

# Kinetics of oxidation reactions between ozone, and lignin and cellulose

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## Keywords

Ozone, Kinetics, Cellulose, Klason Lignin

## Abstract

Ozone is an attractive as an oxidation agent in kraft cellulose bleaching. However, it shows poor selectivity towards lignin and may also attack the cellulose. This paper reports kinetic data on ozone reactions with lignin and cellulose, in aqueous solutions, at pH 2 and 4, and temperature in the range 20-40°C. Pure cellulose and Klason lignin from pine sawdust were used in the experiments. Results show that both lignin and cellulose fitted well a second order reaction scheme (ie. first order with respect to both ozone and substrate concentrations). Lignin oxidation rate constants were up to 60,000 times larger than that of cellulose. Lignin oxidation was not significantly affected by pH whereas cellulose degradation was faster at pH 4. Kinetic parameters, and data on ozone selfdecomposition are also reported.

## 1. Introduction

Environmental pressures on the bleaching Kraft cellulose industry have motivated the search for new bleaching agents alternative to chlorine-based ones. In that context, ozone has been proposed as part of elementary chlorine free (ECF) and total chlorine free bleaching sequences (Andtbacka & Tibbing, 1994; Dillener et al, 1990; Liebergott et al, 1984; Liebergott et al, 1992 a, b; Kappel et al, 1994). However, ozone shows poor selectivity towards lignin and may also oxidise the cellulosic matrix. Ozone is a

highly reactive oxidation agent and nucleophilic, electrophilic and free radical's mechanisms have been suggested to explain its reactions with organic compounds (Stahelin and Hoigné, 1985). These reactions are pH dependent and are catalysed by transition metals.

From a process design and control viewpoint, it is important to understand the effect of process conditions on ozone reactivity towards lignin and cellulose. However, little information has been reported on the kinetics of lignin and cellulose oxidation by ozone in particular, reactions kinetics and overall stoichiometry.

In such context this work is aimed at finding the kinetic constants of ozone oxidation reactions with cellulose and Klason lignin from pinewood. The effect of temperature and pH is also assessed.

## 2.-Methods

The experimental system is based on an ozone generator (Ozacav OEC240X) with 0,5 (moles O<sub>3</sub>/h) rated capacity from pure oxygen.

A 2 dm<sup>3</sup> Pyrex reactor, with temperature and stirring control, was fitted to the temperature and stirring control, was fitted to the ozonator. Inlet and outlet ozone mass flow rate was monitored in all experiments. Prior to discharge to the environment, the exhaust gas was washed with a pH 12 iodine solution to destroy any unreacted ozone.

Typically, kinetic experiments were conducted in batch mode for the liquid and phases, whereas the ozone gas was bubbled through the reactor over a preset period. In the case mass transfer did not affect the process rate. Therefore, all runs were carried out at 200 rpm.

Kinetic data was obtained from experiments at varying experimental time, at a given pH and temperature. Ozone consumption was determined by the balance between the inlet and outlet mass flowrates. Rate constants were estimated from ozone and solutes concentration versus time. Ozone selfdecomposition was accounted for in the calculations. Gas and dissolved ozone concentrations were measured by the iodometric (Kolthoff and Belcher, 1957) and the Indigo (Bader and Hoigne, 1981) methods, respectively.

Pure cellulose samples were obtained from highly bleached Pine Kraft pulp. Samples were subjected to mechanical refining in order to disrupt the fibrous structure and reduce internal mass transfer effects. Cellulose was characterised by the Tappi viscosity (TAPPI, 1994), since this parameter is related to the cellulose degree of polymerisation.

Lignin samples were obtained from Pine sawdust

by the Klason method (TAPPI, 1994). Sawdust samples were hydrolysed with 72% H<sub>2</sub>SO<sub>4</sub> at 20°C for 2 h, and further treated with diluted acid for 4 h. until all carbohydrates were dissolved. The Klason lignin was then pulverised to mesh size 80. Lignin was measured on the basis of the Kappa Number (TAPPI, 1994)

### 3. Results and Discussion

#### 3.1 Ozone Selfdecomposition in Aqueous Solution.

Data on ozone self-decomposition in aqueous solution are reported in Table 1. These values fitted well a first order kinetic scheme in terms of dissolved ozone concentration. Self-decomposition reaction order reported in the literature (Teramoto et al, 1981). Ozone decomposition was faster at higher pH and increased with temperature.

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**TABLE 1: OZONE SELF-DECOMPOSITION IN WATER 1st ORDER RATE CONSTANT**

pH	Temperature °C	First Order Rate Constant (min <sup>-1</sup> )
2	20	0.030
	25	0.030
	30	0.035
	35	0.038
	40	0.043
4	20	0.039
	25	0.050
	30	0.081
	35	0.111
	40	0.268

**TABLE 2: OZONE SELF-DECOMPOSITION KINETIC PARAMETERS**

	pH 2	pH 4
Activation Energy (kJ/mol)	14.7	70.4
Pre-exponential factor (min <sup>-1</sup> )	12.1	10.4

Table 2 shows the corresponding Arrhenius kinetic parameters, which are significantly affected by pH. As temperature increases, ozone decomposition takes place at a faster rate at pH 4, probably due to increased free radical formation, enhanced by hydroxide ions. These free radicals are thought to initiate and propagate ozone decomposition (Sehested et al, 1996; Sotelo et al, 1987; Tomiyasu et al, 1985).

### 3.2 Klason Lignin and Ozone Reactions

Ozone and lignin reacted rapidly and, as shown in Table 3, pH did not have a significant effect on the ozone consumption rate. These values could be described by a second order reaction scheme, in terms of dissolved ozone and residual lignin concentration. All values fitted well a single set of Arrhenius kinetic parameters, shown in Table 4 (correlation coefficient above 0.97).

**TABLE 3: LIGNIN OZONE REACTION 2nd ORDER RATE CONSTANT**

pH	Temperature °C	Second order kinetic constant (min <sup>-1</sup> g <sup>-1</sup> )
2	20	61.3
	25	73.0
	30	97.3
	35	112.0
	40	116.8
4	20	68.8
	25	73.0
	30	97.3
	35	104.0
	40	116.8

**Table 4: Klason Lignin Ozonation Kinetic Parameters**

Mean Activation Energy (kJ/mol)	23.4
Preexponential factor ( $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$ )	$9.2 \cdot 10^5$

Lignin presents a chemical structure rich in phenolic-type aromatic units, which present high electron density. Therefore, at lower pH ozone is likely to react through an electrophilic substitution mechanism. At higher pH, free radical formation is enhanced and these are expected to react with lignin.

### 3.3 Cellulose Ozone reactions.

As in the case of lignin, cellulose ozonation could also be described by a second order kinetic scheme. Corresponding rate constants are presented in Table 5. At pH 4, cellulose decomposes at a much faster rate than at pH 2, at higher temperature. This could indicate that free radical mechanisms play a key role in cellulose oxidation, with negligible attack via electrophilic substitution.

**TABLE 6: CELLULOSE OZONATION KINETIC PARAMETERS**

	pH 2	pH 4
Activation Energy (kJ/mol)	57.9	118.4
Preexponential factor ( $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$ )	$1.80 \cdot 10^{11}$	$54 \cdot 10^{18}$

**TABLE 5: CELLULOSE OZONATION 2nd ORDER RATE CONSTANT**

pH	Temperature °C	Second order kinetic constant ( $\text{min}^{-1} \text{g}^{-1}$ )
2	20	$0.96 \cdot 10^{-3}$
2	25	$1.23 \cdot 10^{-3}$
2	30	$2.72 \cdot 10^{-3}$
2	35	$2.77 \cdot 10^{-3}$
2	40	$4.24 \cdot 10^{-3}$
4	20	$1.20 \cdot 10^{-3}$
4	25	$2.48 \cdot 10^{-3}$
4	30	$6.48 \cdot 10^{-3}$
4	35	$13.57 \cdot 10^{-3}$
4	40	$25.68 \cdot 10^{-3}$

## Conclusions

These results show that the apparent rate constant for cellulose oxidation by ozone in aqueous solutions is 3 to 4 orders of magnitude below pH and temperature, where the rate of lignin oxidation is more than 60,000 times faster than cellulose decomposition.

Lignin oxidation was not significantly affected by pH and free radical as well as electrophilic ozone attack may be involved.

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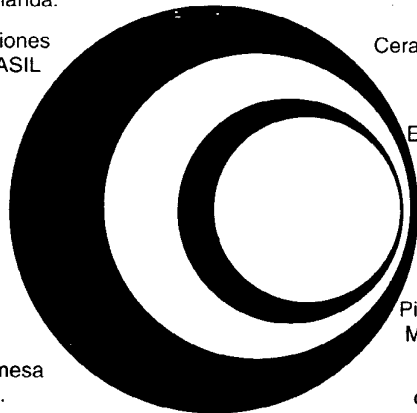
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