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
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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 l80°F.

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A STUDY IN THE OXIDATION OF KRAFT BLACK LIQUOR

by

BHARAT K. SHAH

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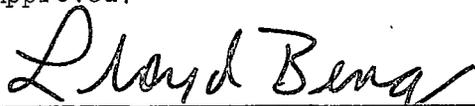fulfillment of the requirements for the degree

of

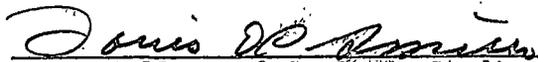MASTER OF SCIENCE

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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 proc-
esses: 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.[4] 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.[4]

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 con-
sists 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). Follow-
ing the digestion period, the pulp fibers are free from lignins and are
ready for separation from the spent cooking liquor. This liquid, to-
gether 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
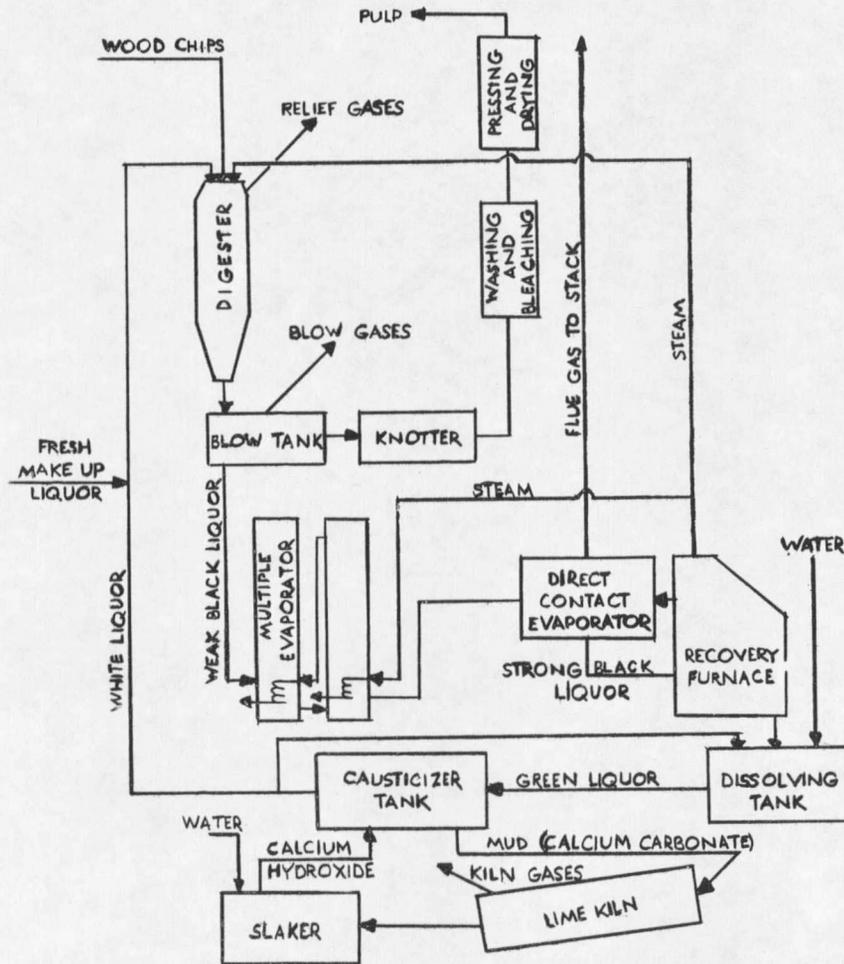
Figure 1.   The Kraft Pulping Process

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[1] 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[1] 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[13] 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[1] 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.[15] If the hot liquor is brought in contact with air, the sodium sulfide is oxidized to sodium thiosulfate:

$$2Na_2S + H_2O + 2O_2 = Na_2S_2O_3 + 2NaOH$$
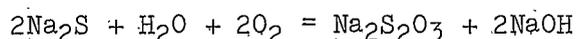
and the methyl mercaptan is oxidized to dimethyl disulfide.

$$4CH_3SH + O_2 = 2(CH_3)_2S_2 + 2H_2O$$
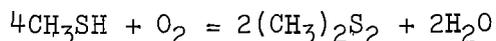
In 1959 Murray[7] published the results of a batch reactor on the kinetics of weak black liquor oxidation. The author studied the reaction rates over a temperature range of 122°F to 196°F and sodium sulfide concentrations up to 16 grams per liter. (g.p.l.) The data obtained from the experiments in a 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

θ = 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:

$$Vln (C + bP) = K\theta + B$$

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 concentra-

tion 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 indi-

cated temperature, the change in rate with temperature was actually very

slight.

Ricca[10] reported that the soluble materials in black liquor catalyze

oxidation. He prepared a synthetic liquor containing the same concen-

tration 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[15,3] have been suggested to explain the formation of stable inorganic sulfur compounds from sodium sulfide.

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

(2) $Na_2S_2O_3 + 2NaOH + 2O_2 = 2Na_2SO_4 + H_2O$
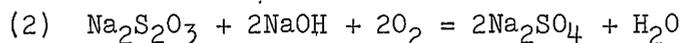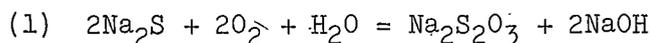
Murray[7] reported that he observed the formation of elemental sulfur at low temperatures during the oxidation of black liquor. The reactions 3 and 4 can explain the formation of elemental sulfur from sodium sulfide.

(3) $Na_2S + H_2O + 1/2\ O_2 = 2NaOH + S$

(4) $2Na_2S + Na_2S_2O_3 + 3H_2O = 4S + 6NaOH$
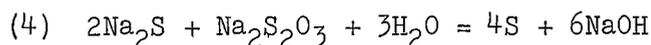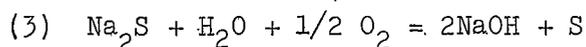
Mechanism of Oxidation

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

$Na_2S\ (l) + O_2\ (g) = Products$

$A\ (l) + B\ (g) = Products$
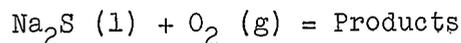
Since the materials in the two separate phases must contact each other before the reaction can occur, the over-all rate expression must account for the resistances provided by the mass transfer step and the chemical