



A study in the oxidation of Kraft black liquor  
by Bharat Keshavlal Shah

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:

Black liquor oxidation was investigated at different conditions to determine the importance of certain variables.

Strong black liquor was obtained from Waldorf-Roerner Paper Products Company and was oxidized in a continuous, stainless Steel, backmix reactor of 0.425 cubic feet volume by bubbling air through the black liquor. The oxidation was carried out at atmospheric pressure and at temperatures Of 180°, 190°, 200° and 210°F. The air flow rate was' 0.25, 0.50 and 0.75 cubic feet per minute. Samples were analysed for sodium sulfide and' sodium thiosulfate.

The rate expression was derived using the two-film model for the oxidation reaction of sodium sulfide. The rate constants were determined graphically. It was found that the reaction rate depends on oxygen absorption and sodium sulfide, concentration. - More conversion of sodium sulfide was obtained at a lower space time. By increasing the air flow rate at a constant temperature, more conversion was obtained. The most effective oxidation occurred at a temperature of 200°F. It was observed that the use of the mixer improved the conversion of sodium sulfide.

One run was made for the oxidation of previously oxidized liquor.

It was observed that a two stage oxidation process could oxidize strong black liquor containing about 25 grams per liter of sodium sulfide to 1.5 grams per liter of sodium sulfide.

A material balance on sulfur suggested that a large amount of converted sulfur was present in compounds other than sodium thiosulfate.

This unaccounted sulfur might be present in the form of polysulfides and sodium sulfate. A thin layer of elemental sulfur was observed for the oxidation run at 180°F.

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Approved:



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## ABSTRACT

Black liquor oxidation was investigated at different conditions to determine the importance of certain variables.

Strong black liquor was obtained from Waldorf-Hoerner Paper Products Company and was oxidized in a continuous, stainless steel, backmix reactor of 0.425 cubic feet volume by bubbling air through the black liquor. The oxidation was carried out at atmospheric pressure and at temperatures of 180°, 190°, 200° and 210°F. The air flow rate was 0.25, 0.50 and 0.75 cubic feet per minute. Samples were analysed for sodium sulfide and sodium thiosulfate.

The rate expression was derived using the two-film model for the oxidation reaction of sodium sulfide. The rate constants were determined graphically. It was found that the reaction rate depends on oxygen absorption and sodium sulfide concentration.

More conversion of sodium sulfide was obtained at a lower space time. By increasing the air flow rate at a constant temperature, more conversion was obtained. The most effective oxidation occurred at a temperature of 200°F. It was observed that the use of the mixer improved the conversion of sodium sulfide.

One run was made for the oxidation of previously oxidized liquor. It was observed that a two stage oxidation process could oxidize strong black liquor containing about 25 grams per liter of sodium sulfide to 1.5 grams per liter of sodium sulfide.

A material balance on sulfur suggested that a large amount of converted sulfur was present in compounds other than sodium thiosulfate. This unaccounted sulfur might be present in the form of polysulfides and sodium sulfate. A thin layer of elemental sulfur was observed for the oxidation run at 180°F.

## INTRODUCTION

The production of pulp in the United States amounted to almost 22 million tons in 1957. This total was produced by the following processes: sulfate (Kraft), 12 million tons; mechanical, 3 million tons; sulfite, 2 1/2 million tons; soda, 1/2 million tons; all others, 4 million tons.<sup>4</sup> Thus, over one half of the pulp produced in the United States comes from the Kraft process. There are about fourteen sulfate (Kraft) pulp mills in the northwest United States.<sup>4</sup>

The problem of the Kraft odor is as old as the Kraft pulping process itself. The odors are mainly organic and inorganic sulfur compounds which are released in varying but substantial amounts at many widely separated parts of the process.

Briefly, the process of producing pulp by the sulfate method consists of treating wood chips and chemicals in the digester, where a reaction takes place which dissolves the noncellulosic part of the wood and leaves the cellulose fibers undissolved (see Figure 1). Following the digestion period, the pulp fibers are free from lignins and are ready for separation from the spent cooking liquor. This liquid, together with the wash water, is known as weak black liquor and contains the spent reagents. The weak black liquor is passed to a series of evaporators where water is progressively removed to a point where the residue can be burned in a furnace to generate steam and regenerate cooking chemicals. The mill shown in Figure 1 has no provision for



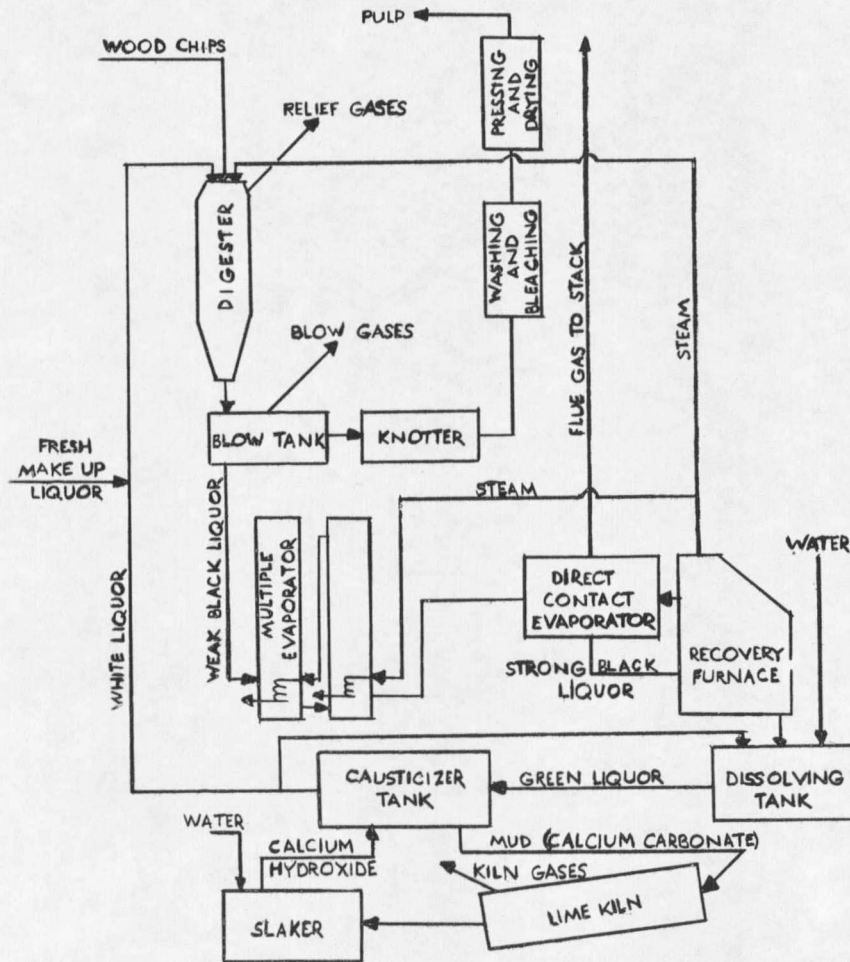


Figure 1. The Kraft Pulping Process

odor control, so that there are substantial amounts of odoriferous gases released from the digester, the evaporators, and the chemical recovery furnace.

The most well-known operation to reduce organic and inorganic sulfur compounds is the black liquor oxidation process. The hot black liquor is contacted with air and the sodium sulfide is oxidized to sodium thiosulfate and other oxidation products. This operation reduces the amount of hydrogen sulfide which escapes in the direct contact evaporator and the recovery furnace.

A large amount of research work has been done for the weak black liquor oxidation. At Waldorf-Hoerner Paper Products Company, the strong black liquor is oxidized instead of the weak black liquor. This study is concerned with the oxidation of strong black liquor at various conditions in order to determine the effect of certain variables on the oxidation process.

## SURVEY OF PREVIOUS WORK

### Literature Survey

The concept of stabilization of some of the sulfur compounds in sulfate black liquor by oxidation was first suggested by M. G. Schmitt<sup>1</sup> in 1938. Schmitt found that in the recovery furnace operation, 12 percent of the sodium and 46 percent of the sulfur were lost. When samples of black liquor were air dried on filter papers and then heated, it was found that the unoxidized sulfur compounds decreased and the oxidized sulfur compounds increased. Schmitt proposed the oxidation of black liquor by aeration.

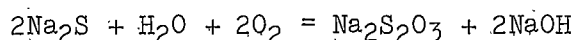
In the period between 1939 and 1942, Bergstroem and Trobeck<sup>1</sup> made a fundamental study of the causes for the changing of the sulfide content of black liquor on storage and found that at elevated temperatures in the presence of air, the sulfide content of the liquor rapidly decreases. On the basis of their oxidation studies, they made the first installation of the oxidation unit of Norrsundet mill in 1952. They found that oxidation reduced the sulfur loss from the liquor going through the vacuum evaporators from 26 percent for unoxidized liquor to an average of 10 percent for oxidized liquor. In the Norrsundet mill in Sweden, reduction in the corrosion in the strong effect of the vacuum evaporators was observed due to the black liquor oxidation. Trobeck also reported an appreciable lime saving per ton of pulp due to the higher sulfidity of white liquor resulting from oxidation of the black liquor. A number of patents have been obtained in Sweden, Canada and the United States

on the design and operation of the Bergstroem-Trobeck System.

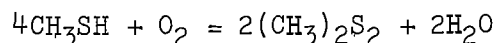
A Bergstroem-Trobeck type oxidation unit was installed in the Kraft pulp mill of Lareto and Pena Pobre near Mexico City. This plant was studied by Trobeck, Lenz and Tirado. In 1961, Tirado<sup>13</sup> conducted small scale oxidation studies. He diffused air into a column of black liquor held at various pressures. Tirado reported that the oxidation of black liquor by air at 28 to 75 psig showed definite gains specifically regarding the conversion of mercaptans, which are difficult to oxidize in the conventional processes. At 50 psig and 65°C, an air rate of about 2.3 times the theoretical amount was required to oxidize the liquor.

Tomlinson and co-workers<sup>1</sup> placed great emphasis on the fact that hydrogen sulfide is lost from the concentrated black liquor in the direct contact evaporators due to its release from the residual sodium sulfide in the liquor by reaction with the sulfur dioxide, sulfur trioxide, and carbon dioxide in the stack gases. They found that when a completely oxidized black liquor was evaporated in a cyclone scrubber, the effluent gas contained only five to eight milligrams of hydrogen sulfide per 100 cubic feet of dry gas at S.T.P. In their laboratory pilot plant work for design purposes, they calculated absorption coefficients using coke and Rasching ring packing and found that the optimum temperature for oxidation of the black liquor to be 70°C. Full scale units have been installed in Windsor and Marathon, Canada.

The study by Bergstroem and Trobeck in Sweden and by Tomlinson in Canada led to a black liquor oxidation process. The weak black liquor from the digesters is an alkaline solution containing various organic and inorganic substances including sodium sulfide and methyl mercaptan.<sup>15</sup> If the hot liquor is brought in contact with air, the sodium sulfide is oxidized to sodium thiosulfate:



and the methyl mercaptan is oxidized to dimethyl disulfide.



In 1959 Murray<sup>7</sup> published the results of a batch reactor on the kinetics of weak black liquor oxidation. The author studied the reaction rates over a temperature range of 122°F to 196°F and sodium sulfide concentrations up to 16 grams per liter. (g.p.l.) The data obtained from the experiments in a batch reactor were taken into account by the following empirical equation:

$$\frac{dw}{d\theta} = K(C + bP)$$

where K = parameter in the oxidation rate equation, liter per hr-sq. ft.

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

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

P = partial pressure of oxygen, atm

$\theta$  = time, hr.

$w$  = total weight of sodium sulfide in the reaction vessel at any time, g.

$\frac{dw}{d\theta}$  = oxidation rate for sodium sulfide in black liquor, g. per hr-sq. ft.

For a constant volume reactor, the equation can be transformed to:

$$\frac{dc}{d\theta} = \frac{K}{V} (C + bP)$$

After integration, the equation becomes:

$$V \ln (C + bP) = K\theta + B$$

where  $B$  = the integration constant

Using graphical techniques, Murray determined the values of the constants  $K$ ,  $B$  and  $b$ .

Murray reported that the maximum rate in the same sulfide concentration range occurred at 160°F when pure oxygen was used as the gas feed to the reaction vessel. Although the maximum rates occurred at the indicated temperature, the change in rate with temperature was actually very slight.

Ricca<sup>10</sup> reported that the soluble materials in black liquor catalyze oxidation. He prepared a synthetic liquor containing the same concentration of the principal inorganic compounds found in the black liquor. He reported that in a static contact system at 75°C, the synthetic liquor oxidized much more slowly than did the black liquor.

#### Conclusions Based on Previous Work

On the basis of the literature survey, certain conclusions can be

drawn from the work done on black liquor oxidation:

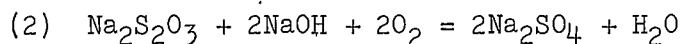
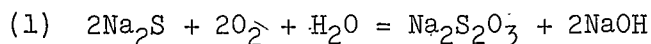
- (1) Although the black liquor oxidation process has been known for at least 25 years, only a small amount of theoretical information is available on the basic mechanism of the process.
- (2) The principal reason for the installation of a black liquor oxidation system is to reduce chemical losses in the recovery furnace and corrosion in the evaporators.
- (3) The basic reaction mechanism of the sodium sulfide with oxygen is reported to be first order, yielding as products, sodium thiosulfate and sodium hydroxide.
- (4) Very little work has been done on the oxidation of strong black liquor.

## THEORY

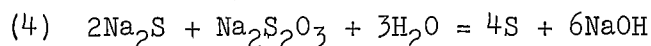
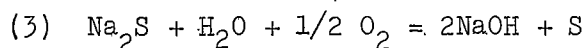
### Black Liquor Oxidation

The black liquor oxidation process is a chemical combination of oxygen with sodium sulfide to form the more stable inorganic sulfur compounds. The transfer of oxygen from the air to the sodium sulfide occurs by a diffusion mechanism.

Reactions 1 and 2<sup>15,3</sup> have been suggested to explain the formation of stable inorganic sulfur compounds from sodium sulfide.

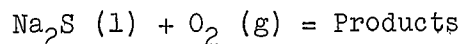


Murray<sup>7</sup> reported that he observed the formation of elemental sulfur at low temperatures during the oxidation of black liquor. The reactions 3 and 4 can explain the formation of elemental sulfur from sodium sulfide.



### Mechanism of Oxidation

In general, the reaction for the oxidation of sodium sulfide can be written as:



Since the materials in the two separate phases must contact each other before the reaction can occur, the over-all rate expression must account for the resistances provided by the mass transfer step and the chemical



reaction step. The relative magnitudes of these processes can vary greatly. However, since the oxidation reaction of sodium sulfide is an infinitely fast reaction, mass transfer will control the reaction mechanism.

In order to derive the rate expression, we used a two-film diffusion model with an infinitely fast chemical reaction of  $A(l) + B(g) = \text{Products}$ .

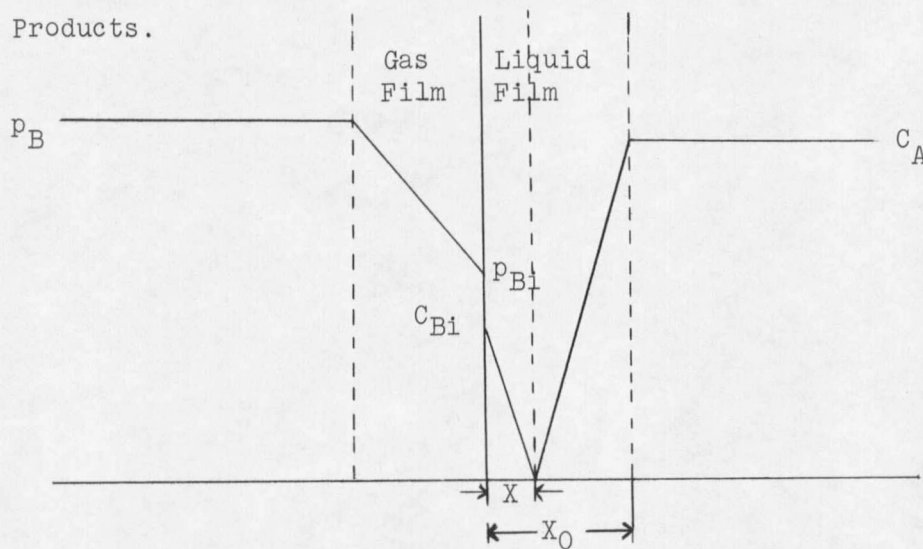


Figure 2. Concentration profile of reactants in films between phases for an infinitely fast irreversible reaction.

Let  $p_B$  = partial pressure of oxygen, atm  
and  $C_A$  = concentration of sodium sulfide, moles per liter.

The rate of disappearance of A and B is given by

$$(5) \quad -r_A = -r_B = K_{Bg} (p_B - p_{Bi}) = K_{Bl} (C_{Bi} - 0) \frac{X_0}{X} =$$

$$K_{Al} (C_A - 0) \frac{X_0}{X_0 - X}$$

$K_{Bg}$ ,  $K_{Bl}$ , and  $K_{Al}$  are the mass transfer coefficients in the gas and liquid phases.

At the interface the relationship between  $p_B$  and  $C_B$  is given by the Henry's Law constant. This assumption is valid for gases which are only slightly soluble in a liquid; since oxygen is only slightly soluble in an aqueous solution, it can be related by Henry's Law.

$$(6) \frac{p_{Bi}}{C_{Bi}} = H_{Bi}$$

Also the movement of material within a film is visualized to occur by diffusion alone; then for A and B moving through the same section of film we have

$$(7) \frac{K_A}{K_B} = \frac{D_A}{D_B}$$

where  $D_A$  and  $D_B$  are the diffusivities of A and B respectively.

Eliminating the unknown values,  $X$ ,  $X_0$ ,  $p_{Bi}$ ,  $C_{Bi}$  in Equations 5, 6 and 7 and also assuming  $H_{Bi} = H_B$  we obtain

$$-r_B = -r_A = \frac{\frac{D_{Al}}{D_{Bl}} C_A + \frac{p_B}{H_B}}{\frac{1}{K_{Bl}} + \frac{1}{H_A K_{Bg}}}$$

Let 
$$K = \frac{1}{\frac{1}{K_{B1}} + \frac{1}{H_A K_{Bg}}}$$

$$b = \frac{D_{A1}}{D_{B1}}$$

$$d = \frac{1}{H_B}$$

then 
$$-r_A = K(bC_A + dp_B)$$

or

(8) 
$$-r_A = K(C_A + d'p_B)$$

where  $-r_A$  = oxidation rate for sodium sulfide in black liquor,  
moles per hr. - sq. ft.

$K$  = parameter in the oxidation rate equation, liter per  
hr. - sq. ft.

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

Let  $a$  = surface area per unit volume, sq. ft. per cu. ft.

Then rewriting the rate equation:

(9) 
$$-r_A a = K_a(C_A + d'p_B)$$

where  $-r_A a$  = oxidation rate for sodium sulfide in black liquor,  
moles per hr. - cu. ft.

$K_a$  = parameter in the oxidation rate equation, liter per  
hr. - cu. ft.

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

Figure 3 shows a material balance on a Backmix Reactor.

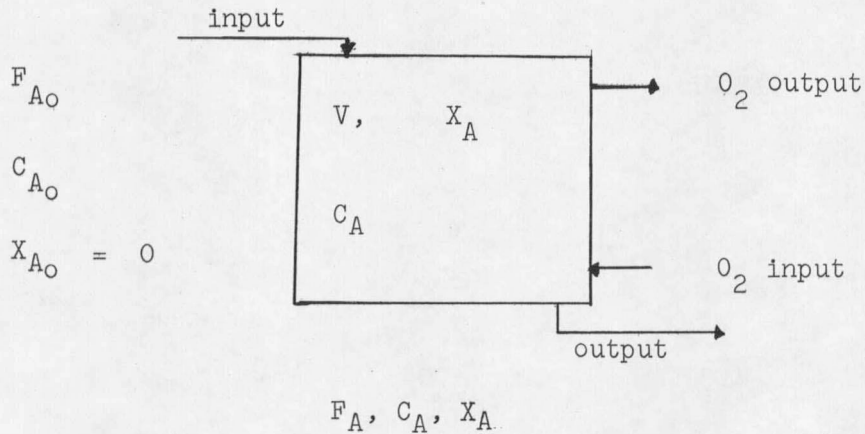


Figure 3. Variables for a Backmix Flow Reactor

- Let
- $F_{A_0}$  = feed rate of sodium sulfide, moles per hr.
  - $X_A$  = fraction of sodium sulfide converted
  - $V$  = volume of reactor occupied by reacting fluid, cu. ft.
  - $v$  = volumetric flow rate, liters per hour
  - $C_A$  = concentration of A, moles per liter.

Therefore,

$$\text{Input of A} = F_{A_0} ,$$

$$\text{Output of A} = F_A = F_{A_0} (1 - X_A) ,$$

$$\text{Disappearance of A by reaction} = (-r_{Aa})(V)$$

Hence, equating terms

$$F_{A_0} - F_{A_0} (1 - X_A) = (-r_{Aa})(V) ,$$

and (10) 
$$-r_{Aa} = \frac{F_{A_0} X_A}{V} = \frac{v C_{A_0} X_A}{V} = \frac{C_{A_0} X_A}{\theta}$$

where

$$\text{space time } \theta = \frac{\text{Volume of the reactor}}{\text{volumetric flow rate}} = \frac{V}{v}$$

At the same reaction temperature, one should obtain different conversion values at different space time which will enable one to calculate reaction rates ( $-r_{Aa}$ ).

## RESEARCH OBJECTIVES

The purpose of this study was to investigate the oxidation of strong black liquor with air. A thermodynamic and kinetic study was made for the oxidation reactions of sodium sulfide. The oxidation was studied in order to determine the factors controlling the reaction mechanism. The strong black liquor oxidation was studied at several temperatures and several air flow rates in order to determine the effect of these variables on the oxidation rate. It is hoped that this study will assist the Waldorf-Hoerner Paper Products Company to carry out their strong black liquor oxidation successfully.

## EQUIPMENT

A schematic diagram of the laboratory oxidation system is shown in Figure 4. A stainless steel oxidation reactor, one foot high and one foot in diameter, was provided with a leakproof seal. A constant height of 6 1/2 inches of black liquor was maintained at all times in this oxidation reactor by means of an overflow tube (5). Nichrome heating coils were wrapped around the reactor to maintain the black liquor in the reactor at a constant temperature. Three Powerstat transformers controlled the heat supplied to the reactor.

The air used in all the experimental work was dry. The air flow rate was controlled by a needle valve and was measured by an orifice meter (6).

The orifice meter consisted of a lucite plate, drilled with a 3/32 inch hole and mounted between two flanges on the air line. Pressure taps, one above and one below the orifice plate, were installed and were connected to a water manometer.

The air was preheated by a Nichrome heating coil around the inlet air line. The air was distributed by means of a circular air header (4) in the bottom of the reactor. The air outlet was located on the top of the oxidation reactor.

A gear pump (2) was used to pump the black liquor from the feed tank to the reactor. The feed header was located two inches above the black

liquor level in the oxidation reactor and introduced the unoxidized hot black liquor into the reactor. The black liquor flow rate was determined by collecting a specified amount of oxidized black liquor in a given period of time. This rate was verified by observing the change in the level of the unoxidized black liquor in the feed tank.

Three thermocouples were used to measure the temperatures of the black liquor feed, the black liquor in the reactor and the inlet air. EMF's of the iron-constantan thermocouples were measured by a Minneapolis Honeywell Brown Electronik Model No. 155X 15 P. The temperatures were controlled by adjustment of the Powerstat transformers.

The feed tank, black liquor feed line, air line and reactor were insulated in order to minimize the heat losses.

A mixer (9) was also installed in the reactor.



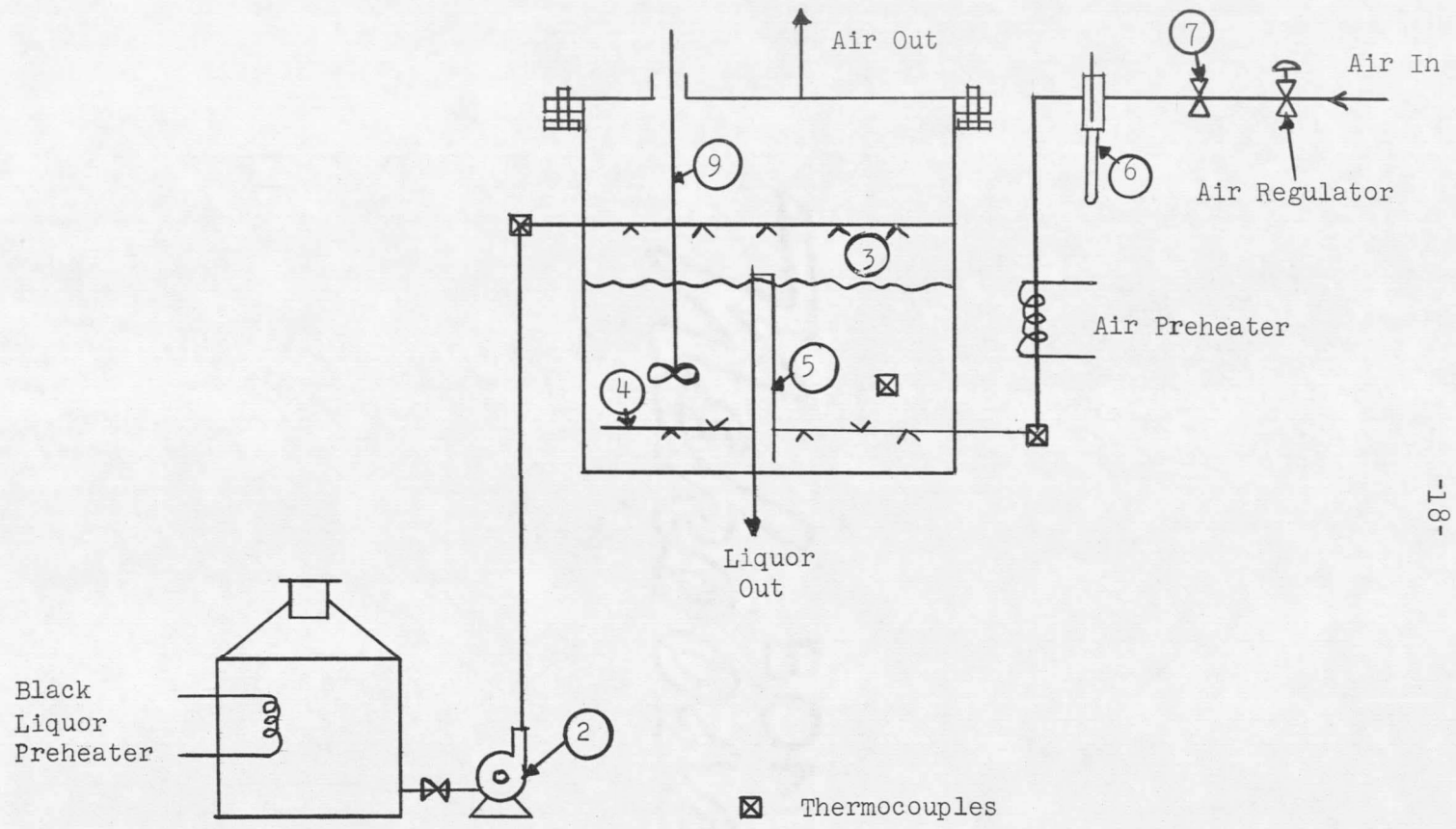


Figure 4. Laboratory Oxidation System

## EXPERIMENTAL PROCEDURE

The strong black liquor used in this study was obtained from the Waldorf-Hoerner Paper Products Company at Missoula, Montana.

The operating procedure and the methods of analysis of the black liquor samples are given below.

### Operating Procedure

Initially, the reactor was filled with strong black liquor to a level of 6 1/2". The black liquor in the reactor was then heated to the desired temperature. When the desired temperature was reached, the preheated feed black liquor was pumped into the reactor at the desired flow rate. At the same time the desired quantity of air was allowed to bubble through the black liquor in the reactor. The black liquor in the reactor was maintained at constant temperature by manual adjustment of the Powerstat transformers. The feed samples were analysed for both sodium sulfide and sodium thiosulfate. The oxidized black liquor samples were also analysed for both sodium sulfide and sodium thiosulfate. These analyses were continued until two samples at an interval of one half hour gave the same concentration of sodium sulfide. After this, the black liquor feed rate was changed and the oxidized liquor samples again were analysed until equilibrium was again attained. For each complete run, the black liquor flow rate was changed at least three times. The same procedure was repeated for all the runs.

### Analytical Methods

A colorimetric method suggested by Strickland and Risk<sup>11</sup> was used for the determination of sodium sulfide in black liquor. The dissolved sulfide reacts quantitatively with p-Phenylenediamine dihydrochloride in the presence of ferric chloride forming a deep color. The color was formed in a fixed volume of aqueous solution containing dye, oxidizing agent (ferric chloride) and wetting agent (alkyl dimethyl benzyl ammonium chloride). The sample was diluted and the optical density measured at a wave length of 600 millimicrons.\* For calibration purposes, the optical density was also measured for a standard solution of sodium sulfide.

A clock reaction reported by Risk and Strickland<sup>12</sup> was used for the determination of sodium thiosulfate in the black liquor. The oxidation of p-Phenylenediamine by ferric chloride is inhibited by the presence of thiosulfate. A well-marked induction period results which is proportional to the amount of thiosulfate present. A calibration curve of the induction time versus the milligrams of thiosulfate was prepared.

Detailed particulars covering the analytical methods described above are presented in Appendix 1.

\*Bausch and Lomb Spectronic 20

## DISCUSSION OF RESULTS

Black liquor oxidation was investigated at different conditions to determine the importance of certain variables on the oxidation process. Since, at Waldorf-Hoerner Paper Products Plant, the oxidation is carried out at a temperature near the boiling point of the black liquor, the temperatures selected for this study were 180°F, 190°F, 200°F and 210°F. Oxidation was carried out at atmospheric pressure with air.

A thermodynamic study was made in order to determine the thermodynamic feasibility of the oxidation of sodium sulfide. The free energy changes of several possible reactions are shown in Table I. The reaction 4 has a positive free energy change which indicates that it is thermodynamically not favorable. The values of free energy change for reactions 1, 2 and 3 indicate that they are thermodynamically favorable. It can be seen that if sodium sulfide, oxygen and water are present in the stoichiometric amount, the conversion of sodium sulfide could be very high. However, the solubility of oxygen in black liquor is very small; and, therefore, the oxidation of black liquor will not be complete.

All the black liquor samples were analyzed for sodium sulfide and sodium thiosulfate. A material balance was made in order to determine the oxidation product distribution. Table II shows the complete material balance on sulfur. The amount of sulfur present as moles per liter of sulfur in sodium thiosulfate and in unknown compounds was calculated and

Table I

The Free Energy Changes for the Oxidation  
Reactions of Sodium Sulfide

Reaction	Free Energy Change at 80°C K cal per g Mole
1. $2\text{Na}_2\text{S} + 2\text{O}_2 + \text{H}_2\text{O} = \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH}$	-187.36
2. $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH} + 2\text{O}_2 = 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	-231.50
3. $\text{Na}_2\text{S} + \text{H}_2\text{O} + 1/2 \text{O}_2 = 2\text{NaOH} + \text{S}$	-34.60
4. $2\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O} = 4\text{S} + 6\text{NaOH}$	+46.50

Table II

Material Balance of Known  
and Unknown Compounds

---

Oxidation at 200°F and 0.50 cu.ft.  
per min. air rate using mixer

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Space Time Hr.	Sodium Sulfide Converted Ex- pressed as Moles per Liter of Sul- fur	Thiosulfate formed Expressed as Moles per Liter of Sul- fur	Unaccounted for Compounds Ex- pressed as Moles per Liter of Sulfur
0.975	0.165	0.072	0.093
1.620	0.199	0.094	0.105
2.160	0.221	0.110	0.111
3.550	0.260	0.140	0.118

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Analysis for Sodium Sulfate\*

Sample	Grams per liter of Sodium Sulfate	Moles per liter of Sodium Sulfate
Unoxidized Black Liquor	3.88	0.0274
Oxidized Black Liquor	5.72	0.0404

\*TAPPI Standard T 625 m-48

plotted in Figure 5 for the black liquor oxidation at 200°F and 0.5 cu. ft. per minute of air flow rate. It can be seen that at lower space times, more converted sulfur was present as unknown compounds than as thiosulfate. But at higher space times, the sulfur in sodium sulfide was converted more to thiosulfate than to unknown compounds. As space time increases, the amount of sulfur present as moles per liter of sulfur in sodium thiosulfate increases at a faster rate than in unknown compounds. For this particular run at a space time of 2.16 hrs., the product distribution was equally distributed between thiosulfate and unknown compounds.

At the beginning of this study, it was believed that the main products of oxidation would be sodium thiosulfate and sodium sulfate. A pair of unoxidized and oxidized black liquor samples were analyzed for sodium sulfate and are reported in Table II. It was found that the oxidized sample contained 0.0404 moles per liter of sulfur as sodium sulfate while the unoxidized sample contained 0.0274 moles per liter of sulfur as sodium sulfate. This indicates that small amounts of the sulfide were oxidized completely to sulfate. This, however, does not completely account for the overall conversion of sulfide.

It is, therefore, believed that the unaccounted sulfur might be present in oxidation states in between the sulfide and thiosulfate form. The stable oxidation states in between the sulfide and thiosulfate are

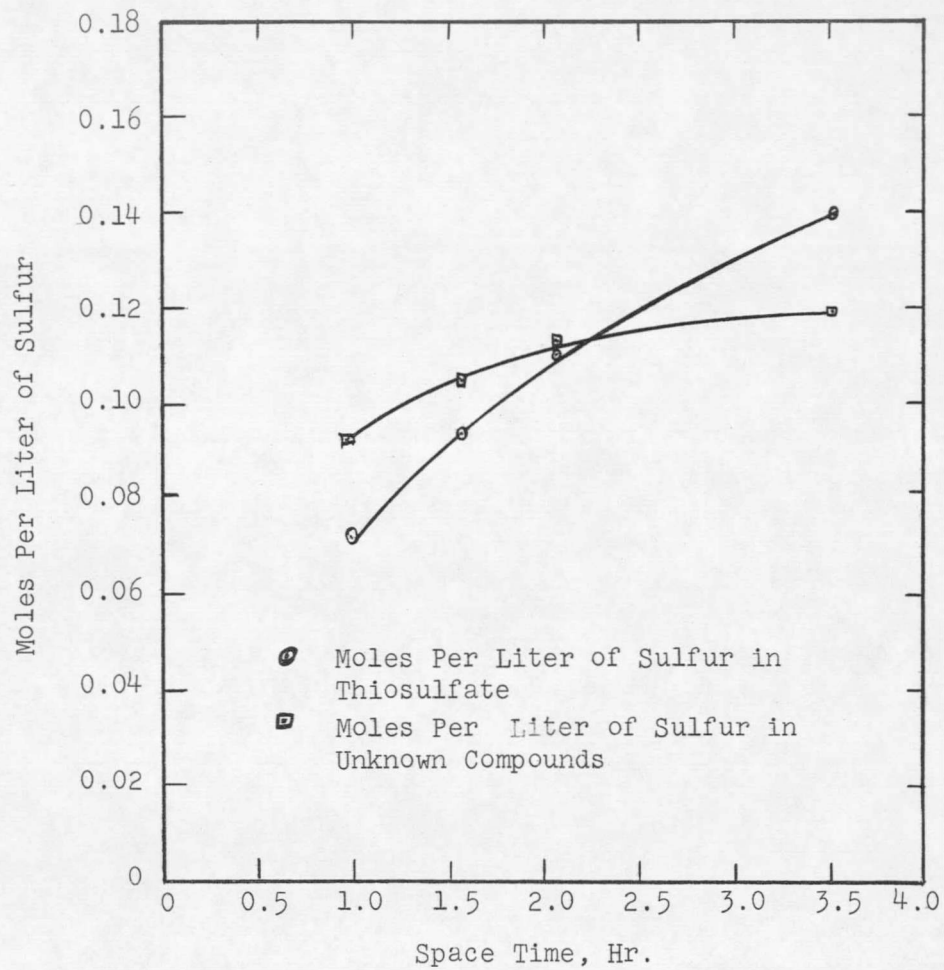


Figure 5. Sulfur Product Distribution Versus Space Time For a Black Liquor Oxidation at 200°F and 0.5 Cu. Ft. Per Minute Air Rate Using Mixer



elemental sulfur and the polysulfides. The elemental sulfur is visible in aqueous solution since it is insoluble. During the experiment, a small layer of elemental sulfur was observed while cleaning the reactor at the low temperature runs of 180°F, but no elemental sulfur was observed in the oxidized liquor at higher temperatures. It, therefore, appears that the elemental sulfur was not a major part of the unaccounted sulfur. The polysulfides are stable in alkaline solution and are possible oxidation products of sulfide. During the experiments, analyses were not made for polysulfides and so the exact amount of polysulfides produced were not known.

Table III shows the conversion of sodium sulfide at 200°F and an air rate of 0.5 cu. ft. per minute with and without the aid of a mixer. The mixer was maintained at a very slow stirring rate; and, hence, the difference in conversion was not appreciable. However, a mixer operating at a higher stirring rate would definitely help the conversion of sodium sulfide.

During the experimental runs, a slight foam problem occurred at the higher air rates. Since this foam problem was not too critical, a cyclone separator would easily separate the foam and a foam breaker would not be essential in actual industrial operation.

The oxidation of previously oxidized liquor was made in order to study the feasibility of a two stage oxidation process. Table IV

TABLE III

Comparison of Conversion of Sodium Sulfide at 200°F and 0.5 Cubic Feet Per Minute Air Rate With and Without the Aid of a Mixer.

Space Time Hr.	<u>Without Mixer</u> Percentage Conversion of Sodium Sulfide	<u>With Mixer</u> Percentage Conversion of Sodium Sulfide
0.93	49	-
0.975	-	52
1.50	59	-
1.62	-	63
2.16	68	70
3.55	-	82
3.90	79.4	-

TABLE IV

Comparison of Oxidation of Unoxidized  
and Oxidized Black Liquor at 200°F  
and 0.5 Cubic Feet Per Minute Air Rate

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Oxidized Black Liquor

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Space Time Hr.	Feed Concentration Grams Per Liter Sodium Sulfide	Equilibrium Concentration Grams Per Liter Sodium Sulfide	Percentage Conversion Sodium Sulfide
0.975	6.3	3.28	48
1.630	6.3	2.71	57
3.900	6.3	1.51	76

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Unoxidized Black Liquor

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0.930	25.2	12.8	49.0
1.500	25.2	10.3	59.0
2.170	25.2	8.05	68.0
3.900	25.2	5.20	79.4

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shows the conversion data for a feed of both unoxidized and oxidized black liquor. The conversions are almost the same for the oxidized and unoxidized black liquor oxidation. Hence, in a two stage strong black liquor oxidation process operating at 200°F, 25 grams per liter of sodium sulfide could be oxidized to as low as 1.5 grams per liter of sodium sulfide.

A plot of percentage conversion versus space time of sodium sulfide at 180°, 190°, 200° and 210°F and at an air flow rate of 0.75 cu. ft. per minute is shown in Figure 6. It can be seen that in the temperature range 180°-200° F, the conversion of sodium sulfide increases with the temperature. However, the conversion of sodium sulfide at 210°F is significantly lower than that at 200°F. Figure 6 also suggests that at the same temperature and air flow rate, the amount of sodium sulfide converted increases with an increase in space time.

Figure 7 is a plot of percentage conversion of sodium sulfide versus temperature at a space time of 1.5 hrs. for the oxidation runs at 180°, 190°, 200° and 210° F and an air flow rate of 0.75 cu. ft. per minute. Figure 7 suggests that the most effective oxidation occurs at a temperature of approximately 200°F.

Figure 8 is a plot of percentage conversion of sodium sulfide versus space time at a temperature of 200°F and air flow rates of 0.25,

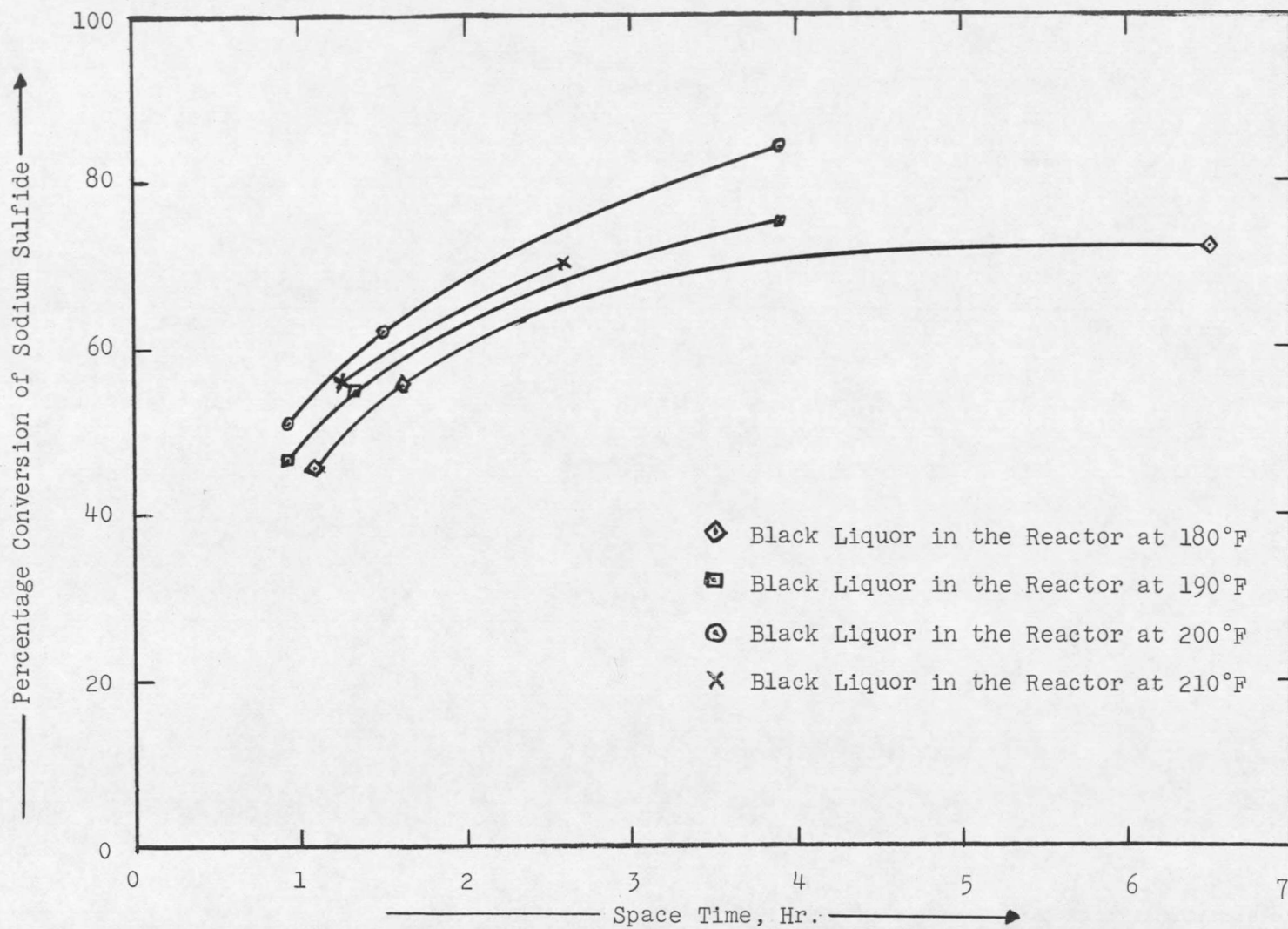


Figure 6. Percentage Conversion of Sodium Sulfide Versus Space Time for Black Liquor Oxidation Runs at 180°, 190° 200° and 210° F and an Air Rate of 0.75 Cu. Ft. Per Minute

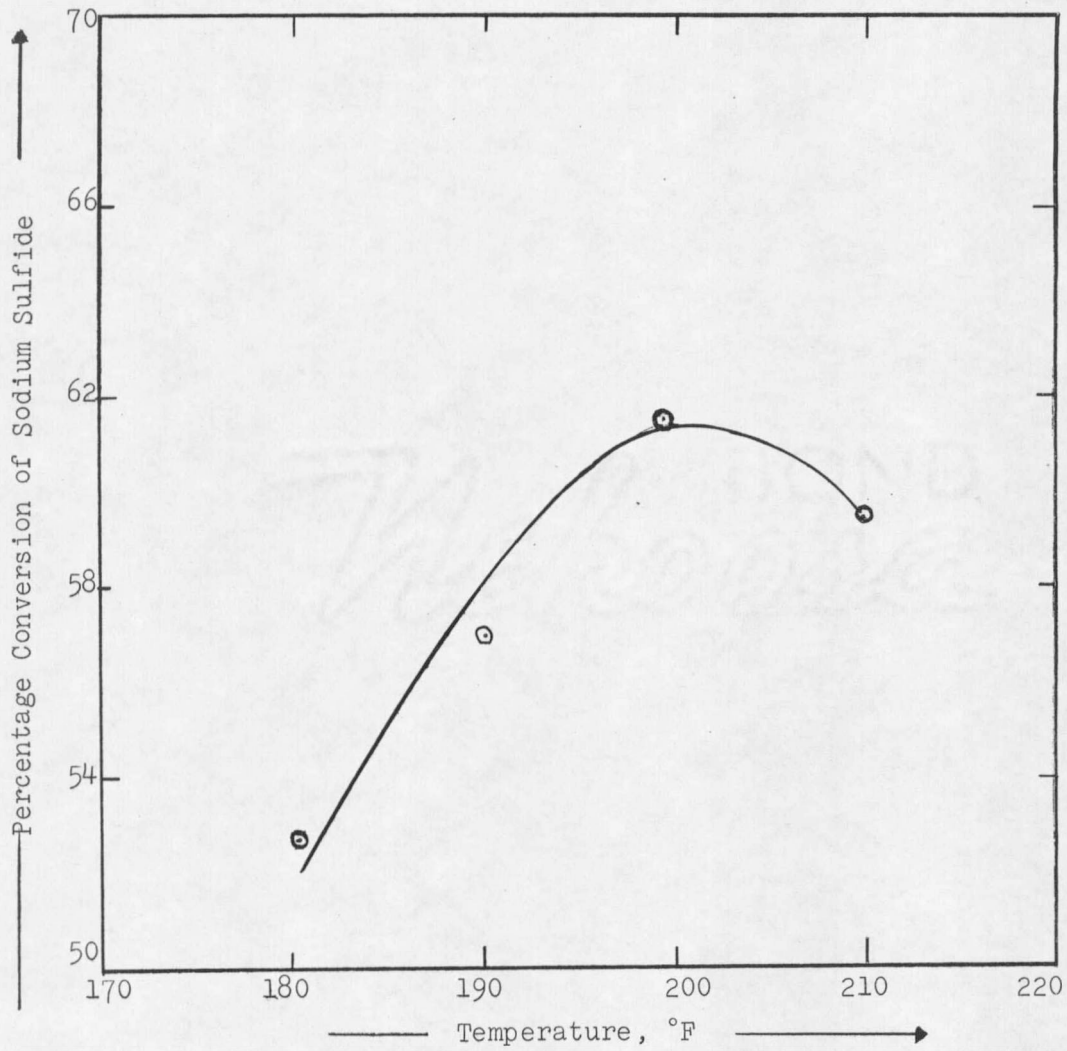


Figure 7. Percentage Conversion of Sodium Sulfide Versus Temperature at a Space Time of 1.5 Hour For the Black Liquor Oxidation Run 180°, 190°, 200° and 210°F and an Air Rate of 0.75 Cu. Ft. Per Minute.

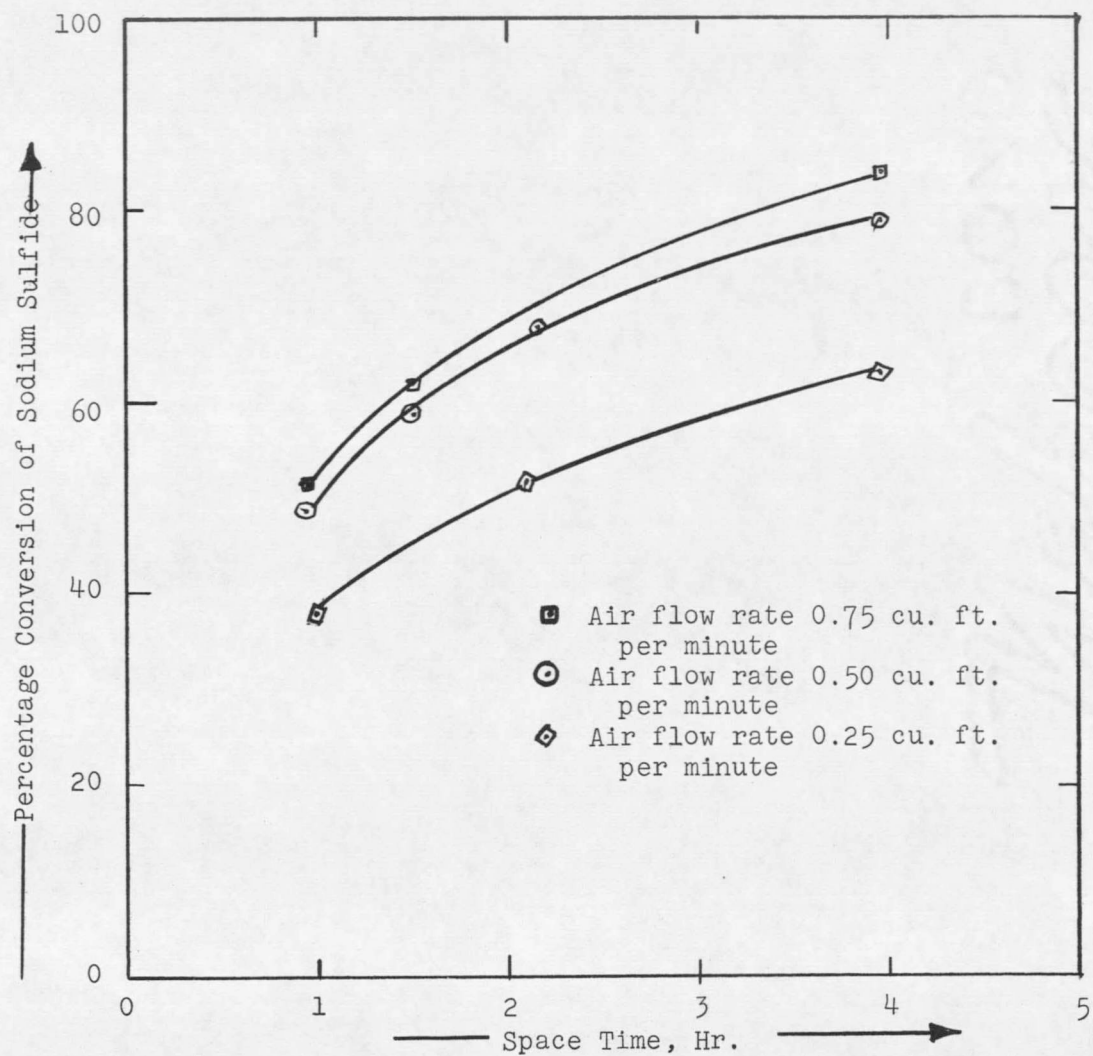


Figure 8. Percentage Conversion of Sodium Sulfide versus Space Time at Air Flow Rates of 0.25, 0.50 and 0.75 Cu. Ft. Per Minute and Temperature of 200°F

0.50 and 0.75 cu. ft. per minute. The data indicates that more conversion of sodium sulfide is obtained at a higher air flow rate. This is to be expected since the increase in air flow increases the turbulence in the reactor.

The rate equation (9), derived in the theory section, was correlated with the experimental data in order to verify the proposed mechanism and the constants  $K_a$  and  $d'$ . The details for the determination of rate constants are described in Appendix II. The values of  $K_a$  and  $d'$  at various temperatures and air flow rates are given in Table V. The value of  $K_a$  is contained in the range of 20 to 30 liters per hr. cu. ft. There appears to be some effect of air flow rate and temperature, but this effect is probably contained within the experimental errors.

An attempt was made to calculate the constants  $K_a$  and  $d'$  by assuming that air was bubbled through black liquor. It has been reported in the literature<sup>6</sup> that Higbie's equation can be used to estimate the liquid phase mass transfer coefficient for air bubbling through a liquid. The equation is:

$$K_L = 2 \sqrt{\frac{\pi}{Dt_e}}$$

where  $D$  = diffusivity of oxygen, sq. cm. per second  
 $t_e$  = life of transient film, second  
 $k_L$  = liquid-phase mass transfer coefficient, cm. per second



TABLE V

Values of Rate Constants  $K_a$  and  $d'$   
at Various Temperatures  
and Air Flow Rates

Run Number	Temperature °F	Air Rate Cu. Ft. Per Minute	$K_a$ Liter Per Hr. Cu. Ft.	$d'$ Moles Per Liter-atmosphere
7	180	0.25	21.0	0.191
10	180	0.75	31.3	0.251
8	190	0.25	21.2	0.171
1	190	0.50	29.8	0.171
2	190	0.75	31.2	0.110
9	200	0.25	27.2	0.323
4	200	0.50	25.6	0.025
*5	200	0.50	25.0	0.114
11	200	0.75	29.0	0.070
#12	200	0.50	28.2	0.030
13	210	0.75	31.0	0.238

\*Runs made with a mixer

#Runs made for oxidized black liquor

Calculated Values of Rate Constants:

$K_a = 48$  liter per hr. cu. ft.

$d' = 0.0004$  moles per liter-atmosphere

For gas bubbles in liquids, Higbie suggested that  $t_e$  might be roughly approximated as the time required for the bubble to rise through a distance equal to its diameter. The average value of  $t_e$  has been reported by Higbie as 0.05 seconds. The calculation of  $K_a$  is shown in Appendix III. The calculated values of  $d'$  and  $K_a$  are reported in Table V. The calculated value of  $K_a$  is higher than that obtained during the experiments. However, the value of  $K_a$  depends largely on the bubble diameter and the time required for the bubble to rise to the surface. An error in these values will cause an error in the constant  $K_a$ . It is out of the scope of this thesis to obtain the exact bubble diameter and the time required for the bubble to rise.

The calculated value of  $d'$  is very small in comparison to the experimental values of  $d'$ . According to the theory,  $d'$  depends on the diffusivities of oxygen and sodium sulfide in black liquor and on Henry's Law constant. Since the ratio of the diffusivities of oxygen and sodium sulfide in black liquor will remain relatively constant, the only thing which can change the calculated value of  $d'$  is Henry's Law constant. The black liquor contains sodium hydroxide which will alter the value of Henry's Law constant and hence is a possible explanation of the large difference.

The details of calculation of constants  $d'$  and  $K_a$  are given in Appendix III.

If the oxidation depends only on sulfide concentration, then oxygen absorption will not affect the rate and the term  $d'$  will be zero. The experimental results indicate that the oxidation of black liquor depends both on oxygen absorption and sulfide concentration.

## CONCLUSIONS

Strong black liquor can be oxidized with high yield at a temperature of 200°F and an air rate of 0.50 to 0.75 cu. ft. per minute in a backmix reactor of 0.425 cu. ft. volume. The oxidation reaction occurs in the liquid phase and the mass transfer rate controls the rate of the reaction. The reaction rate which depends on oxygen absorption and sodium sulfide concentration can be expressed in the following form:

$$-r_{S=a} = K_a (C_{S=a} + d' p_{O_2}).$$

The calculated value of  $K_a$  is in good agreement with the experimental value of  $K_a$ . The experimental value of constant  $d'$  is considerably higher than the calculated value of  $d'$ . This suggests that a mechanism other than the two film diffusional model controls the black liquor oxidation.

During all the experimental work foam generation was not too excessive. This suggests that a foam breaker is not essential in an industrial strong black liquor oxidation process.

A mixer will increase the conversion of sodium sulfide in an industrial oxidation process.

Some of the sulfide is converted to compounds other than sodium thiosulfate. These compounds are probably polysulfides and sodium sulfate.

APPENDICES

## APPENDIX I

### Methods of Analysis

#### 1. Sodium Sulfide in Black Liquor:

##### A. Reagents:

Base Electrolyte -- Dissolve 0.8 grams of  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  in a little water containing 20 milliliters of concentrated hydrochloric acid. Add 10 milliliters of 50% "Roccal" \*wetting agent (alkyl dimethyl benzyl ammonium chloride) and dilute to one liter with water.

p-Phenylenediamine Hydrochloride Solution -- Dissolve 2.5 grams of recrystallized p-phenylenediamine in a little water. Add 10 milliliters of concentrated hydrochloric acid and dilute to 250 milliliters. This solution may be kept for 2 to 3 weeks in a stoppered bottle.

Starch Solution -- Dissolve 2 to 3 grams of starch in one liter of water.

0.1 N Sodium Thiosulfate Solution -- Dissolve 25 grams of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$  and 0.1 grams of sodium carbonate in water and dilute to 1 liter. The thiosulfate solution is standardized against a standard potassium iodate solution.

0.1 N Iodine Solution -- Place 12.7 grams of iodine in a 250 milliliter beaker. Add 40 grams of iodate free potassium iodide and 25 milliliters of water. Stir at intervals to hasten solution of the iodine, and when all has dissolved, dilute to approximately

\*Onyx Oil and Chemical Company

one liter with water. The iodine is standardized against a standard thiosulfate solution.

Standard Sodium Sulfide Solution -- Dissolve 5 grams of  $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$  in 500 milliliters water.

B. Procedure:

(a) Standardization of the Sodium Sulfide Solution -

1. Add 10 milliliters of the  $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$  solution to a flask containing 25 milliliters of 0.1 N iodine solution. The sodium sulfide reacts with iodine to form sodium iodide.
2. Titrate the excess of iodine with a 0.1 N sodium thiosulfate solution to a starch end point.
3. The normality of the sodium sulfide can be calculated as follows:

$$N_{\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}} = \frac{(25)(0.1) - (x)(0.1)}{10}$$

where x = milliliters of 0.1 N sodium thiosulfate solution required for the titration of the excess iodine. The grams per liter of sodium sulfide can be calculated as follows:

$$\text{Grams per liter of } \text{Na}_2\text{S} = \frac{(120)(78)}{(240)} \times (N_{\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}})$$

(b) Determination of Sodium Sulfide in Black Liquor.

1. Add 0.03 milliliters of sample black liquor from a micrometer syringe to 45 milliliters of base electrolyte

in a stoppered 50 milliliter flask.

2. Swirl the tube gently to mix.
3. Let the sample stand not less than 1 minute nor more than 2 minutes.
4. Add 2 milliliters of p-phenylenediamine solution, stopper and mix.
5. Allow blue color to form not less than 10 minutes nor more than 15 minutes.
6. Dilute the contents of the flask to the desired volume (500 milliliters) with water.
7. Measure the optical density at a wave length of 600 millimicrons against a similarly prepared and diluted blank.
8. Determine the apparent sulfide concentration from a previously determined optical density value of a standard sodium sulfide solution.
9. Multiply the apparent sulfide concentration by the recovery factor to obtain the actual sulfide concentration.

C. Calibration of Colorimeter:

- (a) Calibration - Add 0.14 milliliters of standard sulfide solution to 45 milliliters of base electrolyte and generate the blue color as described in Steps 2 through 5 of the procedure for the determination of sodium



sulfide in black liquor. Dilute the standard and blank to the appropriate volume and measure the optical density at a wave length of 600 millimicrons.

- (b) Determination of the maximum amount of  $S^{=}$  in order to remain within Beer's Law. During the calibration of sodium sulfide by the colorimetric method as suggested by Strickland and Risk<sup>11</sup>, it was found that Beer's Law held for concentrations up to six grams per liter of sodium sulfide when the sample size was 0.15 ml. For black liquor samples containing more than 6 grams per liter of sodium sulfide, not all the sulfide reacted to form the blue color as described in the previously procedure. Since our samples were strong black liquor, we expected very high concentrations of sulfide. Therefore, we used a smaller sample size and thereby reduced the amount of sulfide present. Table VI shows the effect of sample size on the concentration of sodium sulfide in the black liquor. It can be seen that any sample size from 0.01 to 0.03 milliliters gives the same result as obtained by the potentiometric method. A sample size of 0.03 milliliters was selected for all the analysis work of sodium sulfide by the colorimetric method.
- (c) Effect of Black Liquor Solids and the Determination of the Recovery Factor - Black Liquor samples of various sizes

TABLE VI

Sample Size of Black Liquor Versus Concentration  
of Sodium Sulfide Determined by  
Colorimetric Method

Concentration of Sodium Sulfide

Grams per Liter of Sodium  
Sulfide by Potentiometric Method\* = 22.40

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Sample Size Milliliter	Concentration Gram Per Liter of Sodium Sulfide by Colorimetric Method
0.06	16.50
0.05	17.70
0.04	18.05
0.03	22.42
0.02	22.50
0.01	22.48

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\*Potentiometric Method involves the titration with silver nitrate in an alkaline ammoniacal solution using a potentiometric end point (silver-silver sulfide//glass electrode cell).

were analyzed. The apparent grams per liter of sodium sulfide versus sample size is plotted in Figure 9. The apparent amount of sodium sulfide decreases as the sample size increases. A sample size of 0.03 milliliter gives a value which is 98% of the extrapolated value (no solids) of 1.276 grams per liter. The recovery factor =  $\frac{1}{0.98} = 1.02$ .

2. Sodium Thiosulfate in Black Liquor:

A. Reagents:

Base Electrolyte -- Dissolve 40 grams of sodium chloride in water. Add 30 milliliters of concentrated hydrochloric acid and dilute to one liter.

p-Phenylenediamine Solution -- Dissolve 2.5 grams of p-phenylenediamine in 6 milliliters of concentrated hydrochloric acid. Dilute to 100 milliliters with water.

Ferric Chloride Solution -- A 4% solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in water.

0.002 M Sodium Thiosulfate Solution -- Dissolve 2.5 grams of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in water and dilute to 200 milliliters. Standardize the thiosulfate solution against a standard potassium iodate solution.

B. Procedure:

1. Add 0.1 milliliters of black liquor to a beaker containing 25 milliliters of base electrolyte.

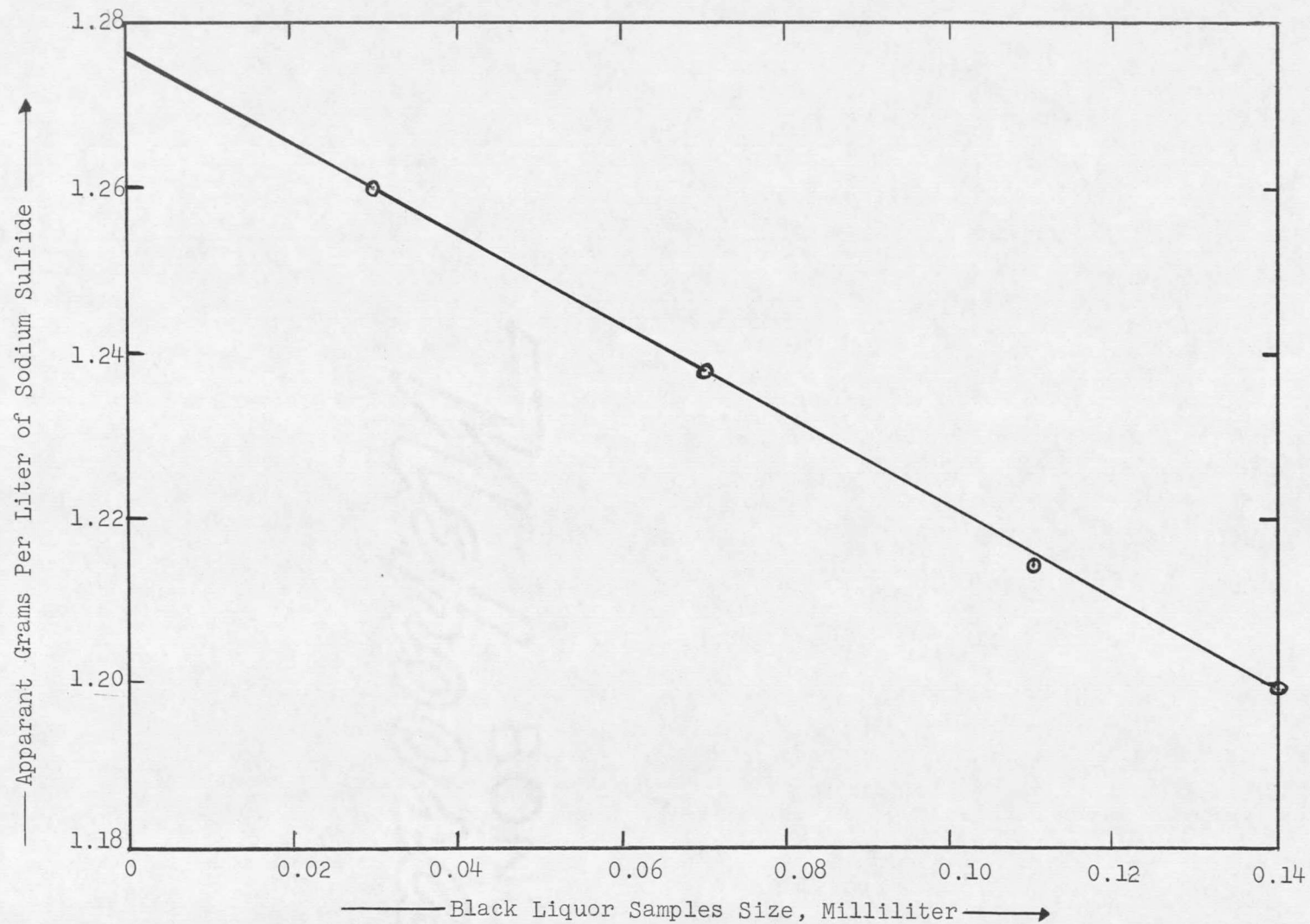


Figure 9. Grams Per Liter of Sodium Sulfide Versus Black Liquor Sample Size to Determine Recovery Factor by Colorimetric Method.

2. Add 1 milliliter of the p-phenylenediamine solution and 26 milliliters of water.
3. Add 1 milliliter of ferric chloride solution and record the time it takes for the solution to turn violet.
4. Determine the milligrams of thiosulfate in the black liquor sample from a previously prepared standard curve of the induction time versus milligrams of sodium thiosulfate.

C. Calibration:

A standard curve of the induction time versus milligrams of thiosulfate is prepared by adding various quantities of a standard thiosulfate solution in place of the black liquor sample and recording induction time as described in the preceding procedure.



















































