A study in the oxidation of Kraft black liquor
by Fredrick James Zadick

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemical Engineering
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Abstract:
Strong black liquor from the Hoerner-Waldorf Paper Products Company was oxidized with oxygen in a diffusion cell at 90°C. The oxygen at atmospheric pressure was allowed to pass over the liquor in the cell, thereby diffusing into and simultaneously reacting with sodium sulfide in the black liquor. Periodically, samples were taken at different distances from the liquid interface and analyzed for sulfide.

Experimental results were correlated to a mathematical model describing the diffusion and simultaneous rapid reaction of oxygen with the sulfide in the black liquor. Constants used in the mathe-matical expression were determined for the black liquor system.

Generally the experimental results agreed well with the theoretical predicted results from the diffusion model. This gives evidence in support of the theory that the oxidation mechanism in the black liquor is diffusion controlled and can be described by a mathematical expression for diffusion with simultaneous rapid (essentially instantaneous) reaction.

The effect of increasing the thiosulfate concentration in black liquor seemed to slow the rate of conversion of sodium sulfide.

Increasing the sulfide concentration in black liquor had neg-ligible effect on the rate of conversion of sodium sulfide to thio-sulfate.

An artificial solution of sodium sulfide was oxidized in the same manner as were the black liquor samples. Results showed the sodium sulfide solution to react very slowly, indicating that the sulfide in black liquor may be catalyzed to react very rapidly.

There was evidence of convection in the diffusion cell caused by external disturbances. This seemed to increase the values of diffusivity of sulfide in the black liquor, which would have been lower in a perfectly undisturbed cell apparatus.

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## ABSTRACT

Strong black liquor from the Hoerner-Waldorf Paper Products Company was oxidized with oxygen in a diffusion cell at $90^\circ$C. The oxygen at atmospheric pressure was allowed to pass over the liquor in the cell, thereby diffusing into and simultaneously reacting with sodium sulfide in the black liquor. Periodically, samples were taken at different distances from the liquid interface and analyzed for sulfide.

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# INTRODUCTION

The Kraft sulfate pulp process accounts for over half of the pulp produced in the United States. Odors from these plants are of growing concern to many communities. These odors, both organic and inorganic in nature, are given off at various units in a Kraft pulp mill.[4] One major source of odor is the escape of hydrogen sulfide from the direct contact evaporators and the recovery furnace used to concentrate and regenerate black liquor in the Kraft process.

The Kraft process starts with the digesting of wood chips by a cooking liquor which is a mixture of sodium sulfide, sodium hydroxide, and sodium carbonate. The purpose of the digestion is to dissolve the noncellulosic material in the chips, leaving the cellulose fibers undissolved. In this step lignins are hydrolyzed to alcohols and acids. After the digestion, the pulp fibers are free from lignins and are separated from the cooking liquor. This liquor is the weak black liquor which contains appreciable amounts of organic sulfur compounds and the spent reagents of the original cooking liquor.

Also present are the unreacted inorganic compounds originally present. This weak black liquor is then concentrated by direct contact evaporators in series to concentrate the liquor to about forty percent solids. The concentrated black liquor is called strong black liquor. The strong liquor is then sprayed into a recovery furnace to regenerate the liquor by breaking down organic compounds and melting the inorganic chemicals.[11]

In order to reduce the odor released in the evaporators and recovery furnace, the black liquor (either weak or strong) can be oxidized. Here the main reaction is the oxidation of sodium sulfide to sodium thiosulfate and other secondary products. This reduces the amount of hydrogen sulfide given off by the evaporators and recovery furnace and also saves adding increased make-up reagents upon regeneration.

Most oxidation studies with black liquor have been concerned with oxidizing the weak black liquor. The Hoerner-Waldorf plant at Missoula, Montana presently oxidizes strong black liquor.

The mechanism of black liquor oxidation has not been well understood. This study is concerned with the oxygen oxidation of strong black liquor in a diffusion cell in which the oxygen is passed over the liquid interface, diffusing through and reacting with the black liquor. It was hoped that this model would give some information on the mechanism of the oxidation.

## SURVEY OF PREVIOUS WORK

Some previous oxidation studies with black liquor have been concerned with direct contact methods such as packed columns and batch reactors in which the liquor was continuously agitated.[2,5] Conclusions drawn from these studies have given little information on the basic mechanism of the oxidation. Experimental results that have been reported contain information on the rates of oxidation for various temperature ranges, air rates, etc., for specific plant conditions.

Murray reported the oxidation rate to follow an empirical equation of the nature

$$V \ln (c \neq bp) = K\theta \neq B$$

where

$V$ = volume of reactor

$B$ = integration constant

$b$ = parameter in oxidation rate equation, grams per liter atmosphere

$p$ = partial pressure of oxygen, atmospheres

$\theta$ = time, hours

$c$ = concentration of sodium sulfide in black liquor, grams per liter

$K$ = parameter in oxidation rate equation, liter per hour square foot

Murray determined values of $K$, $B$, and $b$.

Shah reported that the reaction rate depends on oxygen absorption and sodium sulfide concentration and could be expressed by

$$- r_s a = Ka(C_s \neq d' P_{O_2})$$

where　　$Ka =$ parameter in oxidation rate equation,
liter per hour cubic foot

$d' =$ parameter in oxidation rate equation,
moles per liter atmosphere

$-r_s a =$ oxidation rate of sodium sulfide,
moles per hour cubic foot

$C_s =$ concentration of sodium sulfide,
moles per liter

The value of Ka calculated by Shah was close to the experimental value, but the calculated value of d' was considerably lower than the experimental value, suggesting that a mechanism other than the two-film diffusional model used by Shah would best represent the reaction.[9]

Fones and Sapp found the rate of oxidation of black liquor to be "quite rapid". Their oxidation study showed that the concentration of sulfide decreased with time and the concentration of thiosulfate and sulfate increased with time. After most of the sulfide had been oxidized, the thiosulfate was apparently further oxidized to sulfate.[3]

THEORY

## Black Liquor Oxidation

The following are generally accepted to explain the main reactions in the oxidation of black liquor:

(1) $2Na_2S + 2O_2 + H_2O = Na_2S_2O_3 + 2NaOH$

(2) $Na_2S_2O_3 + 2NaOH + 2O_2 = 2Na_2SO_4 + H_2O$
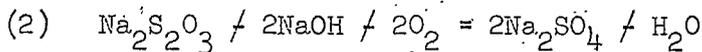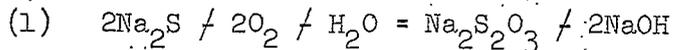
The oxidation is basically the reaction of oxygen with sodium sulfide to make more stable inorganic sulfur compounds, of which sodium thiosulfate is the major product.[2,3,13] The reaction of thiosulfate with sodium hydroxide and oxygen has been reported to occur in greatest proportion after the sodium sulfide has been nearly depleted by oxidation.[3]

Many other reactions have been hypothesized (involving various oxidation states of sulfur) including formation of elemental sulfur. These reactions, however, would be of minor significance in this study.[5,8]

Since the oxygen is in the gaseous state and the black liquor is a liquid, the oxygen must contact the liquor before any reaction can take place. Mass transfer is assumed to control the reaction since previous work indicates that the reaction is essentially instantaneous. Thus, the mass transfer model used to describe the diffusion of oxygen is based on the very rapid reaction between oxygen and sulfide.

## Theory on Simultaneous Diffusion and Reaction

There are two basic theories concerning diffusion with simultaneous reaction. The first is called the two-film theory, based on the assumption that the resistance to diffusion is concentrated within a thin film next to the gas-liquid interface. This film is assumed to have negligible capacity for holding the dissolved solute. In the two-film theory there are two such films actually, one in the gas and one in the liquid.

The other theory is that of unsteady state molecular diffusion of the solute into the whole mass of liquid, the amount of solute dissolving being restricted by the time of exposure of the liquid surface. It is not possible to say which theory is more correct in industrial equipment, due to lack of experimental evidence.[10]

In the two-film theory, as used by Shah in his study of black liquor oxidation, the solute gas A reacts instantaneously with liquid B according to A $+$ B $=$ AB. As the solution first meets the gas, the two substances react immediately at the phase boundary. The product AB will start to diffuse toward the main body of liquid. The liquid near the surface soon runs out of B, and more B starts to diffuse upward from the main body of liquid. Because B is rapidly removed from the region near the surface, the A coming in must diffuse through part of the liquid film in order to meet B diffusing upward. Thus, the reaction zone for A and B moves away from the gas-liquid interface and takes up a stationary position (within a few seconds time) such that

the rate of diffusion of A from the gas phase is equal, mole for mole, to the rate of diffusion of B from the main body of liquid.[10]

The unsteady state diffusion theory used in this study also assumes a rapid reaction between gas A and substance B in the liquid. As A is absorbed, the B molecules near the interface are consumed in the reaction and are replaced by diffusion of more B molecules from the body of liquid. Because the reaction is assumed to take place very rapidly when A meets B, regardless of their concentrations in the reaction zone, the distance at which A and B meet will move farther down from the interface with time.

Thus, for the region up to a distance z' from the interface, the diffusion of A is represented by the diffusion equation[1]

$$(3) \quad D_A \frac{\partial^2 C_A}{\partial z^2} = \frac{\partial C_A}{\partial t}$$

also for $z > z'$, the diffusion of B is given by

$$(4) \quad D_B \frac{\partial^2 C_B}{\partial z^2} = \frac{\partial C_B}{\partial t}$$

where $t$ = time

$C_B$ = concentration of B

$C_A$ = concentration of A

$D_A$, $D_B$ = diffusion coefficients of A and B, respectively, in the liquid body

For the times of exposure of the surface to oxygen in this study, it may be assumed that the liquid layer is infinitely deep, or $z' < z < \infty$. Actually, the concentration of B five inches below the interface remains at essentially the initial concentration of B during the period of the run.

Solutions to equations (3) and (4) are of the form

$$(5) \qquad \frac{C_A}{C_{A_o}} = a_1 + a_2 \ \mathrm{erf} \ \frac{z}{\sqrt{4 \ D_A \ t}}$$

and

$$(6) \qquad \frac{C_B}{C_{B_o}} = b_1 + b_2 \ \mathrm{erf} \ \frac{z}{\sqrt{4 \ D_B \ t}}$$

where $\qquad C_{B_o}$ = initial concentration of B in the liquid

$\qquad\qquad C_{A_o}$ = interfacial liquid phase concentration of A

To solve for all the constants $a_1$, $a_2$, $b_1$, $b_2$, the following initial and boundary conditions are given:

I.C.      at $t = 0$          $C_B = C_{B_o}$

B.C.      at $z = 0$          $C_A = C_{A_o}$

B.C.      at $z = z'(t)$      $C_A = 0$

B.C.      at $z = z'(t)$      $C_B = 0$

B.C.      at $z = z'(t)$      $-D_A \dfrac{\partial C_A}{\partial z} = D_B \dfrac{\partial C_B}{\partial z}$

The last boundary condition comes from the fact that one mole of A reacts stoichiometrically with one mole of B.[1]

At the reaction surface, equation (5) must reduce to

$$(7) \quad C_A(z',t) = 0$$

Then, from the perfect differential

$$(8) \quad dC_A = 0 = \left(\frac{\partial C_A}{\partial z'}\right)_t dz' + \left(\frac{\partial C_A}{\partial t}\right)_{z'} dt$$

the following solution can be obtained:

$$(9) \quad \frac{dz'}{dt} = - \frac{\left(\dfrac{\partial C_A}{\partial t}\right)_{z'}}{\left(\dfrac{\partial C_A}{\partial z'}\right)_t}$$

Substituting equation (5) into equation (9) gives

$$(10) \quad \frac{dz'}{dt} = \frac{z'}{2t}$$

Integrating (10) gives the following equation showing dependence of z' on t:

$$(1\ ) \quad z' = \sqrt{4\alpha t}$$

where $\alpha$ = integration constant

The constant $\alpha$ may be solved indirectly from

$$(12) \quad 1 - \mathrm{erf}\sqrt{\frac{\alpha}{D_B}} = \frac{C_{B_o}}{C_{A_o}} \sqrt{\frac{D_B}{D_A}}\ \mathrm{erf}\sqrt{\frac{\alpha}{D_A}}\ \exp\left(\frac{\alpha}{D_A} - \frac{\alpha}{D_B}\right)$$

It is assumed that $D_B = D_A$ to simplify calculations of $\sqrt{\dfrac{\alpha}{D_B}}$.

This assumption is approximately true, since orders of magnitude

of the values of the diffusivities will not vary by more than a factor

of two, usually. This will not appreciably change the value of $\sqrt{\dfrac{\alpha}{D_B}}$.

(See the Calculation Section in the Appendix.)

The constants determined are:

$$(13) \quad a_1 = C_{A_o}$$

$$(14) \quad a_2 = - \left( \text{erf} \sqrt{\dfrac{\alpha}{D_A}} \right)^{-1}$$

$$(15) \quad b_1 = 1 - \left( 1 - \text{erf} \sqrt{\dfrac{\alpha}{D_B}} \right)^{-1}$$

$$(16) \quad b_2 = \left( 1 - \text{erf} \sqrt{\dfrac{\alpha}{D_B}} \right)^{-1}$$

First, equation (12) must be solved for $\sqrt{\dfrac{\alpha}{D}}$ by insert-

ing given values of $\dfrac{C_{B_o}}{C_{A_o}}$ and $\sqrt{\dfrac{D_B}{D_A}}$. Then we can get $a_2$, $b_1$, and $b_2$.

The average rate of absorption of A up to time t is

$$(17) \quad N_{A_{avg}} = \frac{1}{t} \int_o^t N_A dt = 2 \, \frac{C_{A_o}}{\text{erf} \sqrt{\dfrac{\alpha}{D_A}}} \sqrt{\dfrac{D_A}{\pi t}}$$

## RESEARCH OBJECTIVES

This study was undertaken to investigate the mechanism of the oxidation of strong black liquor with oxygen. A diffusion cell was used which allowed oxygen to simultaneously diffuse and react with the black liquor. Experimental data were fit to a mathematical diffusion-controlled model to describe the oxidation mechanism. All work was carried out at about $90^\circ C$. It is hoped that the information presented in this study will contribute to further progress in oxidation of black liquor in pulp mills.

# EQUIPMENT

The heart of the equipment was a plexiglass diffusion cell consisting of a one centimeter diameter cylindrical hole bored concentrically through a $5\frac{1}{2}$-inch long piece of two-inch diameter plexiglass rod. Ten sample holes just large enough for a 22-gauge syringe were drilled down the length of the rod to enable sampling of the material in the one centimeter diameter hole. The first sample hole was 5/8-inch from the top of the cell and the next four sample holes were spaced 1/4-inch apart. The sixth hole was 3/8-inch down from the fifth hole and the remaining four holes were 1/4-inch apart. See Figure 1 for a view of the diffusion cell.

The sample holes were covered by gum rubber septums to enable sampling by a syringe. The whole cell unit was mounted on one face of a cubical (one cu. ft. in volume) plastic tank with the rubber septums (covering the sample holes) exposed to the outside through a cutaway in the face of the tank. Thus the whole cell could be immersed in a constant temperature bath while the liquor to be oxidized could be sampled from the outside by a syringe.

Oxygen was introduced through a small tube above the liquid interface of the black liquor. The oxygen was first bubbled through water at the same temperature as the water bath before being sent through a liquid trap and finally to the diffusion cell. This saturated the oxygen with water vapor and prevented evaporation of any