. 12, that the experiments with NaOH at 2 hours preheating and with water at 10 hours preheating lead to similar pre-extraction of lignin from the pulp. In contrast, only a small amount of lignin is pre-extracted with water after 2 hours preheating. Figure 13 shows that the oxygen delignification rates for the three different initial conditions are very similar. It can also be seen that the maximum delignification rate is reached at about 7 minutes. This shows that oxygen is needed for the delignification to proceed, irrespective of whether the reactor was initially filled with water or caustic. For this reason, as well as experimental simplicity, the reactor was filled with water in later kinetic experiments. The pre-extraction of lignin from pulp at alkaline conditions may be the result of "peeling delignification".

Figure 14 shows the methanol formation rate versus time for two new experiments with different initial conditions. The TOC and methanol concentration were also measured for these two experiments, Table I.

Figure 15 shows the rates of formation of TOC when the reactor is initially filled with water. These rates were calculated using equation 5 and the concentrations listed in Table I. It can be seen that the rate of formation of organic carbon and methanol in the spent liquor decrease with time.

CONCLUSIONS

The present differential CSTR is suitable for measuring the kinetics of medium consistency oxygen delignification at standard operating conditions. The obtained data appears to con-

Keywords: REACTORS, TANKS, OXYGEN, DELIGNIFICATION, KINETICS, REACTION MECHANISMS.