

HIGH INTENSITY BLACK LIQUOR OXIDATION

A thesis submitted by

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# TABLE OF CONTENTS

	Page
ABSTRACT	1
INTRODUCTION	3
Basis for Experimental Work	3
Thesis Objectives	3
BACKGROUND	5
Rationale for HIBLOX Scheme and Historical Development	5
Chemistry of BLOX	8
Chemistry of ZIMPRO WAO	13
Chemistry of Oxidation of Lignin Model Compounds	13
Kinetics of BLOX	17
Kinetics of ZIMPRO WAO	19
Kinetics of Oxidation of Lignin Model Compounds	20
Kinetics of Oxidation of Other Organic Compounds	21
Black Liquor - Composition and Colloidal Nature	23
Key Black Liquor Properties and Possible Effects of HIBLOX	27
Precipitation Behavior	27
Inorganic Scaling	27
Organic Precipitation	28
Rheology	29
Closure	33
EXPERIMENTAL APPROACH	34
General Considerations	34
Kinetics	36
Chemistry	36
Postoxidation Properties	36

EXPERIMENTAL PROGRAM	38
Apparatus	38
Experimental Procedures	41
HIBLOX Reactions	41
Titrations for Unknown Acids	42
Concentration	42
Viscosity Measurement at High Solids	43
Analytical Procedures	43
pH Measurements	43
Ion Chromatography	43
Sodium Sulfide Measurement	43
Black Liquor Solids Measurement	44
Ultraviolet Spectrophotometry	44
Total Oxygen Demand	44
Black Liquor Heating Value	44
Lignin Molecular Weight Analysis	45
RESULTS AND DISCUSSION	46
General Considerations	46
Comparison of Calculated TOD Reduction and Heating Value Reduction	47
Temperature-TOD Reduction Limits	49
Kinetics	50
Influence of Reactor and Liquor Parameters	50
Kinetic Model of HIBLOX	55
First Reaction	63
Second Reaction	69

Effect of Utilization of Strong Liquor	75
Chemistry	81
Postoxidation Properties	112
Effect of HIBLOX on pH	112
Precipitation Behavior and Rheology	114
Other Property Changes	124
CONCLUSIONS	126
Chemistry	126
Kinetics	127
Postoxidation Properties	128
SUGGESTIONS FOR FUTURE WORK	129
ACKNOWLEDGMENTS	130
LITERATURE CITED	131
APPENDIX I. CALIBRATION OF EXPERIMENTAL EQUIPMENT	134
APPENDIX II. CALCULATION OF OXYGEN CONSUMPTION	135
APPENDIX III. EXPERIMENTAL CONDITIONS AND OXYGEN CONCENTRATION <u>vs.</u> TIME DATA	140
APPENDIX IV. TEMPERATURE-TOD REDUCTION LIMITS	156
APPENDIX V. EFFECT OF REACTION PARAMETERS ON HIBLOX REACTION RATE	157
APPENDIX VI. RATE EXPRESSIONS FOR KINETIC ANALYSIS	163
APPENDIX VII. METHOD FOR CALCULATION OF UNKNOWN ACIDS IN HIBLOX LIQUOR	165



## ABSTRACT

In many cases recovery boiler throughput is limited by the heat release characteristics of the boiler. One approach to overcoming this type of capacity limitation would be to release a significant portion of the heating value of the black liquor upstream of the recovery boiler via high intensity black liquor oxidation. The objective established for this thesis was to provide information concerning the chemistry, kinetics, and postoxidation properties associated with high intensity black liquor oxidation which would facilitate a technical and economic evaluation of the process.

This objective was accomplished via a small scale reactor study. Black liquor was oxidized in a semibatch reactor under a variety of conditions. A characterization was made of the process and the influence of key reactor and liquor parameters was determined.

The kinetics of high intensity black liquor oxidation were modeled as two consecutive reactions, both first order with respect to liquor total oxygen demand. The first reaction primarily involved the oxidation of sodium sulfide to sodium thiosulfate and exhibited mass transfer rate limitations at high sulfide contents. The second reaction involved the oxidation of the thiosulfate to sulfate and the alkaline-oxidative degradation reactions of the liquor organics.

High intensity black liquor oxidation caused substantial changes in both the inorganic and organic fractions of the black liquors. The inorganic sulfurous species were oxidized sequentially from sulfide to thiosulfate to sulfate at increasing extents of reaction. Inhibition of thiosulfate oxidation by the sulfide prevented significant formation of sulfate until all the sulfide was consumed. The reactions involving the liquor organics led to a variety of low

molecular weight acids and a substantial reduction in the amount of precipitable lignin. The total acidification, both by formation of organic acids and alkali consuming reactions involving the inorganics, amounted to roughly 1.15-1.20 millimoles of acidification/millimole oxygen consumed during oxidation. A significant reduction in the pH of the liquor resulted from the formation of the acidic species.

The pH decline caused the postoxidation liquors to exhibit poor rheological properties at high solids contents. The poor rheological properties were traced to the destabilization of the colloidal lignin in the liquor. The poor rheology required the addition of alkali to produce acceptable postoxidation liquor properties.

Since the only source of the needed alkali in a paper mill would be the white liquor system, the use of white liquor as the source of the alkali was investigated. Various amounts of alkali with a sulfide/hydroxide ratio corresponding to a 30% sulfidity white liquor were added to black liquor prior to oxidation. Under these circumstances approximately 0.5 pound alkali/pound oxygen consumed during oxidation was sufficient to restore acceptable liquor properties at 5% total oxygen demand reduction. Increasing amounts of alkali were needed at increasing extents of reaction.

## INTRODUCTION

### BASIS FOR EXPERIMENTAL WORK

In many cases recovery boiler capacity is limited by factors related to the boiler combustion load. The combustion load determines the amount of air required, the amount of flue gas produced, and the amount of heat which must be absorbed by the furnace waterwalls prior to the entry of the exit gas into the furnace heat traps. Factors such as these limit the amount of black liquor of a given heating value that can be burned in a given boiler.

One approach to increasing recovery boiler capacity is to release a significant portion of the heating value of the black liquor upstream of the boiler via high intensity black liquor oxidation (HIBLOX). The successful development of such a system would allow mills to incrementally increase recovery boiler throughput while minimizing the capital investment. An evaluation of the feasibility of this approach requires a great deal of information concerning reaction kinetics, chemistry, and postoxidation liquor properties.

### THESIS OBJECTIVES

The objective of this thesis was to provide information which would facilitate the technical and economic evaluation of the proposed HIBLOX process. Specifically, the thesis was proposed to investigate HIBLOX reaction kinetics and chemistry, as well as two postoxidation properties, precipitation behavior and viscosity, identified via a literature survey as potentially serious problems. These phenomena were characterized and the effects of key liquor and reactor parameters on the HIBLOX process and the ensuing concentration operation were determined.

As the characterization of the selected phenomena progressed, a severe liquor rheology problem became apparent. The extensive oxidation of black liquor led to a product which gelled at high solids. At this point the objectives of the thesis were broadened to include determination of a method of overcoming this problem. Determination of a solution to this gelling problem became a key thesis objective. The experimental work has shown a simple solution to this problem does exist.

This thesis provides a characterization of the chemistry, kinetics, and key postoxidation properties related to HIBLOX and provides a solution to a severe technical problem inherent to the process. The knowledge concerning the chemical changes associated with the oxidation of black liquor has been extended and a kinetic model for the HIBLOX process has been developed. The solution of the gelling problem has overcome the greatest technical problem inherent to HIBLOX and provides a greater understanding of the rheological behavior of black liquor and its dependence on liquor parameters.

## BACKGROUND

### RATIONALE FOR HIBLOX SCHEME AND HISTORICAL DEVELOPMENT

Undesirable capacity limitations are imposed on kraft recovery furnaces due to heat release characteristics (1,2). For example, furnaces are designed for a gas temperature of approximately 1200°F at the entrance to the generating bank. The gas temperature must be below the fusion temperature of the entrained inorganic ash at this point in order that cleanliness can be maintained via sootblowers.

Constraints of this type tend to limit the rate at which black liquor of a given heating value can be burned in a given unit. If greater capacity becomes necessary due to increased pulp production, often the only solution is to purchase an additional recovery boiler. When only a moderate increase in capacity is needed, such a decision may be unacceptable.

The alternatives available for increasing recovery furnace throughput by a moderate amount are limited. Perhaps the best candidate is the fluidized bed incinerator (2). These units have the potential to increase furnace capacity by a controllable amount, but suffer from numerous problems including the lack of inherent capability of recovering the inorganic sulfur as sodium sulfide, possible bed fusion problems, poor energy recovery, and relatively high power requirements. At the present time no wholly satisfactory means exists for increasing boiler throughput by a moderate amount.

The proposed HIBLOX process would present a straightforward means of providing desired incremental capacity. The concept was originated in early 1981 and work began on the development of process flow sheets and material and energy

balances at this time. From this work some ideas regarding the specifics of the process were generated.

The HIBLOX reactor would be inserted in the recovery system either within or following the black liquor evaporation step. The latter concept is shown schematically in Fig. 1. All the black liquor would pass through the reactor, where a portion of the heating value would be released, thus reducing the boiler combustion load/pound of original liquor solids. The reduced combustion load/unit black liquor would lead to greater capacity for heat release limited boilers.

The oxidant would be air or molecular oxygen. The choice of the oxidant could be determined by a combination of technical, economic, and environmental considerations. Among the major considerations would be the cost and availability of oxygen at a particular mill location and the environmental regulations concerning the waste gas from the HIBLOX unit.

The extent of oxidation required for the HIBLOX process would be greater than that currently practiced for odor control. It would be limited on the upper end by the point at which the heating value of the oxidized liquor would be insufficient to maintain stable, autogenous combustion. It is believed the desired oxidation range would be 5-10% of the total oxygen demand (TOD) of the black liquor (3).

Table I illustrates how HIBLOX would compare to other black liquor oxidation schemes. It is evident HIBLOX would be an extension of the current black liquor oxidation (BLOX) process employing somewhat more severe reaction conditions and satisfying somewhat more of the liquor TOD. For this reason, most of the background literature discussed in ensuing sections was gathered from research

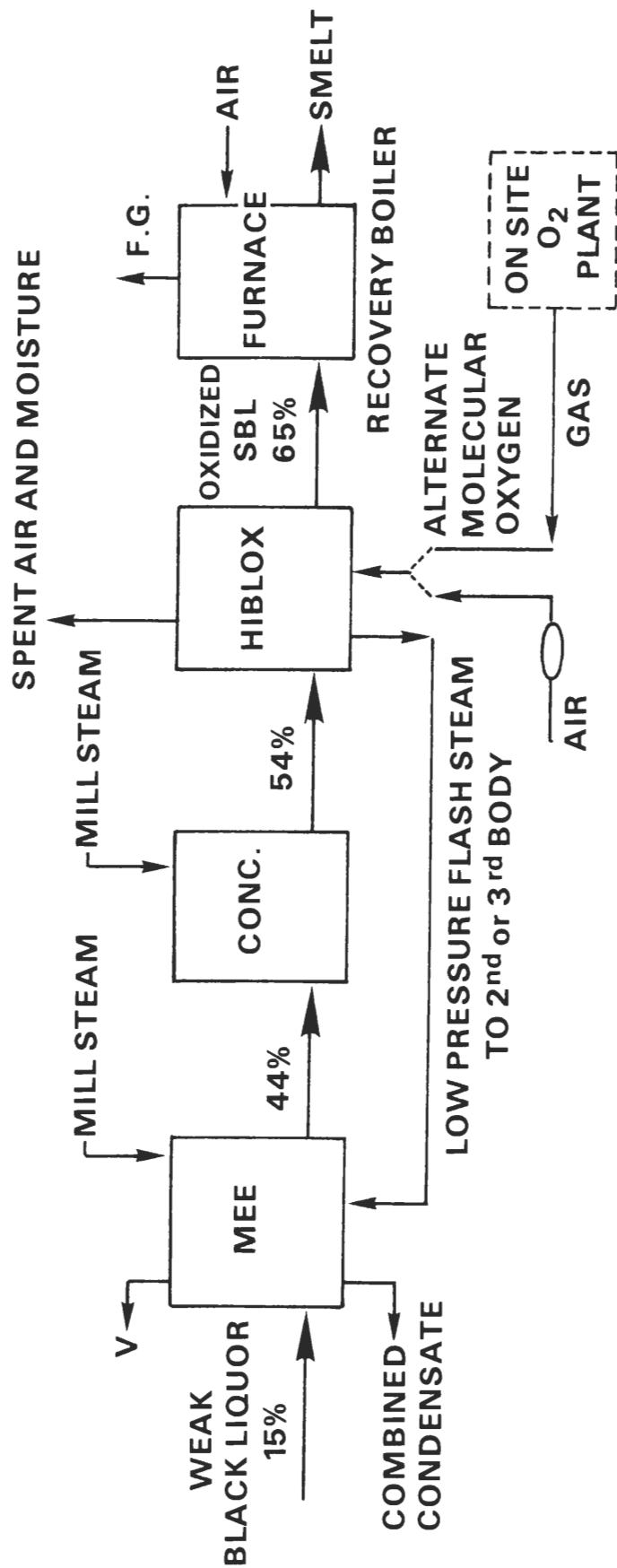


Figure 1. Schematic of HIBLOX process.

related to BLOX. The other process, ZIMPRO wet air oxidation (ZIMPRO WAO), represents a much more severe oxidation, even as adapted for kraft black liquor.

Table 1. Black liquor oxidation approaches.

	Liquor Treated, %	Total Oxygen Demand, %	Temperature, °F	Pressure, psig
Odor Control	100	2-3	200	0
HIBLOX	100	5-10	250-350	50-150
ZIMPRO	100	100	400-700	800-1500
ZIMPRO as modified for kraft process	10-15	50-80	450-550	800-1500

The chemistry and kinetics related to the first 2-3% reduction in black liquor TOD and the postoxidation properties of the oxidized liquors are well known from the work on BLOX for odor control. On the other extreme the products formed from the 100% TOD reduction associated with the ZIMPRO WAO are also known. It is between these extremes where HIBLOX would operate and where information is lacking. A review of the work related to BLOX and ZIMPRO WAO as well as consideration of the properties of black liquor provided a basis for determining the proper experimental approach and the key areas of concern.

#### CHEMISTRY OF BLOX

The major reaction associated with BLOX is the oxidation of sodium sulfide to sodium thiosulfate. Although the actual reaction mechanism is quite complicated and involves a polysulfide intermediate (4,5), the net reaction is usually written  $2 \text{Na}_2\text{S} + 2 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2 \text{NaOH}$ . This stoichiometry, suggesting consumption of one mole oxygen/mole sodium sulfide, has been experimentally verified by a number of investigators (6-8).



However, virtually no  $\text{Na}_2\text{S}$  actually exists in black liquor due to the prevailing pH. Actually the  $\text{NaHS}$  species is predominant and it would probably be oxidized according to  $2 \text{NaHS} + 2 \text{O}_2 \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$ . Since  $\text{NaHS}$  is an alkaline salt and  $\text{Na}_2\text{S}_2\text{O}_3$  is not, a reduction in liquor pH would be expected during oxidation. Surprisingly, the expected pH reduction has not generally been reported in the literature.

A second reaction involving the sulfurous species of the liquor is the oxidation of the sodium thiosulfate to sodium sulfate through a very reactive sulfite intermediate (9,10). This reaction is normally written  $\text{Na}_2\text{S}_2\text{O}_3 + 2 \text{NaOH} + 2 \text{O}_2 \rightarrow 2 \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ . The oxidation of thiosulfate to sulfate is not a desired reaction and the conversion is usually minimal during BLOX.

It has been reported (9,10) that the conversion of thiosulfate to sulfate is accentuated by oxidizing weak rather than strong liquor. The reduced conversion in strong liquor was attributed to inhibition of sulfate formation due to the greater sulfide (and hence its intermediate oxidation product, polysulfide) concentration. Polysulfide apparently prevents sulfate formation by returning the sulfite intermediate to thiosulfate via  $\text{Na}_2\text{S}_2 + \text{Na}_2\text{SO}_3 \rightarrow \text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3$  (9,10). Thus little sulfate can be formed while sulfide and/or polysulfide is present in high concentrations.

Finally, any sodium sulfite present in the liquor can be oxidized to sodium sulfate. This reaction is usually written  $2 \text{Na}_2\text{SO}_3 + \text{O}_2 \rightarrow 2 \text{Na}_2\text{SO}_4$ . Usually only very small quantities of sulfite are present in the liquor and this reaction is of minimal importance.

One investigation which considered the linked chemistry of the key sulfurous species over a wide oxidation range was the work of Fones and Sapp (11). They investigated in-digester black liquor oxidation and followed the progress of the reactions involving the sulfurous species. The status of the sulfurous species as a function of time was determined.

The key results are shown in Fig. 2. The sequential oxidation from sulfide to thiosulfate to sulfate is obvious. Eventually complete conversion to sulfate occurred with essentially no remaining sulfide or thiosulfate.

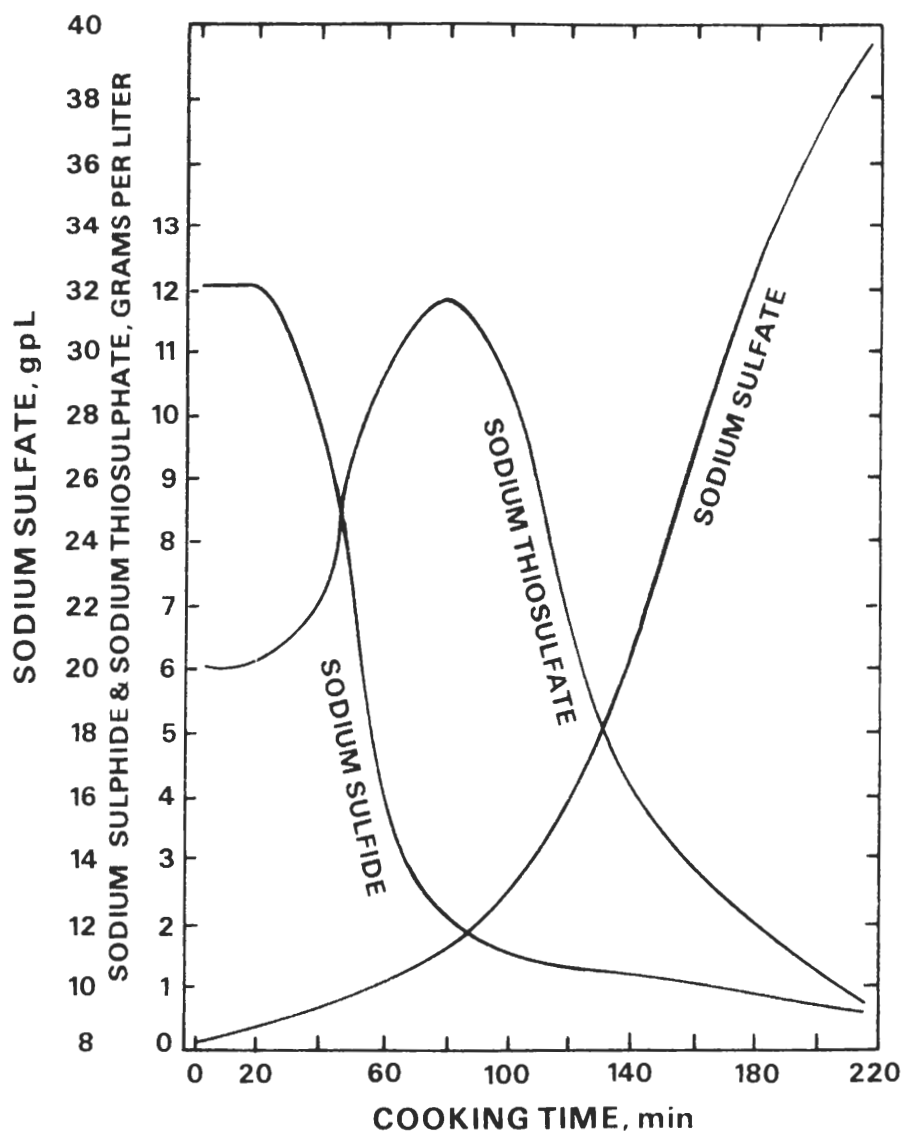


Figure 2. Change in concentration of sodium sulfide, sodium thiosulfate, and sodium sulfate upon oxidation. Taken from Fones and Sapp, Tappi 43(4):369-73(April, 1960).

What is not clear is the extent of liquor TOD reduction associated with a given extent of sulfur conversion. It is also not apparent what other reaction products were formed and what the properties of the highly oxidized liquor were. The lack of information concerning the relationship between extent of reaction and sulfur conversion to sulfate is unfortunate because this relationship is important to the HIBLOX process.

The status of the sulfurous species as affected by the extent of oxidation could have significant implications for boiler odor control strategy. The work of Strohbeen and also Douglas and Price (12,13) has shown sodium sulfate to be stable to the release of hydrogen sulfide during pyrolysis. Sodium thiosulfate does not possess such stability. Hence determination of the extent of reaction necessary for complete conversion of sulfurous species to sulfate would be of substantial value.

Organic compounds are also oxidized during BLOX. However, the amount of the total oxygen consumption attributable to the organic fraction of the liquor is small relative to that consumed by the inorganics. For this reason less emphasis has been placed on determining the chemistry involving the organic species.

The one organic species in black liquor whose oxidation chemistry has been extensively studied is the odorous compound methyl mercaptan. During BLOX a complex series of oxidation and hydrolysis reactions convert the methyl mercaptan to a nonvolatile form (7). These reactions are shown schematically in Fig. 3. The stoichiometry associated with all these reactions is not known, but the initial oxidation to dimethyl disulfide has been shown to follow the stoichiometry suggested by  $4 \text{ CH}_3\text{SH} + \text{O}_2 \rightarrow 2 \text{ CH}_3\text{SSCH}_3 + 2 \text{ H}_2\text{O}$  (7).

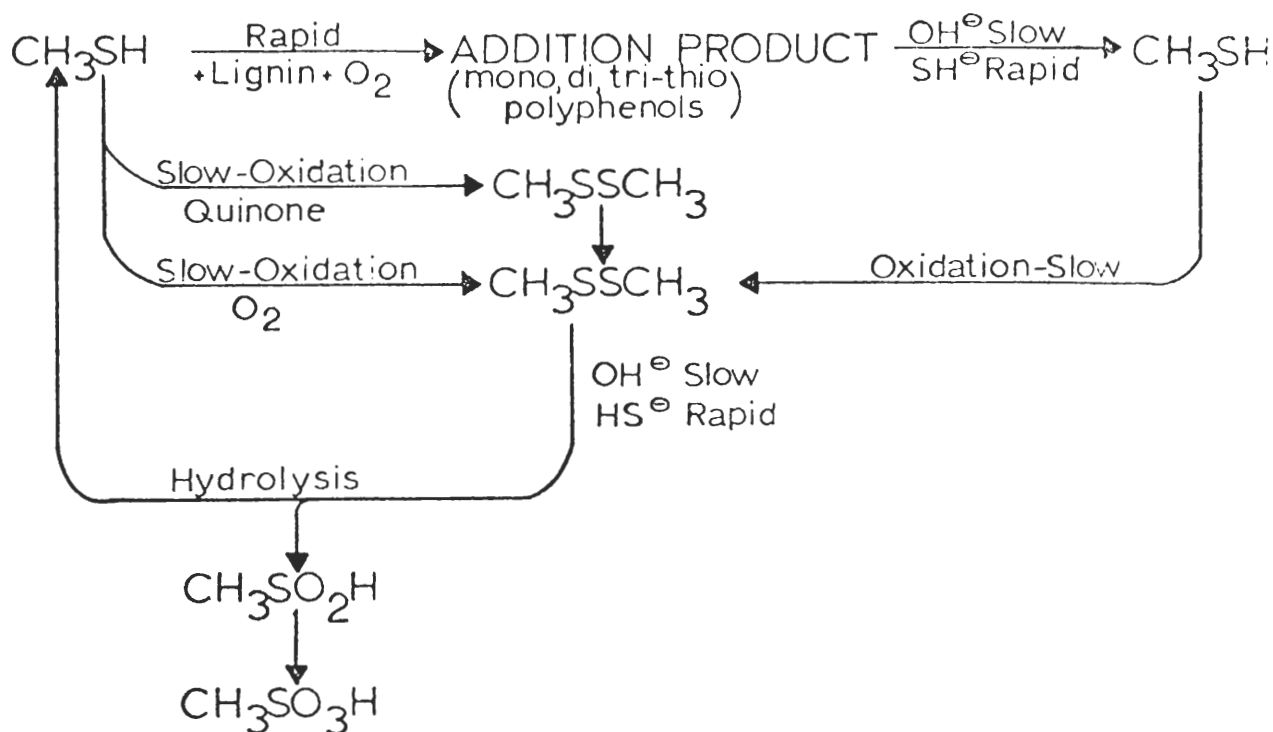


Figure 3. Schematic outline of reactions occurring in black liquor oxidation. Taken from Bentvelzen, et al., Tappi 59(1): 130-3(Jan., 1976).

The lignin and carbohydrates present in the liquor also undergo some oxidation during BLOX. Little effort has been placed on analysis of this chemistry in BLOX studies. Generally, the oxygen consumption greater than that stoichiometrically required for complete oxidation of sulfide to thiosulfate is attributed to reactions involving the organics (7,8) without further explanation. Approximately 20-30% of the total oxygen consumption during BLOX is attributed to the mercaptan, lignin, and carbohydrates.

Among the two general classes of organics, lignin and carbohydrates, the lignin fraction is known to be quite susceptible to alkaline oxidative attack. Cooper's (10) comparison of the heating value reduction due to BLOX and the lignin weight loss indicated the lignin to be the more easily oxidized species.

The specifics of oxidative lignin chemistry will be detailed in a following section.

#### CHEMISTRY OF ZIMPRO WAO

The products associated with the ZIMPRO WAO process are the result of more or less complete oxidation. At 100% TOD reduction, organics are converted to the fully oxidized products, carbon dioxide and water (14-16). Inorganics are also converted to the fully oxidized products. For example, all sulfur is oxidized to the sulfate form (17).

As the extent of oxidation drops below 100%, intermediate oxidation products are found in the product liquors. Sodium acetate is a common product. It appears as a reaction product in black liquors at oxidation levels below 94% TOD reduction (18). The reaction mechanisms associated with ZIMPRO WAO, and hence the stoichiometry, have not been published.

#### CHEMISTRY OF OXIDATION OF LIGNIN MODEL COMPOUNDS

A great deal of work has been done in the area of alkaline oxidation of lignin model compounds. The reaction mechanisms and products have been found to be highly dependent on the particular model compound. Among the reported reaction paths are side chain displacement, oxidative coupling, formation of epoxidated quinols, and ring cleavage between the methoxyl bearing ring carbon and either of the two adjacent ring carbons (muconic acid path) (19-21). The reaction mechanisms and the types of products produced have significant implications for HIBLOX.

Phenols alkylated para to the hydroxyl group undergo oxidative coupling to diphenols as a first step as shown in Fig. 4 (20). Dimerization is then followed by ring fission reactions. The paths and stoichiometry of the fissure reactions are unknown, although mechanisms have been proposed without proof (20). Products isolated from the oxidation of the compound shown in Fig. 4 included carbon dioxide, methanol, acetone, and 2-hydroxy-3 methoxy-5 methylbenzoic acid. The product analysis and pH behavior indicated oxidative degradation proceeded faster than the carbon-carbon coupling (20).

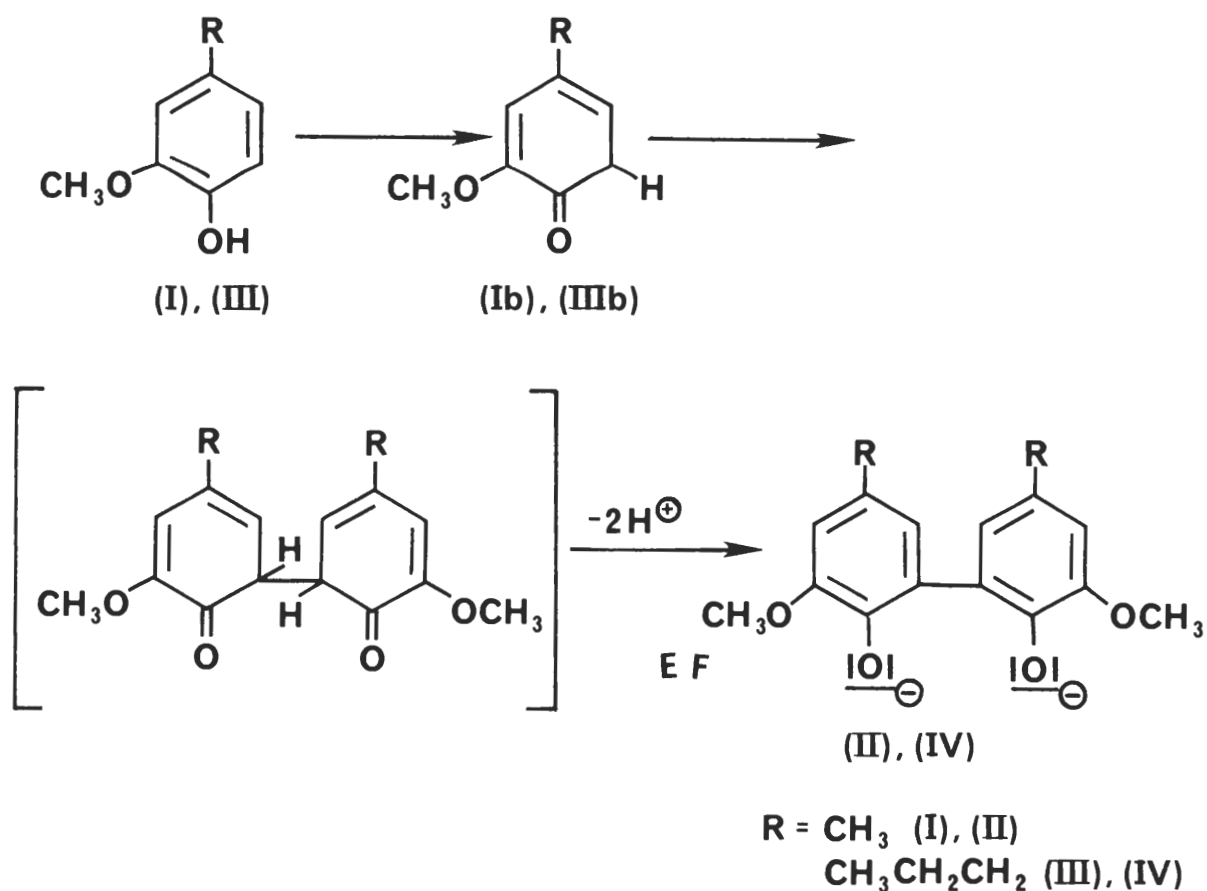


Figure 4. Dimerization (o-carbon-o-carbon coupling) of p-alkylated guaiacol derivatives. Taken from Kratzl, *et al.*, Adv. in Chem. Series 59:157-75, Am. Chem. Soc., 1966.

Nonalkyl substituted phenolics such as that shown in Fig. 5 tend to react via side chain Dakin type elimination reactions as a first step (19). The eliminated chains can then be oxidized to a variety of low molecular weight acids or participate in condensation reactions (22). The postelimination phenolic groups are then attacked in a manner analogous to the alkyl substituted phenolics.

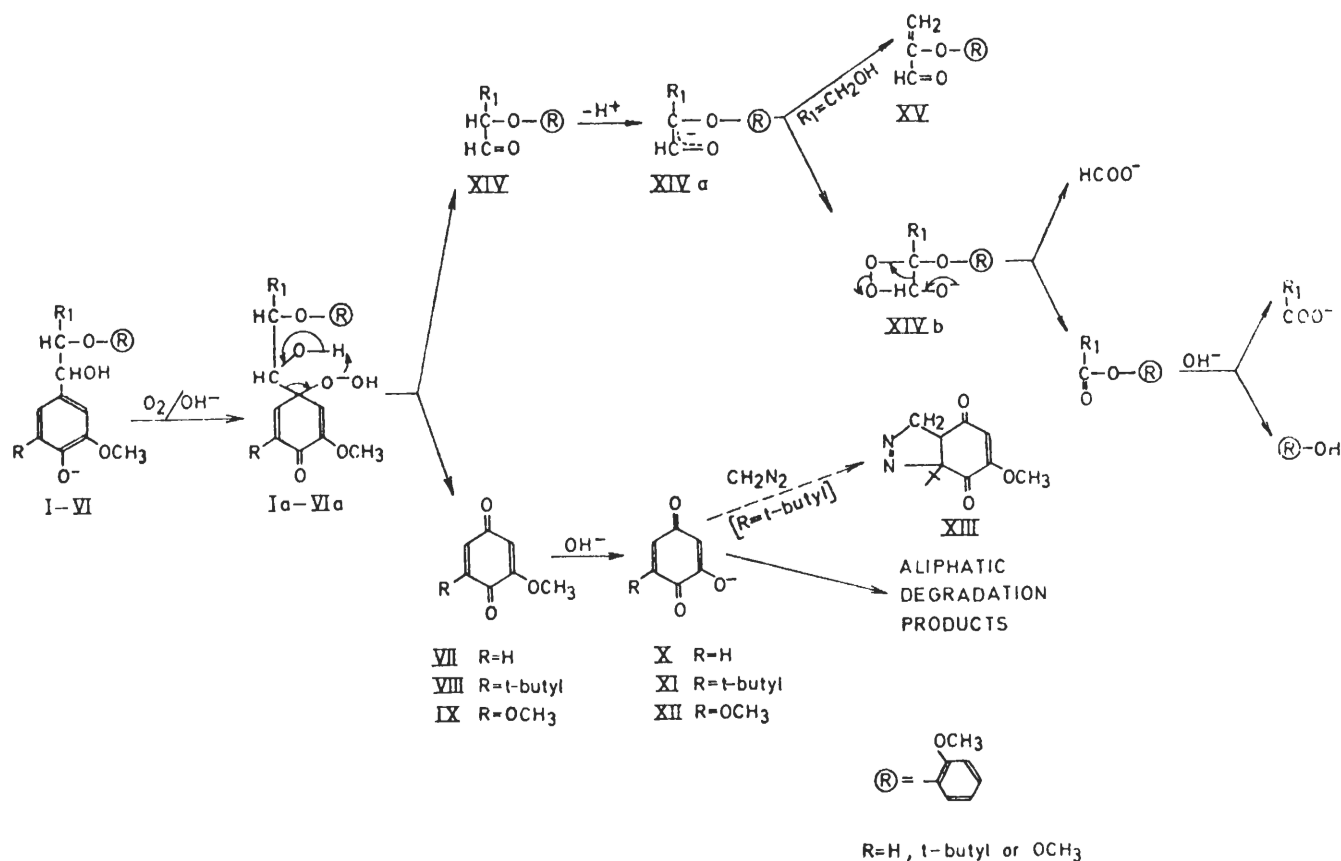


Figure 5. Oxidation of nonalkyl substituted phenolics. Taken from Imsgard, Doctoral Dissertation, RIT, Stockholm, Sweden, 1976.

When a complicated lignin-type structure such as that shown in Fig. 6 is oxidized in alkali, it is apparent any number of low molecular weight acids as well as a host of other products can result. Oxidation of the structure shown in Fig. 7 at 100°C led to the products shown in Table 2 (19).

Regardless of the reaction mechanisms involved, the alkaline oxidation of lignin model compounds invariably leads to various acidic products. The oxidative degradation reactions generally take place along with alkali-promoted (nonoxidative) reactions. The combination of these reactions can eventually lead to complete degradation of the lignin structure.

THE PATHWAYS OF OXIDATIVE DEGRADATION  
OF  $\beta$ -ARYLETHER STRUCTURES

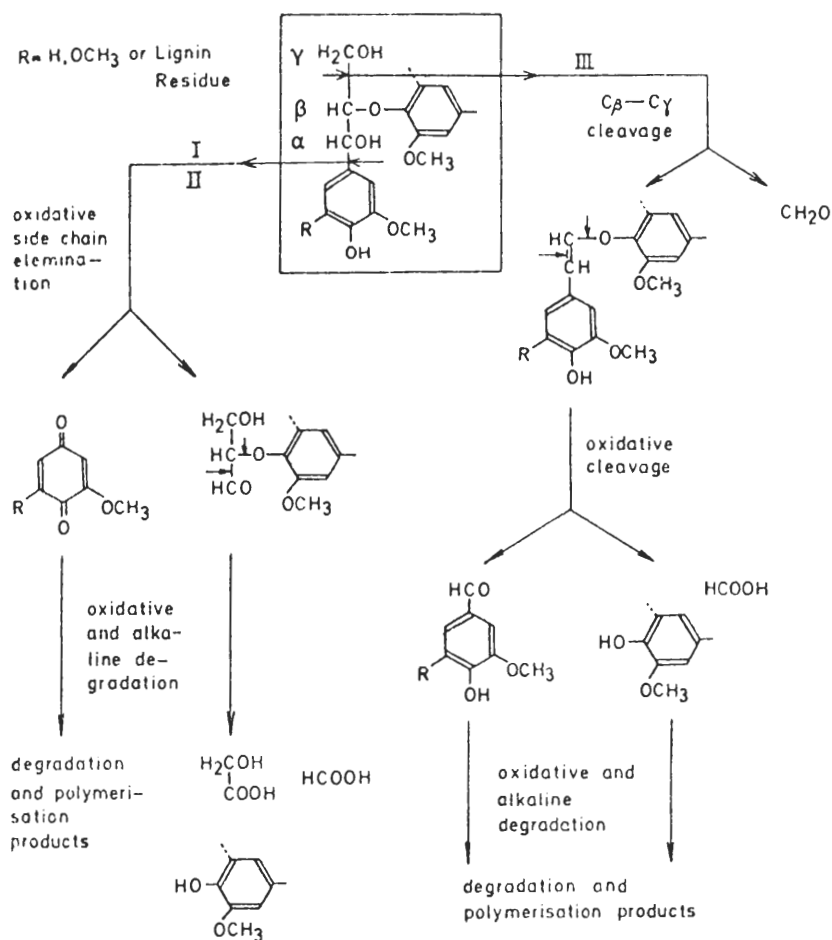


Figure 6. Oxidation of  $\beta$ -arylether structures. Taken from Imsgard, Doctoral Dissertation, RIT, Stockholm, Sweden, 1976.



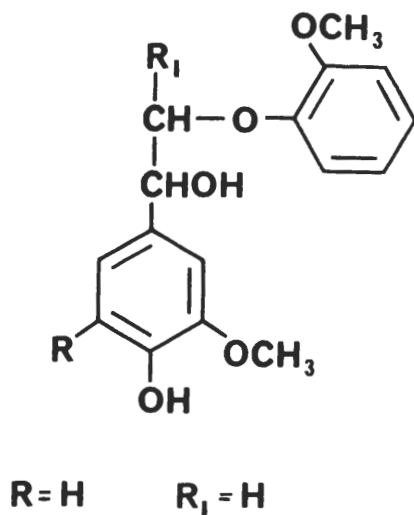


Figure 7. Compound which led to products shown in Table 2. Taken from Imsgard, Doctoral Dissertation, RIT, Stockholm, Sweden, 1976.

Table 2. Products formed from oxidation of the compound shown in Figure 7.

Compound	Yield, %
Formic acid	4
Acetic acid	29
Glycolic acid	15
Oxalic acid	31
Malonic acid	4.2
Succinic acid	3.6
Fumaric acid	1
Guaiacol	3
Vanillin	5

## KINETICS OF BLOX

The kinetics of the main reactions pertinent to BLOX are well established. Detailed studies of the oxidation kinetics of sulfide have been done in both black liquor and alkaline aqueous solutions, and thiosulfate oxidation has been

studied to a lesser extent. From this work kinetic expressions have been developed.

The kinetics of sulfide oxidation in black liquor by air have been delineated by Murray (5) using the following equation:

$$-\frac{dC_s}{dt} = \frac{k_1 k_2 P_{O_2} C_s}{k_1 C_s + k_2 H} \quad (1)$$

where  $k_1$ ,  $k_2$  = rate constants

$P_{O_2}$  = oxygen partial pressure

$C_s$  = sulfide concentration

$H$  = Henry's Law constant

At high sulfide concentrations  $k_1 C_s \gg k_2 H$  and the reaction was zero order in sulfide concentration (i.e., mass transfer limited). At low sulfide concentration  $k_2 H \gg k_1 C_s$  and the reaction became first order with respect to sulfide.

Cooper (10) carried out similar work in a plug flow reactor utilizing molecular oxygen as the oxidant. The experimental method insured Reynolds numbers in excess of 40,000 to maximize mass transfer. Even under these conditions the zero/first order sulfide dependence was noted.

The alkaline aqueous oxidation of sulfide has also been extensively studied. Avrahami and Golding (23) determined a zero/first order scheme analogous to that determined for sulfide in black liquor. An activation energy of 8000 calories/gram mole was determined for the sulfide limited portion of the oxidation reaction. A lower activation energy might be expected for the oxidation of sulfide in black liquor, since the phenolic constituents are reported to act as catalysts (24-26), greatly increasing the reaction rate.

Cooper (10) studied the kinetics of thiosulfate oxidation in black liquor. The concentration of thiosulfate initially increased rapidly as sulfide was oxidized. As the sulfide oxidation was completed, thiosulfate oxidation to sulfate became apparent. A first order reaction with respect to thiosulfate was noted.

Less work has been done concerning the kinetics of oxidation of black liquor organics. However, Cooper (10) and Bentvelzen (7) studied the kinetics of sodium mercaptide oxidation. Zero/first order dependence with respect to mercaptide concentration was noted, a result analogous to the sulfide case. The oxidative kinetics of other organic liquor constituents have not been studied in connection with BLOX.

#### KINETICS OF ZIMPRO WAO

The information concerning the kinetics of ZIMPRO WAO is incomplete. Typical time-temperature relationships for a chosen extent of TOD reduction for some aqueous organic streams are available, but the factors which determine reaction rate are not discussed. Whether the reaction rates are chemically or mass transfer limited is not apparent (18).

Furthermore, as Fig. 8 shows, in some cases oxidation greater than that pertinent to HIBLOX occurs prior to any reported data. In Fig. 8, at 392°F, 30% reduction in TOD occurred prior to measurement of any data. The lack of concern with the first ten percent TOD reduction makes the data not very useful for an evaluation of HIBLOX.

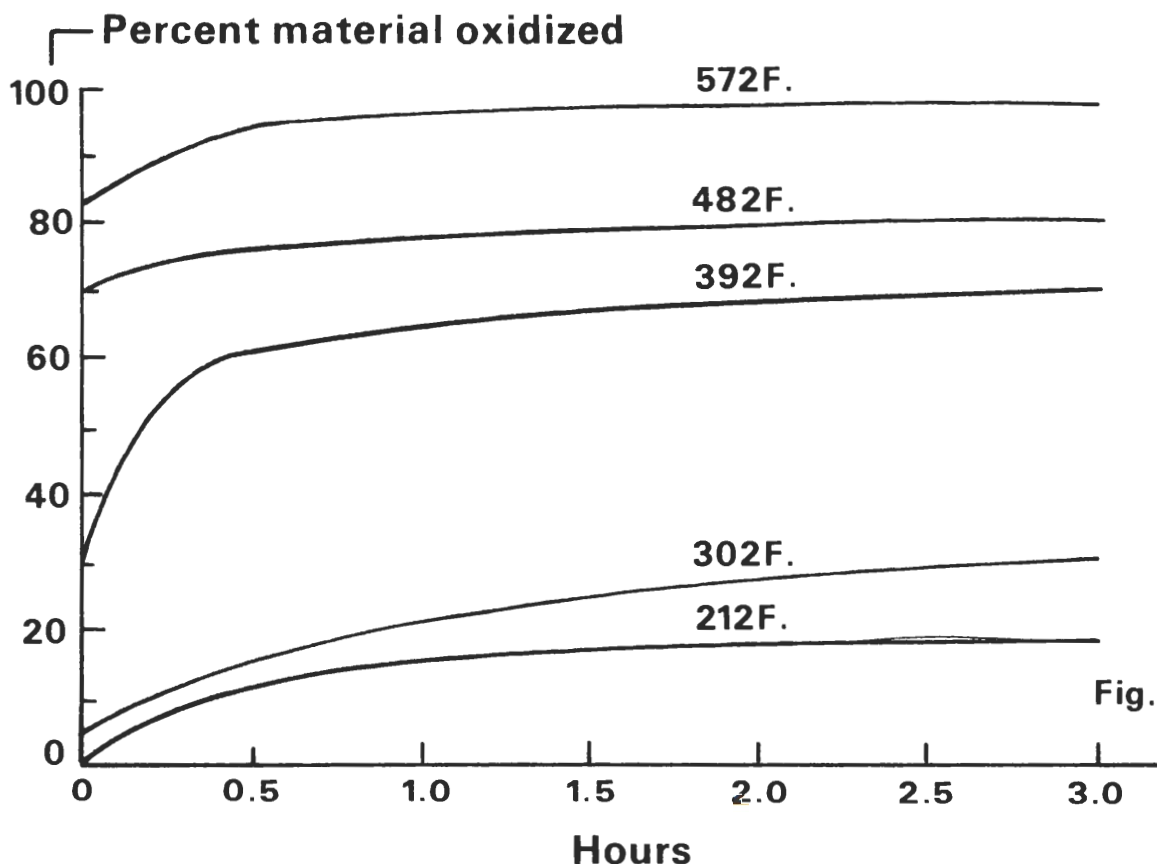


Figure 8. High temperatures give low reaction time and high oxidation. Taken from Zimmermann, F., Chemical Engineering 65:117-20 (Aug., 1958).

#### KINETICS OF OXIDATION OF LIGNIN MODEL COMPOUNDS

The kinetics associated with the oxidation of lignin model compounds are also not well defined. Again, the complexity of the reaction mixture and the numerous reaction products makes kinetic measurements difficult. It is known that the rate of lignin oxidation in alkaline solution is very pH dependent (27).

Figures 9 and 10 show oxygen consumption during oxidation of deciduous alkali lignin at fixed and varying pH. The pH of the solution associated with Fig. 9 was maintained at 10.8 via addition of sodium hydroxide. The pH was allowed to drift in the trial shown in Fig. 10 and declined to less than 8 due to the formation of acidic products. The reduction in oxidation rate with decreasing pH is attributed to increased stability of the phenolic ring at decreasing pH (27).

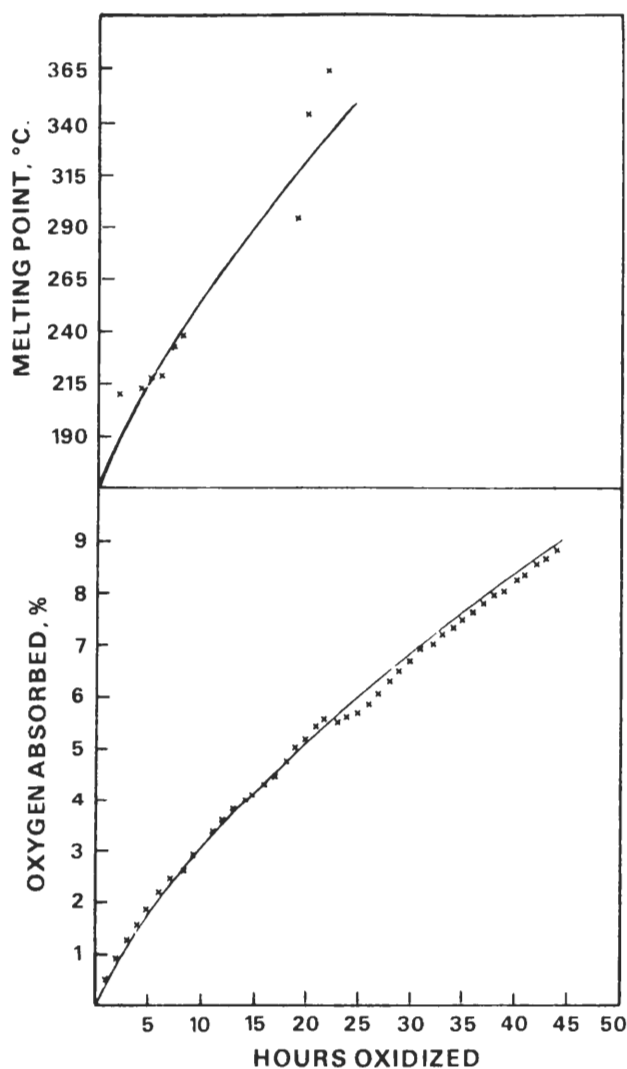


Figure 9. Oxidation at 70°C - pH constant. Taken from Raff and Tomlinson, Can. J. Research 27(11):399-418.

#### KINETICS OF OXIDATION OF OTHER ORGANIC COMPOUNDS

The kinetics related to the oxidation in aqueous media of single organic compounds, including various alcohols and aldehydes, were determined by Taylor and Weygant (28). All exhibited first order kinetics with respect to both the organic compound and oxygen. Activation energies ranging from 16-25 kcal/mole were obtained.

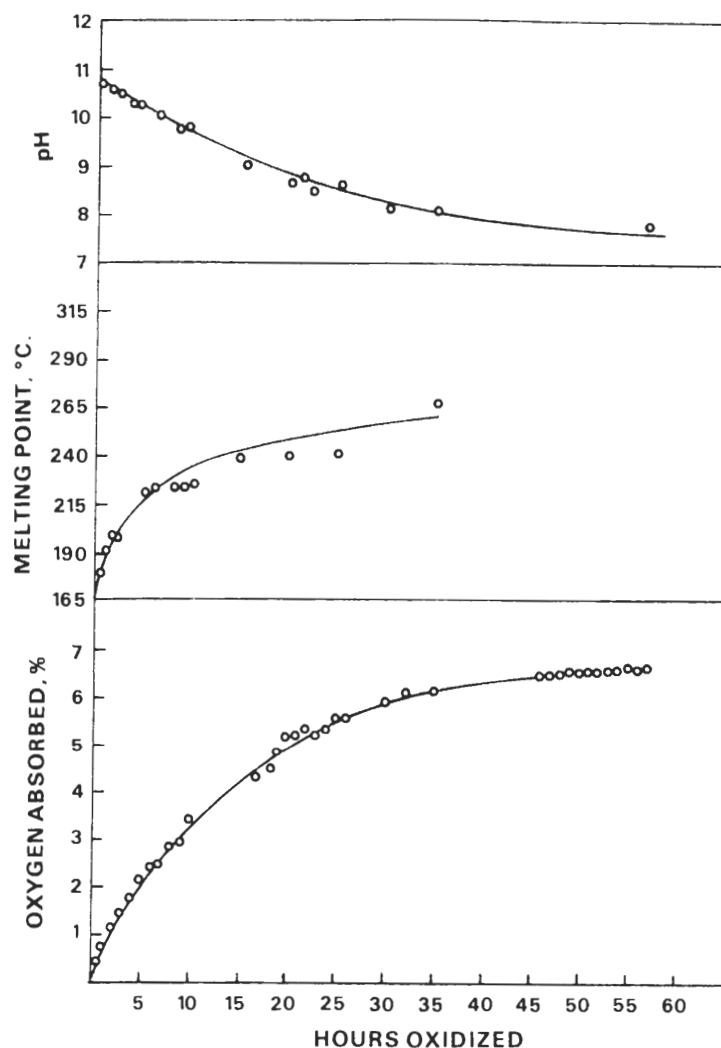


Figure 10. Oxidation at 70°C - pH drift. Taken from Raff and Tomlinson, Can. J. Research 27(11):399-418.

From the previous discussion, it is apparent that greater knowledge of the chemistry and kinetics of black liquor oxidation in the 5-10% TOD reduction range is needed to facilitate evaluation of the HIBLOX process. A kinetic analysis in this oxidation range is lacking. Additionally, while some of the chemistry can be inferred from the related work, information is needed concerning the status of both the inorganic and organic species over the selected oxidation range.

This chemistry is important for several reasons. The conversion of all the sulfur to the sulfate form could have a significant impact on boiler operation due to the previously mentioned stability of sulfate vis-a-vis hydrogen sulfide release during pyrolysis. The possible formation of acidic products from the lignin and carbohydrate liquor fractions also needs investigation due to probable influences on liquor properties.

Given the complex nature of black liquor, it would not be surprising to see liquor properties substantially altered by HIBLOX. The postoxidation liquor properties might well exert a telling influence on the feasibility of HIBLOX. A review of the colloidal nature of black liquor and consideration of the dependence of key liquor properties on measurable parameters as well as the anticipated changes due to oxidation indicated the precipitation behavior and rheology of HIBLOX liquors to be of primary concern to the thesis work.

#### BLACK LIQUOR - COMPOSITION AND COLLOIDAL NATURE

Black liquor is composed of water, inorganic compounds, and organic compounds. The inorganic compounds are those associated with the cook and those present in the wood. The organic compounds include species derived from both the lignin and carbohydrates of the wood. All of these compounds exert some effect on the properties of the liquor.

The inorganics and the carbohydrates are soluble in water. The inorganics are present as the simple low molecular weight inorganic salts and are also associated with organic anions. The degraded carbohydrates are present as sodium salts of various saccharinic acids and/or lactones (29). These compounds do affect black liquor properties, but it is the lignin fraction that imparts particularly unusual properties to the liquor.

Many of the properties of black liquor can be traced to its colloidal nature. In fact, two colloidal systems can exist in black liquor. The colloidal systems are a molecular lignin colloid and association colloids formed by fatty acids and resin acid salts.

The resin acids and fatty acids are present as the sodium salts. The anions of these acids associate to form micelles. The micelles in black liquor exhibit the properties typical of this type of colloidal system. This colloidal system had been removed from the liquor utilized in this thesis via soap skimming.

The other colloid found in black liquor involves the lignin fraction. The lignin in black liquor is quite different from its natural state. Although a small portion of the lignin is dissolved as relatively small molecules, the majority is present as large colloidal macromolecules. The condensed, cross-linked macromolecule contains many structures such as quinones and catechols, but can most easily be considered as a polymer of phenyl propane units.

The average molecular weight of the lignin is a topic currently being debated. One view is that the molecular weight of the lignin ranges from 500-1800, suggesting a degree of polymerization of 3-10. A second opinion is that the molecular weight is much greater, ranging from 2000 to as high as 10,000.

Colloidal lignin has many interesting characteristics. It is thought the lignin polymer exists as a spherical, amorphous macromolecule with varying degrees of polyelectrolytic character (30-32). It has been suggested that the lignin molecule in solution consists of a strongly immobilized network core and a loose surface region where local chain motions are possible. Strong



intermolecular association of lignin through secondary forces has been reported under some conditions (30-32). In these cases, long-range Van der Waal's forces play an important role in the behavior of kraft lignin in aqueous solutions.

Depending on the interaction with solute species and pH, the lignin macromolecule exhibits behavior typical of both lyophilic and lyophobic colloids in aqueous solution. The lyophobic behavior is most often associated with low pH conditions, while lyophilic behavior is typical under high pH conditions. Due to factors such as the irregular particle structure, intermolecular and intramolecular association, the charge distribution, and ion exchangeability, a quantitative interpretation of the colloidal behavior is extremely difficult (31).

In alkaline black liquor, the behavior of colloidal lignin is dependent upon a balance between attractive and repulsive forces acting on the lignin. The attractive forces are those acting on all colloidal particles and are lumped together under the term Van der Waal's forces (33). The attraction energy varies approximately with  $1/(\text{distance})^2$  at distances of separation of a few angstroms and with  $1/(\text{distance})^4$  at larger distances.

The repulsive forces are due to the presence of ionizable groups in the macromolecule. The colloidal lignin is stabilized and kept in solution at high pH by ionized hydrophilic groups, mainly phenolic hydroxyls and carboxyls. These ionized groups prevent the lignin from agglomerating and precipitating due to the electrical charge on the macromolecule. Lignin contains approximately 0.8-1.0 hydroxyl groups per monomeric unit with pKs of 9.4-10.8 and 0.16 carboxyl groups with pKs of approximately 5. Since the phenolic hydroxyl groups are the most numerous, they have the greatest effect on the stability of the

colloid. Ionized phenolic hydroxyl and carboxyl groups in the lignin are shown schematically in Fig. 11.

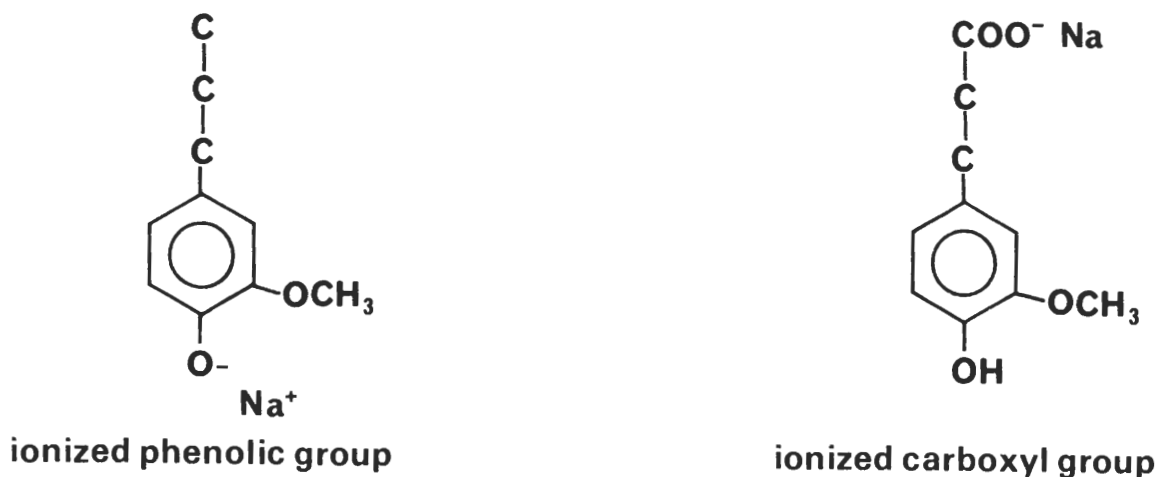


Figure 11. Ionizable groups in lignin.

As long as the repulsive forces due to the ionized hydrophilic groups exceed the attractive force, the colloidal lignin can be kept in solution. However, should the liquor pH decline to approximately 11, dissociated groups begin to accept protons. The repulsive forces decline and the attractive forces begin to cause flocculation. The majority of the lignin will precipitate as the pH drops below 9.

Given the composition and colloidal nature of black liquor, its properties could easily be affected by HIBLOX. Among the properties of greatest concern were precipitation behavior and rheology. The dependence of the properties on liquor parameters and possible HIBLOX effects are detailed below.

## KEY BLACK LIQUOR PROPERTIES AND POSSIBLE EFFECTS OF HIBLOX

### Precipitation Behavior

A number of types of precipitation problems have been noted in black liquor recovery systems. These include "soluble" sodium sulfate-sodium carbonate scaling, "insoluble" calcium carbonate scaling, and the precipitation of organics. Each type of scaling occurs due to a different driving force and presents a different possible problem for the HIBLOX process.

### Inorganic Scaling

Sodium sulfate-sodium carbonate scales can occur when black liquor is concentrated. The precipitation occurs when the solubility limits are exceeded due to the removal of water. Sodium carbonate and sulfate normally constitute 10-15% of the liquor solids, and most liquors exceed their solubility limit at approximately 50% solids. The compounds often precipitate together, forming a solid phase with a composition similar to that of burkeite ( $2 \text{Na}_2\text{SO}_4\text{-Na}_2\text{CO}_3$ ). The solubility limit is affected not only by the amounts of sodium sulfate and carbonate in the liquor, but by the presence of other sodium salts and the total solids content of the liquor. Temperature has been found to exert only a minor effect at temperatures commonly found in evaporators.

The other type of inorganic precipitation seen in black liquor is the hard or insoluble scales, usually composed of calcium carbonate. This type of precipitation is very temperature dependent. The rate of precipitation may double for a temperature increase of 6-10°F and often becomes significant in evaporator tubes at temperatures of 245-256°F.

Inorganic precipitation could be enhanced by HIBLOX. The anticipated formation of sulfate and carbonate salts as reaction products might be expected to

increase the likelihood of burkeite type scaling. This possibility was thought to be one of the more severe potential problems associated with HIBLOX. Temperature dependent precipitation might also be enhanced due to high reactor temperatures, but was thought to be of less concern because the reactor temperatures were not expected to be substantially above the temperatures commonly found in existing multiple effect evaporators.

#### Organic Precipitation

Precipitation of lignin can also occur in black liquor recovery systems. The precipitation of lignin during concentration occurs due to the breakdown of the colloidal lignin system. As previously discussed, the stability of the colloidal system is dependent upon the ionization of hydrophilic groups and a protective shell of water molecules (29). Increasing solids content and especially any decline in liquor pH can destabilize the colloid, leading to precipitation. Komshilov and Letonmyaki (34) have reported precipitation of lignin during black liquor evaporation at between 0.7 and 1.14% active alkali (as Na<sub>2</sub>O, based on o.d. solids).

The possible formation of acidic products from the lignin and carbohydrates during HIBLOX made organic precipitation behavior a great concern. Formation of the acids could lead to a lower liquor pH, which could cause lignin destabilization. However, the tendency toward precipitation could be offset by a decreasing lignin concentration and/or the introduction of ionizable groups during HIBLOX.

No evidence of carbohydrate precipitation during recovery operations could be found. The lactones and/or hydroxy acids in black liquor are reported to be unaffected by pH change and/or concentration (35,2). No deleterious effect on the precipitation behavior of this fraction during HIBLOX was anticipated.

## Rheology

Black liquor is a non-Newtonian liquid. Its viscosity behavior is that of a thixotropic fluid. As such it exhibits considerable shear thinning at high solids contents. At low solids the behavior approaches Newtonian.

While rheology is probably the most important property with respect to processing black liquor, little is known concerning how rheology varies with composition. It is apparent that the viscosity increases substantially with increasing solids content. Empirical expressions (36,37) have been developed to predict viscosity, but these provide no fundamental knowledge.

The work which has been done concerning the effect of composition on rheology has shown that specific organic compounds in the liquor can lead to poor rheological properties, including gelation at as low as 40% solids (38). Eucalyptus liquors are particularly prone to this behavior. The presence of polyphenols and/or ellagic acid is the ostensible cause. The manner in which these compounds exert a negative influence on liquor rheology is not known.

It is reasonable to assume that the organic compounds, especially the polymeric lignin, are the dominant factor determining the liquor rheology. The inorganic salts could not account for observed liquor viscosities. For this reason, the viscosity behavior of black liquor might parallel that of other polymeric solutions.

The viscosity of polymeric solutions increases greatly with concentration. Even a small amount of polymeric material can cause a substantial increase in solution viscosity over that of the pure solvent. One of the most widely used equations for predicting the effect of polymer concentration on solution viscosity is the Huggins equation (39):

$$\frac{N_{sp}}{C} = [N] + k [N]^2 C \quad (2)$$

where  $N_{sp}$  = specific viscosity

$C$  = polymer concentration

$k$  = Huggins constant

$[N]$  = intrinsic viscosity

Polymer molecular weight also affects solution viscosity. In general, the viscosity of linear polymers varies with molecular weight in accordance with the following equation (49):

$$[N] = KM^a \quad (3)$$

where  $[N]$  = intrinsic viscosity

$K$  and  $a$  = constants which must be experimentally determined

$M$  = molecular weight

Both  $K$  and  $a$  are functions of both solvent and polymer type. For branched polymers, the dependence of viscosity on molecular weight follows a similar trend but is not so easily quantified.

Prediction of the viscosity behavior of the polymeric lignin sol in black liquor in terms of its dependence on concentration and molecular weight is difficult. While the viscosity is thought to increase with increases in either parameter, the situation is more complicated. The polymeric lignin exhibits polyelectrolytic behavior which can affect the anticipated results.

Polyelectrolytes exhibit behavior in solution which is quite different from that of nonionizable polymers. In aqueous solution, the mutual repulsion of

charged groups can cause expansion of the polymer chain to levels far greater than would otherwise be possible. The size of the polyelectrolyte coil can be greatly affected by pH and the presence of low molecular weight electrolytes (salts), since both influence the degree of ionization.

Polyelectrolytic polymers can exhibit unexpected properties. Properties which depend on the size of the polymer chain, such as viscosity, are strongly affected by chain expansion. For this reason, the viscosity of polyelectrolytic polymer solutions can markedly increase with decreasing concentration due to greater ionization and hence greater chain expansion. In these cases, when very large chain extensions are reached, the concentration effect reverses. Similar unusual behavior can be caused by varying ionic strength caused by salt addition.

Given the difficulty of making a priori predictions of the rheology of lignin sols, some experimental work has been done. Both the viscosity and molecular weight of lignin sols have been reported to be affected by pH. Benko (41) as well as Yaropolev and Tishchenko (42,43) noted a decrease in the intermolecular associations and molecular weight of lignin sols with increasing pH. Increasing pH has also been reported to eliminate the destabilization of lignin sols by electrolytes (31).

Less is known about the effect of oxidation on the rheology of lignin sols and ultimately on black liquor rheology. The information which is available indicates oxidation increases the viscosity of lignin sols. Raff, et al. (27) reported the lyophilic tendency of alkali lignin and its viscosity in Cellosolve both increased with increasing extent of oxidation. Hydrophilic sols have a tendency to show great increases in viscosity with concentration as shown in Fig. 12.

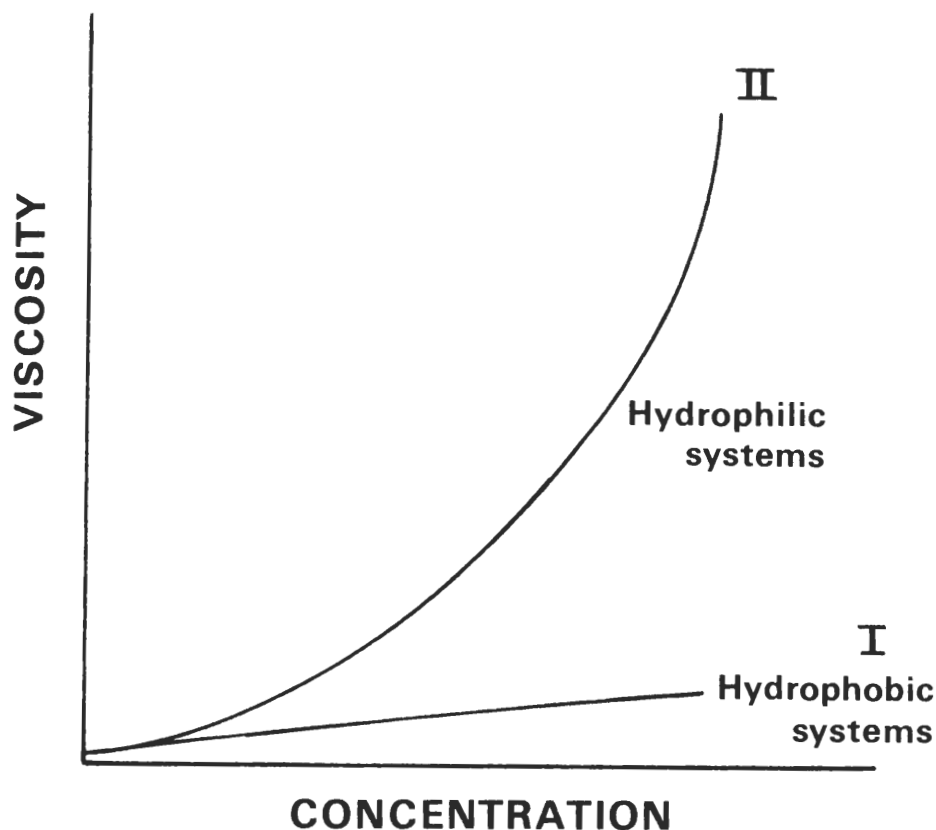


Figure 12. Comparison of viscous behavior of hydrophobic and hydrophilic sols. Taken from Swanson, Class Notes A-235 Colloid Chemistry, IPC, 1981.

The effect of oxidation on black liquor rheology is less certain. The mild oxidation of BLOX apparently does not generally cause a noticeable effect on liquor rheology, although isolated reports of viscosity increases do exist (44,2). Such a viscosity increase with oxidation has not been documented with substantial quantitative evidence, nor explained.

Given the factors which affect viscosity, an a priori prediction of the effect of HIBLOX on liquor rheology would be difficult. HIBLOX could be expected to effect liquor rheology in numerous ways, including positive and negative changes. Whether or not the overall effect would be deleterious would be dependent on the relative magnitudes of the changes. Among the anticipated changes in the liquor which might affect the viscosity and hence the rheology at a given solids content would be the following:



1. Reduction in the concentration of polymeric lignin. This decrease would probably tend to reduce the solution viscosity, although the polyelectrolytic behavior might cause unusual effects.
2. Increase in the number of ionizable groups. The increase in ionizable groups could occur by formation of acids on the C<sub>3</sub> branch of the phenyl propane monomer, ring opening reactions leading to muconic acid and the breaking of aryl ether bonds. Increased polyelectrolytic behavior and increased hydrophilic tendencies could be expected.
3. Reduction of liquor pH due to acid formation. Significant pH reduction could lead to greater viscosity and even destabilization of the lignin colloid. Additionally pH dependent pseudo-polymerization of the carbohydrates would be possible.

#### CLOSURE

The background information detailed the prior state of knowledge concerning the oxidative chemistry and kinetics of black liquor. The key properties and how the properties were dependent on various parameters, including known and anticipated oxidation effects, were also presented. The need for information concerning reaction kinetics, chemistry, and the key postoxidation properties at oxidation levels pertinent to HIBLOX was apparent. From this background an approach designed to provide the needed information was developed. The details of this plan are discussed in the following section.

varied within realistic levels to identify those factors critical to acceptable oxidation. These trials identified a critical rheology problem inherent to the process and related this problem to two major variables.

Table 3. Reactor and liquor parameters examined during HIBLOX trials.

Liquor Parameters	Reactor Parameters
Active alkali level	Temperature
Trace metal content	Pressure
Weight percent solids	Gas flow rate
Sulfide/thiosulfate level	Reactor surface area
	Degree of mixing

The second series of trials centered on the cause of the rheology problem and the means by which it could be overcome. These trials involved addition of alkali to the liquor and were designed to determine how much alkali would solve the problem and how the added alkali would affect the chemistry and kinetics. The alkali was added in a sulfide/hydroxide ratio consistent with white liquor as the alkali source, since the addition of purchased caustic was known to be not economical (3).

An oxidation range of 5-15% TOD reduction was examined during the experimental work. This oxidation range was thought to fully cover the possible oxidation levels which would be suitable for the HIBLOX process. As the gelling phenomenon became apparent, the desirability of minimizing the extent of oxidation became known and the emphasis was placed on the lower end of the proposed range.

## EXPERIMENTAL APPROACH

### GENERAL CONSIDERATIONS

The HIBLOX reactions were carried out in an air sparged batch reaction vessel. The batch reaction vessel was chosen due to the high cost and technical difficulty involved in designing a suitable high temperature, high pressure flow reactor. The sparger design was chosen because of the current use of such reactors in normal BLOX schemes. Air was chosen as the oxidant to allow determination of the oxidation rate via the measurement of the oxygen concentration of the outlet gas.

Prior to beginning the experimental work, the individual pieces of equipment were checked for accuracy and calibrated if necessary, and the mass balance approach used for calculating oxygen consumption was tested using water as the reactant. The details concerning the calibration of the necessary equipment are given in Appendix I. The procedure for applying the mass balances and the testing of the approach using water are described in Appendix II.

For the HIBLOX trials, the program of Appendix II was used with the reaction parameters and oxygen concentration data shown in Appendix III to generate the TOD vs. time data used in the kinetic analysis. The oxygen concentrations were used to calculate the oxygen consumption as a function of time. Subtracting the oxygen consumed from the initial liquor TOD yielded the necessary TOD vs. time data.

Two series of trials were run as part of this thesis. In the first series familiarity was gained with the idiosyncracies of HIBLOX as an industrial process, and the selected reactor and black liquor parameters shown in Table 3 were

varied within realistic levels to identify those factors critical to acceptable oxidation. These trials identified a critical rheology problem inherent to the process and related this problem to two major variables.

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## KINETICS

The complex nature of black liquor made it unlikely that a meaningful rate expression based on specific liquor constituents could be developed. For this reason the kinetic analysis was based on liquor TOD and its relationship to oxygen consumption. This quantity reflected the overall extent of reaction without regard to which liquor species were reacting at a given moment. The oxygen consumption was also indicative of overall trends in reaction chemistry, especially the transition from fast reactions involving easily oxidized species to slower reactions involving less easily oxidized species.

## CHEMISTRY

The chemistry related to HIBLOX was followed by measurement of pertinent species in the pre- and postoxidation liquors and a mass balance to determine the net increase or decrease. The sulfur containing species were assumed to react via the previously presented stoichiometry. The stoichiometry of the reactions leading to the remaining products could not be determined, but the total acid formation and the amounts of individual acids formed were calculated and related to the oxygen consumed. The ion chromatograph was used for analysis whenever possible, since most of the key reaction products were low molecular weight ions, species particularly amenable to analysis via ion chromatography. Acid titration was used to detect those species not measureable by ion chromatography.

## POSTOXIDATION PROPERTIES

The key liquor properties monitored during the experimental work were precipitation behavior and high solids viscosity. These properties were carefully

monitored because of the likelihood of significant changes during HIBLOX and the importance of these properties to development of a feasible process. Precipitation was visually checked after each reaction and samples were taken for analysis if present. Viscosity measurement was done using a Brookfield viscometer because of the difficulty in finding a more accurate method. The viscosities were measured at 90°C, approximately the minimum temperature at which black liquor is handled at high solids in existing recovery systems due to the inability of the centrifugal pumps to handle high viscosity liquors (2).

## EXPERIMENTAL PROGRAM

### APPARATUS

A schematic diagram of the apparatus used for the oxidation work is shown in Fig. 13. The system consisted of the reaction vessel in which the liquor was oxidized and the equipment necessary to monitor the chosen reaction parameters. The system was designed to allow continuous measurement of oxygen consumption, a quantity essential to the chosen method of kinetic analysis.

The reactor was an Autoclave Engineers, Inc., one-liter, bolted-closure vessel capable of withstanding a maximum pressure of 5800 psi at 650°F. The agitated batch reactor is shown in detail in Fig. 14. The agitator was driven by a variable speed motor, and the agitator shaft was equipped with a mechanical foam breaker. Agitator rpm's were measured via a tachometer supplied by the manufacturer as standard equipment.

The reaction vessel was designed to allow measurement and control of important reactor parameters while assuring maximum safety. Pressure was measured using a pressure gage with a 0-1500 psi range. Reactor temperature was measured using an iron-constantan thermocouple placed in a hollowed tube which extended into the reactor body. For safety purposes, a rupture disk was installed for pressure release in case of overload.

Reactor temperature was controlled by a heater and/or internal cooling coils. The reactor was heated via a jacket-type furnace utilizing resistance type windings controlled by a temperature controller. Cold tap water was circulated through the cooling coils when a reduction in temperature was desired.

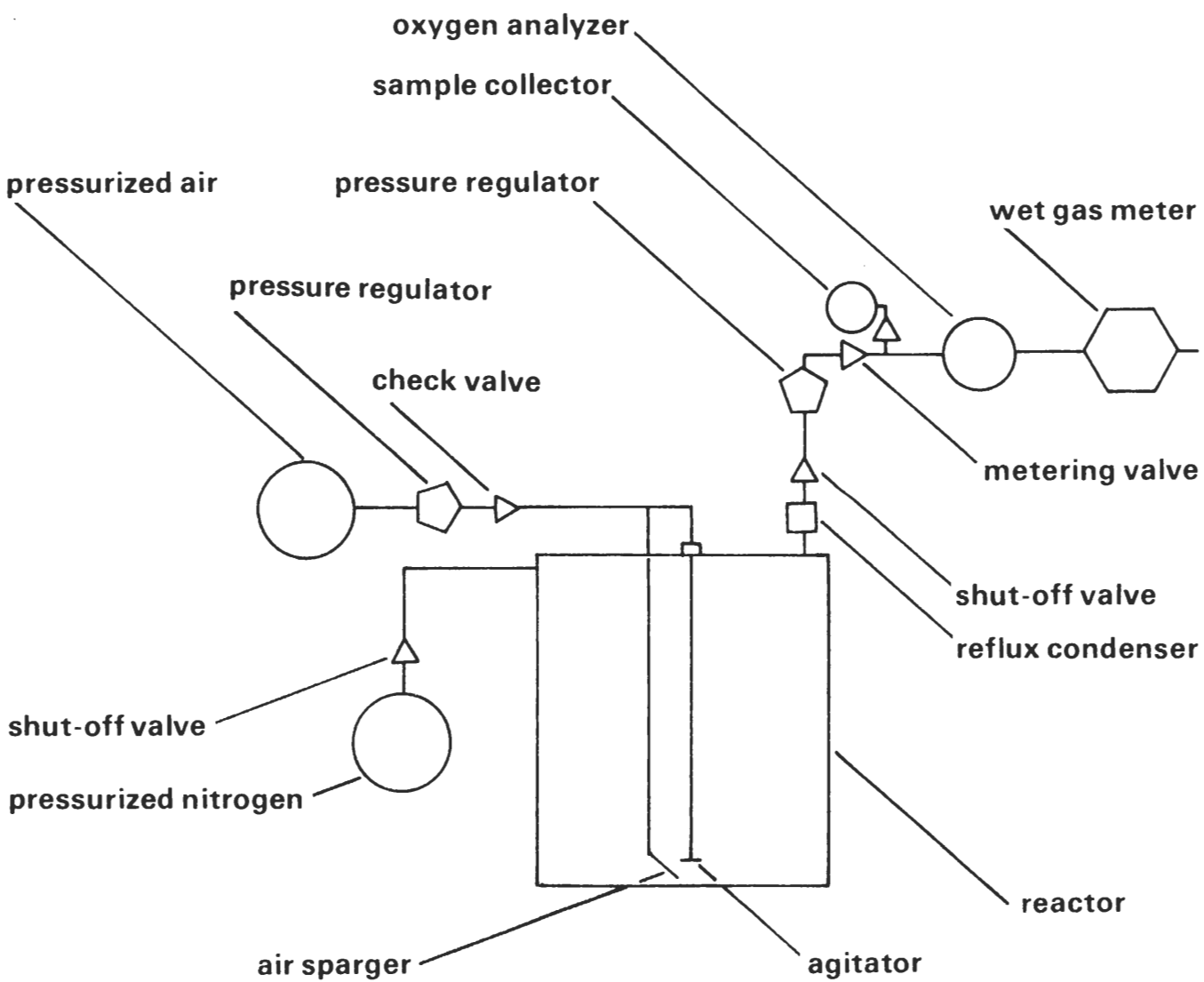


Figure 13. Schematic diagram of experimental system.



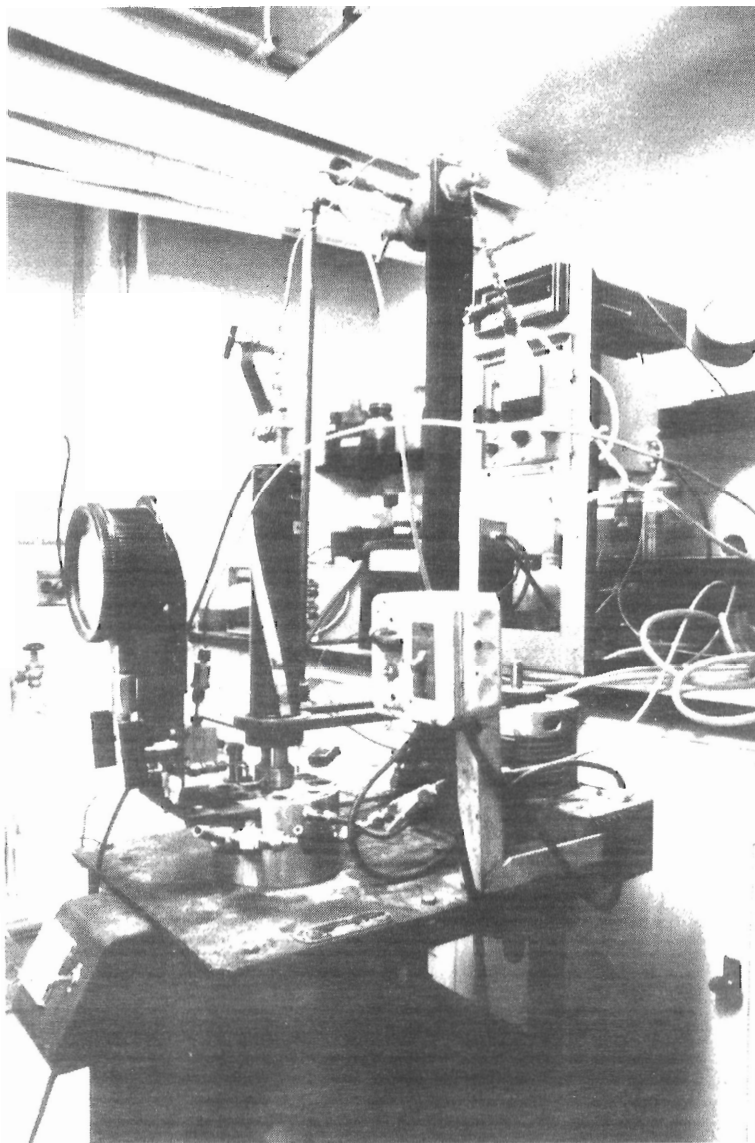


Figure 14. Reactor utilized for HIBLOX trials

Two valves provided access to the reactor body. A valve near the top of the reactor was used to load the reactor with black liquor. A second valve attached to a tube leading to the reactor bottom provided an outlet for removal of the liquor after oxidation.

Two gas systems provided selected gases to the reactor. A pressurized air tank provided air at a regulated pressure. The air feed entered through a tube

near the bottom of the reactor. A check valve eliminated the possibility of flow from the reactor to the air tank. A similar nitrogen feed system provided nitrogen to the reactor when an inert atmosphere was desired.

At the top of the reactor a tube led to the system for controlling gas flow and monitoring the oxygen content in the gas phase. A reflux condenser cooled the exit gas and returned the water in the gas to the reaction vessel. A shut-off valve, a pressure regulator, and a metering valve provided control of the system pressure and the gas flow rate. A sample collector allowed sampling of reaction gases. A wet test meter measured the gas volume and the oxygen content of the exit gas was determined via a Teledyne Model 326A oxygen analyzer. The outlet gas was vented to a hood for removal.

## EXPERIMENTAL PROCEDURES

### HIBLOX Reactions

Prior to each HIBLOX trial the oxygen analyzer was calibrated with water in the reactor. The reactor was heated to reaction temperature, air was passed through the system at the chosen air flow rate, and the analyzer was calibrated. The reactor was then cooled, drained, reheated to boil off any remaining water, and cooled again to ensure no dilution occurred when the black liquor was added.

The black liquor and a hydrocarbon defoamer were then added to the reactor. The reactor was purged with nitrogen to establish an inert atmosphere. The agitator was engaged and the reactor brought to the desired pressure and temperature. When necessary, nitrogen was bled off to regulate the reactor pressure.

When the desired reaction conditions were established, the gas outlet and air inlet valves were simultaneously opened, and gas began flowing through the system. The reaction occurred for a chosen time during which the proper parameters were measured. Reactor temperature was controlled within  $\pm 2^{\circ}\text{C}$  by adjusting the valve controlling the flow of water to the cooling coils.

After the reaction occurred for the desired time, the inlet and outlet valves were simultaneously closed and the reaction quenched by cooling. The reactor was cooled to a temperature of  $< 35^{\circ}\text{C}$  to prevent the loss of volatile compounds upon removal of the liquid. The liquor removal valve was then opened and the liquor was driven from the reactor due to the reactor pressure. The liquor was collected in a beaker to check for full recovery and/or precipitation of material. The reactor was then purged with water for several hours and prepared for the next trial.

#### Titration for Unknown Acids

All black liquor samples were diluted to 10% solids and 100 mL was titrated. The liquors were agitated and the pH was recorded after addition of incremental volumes of 1N NaOH or 1N HCl. All liquors were titrated to a final pH of 2.

#### Concentration

In all cases black liquor samples were concentrated from the postoxidation values to the firing solids range unless gelation occurred. The concentration was done at low temperature under vacuum according to standard procedure. This procedure was chosen to minimize the loss of volatiles in the concentration process.

### Viscosity Measurement at High Solids

The high solids viscosity measurements were made at a water bath temperature of 90°C using a Brookfield viscometer. The samples were concentrated to 63 ± 1% solids, placed in a 400-mL glass beaker, then immersed in the water bath for 30 minutes. The viscometer spindle was then placed in the liquor and rotated for six minutes before any measurements were made. The viscosity was then measured until a consistent value was achieved per the manufacturer's recommendation. Spindle rpm's were set at the minimum value (6 rpm's) to minimize shear thinning.

### ANALYTICAL PROCEDURES

#### pH Measurements

pH measurements were made with a Corning Digital 110 pH meter employing Corning pH electrodes. Dilution to a given solids content was made with distilled water where specified.

#### Ion Chromatography

Ion chromatographic analysis was done using the Dionex ion chromatograph. Standards were supplied by the IPC Analytical Group. Peak height measurements were used in all cases according to standard practice.

#### Sodium Sulfide Measurement

Sodium sulfide measurement was made using an Orion silver sulfide electrode. The electrode was used because the ion chromatograph was not operable for sulfide measurements.

### Black Liquor Solids Measurement

Black liquor solids measurements were made using combustion boat liner as a surface extender and drying overnight at 105°C in a forced air oven except where specified. In the remaining cases solids measurement was done at 48°C and under 30 inches of mercury vacuum to eliminate thermal degradation. For low temperature solids measurement a residence time of approximately one week was used, and a sample of unoxidized liquor of known solids was used as a standard.

### Ultraviolet Spectrophotometry

UV analysis was performed using a Perkin-Elmer Model 576 ST spectrophotometer.

### Total Oxygen Demand

The TOD of the first liquor batch was determined per ASTM Standard D-3250-77 through New York Testing Laboratories. The TOD of the second liquor batch could not be determined in an analogous manner, since the lab ceased doing this test and no alternate could be found. Chemical oxygen demand (COD) tests were run on both liquor batches per ASTM Standard D-1252-78, and the COD ratio was used to determine the second batch TOD as follows:

$$\frac{\frac{1.08 \text{ g COD}}{\text{g solids}} \#2}{\frac{1.12 \text{ g COD}}{\text{g solids}} \#1} \times \frac{0.95 \text{ g TOD} \#1}{\text{g solids}} = \frac{0.92 \text{ g TOD} \#2}{\text{g solids}} \quad (4)$$

### Black Liquor Heating Value

Black liquor heating values were determined according to the method described in Parr Manual No. 120. This procedure is not specific for black liquor and results in some error, especially when attempting to measure small differences in heating values.

### Lignin Molecular Weight Analysis

The molecular weight distributions of the lignin fractions in oxidized and unoxidized black liquor were determined via high pressure liquid chromatography (HPLC). The method and apparatus developed by Lonsky was utilized. The analysis was done after removal of the lignin from the rest of the liquor.

The lignin had been separated from the rest of the liquor solids by precipitation using hydrochloric acid. The precipitated lignin was centrifuged and washed several times to isolate pure samples. The samples were dialyzed and then freeze dried.

The freeze dried samples were acetylated using acetic anhydride in pyridine at room temperature. The acetylated lignin was precipitated over crushed ice, filtered, and washed with dilute hydrochloric acid. The samples were then dissolved in DMSO for HPLC analysis.

## RESULTS AND DISCUSSION

### GENERAL CONSIDERATIONS

As stated in the Experimental section, two series of trials were run to generate the information needed to meet the thesis objectives. The first experimental series established the viability of the experimental approach, determined the temperature requirements for HIBLOX, and provided a characterization of reaction chemistry and kinetics. The trials also yielded information concerning postoxidation liquor properties, including a severe high solids liquor rheology problem which was linked to major reaction variables. HIBLOX, considered per se, appeared to be feasible under chosen conditions, but the high solids rheological properties of the oxidized liquor made the ensuing recovery operations impossible without modification of the process.

The second series of trials centered on the use of alkali addition to overcome the rheology problem. The relationship between the extent of TOD reduction and the necessary alkali addition was quantified. In addition, the effect of alkali addition on reaction chemistry and kinetics was determined. The experiments provided evidence that the rheology problem could be overcome using a moderate alkali addition level.

Before considering specific results, it is necessary to account for differences in the composition of the liquors used in the experimental work, since these differences significantly influenced the results. The weight percent (o.d. solids basis) of the key liquor species is shown in Table 4. The salient point is that the liquor used in the second experimental series had a much higher sulfide content than the first liquor. The sulfide content of the first liquor was reduced by oxidation by ambient air during months of storage.

Table 4. Composition of liquors used in experimental work.

Species	Weight Percent, o.d. solids	
	Liquor No. 1	Liquor No. 2
Sodium sulfide	0.94	4.76
Sodium thiosulfate	5.35	3.65
Sodium sulfite	0.56	0.77
Sodium sulfate	2.00	1.91
Sodium carbonate	11.22	11.46
Sodium oxalate	0.51	0.21
Sodium lactate	4.62	8.46
Sodium formate	4.69	3.51
Sodium acetate	6.32	5.40

A second factor which must be noted prior to considering specific results is the fact that the pH declined substantially during HIBLOX. The magnitude of the pH decline will be discussed in the postoxidation properties section, since this parameter was measured after each trial. The cause of the pH decline will be apparent from the information presented in the section concerning reaction chemistry. The pH decline during HIBLOX was found to exert a profound influence on both HIBLOX kinetics and postoxidation properties, a fact which will be discussed in the pertinent sections.

#### Comparison of Calculated TOD Reduction and Heating Value Reduction

One of the early goals of the experimental work was to establish the validity of utilizing TOD reduction as the measure of extent of reaction. Since the purpose of the HIBLOX process would be to decrease the boiler combustion load by reducing the heating value of the liquor, it was necessary to measure a parameter



directly related to heating value reduction. The calculated TOD reductions were treated throughout this thesis as being equivalent to heating value reductions. The validity of this approach was established by comparing measured heating values to a calculated TOD reduction.

The relationship between heating values and calculated TOD reduction for an oxidized liquor is shown in Table 5. The heating values, which exhibit the normal scatter inherent to the test method, show too much variability to make the test method satisfactory for establishing the TOD reduction via oxidation. However, the range of heating values does encompass the calculated value of 5.9% and the heating value reductions average 5.4%, a figure compatible with the result obtained experimentally.

Table 5. Comparison of calculated percent TOD reduction vs. heating values using Parr Bomb for an oxidized liquor.

HEATING VALUE UNOXIDIZED LIQUOR (BTU/POUND SOLIDS)			
6166	6241		
Average 6204			
HEATING VALUE AFTER OXIDATION (BTU/POUND SOLIDS) - FOUR DETERMINATIONS			
5850	5869	5719	6029
PERCENT REDUCTION OF HEATING VALUE			
5.7	5.4	7.8	2.8
Average 5.4			
CALCULATED PERCENT TOD REDUCTION FROM COMPUTER PROGRAM			
5.9			

### Temperature-TOD Reduction Limits

A second early goal of the experimental work was to determine the minimum temperature requirements which might exist for the HIBLOX process. Determination of the temperature requirements insured the kinetic and chemical analysis would be done over the proper temperature range. An idea of the proper temperature range was gotten from the BLOX process.

At the temperatures used for BLOX ( $\approx 90^{\circ}\text{C}$ ), the oxidation of liquor species other than sodium sulfide proceeds very slowly, if at all. From a practical standpoint, only 2-3% of the liquor TOD can be satisfied regardless of reaction time at this temperature. For this reason, it was necessary to utilize higher temperatures, near or above the liquor boiling point, during HIBLOX.

Above the liquor boiling point, reactor temperature and the minimum reactor pressure become directly linked, in that the pressure must be sufficient to control the amount of water in the vapor phase. Given the rapid rise in the vapor pressure of water with temperature above the normal boiling point, utilization of a relatively low reactor temperature would be highly desirable. For this reason, the minimum temperature-TOD reduction relationship was investigated.

A series of trials was run utilizing the first liquor batch to determine the minimum temperatures necessary to achieve TOD reduction levels of 5-15%. The results of these trials are shown in Table 6. As the table indicates, 5% TOD reduction could be achieved at  $100^{\circ}\text{C}$ , and at least 14.4% reduction was achievable at  $150^{\circ}\text{C}$ .

In fact, these TOD reduction levels are somewhat conservative due to the low sulfide content of the liquor and the method, discussed in Appendix IV, used to generate the results. An average black liquor would possess a greater sulfide

content and therefore slightly greater TOD reduction would be possible. Nevertheless, it is apparent that the temperature range of 100-150°C was the correct range for experimentation.

Table 6. Maximum TOD reduction as a function of temperature.

Temperature, °C	Pressure, psig	TOD Reduction, %
100	100	4.9
130	100	8.8
150	200	14.4 <sup>a</sup>

---

<sup>a</sup>% Oxygen in outlet gas still below 20%.

The determination of the viability of using calculated TOD reduction as the measurement of extent of reaction and determination of the necessary reaction temperature provided a basis for the kinetic analysis. Reaction rate measurements were done over the pertinent temperature range of 100-150°C for a kinetic model using liquor TOD reduction as the key reaction parameter. Additionally, reactor and liquor parameters were varied to determine their effect on reaction kinetics.

## KINETICS

### Influence of Reactor and Liquor Parameters

A number of parameters affected the rate at which oxygen was consumed during the experiments utilizing the low sulfide liquor. Among the factors having the greatest effect on reaction rate were agitator rpm's, temperature, solids content, and liquor sulfide content. Parameters such as initial active alkali level (or pH), reactor pressure, air flow rate, trace metals content, and reactor

surface area exerted a less significant effect or none at all within the ranges examined.

The effects of three parameters - agitator rpm's, temperature, and liquor solids - are shown graphically in Fig. 15 through 17, using the first liquor batch. These graphs depict conditions which were otherwise constant for a given figure. The effect of liquor sulfide content, another parameter significantly affecting reaction rate, will be discussed later.

It is apparent that the reaction rate increased with increases in each of the three parameters, with some exceptions. The rate increased with temperature and also with increasing rpm's up to 500 rpm's, but leveled off at 600 rpm's. Furthermore, the reactor could not be run consistently above 500 rpm's without liquor being thrown into the outlet gas. When the dependence of reaction rate on rpm's was determined, all remaining trials were run at 500 rpm's.

The reaction rate also increased with increasing solids in the range of 20-35% solids. However, at 46% solids, the reaction rate declined. This was attributed to the severe precipitation which occurred at this solids level, a phenomenon which will be detailed in a following section.

The effects of the remaining parameters on the reaction rate are shown in appendix V. These parameters had at most a small effect on reaction rate within the range examined. In most cases this was not particularly surprising, but the fact that initial alkali level had no noticeable effect on reaction rate was somewhat of a surprise, given the dependence of oxidation rates of lignin model compounds on pH. Perhaps a greater alkali level difference was necessary to cause a detectable change in reaction rate, since pH differences after oxidation were minimized by the carbonate-bicarbonate buffer in the liquor.

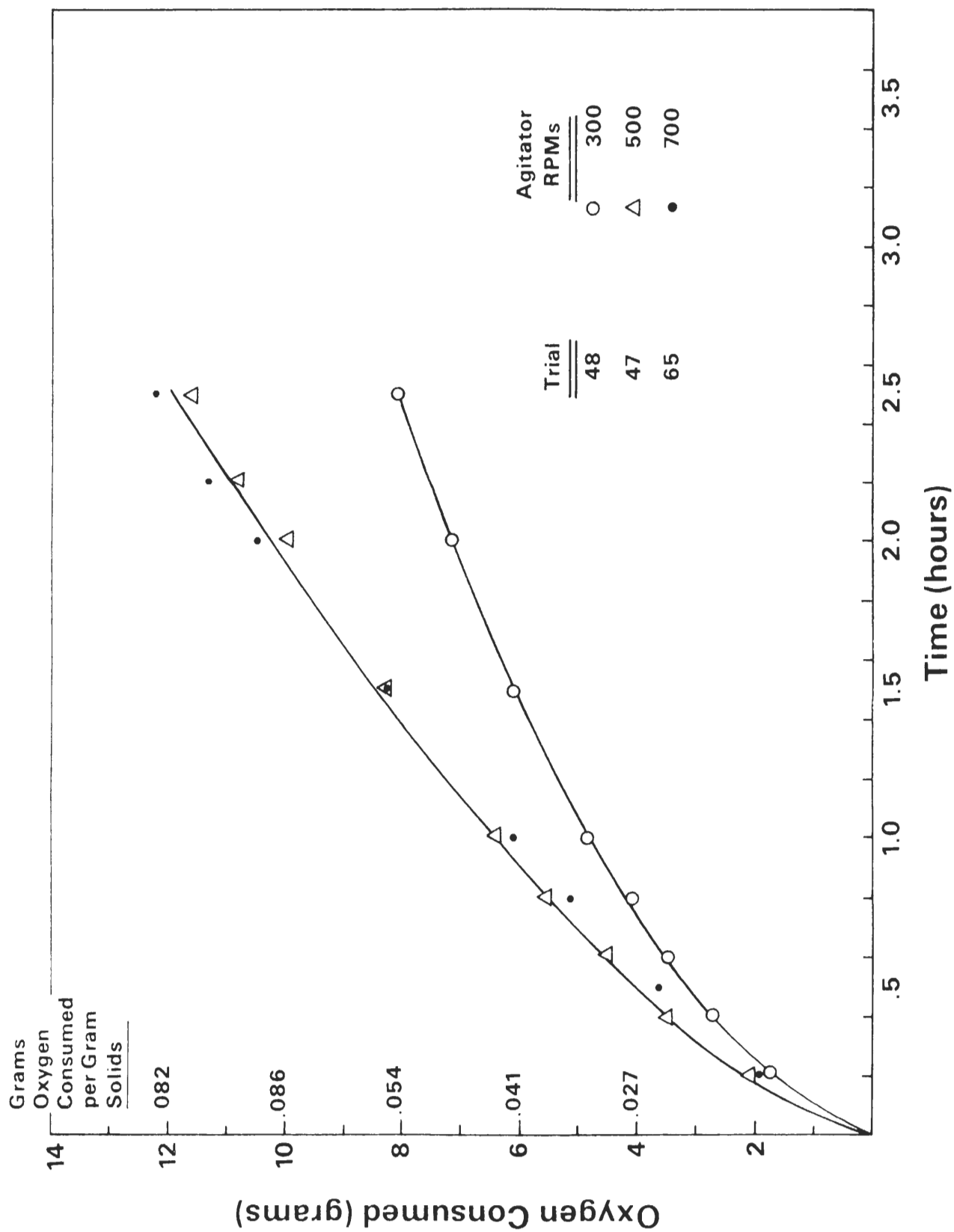


Figure 15. Effect of agitator rpm's on oxygen consumption.

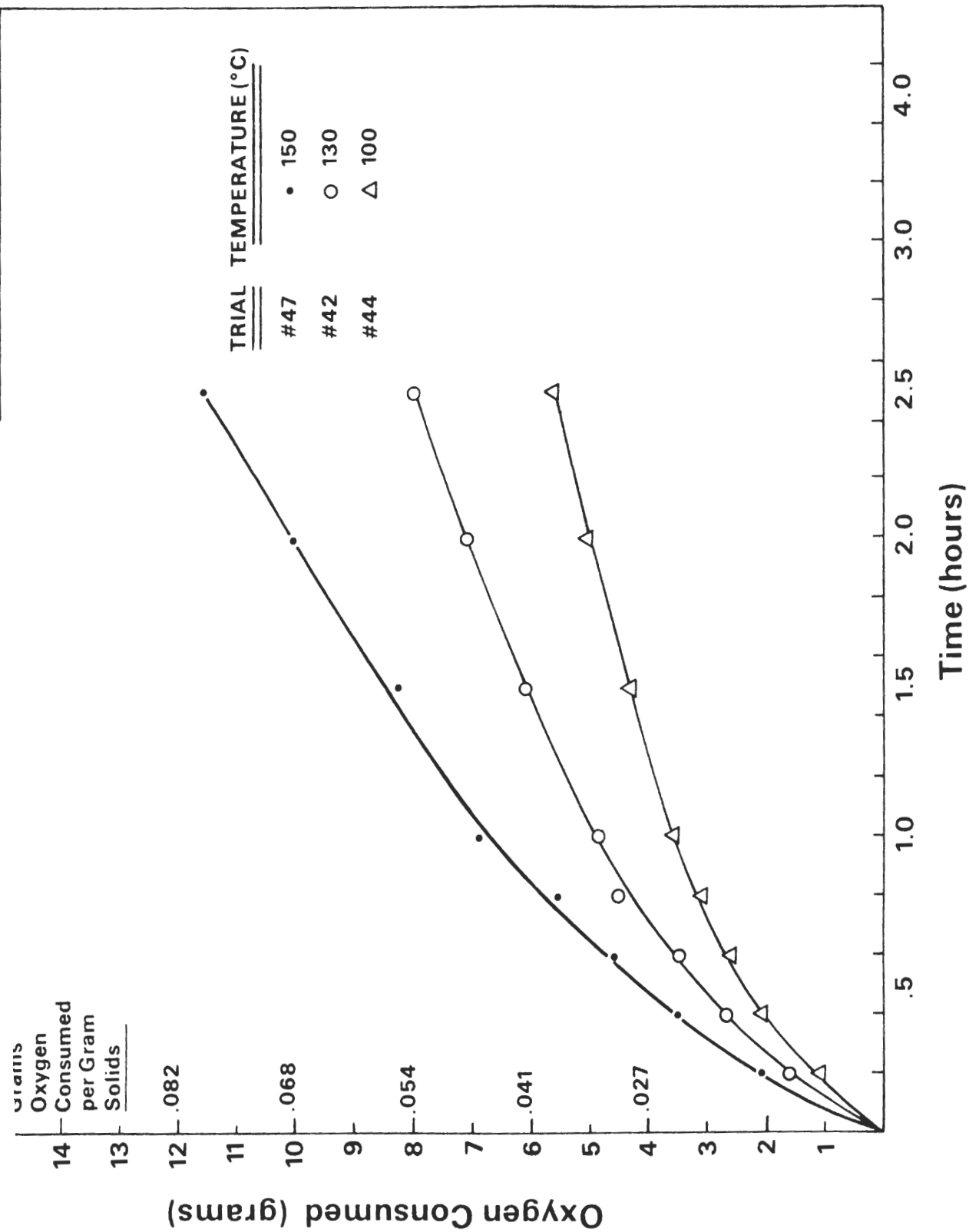


Figure 16. Effect of temperature on oxygen consumption.

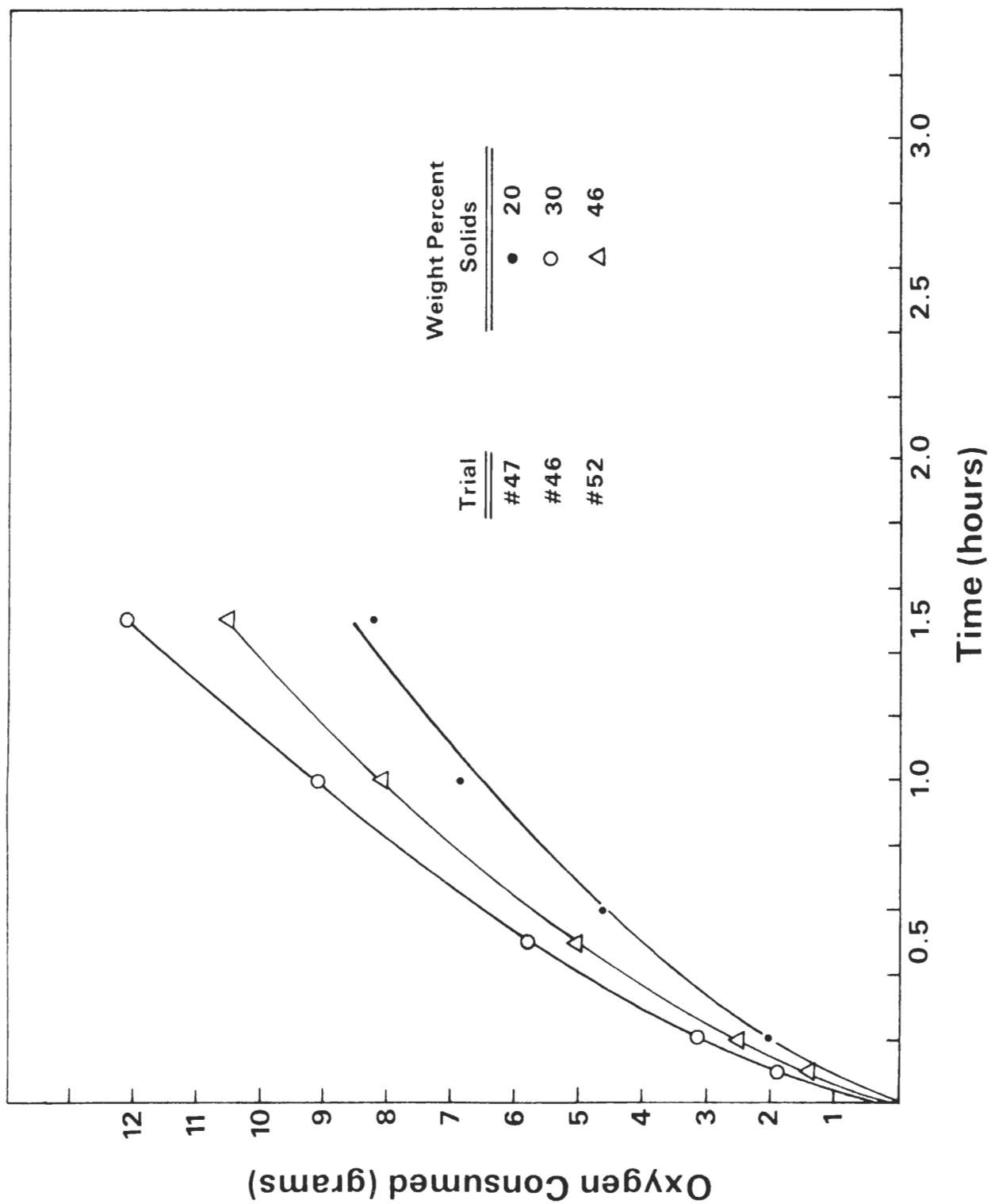


Figure 17. Effect of solids on oxygen consumption.

### Kinetic Model of HIBLOX

Utilizing the data generated from the trials with both liquor batches, a kinetic model was developed for HIBLOX. Given the complex nature of black liquor, it is not surprising that the experimental data did not fit the most simple kinetic expressions. Attempts to fit the data to three typical rate expressions - zero, first and second order with respect to TOD (TOD in grams/liter) - utilizing standard techniques are shown in Fig. 18 through 20. It is evident that none of these models adequately explain the experimental data.

The TOD vs. time data do approximately fit a kinetic model based on two consecutive first order with respect to TOD reactions. The technique used to fit the data to the model and for the remainder of the kinetic work presented later is discussed in Appendix V. The resulting kinetic model is shown in Fig. 21 and 22 for trials involving the high and low sulfide liquors, respectively. In both figures a relatively fast reaction approximating first order kinetics consumed a portion of the TOD, then a slower rate of TOD consumption followed which also approximated a first order plot. Some difference is apparent in the first of the two reactions for the two liquors, but the second reaction followed a similar course in each case.

It must be stressed that the consecutive first order reaction model is largely an empirical fit to the data. Other kinetic models might also fit the experimental data, but the consecutive first order reaction model was selected as the most simple yet realistic model which could be utilized. This approach treats all liquor species as one, TOD, although each undoubtedly possesses its own kinetic characteristics. Many species (e.g., sulfide and thiosulfate)



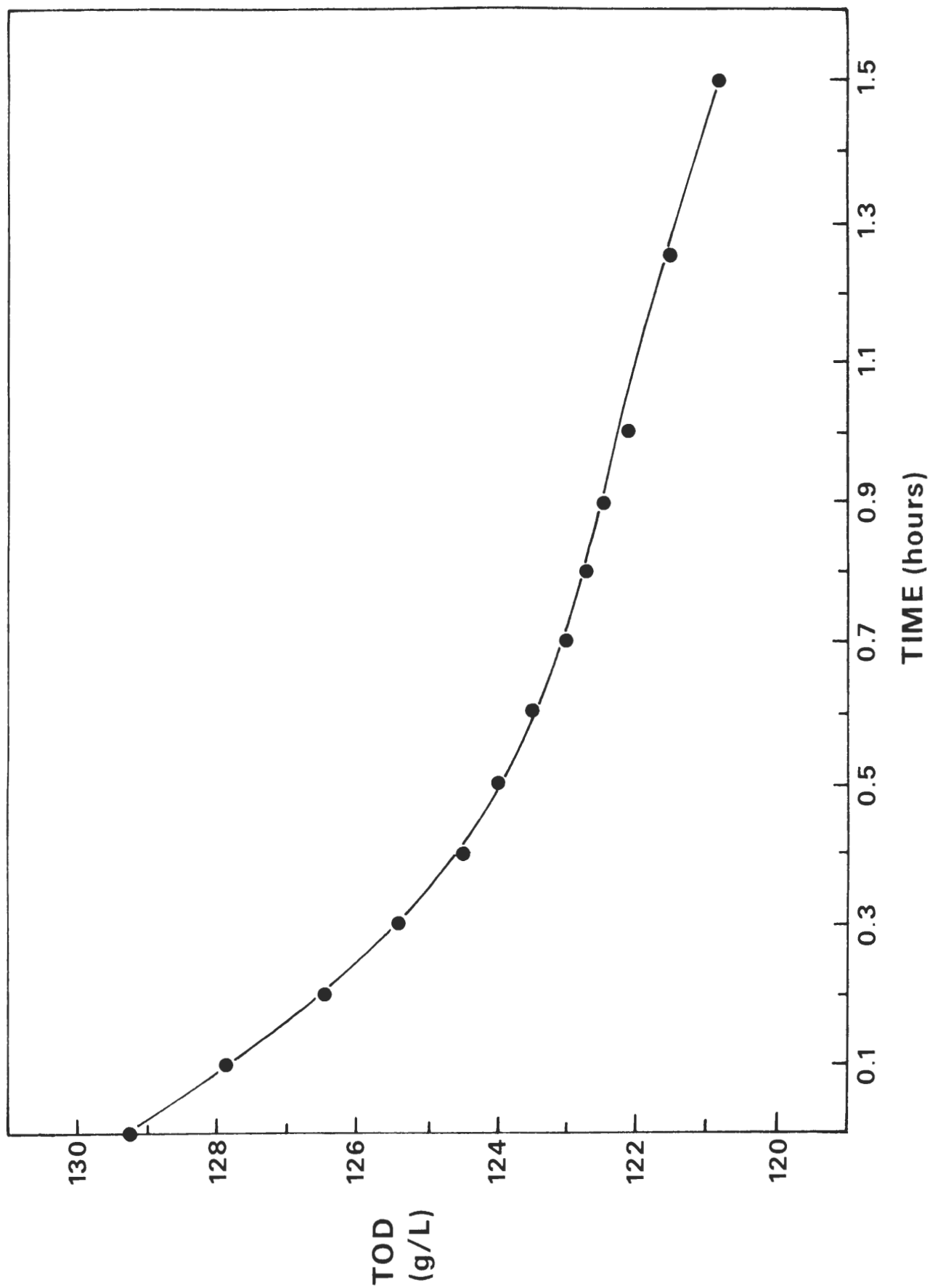


Figure 18. Trial No. 1/liquor No. 2, zero order plot, 21% solids high sulfite liquor, temperature = 150°C.

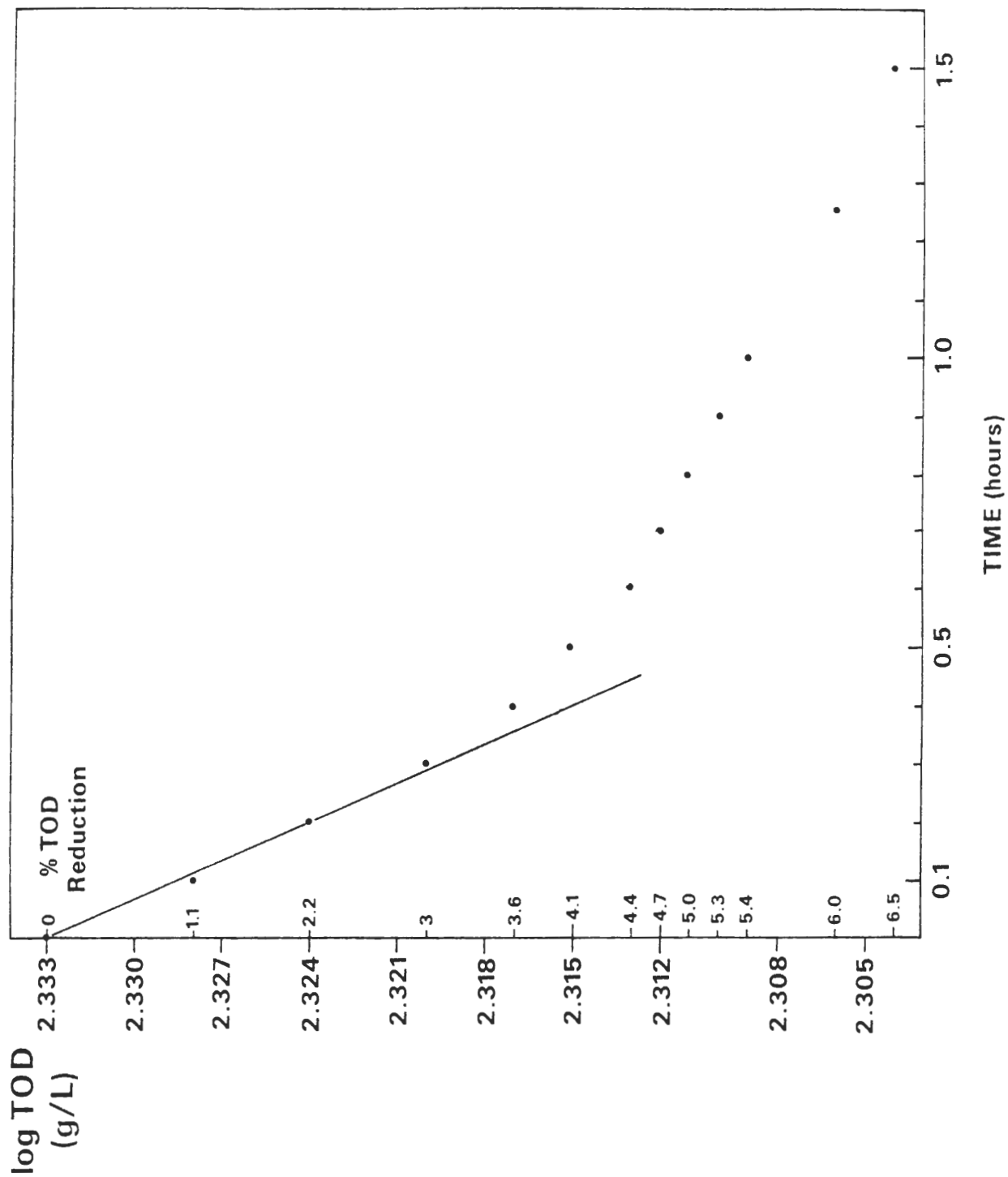


Figure 19. Trial No. 1/liquor No. 2, 21% solids high sulfide liquor, temperature = 150°C, first order plot.

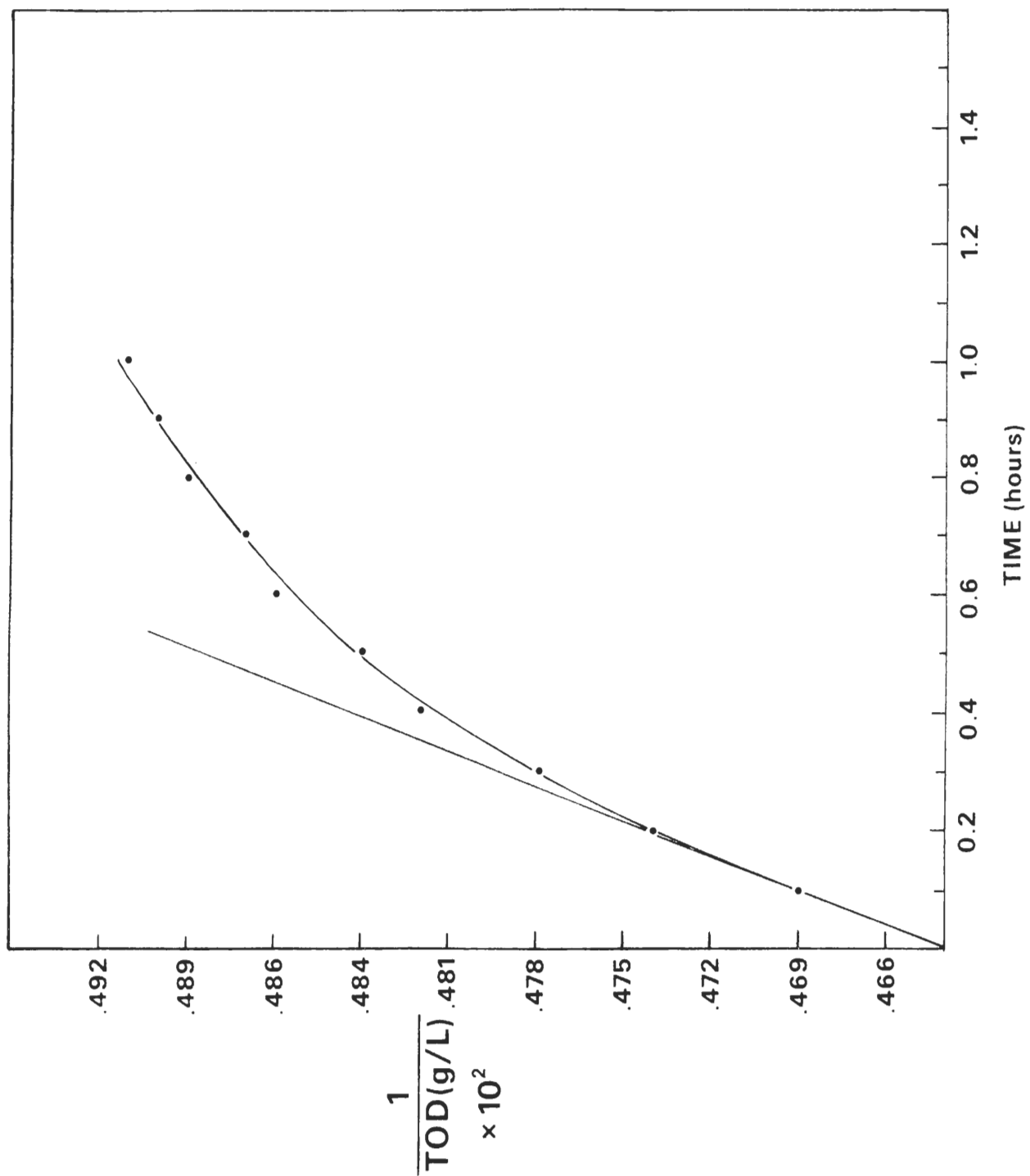


Figure 20. Trial No. 1/liquor No. 2, second order plot.

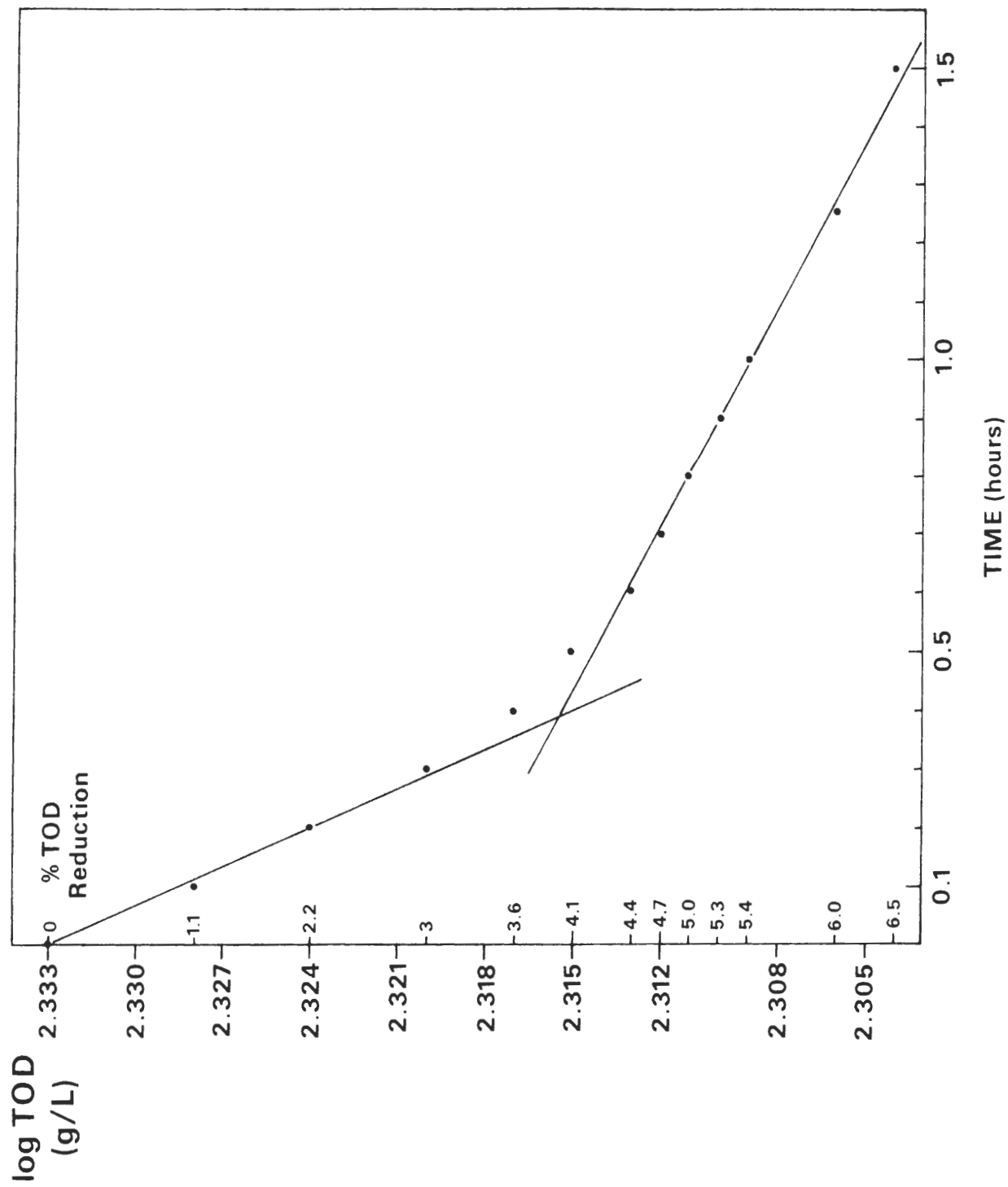


Figure 21. Trial No. 1/liquor No. 2, 21% solids high sulfide liquor, temperature = 150°C.

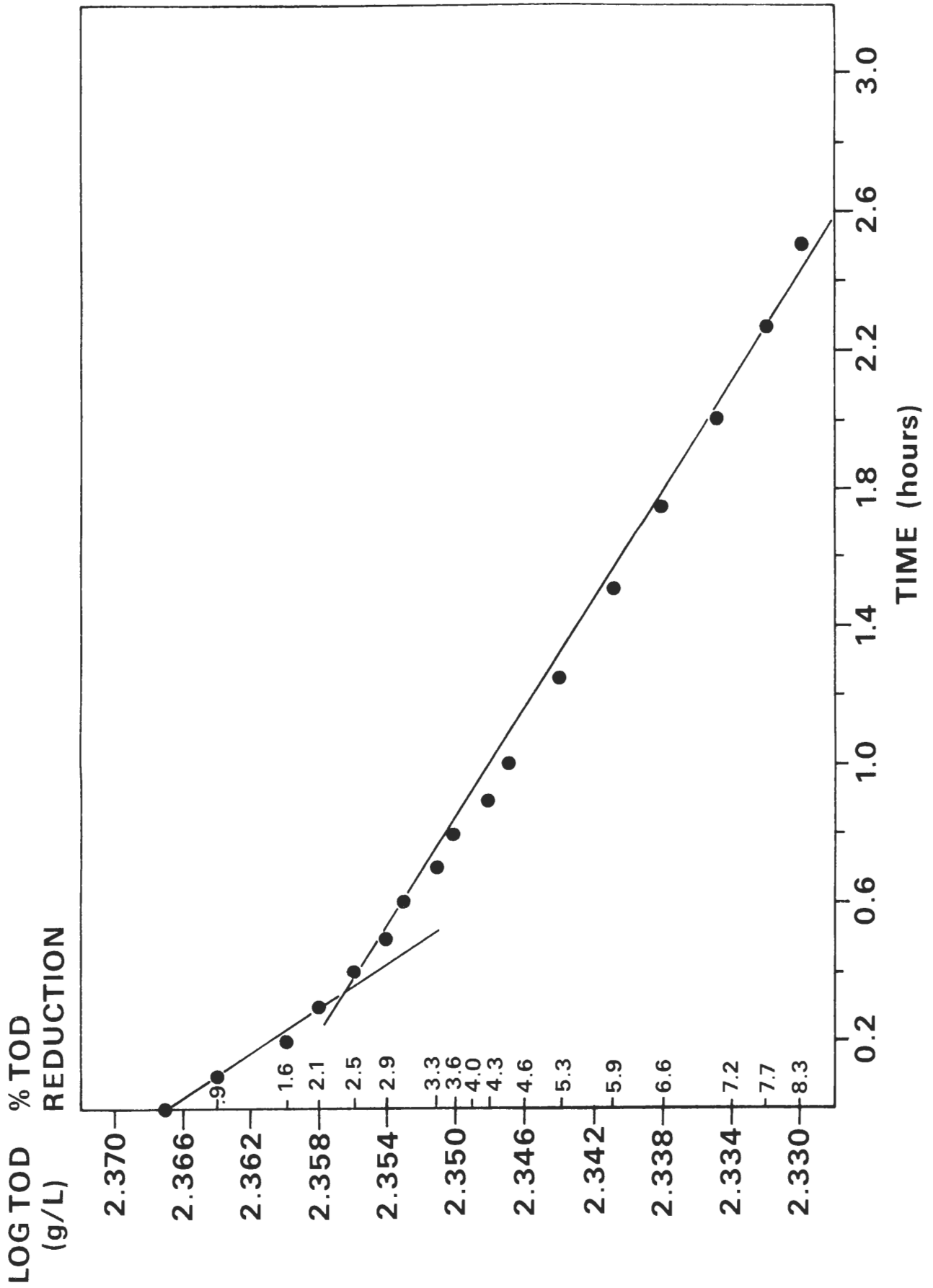


Figure 22. Trial No. 47/liquor No. 2, 22% solids low sulfide liquor, temperature = 150°C.

order combination previously discussed vis-a-vis BLOX. Thus, the proposed kinetic model is undoubtedly a simplification of the actual kinetics but is a simplification which provides a straightforward means for tracking the key parameter describing the extent of reaction.

It was thought that the first reaction might primarily involve the most easily oxidized liquor species, sodium sulfide. The experiments utilizing high sulfide liquor confirmed this suspicion. The experimental data generated from these experiments fit the proposed model well, and the first reaction was faster and consumed a larger portion of the liquor TOD than the first reaction did when the low sulfide liquor was oxidized.

As sodium sulfide was added to the liquor, the oxygen consumed prior to the transition to the second reaction became even greater. Data from such a trial with added active alkali (white liquor, 30% sulfidity as  $\text{Na}_2\text{O}$ ) equal to 3% of the weight of the liquor solids is shown in Fig. 23. Compared to Fig. 21 and 22, a longer and more rapid first reaction is evident. When only sodium hydroxide was added as the alkali, no increase in the rate or duration of the first reaction was noted, so pH effects were not a contributing cause.

In the ensuing analysis of the kinetic model a number of rate constants and oxygen consumptions are discussed. These parameters are defined in Table 7.  $k^*$  and  $k^{**}$  pertain to the initial portion of the first reaction of the kinetic model and thus describe the initial reaction rate for each trial. All rate constants are based on the assumption of first order kinetics with respect to liquor total oxygen demand.

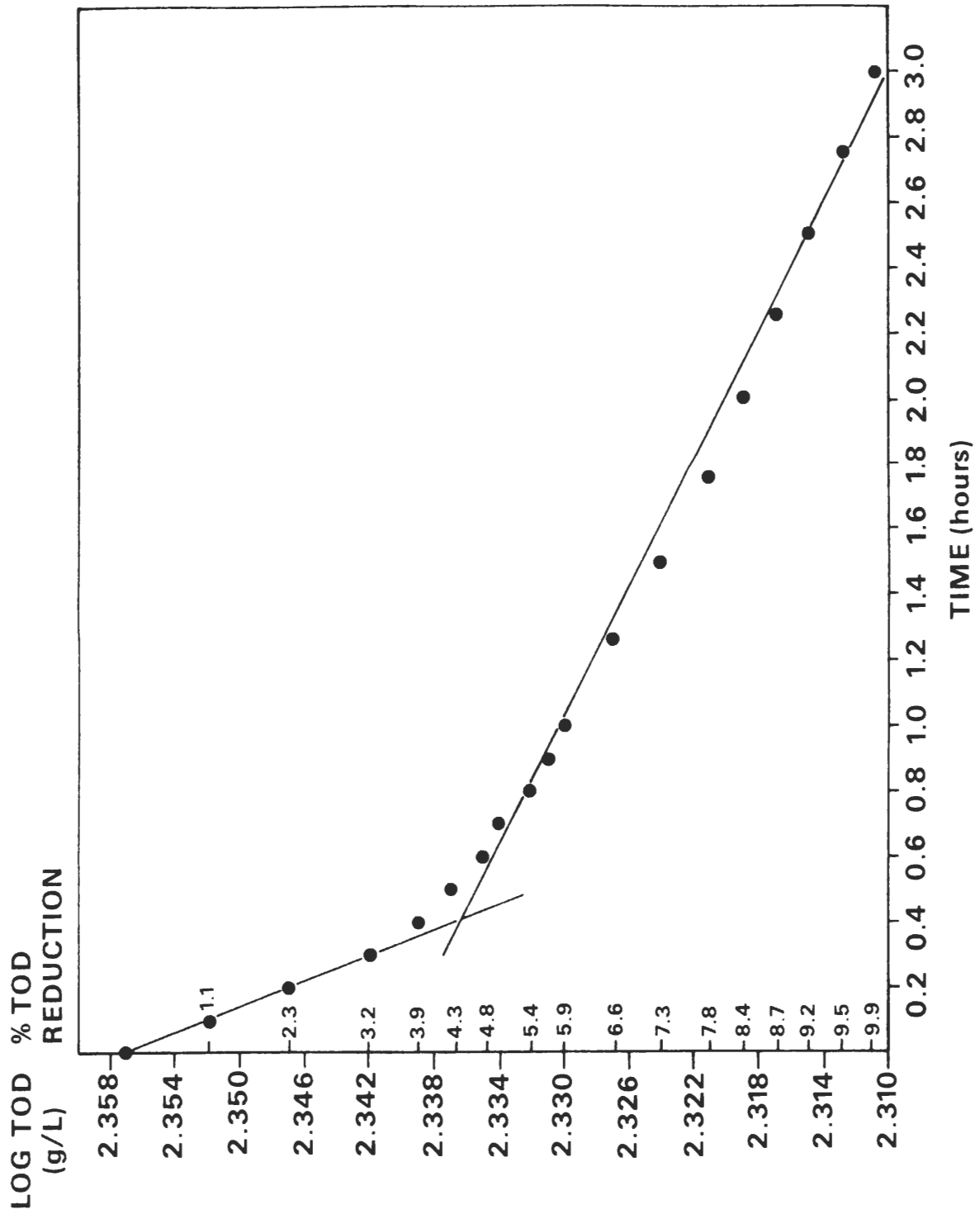


Figure 23. Trial No. 5/liquor No. 2, 22% solids, high sulfide liquor with 3% alkali addition, temperature = 150°C.

Table 7. Definitions of rate constants and oxygen consumptions used in kinetic model.

- $k^*$  = rate constant for data from time zero to first data point
- $k^{**}$  = rate constant for data from time zero to second data point
- $k_1$  = rate constant for entire first reaction of kinetic model
- $k_2$  = rate constant for entire second reaction of kinetic model
- $g^*$  = grams oxygen consumed per gram liquor solids from time zero to first data point
- $g^{**}$  = grams oxygen consumed per gram liquor solids from time zero to second data point

#### First Reaction

Rate constants for the first reaction of the model ( $k^*$ ,  $k^{**}$ , and  $k_1$ ) derived from the experiments using high sulfide liquor are shown in Tables 8 and 9. The  $k_1$  values were based on TOD reductions up to 3.5%, the point at which the rate of reaction began to slow appreciably. Since the  $k^*$  and  $k^{**}$  values were by definition based on only two and three data points, respectively, the values obtained must be viewed in terms of the error which could result from the technique utilized. The  $k_1$  values were also obtained from a limited number of data points and hence the inability to determine these values with a high degree of statistical certainty is acknowledged. However, the rate constants do provide a great deal of information concerning the parameters which were important vis-a-vis reaction kinetics.

The dependence of the reaction rate on key parameters is apparent from the tables. Considering a fixed composition such as 5% alkali addition (Table 8), it is apparent that the rate of reaction increased with temperature as would be expected. The rate constant also increased slightly with sulfide content (Table 9), from 0.0921/hour at 0% alkali addition to 0.1152/hour at 3 and 5% addition.



Table 8. Rate constants and oxygen consumptions for first reaction of kinetic model - effect of temperature on 22% solids, high sulfide liquors with 5% alkali addition.

Rate Constants, (1/hours)	150°C	130°C	100°C
k*	0.1152	0.1152	0.0691
k**	0.1152	0.0921	0.0806
k <sub>1</sub>	0.1152	0.0921	0.0576
Oxygen Consumptions, (grams/gram solids)			
g*	0.011	0.010	0.006
g**	0.021	0.019	0.013

Table 9. Rate constants and oxygen consumptions for first reaction of kinetic model - effect of added alkali at constant temperature on 22% solids, high sulfide liquor.

Rate Constants at 150°C (1/hours)	Alkali Addition (30% Sulfidity)		
	Weight percent of o.d. solids		
	5%	3%	0%
k*	0.1152	0.1152	0.1152
k**	0.1152	0.1152	0.1036
k <sub>1</sub>	0.1152	0.1152	0.0921
Oxygen Consumptions, (grams/gram solids)			
g*	0.011	0.010	0.010
g**	0.021	0.020	0.020

The kinetics of the first reaction can be better understood by examining the rate constants derived from the shortest reaction times. The behavior of the rate constants based on the first two data points,  $k^*$  and  $k^{**}$ , respectively, is worth noting. At constant temperature,  $k^*$  was independent of sulfide concentration, having the same value at all alkali levels.  $k^{**}$  showed nearly the same behavior, dropping only at 0% alkali and then only slightly.

However,  $k^*$  and  $k^{**}$  were affected by temperature, as shown in Table 8. These constants increased with temperature in a manner analogous to  $k_1$ . The dependence of the initial portion of the first reaction of the kinetic model on temperature but not sulfide content while the total first reaction was dependent on both quantities is indicative of the mass transfer rate limitation which prevailed at short reaction times at the high sulfide level.

The mass transfer limitation is also apparent in the grams of oxygen consumed at the shortest reaction times. The parameters  $g^*$  and  $g^{**}$  are the grams of oxygen consumed/gram liquor solids at the first and second recorded data points during the trials. It is apparent that these parameters were relatively insensitive to initial sulfide concentration,  $g^*$  declining only from 0.011 to 0.010 (at 150°C) as the added alkali went from 5 to 0%. Conversely,  $g^*$  was 0.006 at 100°C and 5% added alkali, so temperature obviously greatly affected the initial reaction rate.

As the amount of sulfide declined, the mass transfer limitation ceased and the rate of reaction became sensitive to the sulfide concentration as well as temperature. This dependence is manifested in the higher  $k_1$  value at 5% alkali addition than at 0% even though the temperature was the same. In fact, the  $k_1$  at 130°C and 5% alkali addition was the same as the  $k_1$  at 150°C and no alkali

addition. The  $k_1$  values are the same despite the temperature difference, because in the latter case the reaction rate slowed as the consumption of sulfide made the reaction become kinetically limited.

Table 10 shows the rate constants for the low sulfide liquor. The extremely low sulfide concentrations in these cases precluded the mass transfer limitation. At all times the rate constants and oxygen consumptions were lower than in the cases where high sulfide concentrations existed.

Table 10. Rate constants and oxygen consumptions for first reaction of kinetic model - effect of temperature on 22% solids, low sulfide liquor.

Rate Constants (1/hours)	150°C	130°C	100°C
$k^*$	0.0691	0.0461	0.0461
$k^{**}$	0.0806	0.0576	0.0461
$k_1$	0.0691	0.0461	0.0322
Oxygen Consumptions (grams/gram solids)			
$g^*$	0.009	0.006	0.005
$g^{**}$	0.015	0.011	0.009

For the low sulfide liquors the rate of reaction did not slow appreciably until a greater portion of the liquor TOD than the 150% of the stoichiometric amount for sulfide oxidation previously mentioned was consumed. The TOD represented by sulfide was only approximately 0.6%. If an additional 50% consumption by other species were considered, the total consumption for the first reaction would then be approximately 1.0% of the TOD, but the reaction rate did not slow appreciably until about 2.0% TOD reduction. The  $k_1$  values were calculated for the TOD reductions of 2.0%.

The reason the consumption by the first reaction was large relative to the sulfide content was that substantial conversion of thiosulfate to sulfate occurred at short reaction times when the low sulfide/high thiosulfate liquor was oxidized. Thus, some oxygen consumption associated with thiosulfate oxidation became part of the first reaction of the kinetic model. This phenomenon did not occur with the high sulfide liquors, a fact which is explained in a later section.

An activation energy of 4320 calories/gram mole based on  $k_1$  at 5% alkali addition was calculated for the first reaction as shown in Fig. 24 using the rate constants of Table 8. Such a low value indicates the reaction was only mildly temperature dependent. This observation is consistent with the observed mass transfer limitation from the  $k^*$  and  $k^{**}$  values. The high sulfide liquor was utilized for the activation energy calculations because commercial kraft liquors do not have the low sulfide levels of the first liquor batch.

The 4000 calories/gram mole activation energy is lower than that determined where true first order kinetics prevail. It is half that found by Avrahami and Golding (23) for the aqueous alkaline oxidation of sulfide. Of course, the catalysis of sulfide oxidation by organics could also account for the lower activation energy.

The determination of an initially mass transfer limited reaction at high sulfide concentrations is not surprising. Even at Reynold's numbers exceeding 40,000 and with molecular oxygen as the oxidant, mass transfer limitations initially prevailed during Cooper's work (10). At the slightly higher temperature utilized for HIBLOX the same zero/first order dependence held.

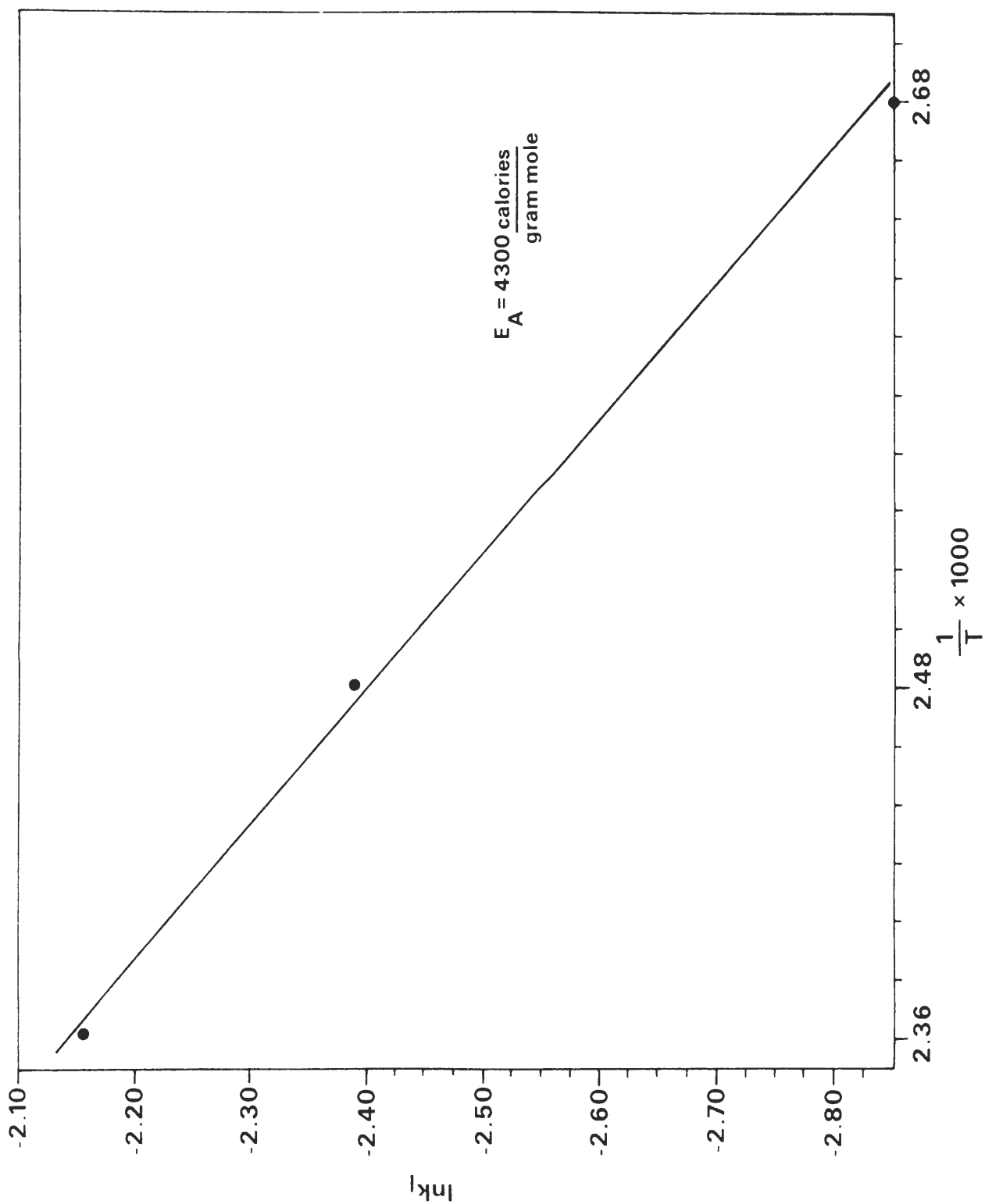


Figure 24. Activation energy for first reaction of kinetic model - 22% solids, high sulfide liquor with 5% alkali addition.

The fact the first reaction can be reasonably modeled as first order with respect to TOD and linked to sulfide content is somewhat fortuitous. Certainly the liquor TOD and sulfide content are not equivalent. Undoubtedly, even during the first reaction, other liquor species which comprise the vast majority of the liquor TOD were also reacting via kinetics idiosyncratic to each species. However, since the sulfide reacted so quickly relative to the remaining liquor TOD, it is the species which dominated the kinetics of the first reaction.

The concept of treating a zero order/first order dependence as purely first order for modeling purposes such as was done for HIBLOX is not uncommon. This approach was satisfactorily used by Galeano and Amsden (45) for sulfide oxidation during BLOX. It also appears suitable for the purposes of this thesis using liquor TOD as opposed to sulfide as the measured reactant.

#### Second Reaction

The second reaction of the kinetic model encompassed the reactions which led to all the observed reaction products except sodium thiosulfate, including sodium lactate, carbonate, acetate, sulfate, oxalate, formate and sulfite. The large number of products associated with this portion of the model and the lack of knowledge concerning the reaction paths and stoichiometry associated with each reaction were the reasons the HIBLOX kinetic model was based on a single parameter, TOD. Within reasonable error, the kinetics of all the reactions were explicable in terms of one first order with respect to TOD reaction. The rate constants calculated for this reaction, assuming first order kinetics, are shown in Tables 11 and 12.

Table 11. Rate constants for second reaction of kinetic model - effects of temperature on low sulfide liquor. (Liquor No. 1.)

Rate Constant (1/hours)	100°C	130°C	150°C
$k_2$	0.0098	0.0181	0.0298

Table 12. Rate constants for second reaction of kinetic model - effects of temperature (top) and alkali addition (bottom) on high sulfide liquor. (Liquor No. 2.)

Rate Constant at 5% Alkali Addition (1/hours)	100°C	130°C	150°C
$k_2$	0.0092	0.0209	0.0314

Rate Constant at 150°C (1/hours)	Alkali Addition (30% Sulfidity) Weight Percent of o.d. Solids		
	0	3	5
$k_2$	0.0253	0.0280	0.0314

The range of TOD reduction over which the rate constants for the second reaction of the model were calculated had to account for the compositional differences in liquor batches. The constants were calculated for TOD reductions beginning at the point at which the first reaction had ceased and the second reaction had definitely begun. The selected points were 2.5 and 4.5% TOD reduction for the low and high sulfide liquors, respectively.

The differences in the starting points for the second reaction necessitated differing terminal points to allow the rate constants to be compared for the different liquor batches. For the low sulfide liquor, only 5% TOD reduction was achievable at 100°C before the reaction slowed to an unmeasurable rate, so to ensure the same TOD reduction range at all temperatures, this value was chosen

as the terminal point. For the high sulfide liquors the second reaction began at greater TOD reduction, and 8% TOD reduction was selected as the terminal point for the rate constant calculation. The choice of the selected TOD reduction ranges were by necessity debatable but represent an attempt to allow a valid comparison of rate constants for very different liquor compositions.

Although it was thought that the rate constants for the second reaction would exhibit less variability with composition than did the rate constants for the first reaction, a number of factors were examined to determine their influence on the reaction kinetics. One parameter examined was initial alkali level, especially sulfide content, due to its effect on thiosulfate level and liquor pH. Differences in the organic composition of the two liquor batches, though not easily quantifiable, were also a potential source of variability in reaction rate, since certain structures would exhibit greater susceptibility to oxidative-alkali attack than others.

Considering Tables 11 and 12 it is apparent that the rate constants were not tremendously affected by liquor composition within the range examined. The rate constants for the high sulfide liquors might be seen as being slightly affected by sulfide/alkali content, increasing from 0.0253/hour at no alkali addition to 0.0314/hour at the maximum addition. The low sulfide batch with a different organic composition yielded a  $k_2$  value of 0.0298/hour at 150°C, about the average of the values from the other liquor. A value of  $0.0284 \pm 0.0031$  would encompass all the values of the rate constant determined at 150°C regardless of varying sulfide level and/or organic composition.



Furthermore, the variation in the rate constants was reduced when the TOD range over which the constants of Table 12 were calculated was adjusted for the additional oxygen demand caused by the alkali additions. The rate constants then became 0.0276, 0.0280, and 0.0253/hour at 5, 3, and 0% alkali addition, respectively. The error caused by rounding off numbers in the calculations would account for the variability in these numbers, so the effect of sulfide addition was negligible.

Activation energies for the second reaction of the model were calculated from the rate constants as illustrated in Fig. 25 and 26. The values obtained were 6900 and 7600 calories/gram mole for the first and second liquor batches, respectively. These values are reasonably consistent given the typical variability in black liquor organics, pH differences, and the problems inherent to offsetting the pertinent TOD reduction ranges for varying sulfide levels.

In both cases the activation energies are rather low, substantially less than the 16-25 kilocalories/mole observed by Taylor and Weygant (28) for single organic compounds. Since mass transfer limitations did not limit the rate of reaction, some other factor(s) must have minimized the temperature sensitivity. Unlike the work of Taylor and Weygant, HIBLOX involved both oxidative and alkali promoted reactions. This fact may account for the relatively low temperature sensitivity of the reaction rate.

The declining pH with increasing extent of reaction caused a reduction in alkali levels and increased the stability of the phenolic structures of the liquor. Since a large portion of the second reaction of the kinetic model involved degradation of the lignin fraction, the combination of less alkali for attack on the lignin and the greater stability of the phenolic structures at lower

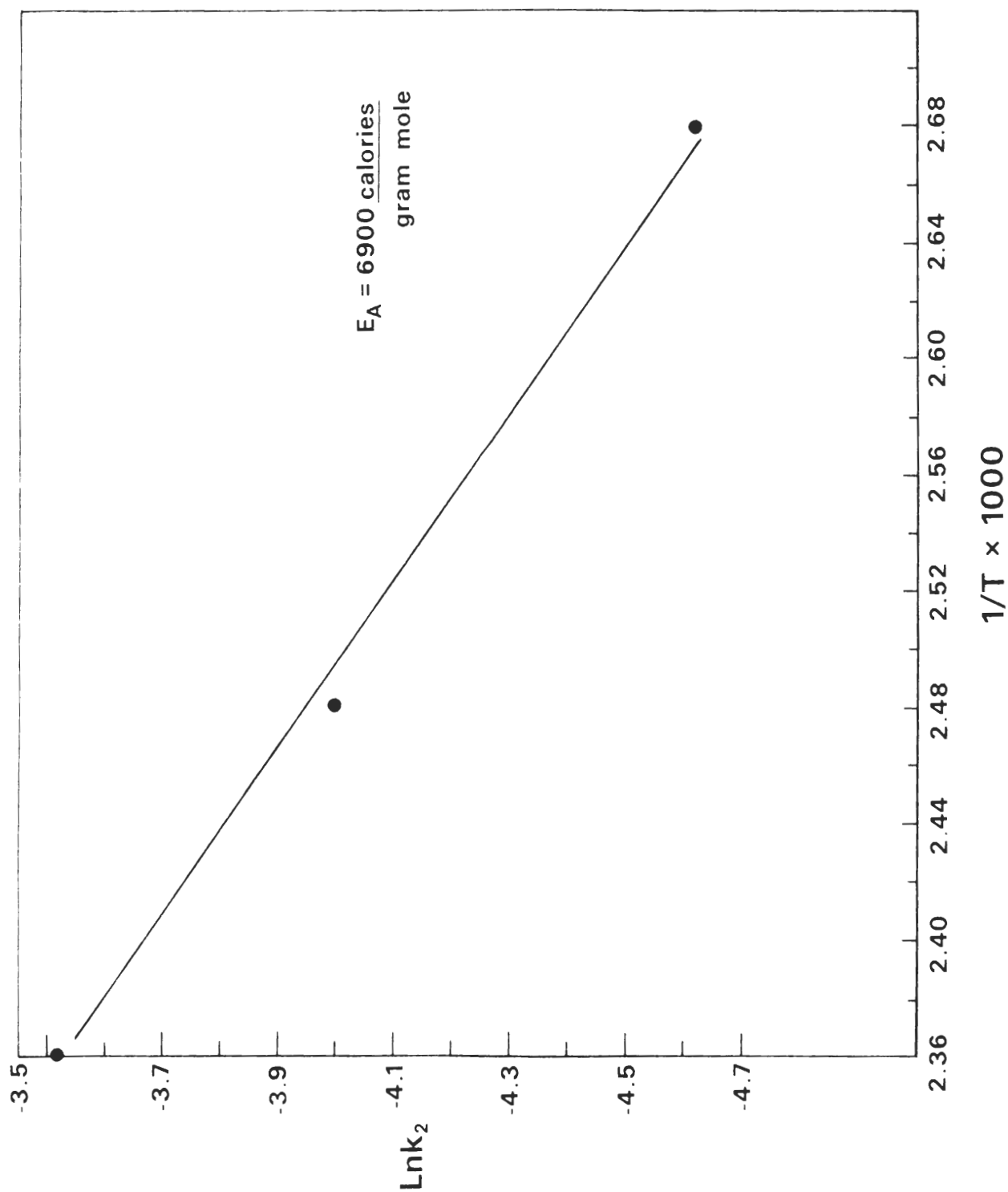


Figure 25. Activation energy for second reaction of kinetic model - 22% solids, low sulfide liquor with no alkali addition.

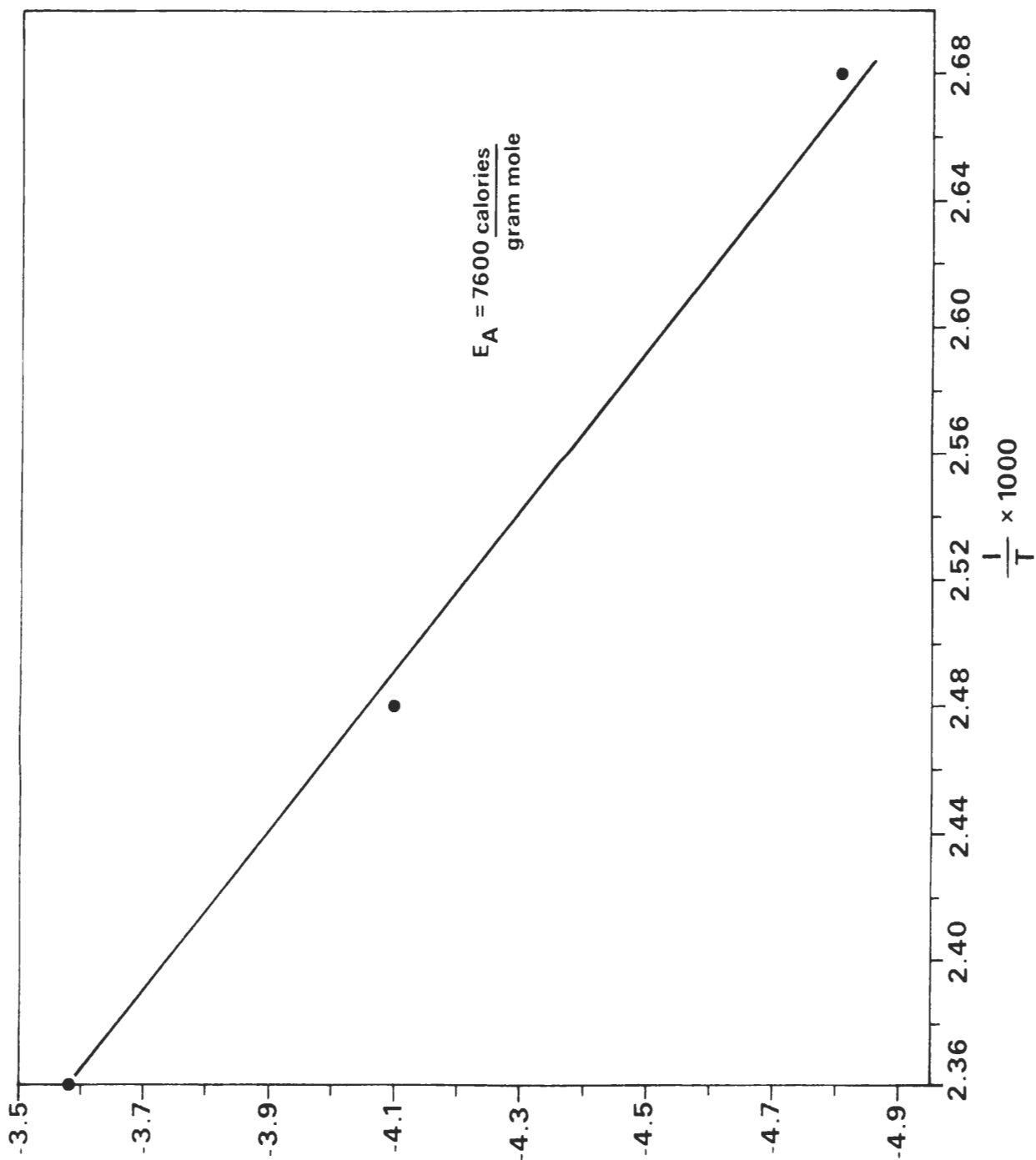


Figure 26. Activation energy for second reaction of kinetic model - 22% solids, high sulfide liquor with 5% alkali addition.

pH's would account for a substantial reduction in reaction rate. Considering the previously discussed work of Raff and Tomlinson (27), a pH change of less than one unit was shown to significantly slow the rate of oxygen absorption by lignin. Given the substantial pH change which occurred during HIBLOX, a great retarding effect would be anticipated.

Thus the pH decline was probably the main cause of the slowing of reaction rate rather than the reduction in TOD concentration since a great deal of TOD remained at the end of every trial. Given this scenario, reactor temperature might play a less significant role in reaction rate than would otherwise be anticipated. Further explanation of the factors determining the rate of reaction is found in the following section on high solids oxidation.

#### Effect of Utilization of Strong Liquor

Liquor was oxidized at 45% solids to examine the effects of a number of parameters influenced by solids content. The use of strong rather than weak liquor was expected to exert several effects on HIBLOX kinetics. If it were true that first order kinetics were in existence, doubling the solids (and TOD) would be expected to double the rate of reaction relative to the 22% solids cases. However, several factors besides liquor TOD were changed by the increase in solids content.

The use of strong liquor was expected to accentuate the mass transfer influences on reaction rate which prevailed at short reaction times during oxidation of weak liquor. Liquid side resistance generally determines mass transfer rates under experimental conditions such as those utilized during the experiments pertaining to HIBLOX (46). For this reason the increased solids content and the corresponding viscosity increase were expected to prevent the

doubling of reaction rate which could otherwise result from the doubling of the initial sulfide content of the liquor. Fortunately, the viscosity was expected to remain relatively low due to the high temperature (150°C), so a substantial decrease in reaction rate was not anticipated.

The doubling of solids content relative to the previous case also increased the initial liquor pH. The change in pH could have influenced the rate of pH dependent reactions, especially those involving the lignin fraction. However, the change in initial liquor pH was no greater than that caused by the alkali additions at low solids which were shown to exert only a slight influence on the rates of the second reaction of the kinetic model. Hence, only a small influence on reaction rate was expected.

TOD vs. time curves for  $44 \pm 1\%$  solids liquors oxidized under the same conditions as the weak liquors are shown in Fig. 27 and 28. The former graph is for the low sulfide liquor, while the latter was developed from the higher sulfide liquor with 5% alkali addition. It is apparent from these graphs that the consecutive first order reaction model can still be applied.

Rate constants and selected oxygen consumptions for the high solids trials are shown in Table 13. Comparing high and low solids trials at 5% alkali addition, the total oxygen consumptions were nearly the same. Hence the consumption per gram of solids was lower at the higher solids level. For example,  $g^*$  and  $g^{**}$  were 0.011 and 0.021 gram at 22% solids and 0.005 and 0.010 gram at 44% solids. These values indicated that despite the much greater liquor sulfide content, the initial rate of reaction remained constant at the mass transfer rate. With the rate of reaction essentially independent of sulfide content, the rate constants  $k^*$ ,  $k^{**}$ , and  $k_1$  were reduced relative to the low solids values, since the rate of reaction relative to the liquor TOD was lower.

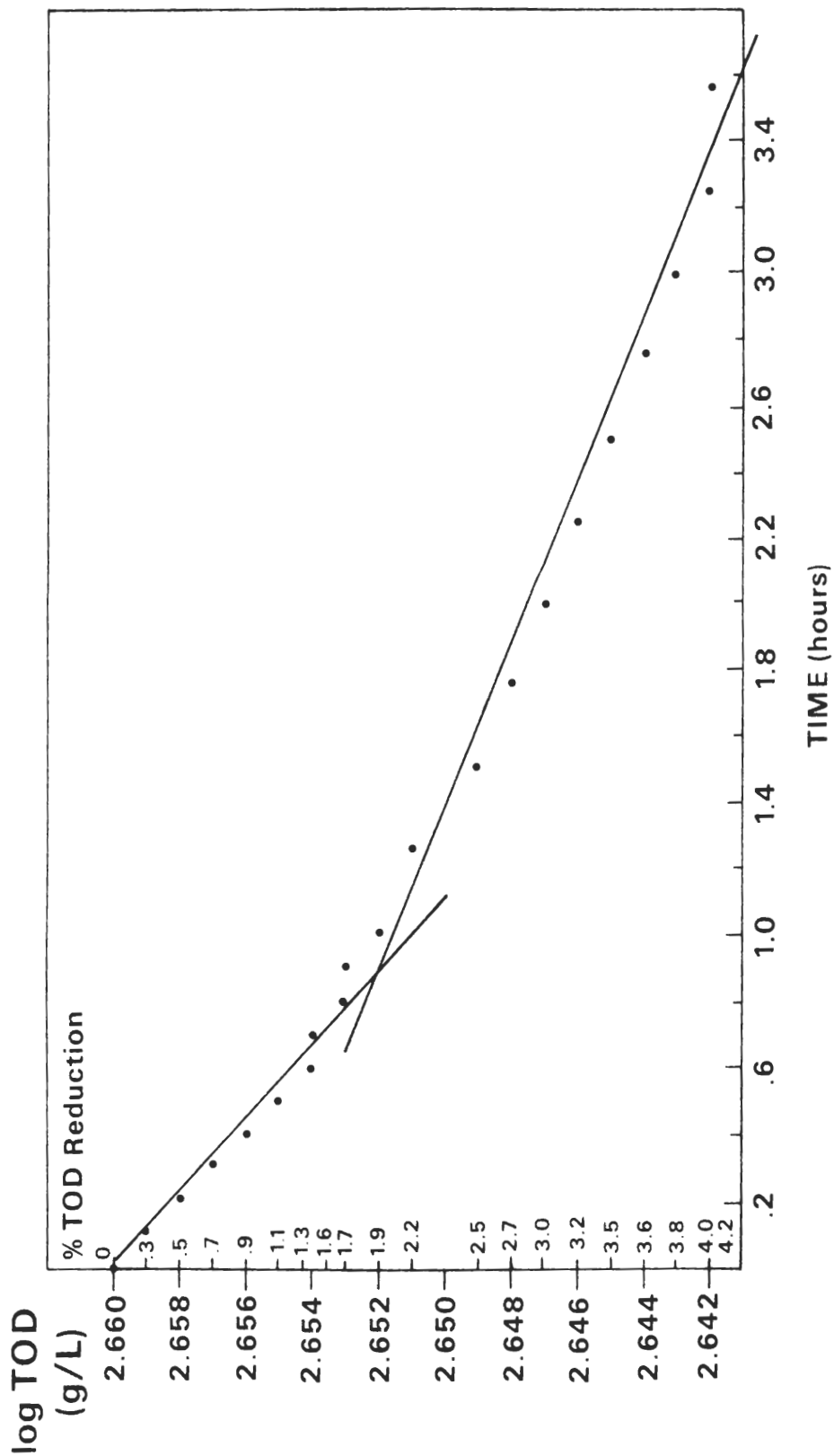


Figure 27. Trial No. 51/liquor No. 1, 45% solids, low sulfide liquor, temperature = 150°C.

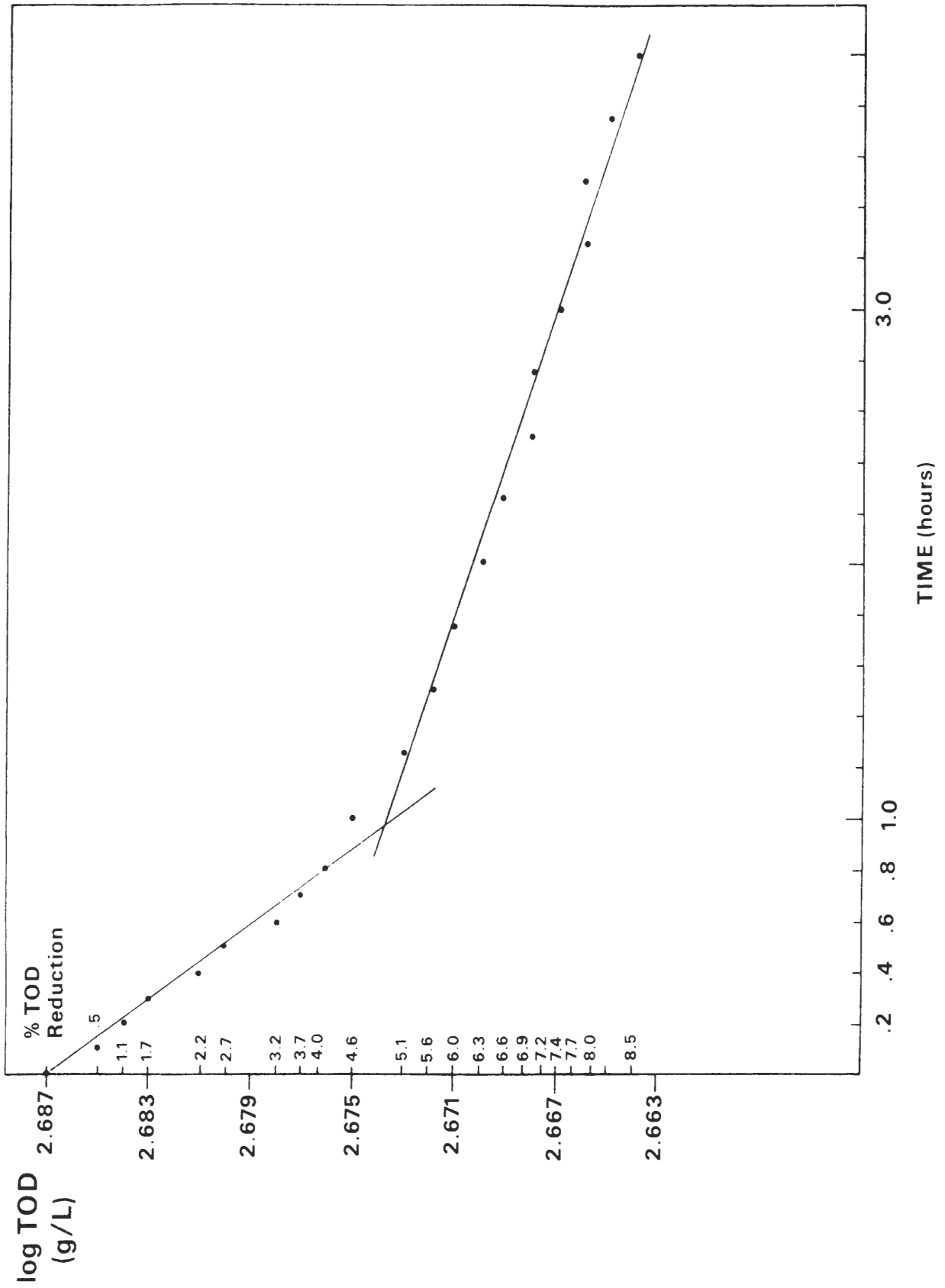


Figure 28. Trial No. 12/liquor No. 2, 43% solids, high sulfide liquor with 5% alkali addition, temperature = 150°C.

Table 13. Rate constants and oxygen consumptions for strong liquor - low sulfide liquor and high sulfide liquor with 5% alkali addition. In parentheses are comparable values from the 22% solids trials.

Rate Constants at 150°C (1/hours)	Low Sulfide	High Sulfide Plus 5% Alkali
k*	0.0230 (0.0691)	0.0461 (0.1152)
k**	0.0230 (0.0806)	0.0345 (0.1152)
k <sub>1</sub>	0.0184 (0.0691)	0.0329 (0.1152)
k <sub>2</sub>	0.0092 (0.0298)	0.0107 (0.0314)
Oxygen Consumptions (grams/gram solids)		
g*	0.002 (0.009)	0.005 (0.011)
g**	0.004 (0.015)	0.010 (0.021)

The rate constants for the second reaction of the model were also substantially lower than those derived from the low solids runs. The rate of oxygen consumption in grams over the same range of TOD reduction was only slightly increased at higher solids. For example, over the range 6-6.3% TOD reduction, the rate of oxygen consumption for the 5% alkali addition liquor was 4.0 grams/hour at 43% solids compared to 3.4 grams/hour at 22% solids. Given a truly kinetically limited reaction, the oxygen consumption rate should have doubled at the higher solids.

The fact that the rate of oxygen consumption was only slightly increased at higher solids might be further evidence of liquor pH being the factor limiting the rate of the second reaction of the kinetic model. Increasing the solids content of the liquor increased the alkali content of the starting material and hence its pH, but also increased the moles of acids formed at a given extent of



TOD reduction. The pH of the oxidized high solids liquor declined in a manner similar to the low solids liquor and the reaction rate did the same.

Attempts to positively determine the influence of liquor pH on the rate of the second reaction of the model were inconclusive at all solids levels. Even though the initial pH was adjusted to different values, the postoxidation pH's showed less variability due to the buffering capability of the carbonate in the liquor. By the time the second reaction of the model had begun, the pH's had declined in a similar manner in all cases, so the effect of pH was not clarified.

The rates of some of the reactions included in the second reaction of the kinetic model would not be expected to be influenced to a large extent by pH. An example is the oxidation of sodium thiosulfate to sodium sulfate. In this case the doubling of the thiosulfate concentration would undoubtedly result in an increased reaction rate. Perhaps reactions of this type account for the slight increase in reaction rate with increasing solids. However, since such a great portion of the second reaction of the model involved the lignin fraction of the liquor, the overall rate would not be very solids dependent.

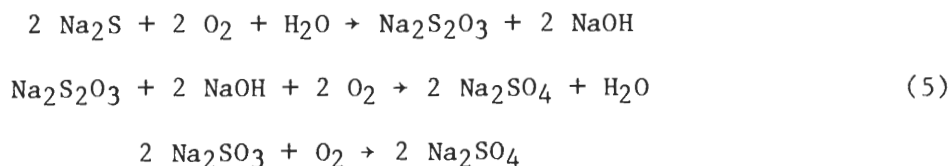
A second possible explanation for the observed reaction rate behavior is the rheology changes which occurred during oxidation at high solids. While no viscosity change during oxidation was noted at low solids, the viscosity changes which occurred at high solids (detailed in the section concerning postoxidation properties) were considerable. It is conceivable that the change in rheological properties at high solids prevented the kinetically possible increase in reaction rate.

# CHEMISTRY

HIBLOX caused substantial chemical changes in the black liquors. These changes were apparent in both the inorganic and organic fractions of the liquor. A variety of reaction products were formed, giving the postoxidation liquors a chemical nature substantially different than the starting liquor.

For a constant liquor composition the chemical changes caused by HIBLOX were remarkably consistent throughout the experimental work. No reactor and/or liquor parameters exerted an appreciable effect on the type of reaction products formed, and increasing the extent of reaction simply increased the yield of the products. The chemistry can best be approached by first considering the chemistry involving the inorganic sulfur species, then considering the remaining reactions.

As previously noted, the oxidative reactions involving the inorganic sulfurous compounds in black liquor are generally written as follows:



Although the reaction mechanisms are more complicated, the oxygen consumption has been found to be consistent with this stoichiometry. Hence, this stoichiometry was used in the mass balances derived for HIBLOX.

While the equations written in the above manner would make it appear that the oxidation of sodium sulfide was not an alkali consuming reaction, such was not the case. In reality little or no sodium sulfide existed in the black liquor.

Rather, the sulfide existed as  $(HS^-)$  and was oxidized according to  $2 NaHS + 2 O_2 \rightarrow Na_2S_2O_3 + H_2O$ . This scheme indicates the consumption of alkali which occurred when the sulfide was oxidized. The reduction of alkali attributable to this reaction was of great significance in terms of its effect on postoxidation liquor properties.

For TOD reductions  $> 5\%$  all the sulfide in the liquors was oxidized to sodium thiosulfate. Liquors oxidized to 5-6% TOD reduction showed a substantial increase in the concentration of thiosulfate. At high initial sulfide concentrations a large percentage of the oxygen consumed during HIBLOX could be attributed to this reaction.

The oxidation of sulfide to thiosulfate constituted a majority of the TOD reduction associated with the first reaction discussed in the section concerning reaction kinetics. For example, in Fig. 23, the oxygen consumed via the first reaction was 4.9 grams, 145% of the stoichiometric amount required for complete oxidation of sulfide. Other authors (7,10) have reported 120-130% of the stoichiometric consumption for complete sulfide removal.

The thiosulfate formed from sulfide oxidation as well as the thiosulfate and sulfite originally present in the liquor was then slowly oxidized to sodium sulfate. Apparently these reactions were part of the TOD reduction associated with the second reaction discussed in the kinetics section. As greater amounts of liquor TOD were satisfied, increasing amounts of sulfate were found. Ultimately, 100% conversion to sulfate was achievable, but a relatively large extent of reaction was necessary.

Tables 14 through 17 show the relationship between extent of reaction and status of the sulfurous species for various initial liquor compositions. Ranges for the starting liquor compositions (0% TOD reductions) are given in the tables where some variability existed in different trials. Precise values for each trial can be found in the mass balances presented later in this section. It is apparent that an extent of reaction on the high side if not beyond the anticipated maximum 10% TOD reduction of HIBLOX is necessary for total conversion to sulfate. Furthermore, the presence of greater initial sulfide concentrations inhibited the formation of sulfate.

Table 14. Grams of sulfurous species as a function of percent TOD reduction - low sulfide liquor.

Species	Percent TOD Reduction				
	0	5.0	7.4	8.3	12.9
Sulfide	0.59	0	0	0	0
Thiosulfate	5.64	4.59	2.64	2.30	0
Sulfite	0.24	0.20	0.20	0.20	0
Sulfate	1.98	5.40	8.33	9.48	13.50

Table 15. Grams of sulfurous species as a function of percent TOD reduction - high sulfide liquor with no alkali addition.

Species	Percent TOD Reduction	
	0	6.4
Sulfide	2.74	0
Thiosulfate	3.68	7.16
Sulfite	0.69	0.14
Sulfate	1.81	4.38

Table 16. Grams of sulfurous species as a function of percent TOD reduction - high sulfide liquor with 3% alkali addition.

Species	Percent TOD Reduction			
	0	5.9	7.3	9.9
Sulfide	3.33-3.40	0	0	0
Thiosulfate	3.81-3.86	9.56	8.84	6.20
Sulfite	0.71-0.72	0.41	0.34	0.20
Sulfate	1.87-1.90	2.43	3.81	8.78

Table 17. Grams of sulfurous species as a function of percent TOD reduction - high sulfide liquor with 5% alkali addition.

Species	Percent TOD Reduction				
	0	5.6	6.4	7.7	9.3
Sulfide	3.55-3.89	0	0	0	0
Thiosulfate	3.60-4.06	10.28	10.00	9.40	9.38
Sulfite	0.67-0.76	0.48	0.48	0.47	0.27
Sulfate	1.77-2.00	2.45	2.72	2.70	4.93

The inhibition of thiosulfate oxidation by sulfide is readily apparent from these figures. For example, at 5% active alkali addition substantially less sulfate was formed at approximately 6% TOD reduction than in the case where no sulfide was added. Adjusting the former case for the additional oxygen demand of the added sulfide reduces the difference slightly, but the inhibition remains apparent. The liquor with no sulfide addition had roughly the same sulfate content at approximately 6% TOD reduction as the liquor with added alkali had at approximately 9% TOD reduction. The additional oxygen demand due to the added sulfide represents only approximately 25% of the additional oxygen consumption needed to reach the same sulfate level.

The observed inhibition is easily explained. As previously noted, it can be attributed to a reaction between polysulfide (the intermediate oxidation product of sulfide) and sulfite (the intermediate oxidation product of thiosulfate) which prevents sulfate formation by returning the sulfite to thiosulfate. Since polysulfide resulted from the presence of sulfide, increasing sulfide content was detrimental with respect to the desired conversion of all inorganic sulfur to sulfate.

Thus, the extent of reaction necessary for complete conversion of inorganic sulfur to sulfate was most dependent on initial sulfide concentration. At the lowest sulfide level complete conversion to sulfate was possible at  $\approx 12\%$  TOD reduction. At the highest initial sulfide concentration, a substantial amount of thiosulfate remained at 10% TOD reduction, and the rate of decline indicates complete conversion was not achievable without oxidation well beyond the proposed HIBLOX range.

Organic compounds present in the liquor were also significantly affected by HIBLOX. High molecular weight species were degraded by oxidation to low molecular weight acid salts. Among the reaction products were carbonate, lactate, formate, acetate, and oxalate ions (as sodium salts). All of these products were formed in every trial, with the amounts of each increasing with increasing extent of reaction for a fixed starting liquor composition.

The reactions paths and stoichiometry by which individual organic species were formed could not be determined. Since the reaction paths leading to specific low molecular weight products cannot be determined for known lignin model compounds, determination of these paths for a complex black liquor which includes condensed alkali lignin of unknown structure as well as carbohydrates

would be impossible. Both the lignin and carbohydrates must be considered possible sources of each of the observed reaction products.

The lignin fraction was the more likely source of a number of the observed reaction products. Using the chemistry of model compounds as a basis, it is easy to envision how certain products were formed from the lignin fraction. Formic, acetic, and oxalic acids most likely resulted from oxidation of the low molecular weight species formed by Dakin-type elimination reactions. These products invariably result from the oxidation of structures which are capable of undergoing Dakin-type elimination reactions (i.e., those with substituted groups on the carbon chain off the phenolic ring). Conversely, the oxidation of para alkylated structures generally does not yield these products (19).

Some of the carbonate undoubtedly was formed from the lignin as well. Carbons present in the aromatic ring have been traced to carbonate formation by  $C^{14}$  labelling utilizing model compounds, even at relatively low temperatures (47). At the higher temperature associated with HIBLOX, substantial aromatic ring degradation was anticipated.

The lignin was apparently quite susceptible to oxygen-alkali degradation. Precipitation of the lignin fractions from equal amounts of oxidized and unoxidized liquor indicated substantial lignin degradation during HIBLOX. A 46.5% reduction in weight of precipitable lignin was noted for oxidation to 9.3% TOD reduction. Such a weight reduction is indicative of substantial degradation of the high molecular weight lignin fraction, and thus a large amount of the products formed apparently were from the lignin fraction.

The carbohydrates also were a potential source of several of the reaction products. One product probably attributable to the carbohydrates was lactic acid. Lactic acid is formed in high yield from the alkaline-oxidative degradation of polysaccharides and has been found to be a degradation product of monosaccharides and "sugar alcohols" as well. Reaction mechanisms have been proposed by Sjostrom and Malinen (48) and Sjostrom (49). Furthermore, lactic acid is not a common product of alkaline-oxidative degradation of lignin model compounds.

Other observed products could also have resulted from the carbohydrates. The carbohydrate fraction was a potential source of formic and acetic acids (49), although most likely in smaller amounts than from the lignin (19). Lastly, carbonate is also a product which could result from oxidative degradation of the carbohydrates (47), but carbonate formation has been found to be highly dependent on the structure of the individual starting compound.

In addition to the compounds discussed to this point, many additional products were formed during HIBLOX. Some of these products were not acidic or basic enough to be detected by ion chromatography. Examples of such species are methanol and ethanol, both of which were found in small quantities in the reactor off-gas. Long chain hydrocarbon acids were also not detectable.

Other reaction products were acidic enough for detection, but of high molecular weight (e.g., acids in the colloidal lignin) and thus could not be detected by ion chromatography. Species not detectable by ion chromatography were indirectly detected by acid titration as detailed in Appendix VII and reported as moles of "unknown acids." Any previously undetected species which would accept a proton at  $\text{pH} > 2$  was reported as an unknown acid.



UV spectrophotometry of unoxidized and HIBLOX liquor detected additional changes in liquor composition. A liquor oxidized to 8.3% TOD reduction showed roughly 65% greater absorption than the starting material at the wavelengths associated with both the quinone (430  $\mu\text{m}$ ) and phenolic (280  $\mu\text{m}$ ) groups in the lignin. The absorption due to nonphenolic aromatics (200  $\mu\text{m}$ ) was greater for the unoxidized liquor.

The greater quinone and phenolic content of the oxidized liquor is especially noteworthy when the degradation of the lignin during HIBLOX is considered. As previously mentioned the total precipitable lignin content of the liquor decreased significantly during oxidation. The increase in phenolics and quinones is especially significant given the decrease in lignin concentration.

While the reaction mechanisms which led to the detected products could not be determined, mass balances were constructed which determined the net chemical changes in the HIBLOX liquors. As the individual reaction mechanisms have little relevance to the ultimate feasibility of the process, the mass balances adequately illustrate the important chemical changes in the liquor. Since the formation of the acidic species did greatly affect the postoxidation properties, the key concern was the total moles of acidic species formed as effected by extent of reaction and/or other variables.

Mass balances based on HIBLOX trials are shown in Tables 18 through 27. The top portion of each chart shows the oxygen consumed via the reactions of known stoichiometry. Next the amounts of the other species formed and the moles of these acids formed/mole of oxygen not accounted for via the reactions of known stoichiometry are shown. The "unknowns" represent the acidic species detected

via titration as discussed in Appendix VII. Finally, the total acidification/mole of oxygen consumed and the initial and final compositions for each trial are shown.

Tables 18 through 20 are based on trials involving the first low sulfur liquor. These balances illustrate the effect of temperature and increasing extent of reaction. The tables show the net increase or decrease in the amounts of liquor constituents.

Table 18. Mass balance for low sulfide liquor (0% alkali addition) oxidized to 5.0% TOD reduction at 100°C.

Mass Balance for Trial No. 44 Liquor Batch No. 1

6.91 Grams = 215.9 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
8.5	Sulfide → thiosulfate
17.2	Thiosulfate → sulfate
0.1	Sulfite → sulfate
<u>25.8%</u>	

Net Millimoles Formed

Thiosulfate -9.4                      Sulfate 35.6

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	5.9	Formate	45.6
Carbonate	90.7	Lactate	2.2
Unknown	33.9	Acetate	36.3

Total 214.6

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 25.8\% = 74.2\%$$

or

$$(215.9 - 55.9) = 160.0 \text{ millimoles}$$

214.6	Millimoles Acids Derived from Organics = 1.34 Millimoles
<u>160.0</u>	Millimoles Oxygen Attributable to                      Millimole
	Reactions Involving Organics

Table 18 (Continued). Mass balance for low sulfide liquor (0% alkali addition) oxidized to 5.0% TOD reduction at 100°C.

240.8	Net Millimoles Total Product = 1.12 Millimoles	
215.9	Millimoles Total Oxygen Consumed by All Reactions	Millimole
274.0	Total Millimoles [H <sup>+</sup> ] Formed and [OH <sup>-</sup> ] Consumed	= 1.27 Equivalents Total Acidification
215.9	Millimoles Total Oxygen Consumed by All Reactions	Millimole Oxygen Consumed

#### PREOXIDATION COMPOSITION

284 mL, density 1.226 grams/mL,  
diluted to 600 mL at 22.1% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	0.17	0.59
Thiosulfate	1.62	5.64
Sulfite	0.07	0.24
Sulfate	0.57	1.98
Oxalate	0.14	0.49
Carbonate	2.68	9.33
Formate	1.31	4.56
Lactate	1.55	5.40
Acetate	1.92	6.69

#### POSTOXIDATION COMPOSITION

600 mL, density 1.124 grams/mL

Species	Weight Percent	Grams
Thiosulfate	0.68	4.59
Sulfite	0.03	0.20
Sulfate	0.80	5.40
Oxalate	0.15	1.01
Carbonate	2.19	14.77
Formate	0.98	6.61
Lactate	0.83	5.60
Acetate	1.31	8.83

Table 19. Mass balance for low sulfide liquor (0% alkali addition) oxidized to 7.4% TOD reduction at 130°C.

Mass Balance for Trial No. 40 Liquor Batch No. 1

10.40 Grams = 324.8 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
5.7	Sulfide $\rightarrow$ thiosulfate
22.2	Thiosulfate $\rightarrow$ sulfate
0.1	Sulfite $\rightarrow$ sulfate
<u>28.0%</u>	

Net Millimoles Formed

Thiosulfate -26.8      Sulfate 72.5

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	7.5	Formate	53.6
Carbonate	117.2	Lactate	12.3
Unknowns	64.9	Acetate	43.7

Total 299.2

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 28.0\% = 72.0\%$$

or

$$(324.8 - 85.2) = 239.6 \text{ millimoles}$$

<u>299.2</u>	Millimoles Acids Derived from Organics = 1.25 Millimoles
239.6	Millimoles Oxygen Attributable to Reactions Involving Organics

<u>344.9</u>	Net Millimoles Total Product = 1.06 Millimoles
324.8	Millimoles Total Oxygen Consumed by All Reactions

<u>397.1</u>	Total Millimoles $[H^+]$ Formed and $[OH^-]$ Consumed	= 1.22 Equivalents
324.8	Millimoles Total Oxygen Consumed by All Reactions	Total Acidification
		Millimole Oxygen Consumed

Table 19 (Continued). Mass balance for low sulfide liquor (0% alkali addition) oxidized to 7.4% TOD reduction at 130°C.

PREOXIDATION COMPOSITION

284 mL, density 1.226 grams/mL,  
diluted to 600 mL at 22.1% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	0.17	0.59
Thiosulfate	1.62	5.64
Sulfite	0.07	0.24
Sulfate	0.57	1.98
Oxalate	0.14	0.49
Carbonate	2.68	9.33
Formate	1.31	4.56
Lactate	1.55	5.40
Acetate	1.92	6.69

POSTOXIDATION COMPOSITION

600 mL, density 1.128 grams/mL

Species	Weight Percent	Grams
Thiosulfate	0.39	2.64
Sulfite	0.03	0.20
Sulfate	1.23	8.33
Oxalate	0.17	1.15
Carbonate	2.45	16.36
Formate	1.03	6.97
Lactate	0.96	6.50
Acetate	1.37	9.27

Table 20. Mass balance for low sulfide liquor (0% alkali addition) oxidized to 8.3% TOD reduction at 150°C.

Mass Balance for Trial No. 47 Liquor Batch No. 1

11.61 Grams = 362.8 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
5.1	Sulfide $\longrightarrow$ thiosulfate
21.5	Thiosulfate $\longrightarrow$ sulfate
0.1	Sulfite $\longrightarrow$ sulfate
<u>26.7%</u>	

Net Millimoles Formed

Thiosulfate -29.8      Sulfate 78.1

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	9.8	Formate	65.6
Carbonate	127.7	Lactate	10.0
Unknown	94.6	Acetate	54.1

Total 361.8

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 26.7\% = 73.3\%$$

or

$$(362.8 - 96.9) = 265.9 \text{ millimoles}$$

361.8	Millimoles Acids Derived from Organics = 1.36 Millimoles
265.9	Millimoles Oxygen Attributable to      Millimole
	Reactions Involving Organics

410.1	Net Millimoles Total Product = 1.13 Millimoles
362.8	Millimoles Total Oxygen      Millimole
	Consumed by All Reactions

467.6	Total Millimoles $[H^+]$ Formed	= 1.29 Equivalents
	and $[OH^-]$ Consumed	Total Acidification
362.8	Millimoles Total Oxygen	Millimole Oxygen Consumed
	Consumed by All Reactions	

Table 20 (Continued). Mass balance for low sulfide liquor (0% alkali addition) oxidized to 8.3% TOD reduction at 150°C.

PREOXIDATION COMPOSITION

284 mL, density 1.226 grams/mL,  
diluted to 600 mL at 22.1% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	0.17	0.59
Thiosulfate	1.62	5.64
Sulfite	0.07	0.24
Sulfate	0.57	1.98
Oxalate	0.14	0.49
Carbonate	2.68	9.33
Formate	1.31	4.56
Lactate	1.55	5.40
Acetate	1.92	6.69

POSTOXIDATION COMPOSITION

600 mL, density 1.128 grams/mL

Species	Weight Percent	Grams
Thiosulfate	0.34	2.30
Sulfite	0.03	0.20
Sulfate	1.40	9.48
Oxalate	0.20	1.35
Carbonate	2.51	16.99
Formate	1.11	7.51
Lactate	0.93	6.29
Acetate	1.46	9.88

The tables show the effect of reaction temperature on HIBLOX chemistry. It is apparent that reaction temperature did not substantially alter reaction chemistry over the investigated temperature range. Essentially the same products were formed at both 100 and 150°C.

The total acidification was calculated by summing the alkali consumed and/or the protons generated in the formation or consumption of each species during HIBLOX. For example, each reaction involving the inorganic sulfurous species consumed a known amount of alkali, so this consumption totalled a certain value for each trial. Additionally, the formation of organic acids led to a certain number of protons being released, two moles of protons for each mole of oxalic formed and one for each mole of monoprotic acid formed. Finally, each mole of carbohydrate formed was assumed to equal the loss of one mole of hydroxide by  $\text{CO}_2 + \text{NaOH} \rightarrow \text{NaHCO}_3$ . Summing the total acidification and dividing by the total oxygen consumption led to the desired quantity.

Many more trials were run utilizing the low sulfide liquor and the post-oxidation compositions determined. Mass balances could be constructed for each of these trials, but the balances are not presented because no new information was gained vis-a-vis reaction chemistry. It was apparent from the postoxidation compositions that factors such as pressure, gas, flow rate, etc., exerted no influence on reaction chemistry.

Tables 21 through 27 are based on trials involving the second high sulfide liquor batch and alkali addition. It is apparent from these tables that the chemistry involving this different liquor was generally similar to that of the first liquor batch. The best comparison is for the trial where no alkali was added to the liquor.



Table 21. Mass balance for high sulfide liquor (0% alkali addition) oxidized to 6.4% TOD reduction at 150°C.

Mass Balance for Trial No. 1 Liquor Batch No. 2

8.42 Grams = 263.1 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
32.5	Sulfide $\longrightarrow$ thiosulfate
8.9	Thiosulfate $\longrightarrow$ sulfate
1.3	Sulfite $\longrightarrow$ sulfate
<u>42.7%</u>	

Net Millimoles Formed

Thiosulfate 26.1                      Sulfate 31.1

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	7.8	Formate	38.9
Carbonate	65.5	Lactate	37.8
Unknown	6.7	Acetate	45.8

Total 202.5

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 42.7\% = 57.3\%$$

or

$$(263.1 - 112.3) = 150.8 \text{ millimoles}$$

202.5	Millimoles Acids Derived from Organics = 1.34 Millimoles
150.8	Millimoles Oxygen Attributable to                      Millimole
	Reactions Involving Organics

259.7	Net Millimoles Total Product = 0.99 Millimole
263.1	Millimoles Total Oxygen                      Millimole
	Consumed by All Reactions

320.1	Total Millimoles $[H^+]$ Formed                      = 1.22 Equivalents
263.1	and $[OH^-]$ Consumed                      Total Acidification
	Millimoles Total Oxygen                      Millimole Oxygen Consumed
	Consumed by All Reactions

Table 21 (Continued). Mass balance for high sulfide liquor (0% alkali addition) oxidized to 6.4% TOD reduction at 150°C.

PREOXIDATION COMPOSITION

211.9 mL, density 1.295 grams/mL,  
diluted to 600 mL at 21.0% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	1.00	2.74
Thiosulfate	1.34	3.68
Sulfite	0.25	0.69
Sulfate	0.66	1.81
Oxalate	0.07	0.19
Carbonate	3.32	9.12
Formate	1.19	3.26
Lactate	3.44	9.43
Acetate	1.99	5.47

POSTOXIDATION COMPOSITION

600 mL, density 1.125 grams/mL

Species	Weight Percent	Grams
Thiosulfate	1.06	7.16
Sulfite	0.02	0.14
Sulfate	0.65	4.38
Oxalate	0.13	0.88
Carbonate	1.93	13.05
Formate	0.74	5.01
Lactate	1.89	12.79
Acetate	1.21	8.17

Table 22. Mass balance for high sulfide liquor (3% alkali addition) oxidized to 5.9% TOD reduction at 150°C.

Mass Balance for Trial No. 4 Liquor Batch No. 2

7.91 Grams = 247.2 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
42.4	Sulfide $\longrightarrow$ thiosulfate
0.8	Thiosulfate $\longrightarrow$ sulfate
0.8	Sulfite $\longrightarrow$ sulfate
<u>44.0%</u>	

Net Millimoles Formed

Thiosulfate 51.3                      Sulfate 5.8

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	4.7	Formate	25.8
Carbonate	49.3	Lactate	35.5
Unknown	5.5	Acetate	42.5

Total 163.3

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 44.0\% = 56.0\%$$

or

$$(247.2 - 108.8) = 138.4 \text{ millimoles}$$

163.3	Millimoles Acids Derived from Organics = 1.18 Millimoles
138.4	Millimoles Oxygen Attributable to Reactions Involving Organics

220.4	Net Millimoles Total Product = 0.89 Millimole
247.2	Millimoles Total Oxygen Consumed by All Reactions

274.7	Total Millimoles $[H^+]$ Formed and $[OH^-]$ Consumed	= 1.11 Equivalents
247.2	Millimoles Total Oxygen Consumed by All Reactions	Total Acidification

Table 22 (Continued). Mass balance for high sulfide liquor (3% alkali addition) oxidized to 5.9% TOD reduction at 150°C.

PREOXIDATION COMPOSITION

219.3 mL, density 1.295 grams/mL,  
diluted to 600 mL at 21.6% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	1.00	2.84 + 0.51 <sup>a</sup>
Thiosulfate	1.34	3.81
Sulfite	0.25	0.71
Sulfate	0.66	1.87
Oxalate	0.07	0.20
Carbonate	3.32	9.43
Formate	1.19	3.38
Lactate	3.44	9.77
Acetate	1.99	5.65

POSTOXIDATION COMPOSITION

600 mL, density 1.130 grams/mL

Species	Weight Percent	Grams
Thiosulfate	1.41	9.56
Sulfite	0.06	0.41
Sulfate	0.36	2.43
Oxalate	0.09	0.61
Carbonate	1.83	12.39
Formate	0.67	4.54
Lactate	1.91	12.93
Acetate	1.20	8.16

<sup>a</sup>From alkali addition.

6 16.491 H4241

Table 23. Mass balance for high sulfide liquor (3% alkali addition) oxidized to 7.3% TOD reduction at 150°C.

Mass Balance for Trial No. 3 Liquor Batch No. 2

9.98 Grams = 311.9 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
34.0	Sulfide $\rightarrow$ thiosulfate
5.5	Thiosulfate $\rightarrow$ sulfate
0.8	Sulfite $\rightarrow$ sulfate
<u>40.3%</u>	

Net Millimoles Formed

Thiosulfate 44.5                      Sulfate 19.9

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	8.5	Formate	28.0
Carbonate	80.7	Lactate	37.6
Unknown	35.0	Acetate	37.5

Total 227.3

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 40.3\% = 59.7\%$$

or

$$(311.9 - 125.7) = 186.2 \text{ millimoles}$$

<u>227.3</u>	Millimoles Acids Derived from Organics = 1.22 Millimoles
186.2	Millimoles Oxygen Attributable to                      Millimole
	Reactions Involving Organics

<u>291.7</u>	Net Millimoles Total Product = 0.94 Millimole
311.9	Millimoles Total Oxygen                      Millimole
	Consumed by All Reactions

<u>356.8</u>	Total Millimoles $[H^+]$ Formed	= 1.14 Equivalents
	and $[OH^-]$ Consumed	Total Acidification
311.9	Millimoles Total Oxygen	Millimole Oxygen Consumed
	Consumed by All Reactions	

Table 23 (Continued). Mass balance for high sulfide liquor (3% alkali addition) oxidized to 7.3% TOD reduction at 150°C.

PREOXIDATION COMPOSITION

222.6 mL, density 1.295 grams/mL,  
diluted to 600 mL at 21.9% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	1.00	2.88 + 0.51
Thiosulfate	1.34	3.86
Sulfite	0.25	0.72
Sulfate	0.66	1.90
Oxalate	0.07	0.20
Carbonate	3.32	9.57
Formate	1.19	3.43
Lactate	3.44	9.91
Acetate	1.99	5.74

POSTOXIDATION COMPOSITION

600 mL, density 1.133 grams/mL

Species	Weight Percent	Grams
Thiosulfate	1.30	8.84
Sulfite	0.05	0.34
Sulfate	0.56	3.81
Oxalate	0.14	0.95
Carbonate	2.12	14.41
Formate	0.69	4.69
Lactate	1.95	13.26
Acetate	1.17	7.95

Table 24. Mass balance for high sulfide liquor (3% alkali addition) oxidized to 9.9% TOD reduction at 150°C.

Mass Balance for Trial No. 5 Liquor Batch No. 2

13.54 Grams = 423.0 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
25.1	Sulfide → thiosulfate
15.0	Thiosulfate → sulfate
0.8	Sulfite → sulfate
<u>40.9%</u>	

Net Millimoles Formed

Thiosulfate 71.7                      Sulfate 21.4

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	9.3	Formate	44.7
Carbonate	96.8	Lactate	49.1
Unknown	67.3	Acetate	52.7

Total 319.9

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 40.9\% = 59.1\%$$

or

$$(423.0 - 167.0) = 256.0 \text{ millimoles}$$

<u>319.9</u>	Millimoles Acids Derived from Organics = 1.25 Millimoles
256.0	Millimoles Oxygen Attributable to                      Millimole
	Reactions Involving Organics

<u>413.0</u>	Net Millimoles Total Product = 0.98 Millimole
423.0	Millimoles Total Oxygen                      Millimole
	Consumed by All Reactions

<u>450.0</u>	Total Millimoles [H <sup>+</sup> ] Formed                      = 1.06 Equivalents
	and [OH <sup>-</sup> ] Consumed                      Total Acidification
423.0	Millimoles Total Oxygen                      Millimole Oxygen Consumed
	Consumed by All Reactions

Table 24 (Continued). Mass balance for high sulfide liquor (3% alkali addition) oxidized to 9.9% TOD reduction at 150°C.

PREOXIDATION COMPOSITION

222.6 mL, density 1.123 grams/mL,  
diluted to 600 mL at 21.9% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	1.00	2.88 + 0.51
Thiosulfate	1.34	3.86
Sulfite	0.25	0.72
Sulfate	0.66	1.90
Oxalate	0.07	0.20
Carbonate	3.32	9.57
Formate	1.19	3.43
Lactate	3.44	9.92
Acetate	1.99	5.74

POSTOXIDATION COMPOSITION

600 mL, density 1.134 grams/mL

Species	Weight Percent	Grams
Thiosulfate	0.92	6.26
Sulfite	0.03	0.20
Sulfate	1.29	8.78
Oxalate	0.15	1.02
Carbonate	2.26	15.38
Formate	0.80	5.44
Lactate	2.10	14.29
Acetate	1.30	8.85



Table 25. Mass balance for high sulfide liquor (5% alkali addition) oxidized to 5.6% TOD reduction at 130°C.

Mass Balance for Trial No. 6 Liquor Batch No. 2

7.85 Grams = 245.3 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
48.3	Sulfide $\rightarrow$ thiosulfate
1.7	Thiosulfate $\rightarrow$ sulfate
0.7	Sulfite $\rightarrow$ sulfate
<u>50.7%</u>	

Net Millimoles Formed

Thiosulfate 57.2                      Sulfate 6.8

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	5.3	Formate	29.7
Carbonate	51.8	Lactate	33.4
Unknown	7.0	Acetate	40.1

Total 166.3

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 50.7\% = 49.3\%$$

or

$$(245.3 - 124.4) = 120.9 \text{ millimoles}$$

166.3	Millimoles Acids Derived from Organics = 1.38 Millimoles
120.9	Millimoles Oxygen Attributable to Reactions Involving Organics

236.3	Net Millimoles Total Product = 0.94 Millimole
245.3	Millimoles Total Oxygen Consumed by All Reactions

293.5	Total Millimoles $[H^+]$ Formed and $[OH^-]$ Consumed	= 1.20 Equivalents
245.3	Millimoles Total Oxygen Consumed by All Reactions	Total Acidification
		Millimole Oxygen Consumed

Table 25 (Continued). Mass balance for high sulfide liquor (5% alkali addition) oxidized to 5.6% TOD reduction at 130°C.

PREOXIDATION COMPOSITION

227.0 mL, density 1.295 grams/mL,  
diluted to 600 mL at 22.3% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	1.00	2.94 + 0.85
Thiosulfate	1.34	3.94
Sulfite	0.25	0.74
Sulfate	0.66	1.94
Oxalate	0.07	0.21
Carbonate	3.32	9.76
Formate	1.19	3.50
Lactate	3.44	10.11
Acetate	1.99	5.85

POSTOXIDATION COMPOSITION

600 mL, density 1.135 grams/mL

Species	Weight Percent	Grams
Thiosulfate	1.51	10.28
Sulfite	0.07	0.48
Sulfate	0.38	2.59
Oxalate	0.10	0.68
Carbonate	1.89	12.87
Formate	0.71	4.84
Lactate	1.92	13.08
Acetate	1.21	8.22

Table 26. Mass balance for high sulfide liquor (5% alkali addition) oxidized to 7.5% TOD reduction at 150°C.

Mass Balance for Trial No. 2 Liquor Batch No. 2

9.81 Grams = 306.6 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
36.2	Sulfide $\rightarrow$ thiosulfate
2.4	Thiosulfate $\rightarrow$ sulfate
0.4	Sulfite $\rightarrow$ sulfate
<u>39.0%</u>	

Net Millimoles Formed

Thiosulfate 51.8                      Sulfate 9.7

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	8.7	Formate	37.8
Carbonate	77.2	Lactate	46.4
Unknown	20.0	Acetate	49.7

Total 239.8

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 39.0\% = 61.0\%$$

or

$$(306.6 - 119.6) = 187.0 \text{ millimoles}$$

239.8	Millimoles Acids Derived from Organics = 1.28 Millimoles
187.0	Millimoles Oxygen Attributable to Reactions Involving Organics

301.3	Net Millimoles Total Product = 0.98 Millimole
306.6	Millimoles Total Oxygen Consumed by All Reactions

366.6	Total Millimoles $[H^+]$ Formed and $[OH^-]$ Consumed	= 1.20 Equivalents
306.6	Millimoles Total Oxygen Consumed by All Reactions	Total Acidification
		Millimole Oxygen Consumed

Table 26 (Continued). Mass balance for high sulfide liquor (5% alkali addition) oxidized to 7.5% TOD reduction at 150°C.

PREOXIDATION COMPOSITION

207.7 mL, density 1.295 grams/mL,  
diluted to 600 mL at 20.6% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	1.00	2.69 + 0.86
Thiosulfate	1.34	3.60
Sulfite	0.25	0.67
Sulfate	0.66	1.72
Oxalate	0.07	0.19
Carbonate	3.32	8.93
Formate	1.19	3.20
Lactate	3.44	9.25
Acetate	1.99	5.35

POSTOXIDATION COMPOSITION

600 mL, density 1.127 grams/mL

Species	Weight Percent	Grams
Thiosulfate	1.39	9.40
Sulfite	0.07	0.47
Sulfate	0.40	2.57
Oxalate	0.14	0.95
Carbonate	2.01	13.56
Formate	0.72	4.90
Lactate	1.98	13.38
Acetate	1.22	8.28

Table 27. Mass balance for high sulfide liquor (5% alkali addition) oxidized to 9.3% TOD reduction at 150°C.

Mass Balance for Trial No. 7 Liquor Batch No. 2

13.38 Grams = 418.0 Millimoles Total Oxygen Consumed

Percent of Total Oxygen Consumption	Reaction of Known Stoichiometry
29.1	Sulfide → thiosulfate
6.4	Thiosulfate → sulfate
0.7	Sulfite → sulfate
<u>36.2%</u>	

Net Millimoles Formed

Thiosulfate 47.5                      Sulfate 30.5

Net Millimoles of Acidic Species Formed from Organics  
Via Unknown Stoichiometry

Oxalate	9.9	Formate	45.9
Carbonate	104.7	Lactate	69.6
Unknown	59.3	Acetate	55.9

Total 345.3

Oxygen Consumption Attributable to Reactions  
Involving Liquor Organics

$$100\% - 36.2\% = 63.8\%$$

or

$$(418.0 - 151.4) = 266.7 \text{ millimoles}$$

345.3	Millimoles Acids Derived from Organics = 1.29 Millimoles
<u>266.7</u>	Millimoles Oxygen Attributable to                      Millimole
	Reactions Involving Organics

415.9	Net Millimoles Total Product = 0.99 Millimole
<u>418.0</u>	Millimoles Total Oxygen                      Millimole
	Consumed by All Reactions

501.2	Total Millimoles [H <sup>+</sup> ] Formed	= 1.20 Equivalents
<u>418.0</u>	and [OH <sup>-</sup> ] Consumed	Total Acidification
	Millimoles Total Oxygen	Millimole Oxygen Consumed
	Consumed by All Reactions	

Table 27 (Continued). Mass balance for high sulfide liquor (5% alkali addition) oxidized to 9.3% TOD reduction at 150°C.

PREOXIDATION COMPOSITION

234.2 mL, density 1.295 grams/mL,  
diluted to 600 mL at 22.9% solids prior to oxidation

Species	Weight Percent (before dilution, wet basis)	Grams
Sulfide	1.00	3.03 + 0.86
Thiosulfate	1.34	4.06
Sulfite	0.25	0.76
Sulfate	0.66	2.00
Oxalate	0.07	0.23
Carbonate	3.32	10.07
Formate	1.19	3.93
Lactate	3.44	11.36
Acetate	1.99	6.57

POSTOXIDATION COMPOSITION

600 mL, density 1.141 grams/mL

Species	Weight Percent	Grams
Thiosulfate	1.37	9.38
Sulfite	0.04	0.27
Sulfate	0.72	4.93
Oxalate	0.16	1.10
Carbonate	2.39	16.35
Formate	0.88	6.00
Lactate	2.56	17.55
Acetate	1.44	9.87

This trial, shown in Table 21, involved the second liquor batch as it was received. The extent of reaction for this trial was 6.4% TOD reduction, making it most comparable to Table 19. While the chemistry was for the most part similar to that associated with the first liquor batch, some differences are apparent.

The most striking differences between this mass balance and those previously discussed are a large change in the amount of consumption attributable to the sulfurous species and a redistribution of the relative amounts of acid salts formed. The greater consumption by the sulfurous species is directly attributable to the greater initial sulfide content. Since the sulfide was by far the most easily oxidized substance, the percentage of the total consumption due to the sulfurous species was much greater for the high sulfide liquor.

The differences in the products formed from the organics are less easily explained. It is apparent that substantially greater lactic acid was formed from the second liquor than from the first. The greater lactic acid formation occurred at the expense of the other acids, especially formic. The change in the relative amounts of acids is not overwhelming given expected differences in the liquor compositions. Most importantly, the total acidification relative to the oxygen consumption remained roughly the same as for the first liquor composition.

Except for Table 21 the balances for the high sulfide liquor are derived from trials that also involved alkali addition. These balances are in order of increasing TOD reduction with the 5% alkali addition trials following the 3% addition trials. All the trials were run at 150°C except No. 6, which was run at 130°C. The increasing formation of the same products with increasing TOD

reduction and the same lack of temperature sensitivity as existed with the low sulfide liquor is apparent.

As sulfide was added to the liquor, the greater oxygen consumption by the inorganics relative to the first liquor batch became even more pronounced. At 3% active alkali addition the percentage of the total consumption attributable to the sulfurous inorganics rose to 44% at 5.9% TOD reduction. At 5% active alkali addition the oxygen consumption by this fraction rose to 50.7% of the total at 5.6% TOD reduction.

The chemistry of the organic fraction was not appreciably changed by the alkali addition. The organics reacted to form the same products in roughly the same amounts after adjustment for the greater oxygen demand of the added sulfide. No fundamental change in reaction chemistry was apparent at any alkali level.

To summarize the chemistry of HIBLOX, the oxidation of sulfide to thio-sulfate was the key reaction, much as during BLOX. The consumption via this reaction constituted as much as 50.7% of the total consumption at the highest sulfide content and the minimal extent of oxidation. After the entire sulfide content was satisfied, significant oxidation of thiosulfate to sulfate became apparent. Oxidation beyond the 10% maximum TOD reduction was necessary for complete conversion to sulfate.

At the same time that the inorganics were being oxidized, less rapid degradation of the lignin and carbohydrates by oxidative-alkali mechanisms apparently similar to those proposed for model compounds occurred. These degradation reactions led to a host of low molecular weight acid salts. The specific salts formed were not affected by reaction conditions and increased with increasing extent of reaction.



The chemistry of HIBLOX is of greatest importance in terms of its effect on postoxidation liquor properties. The effect of the chemical changes during HIBLOX on liquor properties was quite significant. These changes and their effect on process feasibility are detailed in the following section.

#### POSTOXIDATION PROPERTIES

The postoxidation properties having the greatest impact on HIBLOX feasibility were, as expected, precipitation behavior and rheology. These properties were greatly affected by HIBLOX, primarily because of the formation of the acidic species and the resulting change in liquor pH. Prior to discussing these properties, it is necessary to consider the effect of HIBLOX on liquor pH.

##### Effect of HIBLOX on pH

The formation of the acidic species previously discussed led to a substantial reduction in liquor pH during HIBLOX. The decrease in liquor pH with increasing extent of reaction was large initially, but the rate of decline slowed greatly as the carbonate-bicarbonate buffering effect became significant. The pH decline caused by HIBLOX was analogous to that caused by acid titration of the black liquor.

The effect of HIBLOX on liquor pH under various circumstances is shown in Tables 28 and 29. Table 28 shows the behavior of the first liquor batch with no added alkali. Table 29 shows the behavior of the second batch with various alkali addition levels.

Table 28. pH decline during HIBLOX - low sulfide liquor.

Percent TOD Reduction	pH at 22% Solids
0	12.7
5.4	10.5
5.8	10.2
7.0	9.9
8.1	9.8
9.0	9.6
12.9	9.4
14.5	9.2

Table 29. pH decline during HIBLOX - high sulfide liquor and added alkali.

Extent of Oxidation, % TOD reduction	Alkali <sup>a</sup> Addition	pH at 22% Solids
0	0	13.3
5.4	0	10.8
0	3	14 <sup>b</sup>
5.9	3	12.8
7.3	3	11.8
9.9	3	10.3
0	5	14 <sup>b</sup>
6.4	5	13.1
7.2	5	12.8
9.3	5	10.9

<sup>a</sup>Weight percent alkali addition (o.d. solids basis), -30% sulfidity as Na<sub>2</sub>O.

<sup>b</sup>Maximum reading of pH meter.

### Precipitation Behavior and Rheology

The deleterious effect of HIBLOX on postoxidation liquor properties was first manifested as precipitation of material and/or reactor plugging during oxidation utilizing the first liquor batch. When minimal precipitation occurred, it was apparent as small specks deposited on reactor surfaces and present in the liquor and the water used to rinse the reactor after each trial. When more severe precipitation occurred, a sizable reduction in the removable liquor volume resulted, and large chunks of material were deposited throughout the reactor. In these cases two distinct phases were present, a tacky solid phase plugging the reactor and a reasonably free-flowing liquid.

An example of the severity of the precipitation/plugging problem is shown in Fig. 29. This photograph shows the deposition of material on the reactor cooling coils following a HIBLOX trial utilizing 45% liquor and oxidizing to 15% TOD reduction. In this case the reactor was totally plugged with precipitated material.

For a fixed liquor composition, precipitation and plugging were found to be dependent upon two independent variables, extent of reaction and liquor solids content. The precipitation/plugging problem became increasingly likely with increases in either parameter. Table 30 shows when and to what degree precipitation/plugging occurred during trials utilizing the first liquor batch. Problems occurred at as low as 22% solids at 13% TOD reduction and at 4% TOD reduction at 45% solids.

It is apparent from Table 30 that within the 5-10% TOD reduction range the precipitation problem could be avoided by maintaining low solids levels. At 20% solids the HIBLOX liquors were indistinguishable from unoxidized liquor vis-a-vis

precipitation and rheology. Hence, much of the work involving reaction chemistry and kinetics was done at the low solids values.

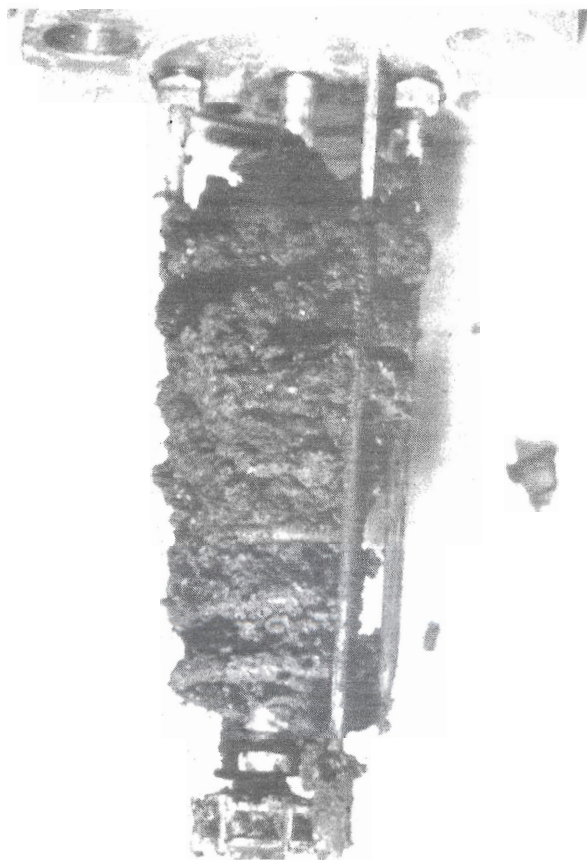


Figure 29. Plugging of reactor during HIBLOX.

Table 30. Occurrence of precipitation/plugging during HIBLOX utilizing first liquor batch.

Liquor Solids	% TOD Reduction	Plugging/ Precipitation
22%	Less than 13	None
	13-14.5	Slight precipitation
35%	Less than 5	None
	5.7	Slight precipitation
	7.5	Moderate precipitation Reactor not plugged
45%	2 or less	None
	4.2 or more	Severe precipitation Reactor plugged

Samples of the precipitate were collected and analyzed via ion chromatography. It was thought that the precipitate might be mainly inorganic salts and therefore detectable by ion chromatography, but little inorganic material was found. The amounts of various species in the precipitate are shown in Table 31. The bulk of the precipitate was unidentifiable organic material.

Table 31. Detectable species in HIBLOX precipitate.

Inorganics	Weight Percent of Air Dried Solids
Sodium chloride	0.21
Sodium sulfate	3.75
Sodium oxalate	0.84
Sodium carbonate	<u>7.40</u>
Total Inorganics	12.20
Organics	
Sodium formate	2.43
Sodium lactate	2.51
Sodium acetate	<u>3.25</u>
Total known species	20.39%

The organic nature of the precipitate and the pH change associated with HIBLOX suggested that the precipitation might be due to destabilization of the colloidal lignin. In fact, as Fig. 30 indicates, it is surprising that the lignin could be kept stable even at 20% solids at the pH's resulting from HIBLOX. Under normal circumstances, considerable lignin precipitation would be expected.

Apparently, the creation of addition ionizable groups and the reduction in the lignin concentration at fixed solids improved the stability of the lignin fraction of the liquor. This increased stability could be attributed to acidic groups formed in the lignin, the breaking of aryl ether bonds, and the reduction

in the lignin concentration as some of the lignin was consumed. These factors improved the stability enough to prevent precipitation under conditions which would normally result in precipitation, but apparently could not overcome the pH decline in all cases, especially at high solids.

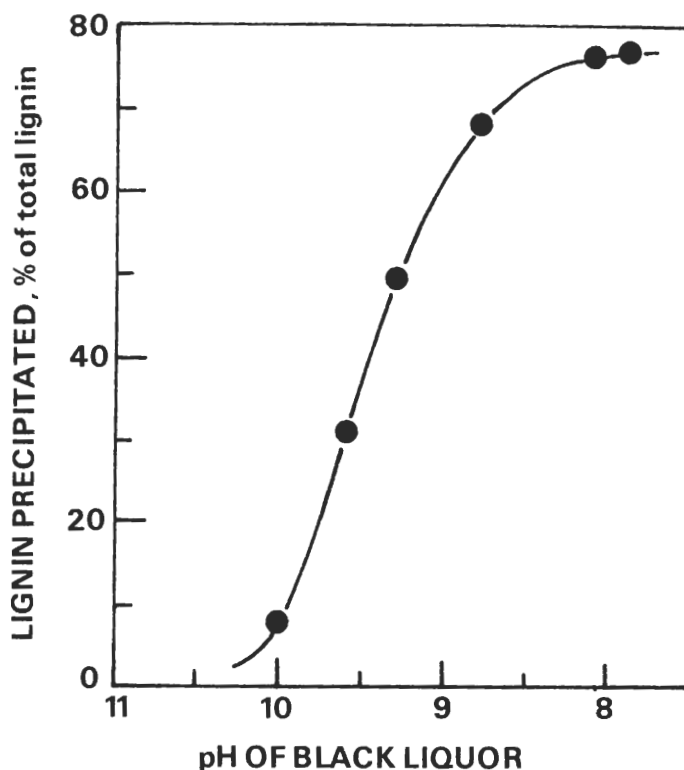


Figure 30. Precipitation of lignin from unoxidized black liquor during acidification.

The maintenance of low solids solved the problem of precipitation/plugging during HIBLOX, but concentration of the liquor would be necessary for ensuing recovery operations. For this reason, the low solids oxidized liquors from the first liquor batch which exhibited no adverse properties during HIBLOX were concentrated to firing solids. The determination of acceptable rheological properties at high solids would help establish HIBLOX as a technically feasible process.

Unfortunately, upon concentration the liquors exhibited unacceptable rheological properties. As the solids contents approached 35% the liquors became unusually viscous. As the 40% solids level was reached, the liquors resembled tar. At 50% solids the liquors were fully gelled. The appearance was that of a solid, and the liquor could not be made to flow even at elevated temperature.

The fact that the lignin fraction was the gel causing agent was proven by separate oxidation and concentration of the lignin and acid soluble fractions of the black liquor. The lignin was precipitated via acidification and separated from the acid soluble fraction by centrifugation. The two fractions were then dissolved in aqueous sodium hydroxide solutions, oxidized and concentrated. The specifics concerning these trials and the results obtained are shown in Table 32. The observation that the lignin gelled while the acid solubles did not is indicative that the lignin was the gel causing agent.

Table 32. Oxidation of lignin and acid soluble fractions.

Fraction	Preoxidation Solids, %	% TOD Reduction <sup>a</sup>	Results of Concentration
Acid solubles	9.5	4.2	No gel formation
Lignin	12	4.8	Gelled

<sup>a</sup>Assuming 1 gram TOD/gram solids.

In an attempt to determine how pH influenced liquor rheology, sodium hydroxide was added in varying amounts to samples of 20% solids oxidized liquors prior to concentration. It was quickly determined that the poor rheology at high solids could be improved by caustic addition. This effect was manifested by the ability of the liquor to exist as a liquid at progressively higher solids

contents as increasing amounts of sodium hydroxide were added. For a liquor oxidized to 5% TOD reduction, approximately 0.5 gram sodium hydroxide/gram oxygen consumed was sufficient to allow the oxidized liquor to exist as a viscous liquid at 60% solids and elevated temperature.

With the knowledge that the alkali addition would solve the rheology problem but would also involve substantial cost, an alternate solution was sought. It has been reported (50,51) that the presence of trace quantities of transition metals can influence the relative rates of carbohydrate and lignin degradation under oxidative conditions.  $Mn^{2+}$  and  $Fe^{2+}$  ions were reported to accelerate the degradation of the lignin and cellulose fractions, respectively, while retarding the rate of degradation of the other constituent. However, combinations of various metal ions exerted unpredictable effects.

It was hoped that the transition metal effect could advantageously be applied to HIBLOX. If one liquor fraction contributed more moles of acid/mole oxygen consumed than the other, suppression of that fraction's tendency to react would be advantageous. Also, the amount of stabilizing acid groups formed within the lignin macromolecule might be affected by the presence of transition metal ions.

The unoxidized black liquor already contained varying quantities of many metals. The specific metals and the amounts of each are shown in Table 33. It would be impractical to remove any or all of them, so the desired  $Mn^{2+}$  and  $Fe^{2+}$  ions were simply added to those already present.

Approximately 1500 ppm of the chosen ions were added to the black liquor prior to oxidation in two trials. The liquors were oxidized to 6.0% TOD reduction and then concentrated. Neither ion had any effect on the liquor rheology,



since both liquors gelled at just over 40% solids in a manner analogous to the liquor without added ions. Thus, active alkali addition remained the only possible solution to the rheology problem.

Table 33. Determination of metals in black liquor.

Analysis	Weight Percent Black Liquor Solids
Aluminum	0.012
Cadmium	Not detected
Calcium	0.033
Cobalt	Not detected
Copper	0.00087
Iron	0.017
Lanthanum	No calibration
Magnesium	0.011
Manganese	0.012
Nickel	Not detected
Potassium	2.03
Silicon	0.092
Sodium	17.5
Strontium	No calibration
Vanadium	0.004
Zinc	Not detected

Note: The above values represent duplicate determinations.

Basis of report: Ovendry.

Method: Potassium and sodium - perchloric acid digestion followed by flame emission. All others - emission spectrographic analysis.

With alkali addition the only known solution to the liquor rheology problems, a preliminary cost analysis was done to determine the economic consequences of adding 0.5 gram alkali/gram oxygen consumed for oxidation to 5% TOD reduction (3). The use of purchased sodium hydroxide was clearly uneconomical. The alternate source of alkali was white liquor. If the amount of alkali needed could be held to the anticipated 0.5 gram/gram oxygen consumed at 5% TOD reduction, the economics of the process still might be favorable.

At this point a series of trials was run to quantify the relationship between amount of alkali added and liquor rheology. The trials utilized a fresh liquor, batch No. 2, and white liquor (30% sulfidity as  $\text{Na}_2\text{O}$ ) as the alkali. Specifically, the goal was to determine the minimum alkali addition which would eliminate the precipitation/plugging problem and produce a liquor with a high solids rheology compatible with the use of existing pumping equipment.

No precipitation/plugging was noted in the experimental series utilizing the second liquor batch and oxidizing to the same extent as with the first batch. The problem was avoided because the higher inherent liquor pH and the alkali addition prevented the postoxidation pH from reaching the range at which problems occurred. The lowest postoxidation pH reached in these trials was 10.3 at 22% solids, far above the pH range of the liquors in which precipitation/plugging occurred.

The key results from these trials related to viscosity behavior are shown in Table 34. At approximately 6.5% TOD reduction, the viscosity of HIBLOX liquor at  $63 \pm 1\%$  solids was  $> 100,000$  cp with no alkali addition. Alkali additions of 0.37 and 0.48 gram/gram oxygen consumed resulted in viscosities of 865 and 600 cp, respectively.

Table 34. Effect of alkali addition and extent of oxidation on high solids viscosity.

% TOD Reduction	Oxidized Liquors				Unoxidized
	5.6	6.0	8.5	6.4	0
<u>Grams alkali added</u> <u>Gram oxygen consumed</u>	0.37	0.48	0.64	0	0
pH at 44% solids	13.1	13.0	12.0	11.6	14
Viscosity (cp) at 63 $\pm$ 1% solids at 90°C	865	600	630	100,000	420

These results clearly show the viscosity of the oxidized liquor can be reduced to approximately that of the unoxidized liquor by means of alkali addition. At 5-6% TOD reduction, alkali addition of 0.5 gram/gram oxygen consumed appears to be adequate. The viscosity would be equal to or only slightly greater than that of the unoxidized liquor, and by utilizing a slightly higher operation temperature an acceptable situation should result.

The results shown in Table 34 demonstrate the futility of extending the reaction to the upper end of the proposed range. At 8.5% TOD reduction, not only is a much larger amount of alkali needed, but also a larger ratio in terms of grams added/grams oxygen consumed. Given the requirements put on the causticizing system by utilizing white liquor addition (3), the minimal extent of oxidation offers the best chance of economic viability.

Figure 31 shows a titration curve generated by adding concentrated sodium hydroxide to a high solids oxidized liquor. It is apparent that no sharp "gel point" exists, but rather that the high viscosity disappears gradually with increasing alkali addition. If sufficient alkali is added, the viscosity drops below that of unoxidized liquor. Of course, some of the reduced viscosity is explicable in terms of the reduced lignin/total solids ratio (at constant total solids) as alkali is added. However, the decline is greater than that attributable to the dilution effect.

It is interesting to note that the viscosity change due to HIBLOX goes beyond that attributable to the pH change as well. The HIBLOX liquor with a pH of 11.6 had a viscosity of 100,000 cp. However, a sample of unoxidized liquor had a viscosity of 1150 cp at the same pH, although some precipitated lignin was evident as small clumps in the liquor. Undoubtedly, chemical changes in the lignin were responsible for this behavior.

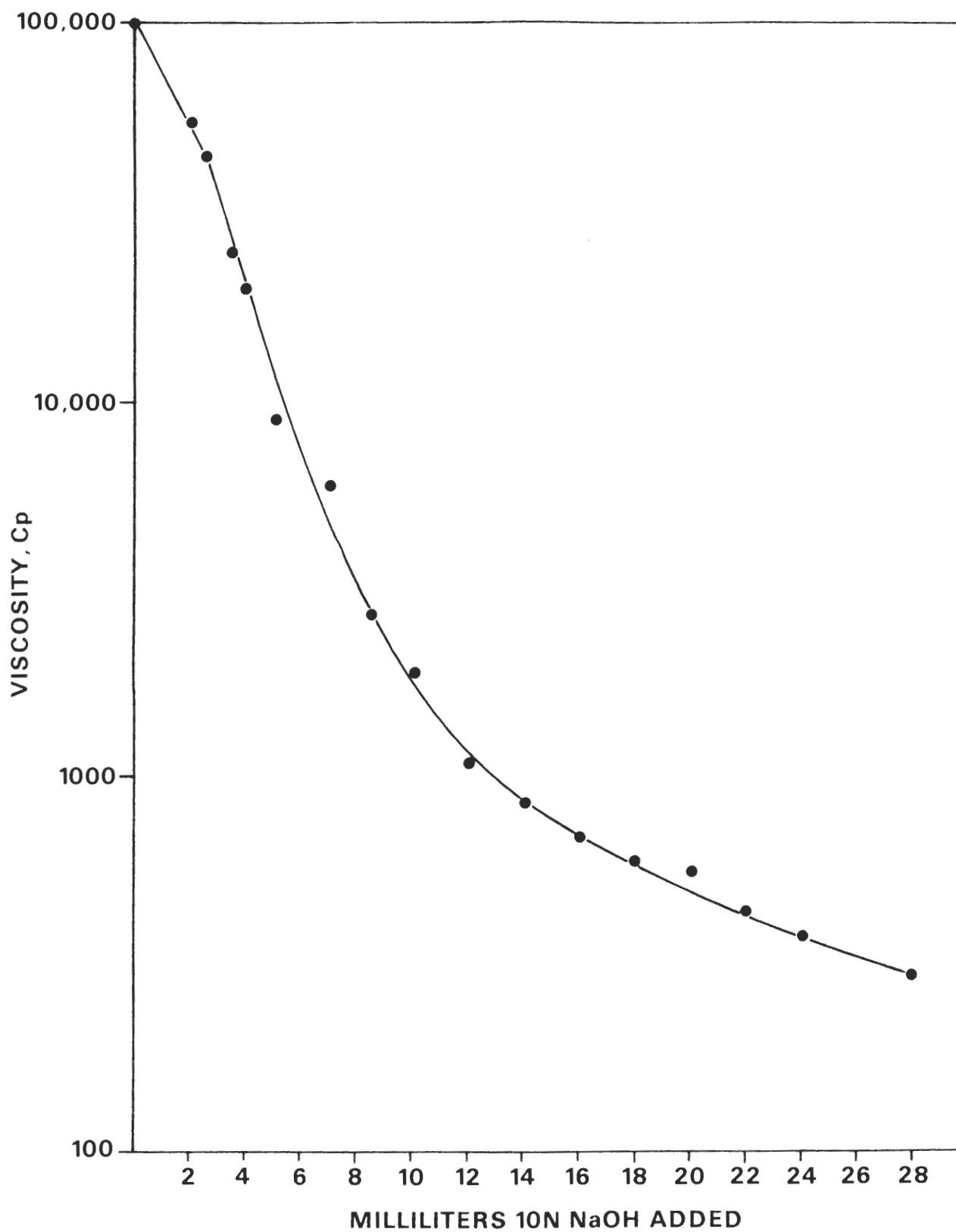


Figure 31. Effect of alkali addition on viscosity of oxidized liquor at 63% solids.

The molecular size distribution of an oxidized liquor (9.3% TOD reduction) was compared to that of the unoxidized liquor using HPLC. The average molecular size of the lignin in the oxidized liquor was larger than that of the unoxidized liquor. It appears either that the oxidation primarily degraded low molecular weight species or that condensation reactions took place during oxidation that increased the molecular weight of the lignin that was not degraded to low molecular weight acids. Given the dissociation of ionizable groups in alkali and the additional ionizable groups in oxidized lignin, the size differential could be enhanced in black liquor. These phenomena might explain the surprisingly high viscosity of high solids HIBLOX liquors even when the pH was sufficient to prevent gelling.

#### Other Property Changes

In addition to affecting liquor rheology and precipitation behavior, HIBLOX caused numerous less significant property changes. Among the properties changed were liquor solids content, odor, and color. Although these changes were of minor importance relative to the rheology change, they could be of some importance to the evaluation of the process.

HIBLOX caused a change in liquor solids content. The change in liquor solids was equivalent to 100% incorporation of the oxygen into the liquor solids. The measured change in solids was less than that associated with 100% incorporation when drying at 105°C but reached the higher level when drying under vacuum at 48°C. The lower solids at 105°C was due to thermal degradation of bicarbonate in the oxidized liquor, causing the loss of volatile material.

A second minor property change was the loss of the characteristic odor of black liquor during oxidation. The oxidized liquor exhibited a somewhat sweet

odor as opposed to the normal hydrogen sulfide odor. The off-gas from the reactor had the normal pungent odor, indicating some malodorous compounds did reach the gaseous phase.

Finally, the color of HIBLOX liquor was much darker than that of normal liquor. This color change was not apparent at normal solids contents. However, upon dilution to extremely low solids ( $\approx$  100 ppm liquor solids), the unoxidized liquor became much lighter than the oxidized liquor.

## CONCLUSIONS

A description of the chemistry, kinetics, and postoxidation properties associated with the oxidation of black liquor in the 5-10% TOD reduction range has been completed in accordance with the stated thesis objectives. In addition, the dependence of the liquor rheological properties on pH has been demonstrated. The conclusions pertinent to each area of research are detailed below.

### CHEMISTRY

HIBLOX caused significant chemical changes in both the inorganic and organic fractions of the black liquors. The inorganic sulfur was oxidized sequentially from sulfide to thiosulfate to sulfate at increasing extents of reaction. Full conversion of sulfide to thiosulfate occurred in all cases, and full conversion to sulfate required in excess of 10% TOD reduction. The extent of oxidation necessary for full conversion to sulfate was shown to be highly dependent on the initial sulfide concentration.

The reactions involving the organic fraction led to low molecular weight acids. Among the products were acetic acid, formic acid, lactic acid, oxalic acid, and carbonic acid (all as sodium salts). Considering both the formation of organic acids and the consumption of alkali during oxidation of the inorganics, an acidification equivalent to the addition of 1.15-1.20 moles of monoprotic acid/mole oxygen consumed occurred during oxidation. Acidification of the oxidized liquor followed by HPLC indicated HIBLOX caused substantial degradation of the high molecular weight lignin, and thus a large percentage of the observed products originated from this fraction. However, the carbohydrates were also a potential source of several of the observed products.

## KINETICS

The kinetics of HIBLOX were shown to be expressable in terms of a single liquor parameter, TOD, and to fit a kinetic model involving successive first order reactions with respect to this parameter. The first reaction mainly involved the oxidation of the sulfide in the liquor to thiosulfate. When this reaction was complete the remaining liquor TOD was reduced by oxidative-alkali reactions which again could be expressed as first order with respect to TOD.

Upon detailed examination the rate of the first reaction of the kinetic model was found to be dependent on both temperature and sulfide content and to exhibit zero order followed by first order dependence with respect to TOD at high sulfide concentration. At high sulfide concentration the first reaction yielded an activation energy of 4300 calories/gram mole, about half that found for the aqueous oxidation of sulfide at lower concentrations. The reduced temperature dependence was due to mass transfer rate limitations which occurred at high sulfide levels. At lower sulfide levels the rate of reaction was relatively slow and dependent on sulfide concentration.

The second reaction of the kinetic model was slower in terms of TOD consumption and more temperature dependent. Activation energies of 6900 and 7600 calories/gram mole were calculated for this reaction, using different liquor batches. The rate of this reaction was not found to be particularly dependent on the concentration of a single liquor species.

The rate of this reaction was affected by a factor other than the TOD reduction. The reduction in reaction rate as TOD was consumed could also be attributed to the pH decline which occurred during oxidation and its effect on



lignin stability and the rate of alkali promoted reactions. Buffering due to high carbonate levels obscured the effect of initial alkali level on reaction rate by minimizing pH differences during the second reaction of the model.

#### POSTOXIDATION PROPERTIES

HIBLOX lead to a product which exhibited normal behavior at low solids but gelled at higher solids levels. The gelling problem was traced to destabilization of the colloidal lignin. The destabilization of the colloidal lignin was in turn traced to the lowering of the liquor pH caused by the formation of the low molecular weight acids.

The gelling tendency could be overcome by the addition of alkali. The elimination of the gelling tendency was gradual as alkali was added, and the amount of alkali needed to prevent gelation was dependent on both the initial liquor alkali level and the extent of TOD reduction in a particular trial. Using 30% sulfidity white liquor, approximately 0.5 gram of alkali solids/gram oxygen consumed was necessary to restore acceptable liquor properties for a typical black liquor.

## SUGGESTIONS FOR FUTURE WORK

A characterization of the key phenomena associated with HIBLOX has now been developed. At this point the knowledge of reaction chemistry, kinetics, and postoxidation properties can be used to reach a decision concerning the likely technical and economic feasibility of the process. The HIBLOX process must be compared to other methods available for gaining incremental capacity and the most promising approach chosen for further research. Should HIBLOX present the most viable approach, further development will be necessary.

Analysis of the burnability of HIBLOX liquors would be the next logical research project. Currently, nothing is known about how the oxidized liquor would behave in a recovery furnace. The determination of acceptable burnability characteristics for HIBLOX liquors would establish the technical viability of the process, although economic considerations still might preclude its implementation.

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APPENDIX I

CALIBRATION OF EXPERIMENTAL EQUIPMENT

Before beginning the HIBLOX trials the experimental equipment was calibrated. Those pieces which were not functioning properly were adjusted to ensure proper performance. The wet gas meter was calibrated vs. a dry gas meter and found to be accurate within 3%. The chart recorder and oxygen analyzer were calibrated using a dc voltage standard. The pressure gages were calibrated vs. a dead weight tester and found to be accurate within 5 psi. Finally, the rpm meter was calibrated vs. a hand held tachometer and found to be accurate within 10 rpm's.

## APPENDIX II

### CALCULATION OF OXYGEN CONSUMPTION

#### APPROACH

The oxygen consumed during each trial was calculated as a function of time via a mass balance over the reactor system. The balance was based on the use of nitrogen as a tie-element. The oxygen consumed was calculated using the proper equations for incremental gas volumes passing through the wet gas meter. The total oxygen consumed in a given trial was the sum of the consumptions over each increment. The approach taken in constructing the balance is shown below.

#### Nitrogen Balance

$$\text{accumulation} = \text{in-out}$$

since there is no generation or consumption.

The nitrogen-out was calculated from the experimental data utilizing the average nitrogen concentration over each increment, and the accumulation was calculated from the outlet concentration and reactor volume with the assumption of a well mixed gas phase. The nitrogen-in was the sum of the other two quantities.

#### Oxygen Balance

$$\text{accumulation} = \text{in-out-consumption}$$

The oxygen-out was calculated from the experimental data in a manner similar to the nitrogen-out calculation. The oxygen-in was  $21/79 \times \text{nitrogen-in}$ , and the accumulation of oxygen was  $-1 \times \text{the nitrogen accumulation}$ . The oxygen consumed was then directly calculated from the other quantities.



The general shape of the outlet oxygen concentration curves is shown in Fig. 32. From time zero to some time  $t_1$  the oxygen concentration was always zero due to the time lag caused by the condenser, reaction gas volume, and piping. The magnitude of the lag was dependent on factors such as reactor pressure and gas flow rate. Adjustment was made for the time lag in the mass balance calculations.

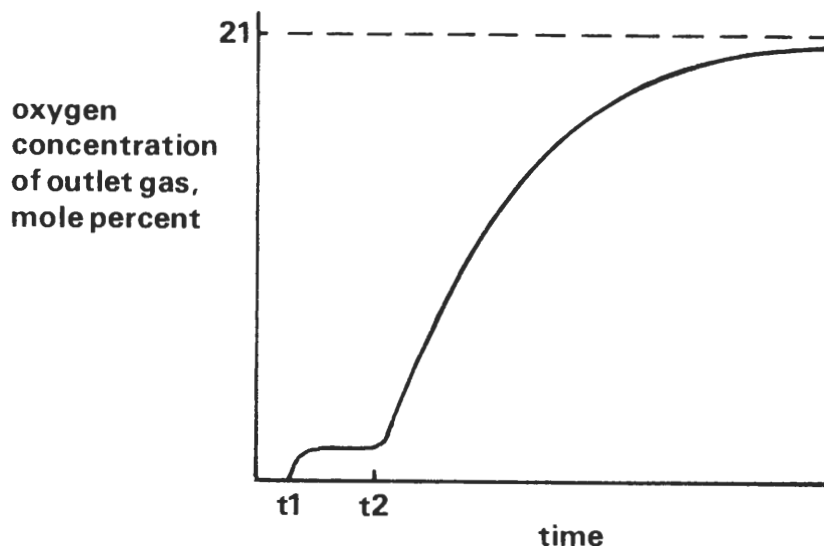


Figure 32. Typical oxygen concentration of outlet gas vs. time curve.

From Fig. 32 it is apparent that the most rapid changes in outlet gas oxygen concentration occurred in the early stages of the trials. For this reason the gas volume increments used for the mass balance calculations were set at  $0.2 \text{ ft}^3$  up to a gas volume of  $2 \text{ ft}^3$  at  $0.5 \text{ ft}^3$  thereafter. In this manner error caused by utilizing the average oxygen concentration in the oxygen out term was minimized.

#### COMPUTER PROGRAM

A simple program was written to perform the computations necessary for the mass balance. The same program was used for the calculation of oxygen consumption

in every trial with the parameters that varied being entered each time the program was used. The program is shown below.

XBLOX/7 PROGRAM FOR OXYGEN CONSUMPTION DURING HIBLOX

```
100  3 RESET FREE
200  FILE 5(KIND=REMOTE,MYUSE=10)
300  FILE 6(KIND=PRINTER)
400  WRITE(5,123)
500  123  FORMAT('INPUT PR,TR,TWGM,PBARO,PH2O,VTOT,PAR,TOD')
600  READ(5,/)PR,TR,TWGM,PBARO,PH2O,VTOT,PWR,TOD
700  A1=0.0
800  VWGM=0.0
810  XYZ=0.0
900  VR=0.016
1000 C1=0.0
1100 DO 1 VWGM=.2,2,.2
1200 WRITE(5,2)
1300  2   FORMAT("INPUT P01,ABC")
1400 READ(5,/)P01,ABC
1500 A1=(VR*144.*(PR-PWR)*(ABC-XYZ))/(1545.*TR)
1600 A2=-A1
1700 O2=(PBARO-PH2O)*0.2*14.7*144.*(1.00-P01)/(760.*1545.*TWGM)
1800 F2=O2+A2
1900 F1=21./79.*F2
2000 O1=(PBARO-PH2O)*0.2*14.7*144.*P01/(76.0*1545.*TWGM)
2100 C1=C1+F1-O1-A1
2200 GC1=32.*C1*454.
2210 XYZ=ABC
2300  1   WRITE(6,/)VWGM,GC1,A1,A2,O2,F2,F1,O1,C1
2500 DO 3 VWGM=2.5,VTOT,.5
2600 WRITE(5,4)
2700  4   FORMAT('INPUT P01,ABC')
2800 READ(5,/)P01,ABC
2900 A1=(VR*144.*(PR-PWR)*(ABC-XYZ))/(1545.*TR)
3000 A2=-A1
3100 O2=(PBARO-PH2O)*0.5*14.7*144.*(1.00-P01)/(760.*1545.*TWGM)
3200 F2=O2+A2
3350 F1=21./79.*F2
3400 O1=(PBARO-PH2O)*0.5*14.7*144.*P01/(760.*1545.*TWGM)
3500 C1=C1+F1-O1-A1
3600 GC1=32.*C1*454.
3610 XYZ=ABC
3700  3   WRITE(6,/)VWGM,GC1,A1,A1,O2,F2,F1,O1,C1
3900 PTODR=100.*GC1/TOD
4000 WRITE(6,/)PTODR
4100 END
```

SYMBOLS

PR	=	reactor pressure, psia
TR	=	reactor temperature, degrees Rankin
TWGM	=	wet gas meter temperature, degrees Rankin
PBARO	=	barometric pressure after correction for pressure drop across wet gas meter, mm mercury
PH2O	=	partial pressure water in outlet gas, mm mercury
VTOT	=	total gas volume thru wet gas meter, cubic feet
PWR	=	partial pressure water in reactor, psia
VR	=	reactor volume, cubic feet
C1	=	oxygen consumed, pound moles
PO1	=	oxygen concentration at VWGM = .1, .3, .5...1.9; 2.25, 2.75...VTOT-.25
ABC	=	oxygen concentration at VWGM = .2, .4, .6 ...2; 2.5, 3, 3.5...VTOT
XYZ	=	dummy variable
A1	=	oxygen accumulation over incremental gas volume, pound moles
A2	=	nitrogen accumulation over incremental gas volume, pound moles
O2	=	nitrogen out over incremental gas volume, pound moles
F2	=	nitrogen in over incremental gas volume, pound moles
F1	=	oxygen in over incremental gas volume, pound moles
O1	=	oxygen out over incremental gas volume, pound moles
GC1	=	oxygen consumed, grams
TOD	=	total oxygen demand, grams
PTODR	=	percent reduction in TOD
VWGM	=	gas volume thru wet gas meter, cubic feet

## TESTING OF PROGRAM

The validity of the chosen approach was established by running "blanks" using water rather than black liquor as the coreactant. Air was passed through the water per the standard experimental procedure under varying conditions and the "consumption" calculated. In these cases consumption of zero grams was the proper result.

The results of several runs are shown in Table 35. The maximum oxygen consumption was calculated to be 0.12 gram. Compared to the magnitude of the liquor TOD's utilized in the experiments, this error was insignificant.

Table 35. Calculated oxygen consumption for blank trials.

Temperature, °C	Pressure, psia	Calculated Oxygen Consumption, grams
100	114.7	-0.02
130	114.7	-0.02
150	214.7	-0.03
177	314.7	-0.12

### APPENDIX III

#### EXPERIMENTAL CONDITIONS AND OXYGEN CONCENTRATION VS. TIME DATA

The charts of this appendix show the experimental conditions utilized for each trial discussed in the text and the outlet gas oxygen concentration as a function of the volume of gas through the wet gas meter. The oxygen consumed as a function of time was then calculable from the gas flow rate. The liquor batch and trial numbers correspond to those detailed in IPC Laboratory Notebooks No. 3346 and 3619. The data for each trial were used with the computer program of Appendix II to generate oxygen consumption vs. time data. Subtracting the oxygen consumption from the initial liquor TOD gave the TOD vs. time data used in the kinetic model.

Liquor Batch No. 2, Trial No. 1

PR = 214.7	PBARO = 739.0	PWR = 67
TR = 762	PH2O = 22.5	Q = 2
TWGM = 535	VTOT = 3	TOD = 129.3

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.2	1.6
2.8	0.1	17.5	1.7
4.3	0.2	17.6	1.8
4.8	0.3	17.7	1.9
5.2	0.4	17.8	2.0
6.6	0.5	17.9	2.25
8.2	0.6	17.9	2.5
9.6	0.7	17.9	2.75
11.9	0.8	17.9	3.0
13.3	0.9		
14.6	1.0		
15.2	1.1		
15.7	1.2		
15.9	1.3		
16.3	1.4		
16.6	1.5		

Liquor Batch No. 2, Trial No. 2

PR = 214.7	PBARO = 723.6	PWR = 67
TR = 762	PH2O = 23.2	Q = 2
TWGM = 536	VTOT = 3	TOD = 127.6

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	16.5	1.6
2	0.1	16.8	1.7
2.3	0.2	17.0	1.8
2.6	0.3	17.2	1.9
2.9	0.4	17.3	2.0
3.4	0.5	17.5	2.25
4.7	0.6	17.75	2.5
6.3	0.7	17.9	2.75
8.4	0.8	17.9	3.0
10.4	0.9		
11.7	1.0		
12.5	1.1		
13.8	1.2		
15.0	1.3		
15.75	1.4		
16.1	1.5		

Liquor Batch No. 2, Trial No. 3

PR = 214.7	PBARO = 743	PWR = 67
TR = 762	PH2O = 21.0	Q = 2
TWGM = 533	VTOT = 3	TOD = 136.4

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	15.7	1.6
2.5	0.1	16.0	1.7
2.7	0.2	16.3	1.8
3.2	0.3	16.5	1.9
3.75	0.4	16.7	2.0
4.7	0.5	17.0	2.25
6.25	0.6	17.2	2.5
8.7	0.7	17.5	2.75
10.6	0.8	17.9	3.0
11.0	0.9		
13.0	1.0		
14.1	1.1		
14.4	1.2		
14.9	1.3		
15.1	1.4		
15.4	1.5		

Liquor Batch No. 2, Trial No. 4

PR = 214.7	PBARO = 739.3	PWR = 67
TR = 762	PH2O = 20.3	Q = 2
TWGM = 532	VTOT = 2	TOD = 134.4

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	16.5	1.6
1.9	0.1	16.7	1.7
2.25	0.2	16.75	1.8
2.8	0.3	16.75	1.9
3.4	0.4	16.75	2.0
4.4	0.5		
6.2	0.6		
9.0	0.7		
12.0	0.8		
13.4	0.9		
14.2	1.0		
15.1	1.1		
15.3	1.2		
15.5	1.3		
16.0	1.4		
16.25	1.5		

Liquor Batch No. 2, Trial No. 6

PR = 214.7	PBARO = 735.9	PWR = 39.3
TR = 726	PH2O = 24	Q = 2
TWGM = 537	VTOT = 2.5	TOD = 139.3

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.1	1.6
2.1	0.1	17.3	1.7
2.6	0.2	17.3	1.8
3.5	0.3	17.4	1.9
4.75	0.4	17.4	2.0
6.0	0.5	17.5	2.25
7.25	0.6	17.75	2.5
8.9	0.7		
11.0	0.8		
12.8	0.9		
14.0	1.0		
15.2	1.1		
15.7	1.2		
16.2	1.3		
16.5	1.4		
16.7	1.5		

Liquor Batch No. 2, Trial No. 8

PR = 214.7	PBARO = 748.7	PWR = 67
TR = 762	PH2O = 22.5	Q = 2
TWGM = 535	VTOT = 2	TOD = 138

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	15.25	1.6
2	0.1	15.7	1.7
2.6	0.2	16.0	1.8
3.0	0.3	16.2	1.9
3.6	0.4	16.3	2.0
4.4	0.5		
5.4	0.6		
7.4	0.7		
9.75	0.8		
11.6	0.9		
12.2	1.0		
12.7	1.1		
13.6	1.2		
13.8	1.3		
14.25	1.4		
14.9	1.5		



Liquor Batch No. 1, Trial No. 40

PR = 114.7	PBARO = 733.2	PWR = 39.3
TR = 726	PH2O = 22.5	Q = 4
TWGM = 535	VTOT = 16	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	18.4	1.6
10.25	0.1	18.5	1.7
12.75	0.2	18.5	1.8
13.5	0.3	18.6	1.9
14.0	0.4	18.7	2.0
14.75	0.5	19.0	2.25
15.7	0.6	19.1	2.5
16.25	0.7	19.25	2.75
16.75	0.8	19.3	3.0
17.25	0.9	19.4	3.25
17.6	1.0	19.5	3.5
17.8	1.1	19.5	3.75
18.0	1.2	19.6	4.0
18.1	1.3	19.6	4.25
18.2	1.4		
18.3	1.5		
19.7	4.5	10.0	9.5
19.75	4.75	20.0	9.75
19.8	5.0	20.0	10.0
19.8	5.25	20.0	10.25
19.9	5.5	20.0	10.5
19.9	5.75	20.0	10.75
19.9	6.0	20.0	11.0
19.9	6.25	20.0	11.25
19.9	6.5	20.0	11.5
19.9	6.75	20.0	11.75
19.9	7.0	20.1	12.0
19.9	7.25	20.1	12.25
19.9	7.5	20.1	12.5
19.9	7.75	20.1	12.75
19.9	8.0	20.1	13.0
19.9	8.25	20.1	13.25
20.0	8.5	20.1	13.5
20.0	8.75	20.1	13.75
20.0	9.0	20.2	14.0
20.0	9.25	20.2	14.25
20.2	14.5		
20.2	14.75		
20.2	15.0		
20.2	15.25		
20.2	15.5		
20.2	15.75		
20.2	16.0		

Liquor Batch No. 1, Trial No. 42

PR = 114.7	PBARO = 745.7	PWR = 39.3
TR = 726	PH2O = 21.8	Q = 2
TWGM = 534	VTOT = 12.5	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.25	1.6
8.3	0.1	17.8	1.7
10.75	0.2	17.9	1.8
11.5	0.3	17.9	1.9
12.5	0.4	18.0	2.0
13.5	0.5	18.1	2.25
14.5	0.6	18.3	2.5
15.25	0.7	18.4	2.75
15.75	0.8	18.4	3.0
16.25	0.9	18.5	3.25
16.5	1.0	18.6	3.5
16.75	1.1	18.75	3.75
16.8	1.2	18.9	4.0
16.9	1.3	18.9	4.25
16.9	1.4		
16.9	1.5		
19.0	4.5	19.7	9.5
19.1	4.75	19.75	9.75
19.2	5.0	19.75	10.0
19.25	5.25	19.8	10.25
19.3	5.5	19.8	10.5
19.4	5.75	19.8	10.75
19.4	6.0	19.8	11.0
19.5	6.25	19.9	11.25
19.5	6.5	19.9	11.5
19.6	6.75	19.9	11.75
19.6	7.0	20.0	12.0
19.7	7.25	20.0	12.25
19.7	7.5	20.0	12.5
19.7	7.75		
19.7	8.0		
19.7	8.25		
19.7	8.5		
19.7	8.75		
19.7	9.0		
19.7	9.25		

Liquor Batch No. 1, Trial No. 44

PR = 114.7	PBARO = 739.9	PWR = 14.7
TR = 672	PH2O = 20.0	Q = 2
TWGM = 533	VTOT = 7.5	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	18.25	1.6
8.75	0.1	18.5	1.7
10.0	0.2	18.5	1.8
13.0	0.3	18.7	1.9
14.0	0.4	18.75	2.0
15.0	0.5	19.0	2.25
15.75	0.6	19.25	2.5
16.3	0.7	19.25	2.75
16.75	0.8	19.4	3.0
16.9	0.9	19.5	3.25
17.1	1.0	19.6	3.5
17.2	1.1	19.7	3.75
17.5	1.2	19.75	4.0
17.8	1.3	19.75	4.25
18.0	1.4		
18.2	1.5		
19.75	4.5		
19.75	4.75		
19.8	5.0		
19.8	5.25		
19.9	5.5		
19.9	5.75		
19.9	6.0		
19.9	6.25		
19.9	6.5		
19.9	6.75		
19.9	7.0		
20.0	7.25		
20.0	7.5		

Liquor Batch No. 1, Trial No. 46

PR = 214.7	PBARO = 750.2	PWR = 69
TR = 672	PH2O = 20.3	Q = 4
TWGM = 532	VTOT = 9.0	TOD = 211.2

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	16.25	1.6
5.5	0.1	16.4	1.7
8.2	0.2	16.5	1.8
9.75	0.3	16.6	1.9
10.8	0.4	16.7	2.0
11.8	0.5	17.0	2.25
12.5	0.6	17.2	2.5
13.4	0.7	17.4	2.75
14.3	0.8	17.4	3.0
14.75	0.9	17.5	3.25
15.25	1.0	17.5	3.5
15.5	1.1	17.5	3.25
15.75	1.2	17.5	3.5
16.0	1.3	17.5	3.75
16.1	1.4	17.6	4.0
16.2	1.5	17.6	4.25
17.7	4.5		
17.7	4.75		
17.75	5.0		
17.8	5.25		
17.9	5.5		
18.0	5.75		
18.0	6.0		
18.0	6.25		
18.1	6.5		
18.1	6.75		
18.1	7.0		
18.1	7.25		
18.2	7.5		
18.2	7.75		
18.25	8.0		
18.25	8.25		
18.25	8.5		
18.25	8.75		
18.25	9.0		

Liquor Batch No. 1, Trial No. 47

PR = 214.7	PBARO = 752.5	PWR = 67
TR = 762	PH2O = 20	Q = 4
TWGM = 533	VTOT = 5	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	15.9	1.6
3.75	0.1	16.1	1.7
6.1	0.2	16.2	1.8
8.6	0.3	16.25	1.9
10.25	0.4	16.4	2.0
11.5	0.5	16.6	2.25
12.3	0.6	16.8	2.5
13.3	0.7	17.0	2.75
14.0	0.8	17.0	3.0
14.3	0.9	17.2	3.25
14.75	1.0	17.25	3.5
14.9	1.1	17.25	3.75
15.2	1.2	17.25	4.0
15.3	1.3	17.4	4.25
15.5	1.4		
15.75	1.5		
17.5	4.5		
17.6	4.75		
17.6	5.0		

Liquor Batch No. 1, Trial No. 48

PR = 214.7	PBARO = 753.9	PWR = 69
TR = 762	PH2O = 21.8	Q = 2
TWGM = 534	VTOT = 5.0	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.6	1.6
5.1	0.1	17.6	1.7
8.6	0.2	17.7	1.8
10.3	0.3	17.7	1.9
12.4	0.4	17.75	2.0
13.75	0.5	17.8	2.25
14.75	0.6	18.0	2.5
15.5	0.7	18.1	2.75
16.1	0.8	18.2	3.0
16.3	0.9	18.3	3.25
16.7	1.0	18.5	3.5
17.0	1.1	18.6	3.75
17.1	1.2	18.7	4.0
17.2	1.3	18.8	4.25
17.3	1.4	18.9	4.75
17.5	1.5	18.9	5.0

Liquor Batch No. 1, Trial No. 51

PR = 314.7	PBARO = 738.4	PWR = 39.3
TR = 726	PH2O = 25.5	Q = 2
TWGM = 539	VTOT = 5.0	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.25	1.7
3.6	0.1	17.3	1.8
6.5	0.2	17.4	1.9
9.25	0.3	17.5	2.0
11.2	0.4	17.7	2.25
12.7	0.5	17.75	2.5
13.6	0.6	17.9	2.75
14.75	0.7	18.0	3.0
15.3	0.8	18.0	3.25
15.7	0.9	18.0	3.5
16.1	1.0	18.1	3.75
16.2	1.1	18.2	4.0
16.5	1.2	18.3	4.25
16.6	1.3	18.4	4.5
16.8	1.4	18.5	4.75
17.1	1.5	18.6	5.0
17.2	1.6		

Liquor Batch No. 1, Trial No. 52

PR = 214.7	PBARO = 743.9	PWR = 69
TR = 762	PH2O = 23.2	Q = 4
TWGM = 536	VTOT = 7.0	TOD = 274.3

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.0	2.25
6.3	0.1	17.1	2.5
9.8	0.2	17.2	2.75
12.0	0.3	17.3	3.0
12.9	0.4	17.5	3.25
13.6	0.5	17.7	3.5
14.3	0.6	17.5	3.25
14.8	0.7	17.7	3.5
15.1	0.8	17.8	3.75
15.1	0.9	17.9	4.0
15.3	1.0	18.0	4.25
15.5	1.1	18.1	4.5
15.9	1.2	18.3	4.75
16.1	1.3	18.5	5.0
16.3	1.4	18.6	5.25
16.4	1.5	18.7	5.5
16.5	1.6	18.7	5.75
16.7	1.7	18.7	6.0
16.8	1.8	18.8	6.25
16.9	1.9	18.9	6.5
16.9	2.0	<b>19.2</b>	<b>6.05</b>

Liquor Batch No. 1, Trial No. 53

PR = 114.7	PBARO = 739.9	PWR = 39.3
TR = 726	PH2O = 26.2	Q = 2
TWGM = 540	VTOT = 4.0	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	16.9	1.5
8.25	0.1	16.9	1.6
9.7	0.2	17.0	1.7
11.25	0.3	17.1	1.8
12.25	0.4	17.25	1.9
13.1	0.5	17.4	2.0
13.8	0.6	17.7	2.25
14.6	0.7	17.9	2.5
15.2	0.8	18.0	2.75
15.4	0.9	18.1	3.0
16.0	1.0	18.3	3.25
16.25	1.1	18.4	3.5
16.7	1.2	18.4	3.75
16.7	1.3	18.5	4.0
16.8	1.4		

Liquor Batch No. 1, Trial No. 54

PR = 114.7	PBARO = 740.9	PWR = 39.3
TR = 726	PH2O = 25.5	Q = 2
TWGM = 539	VTOT = 4	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.0	1.6
7.25	0.1	17.2	1.7
9.25	0.2	17.25	1.8
10.75	0.3	17.4	1.9
12.3	0.4	17.5	2.0
13.0	0.5	17.7	2.25
13.75	0.6	17.9	2.5
14.3	0.7	17.9	2.75
15.25	0.8	18.1	3.0
15.6	0.9	18.3	3.25
15.7	1.0	18.4	3.5
16.0	1.1	18.6	3.75
16.25	1.2	18.75	4.0
16.4	1.3		
16.6	1.4		
16.75	1.5		

Liquor Batch No. 1, Trial No. 56

PR = 114.7	PBARO = 738.6	PWR = 39.3
TR = 726	PH2O = 23.2	Q = 2
TWGM = 536	VTOT = 4	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	18.25	1.6
7.0	0.1	18.5	1.7
9.3	0.2	18.6	1.8
11.0	0.3	18.7	1.9
12.5	0.4	18.75	2.0
13.75	0.5	18.9	2.25
14.8	0.6	19.0	2.5
15.5	0.7	19.1	2.75
16.25	0.8	19.2	3.0
17.0	0.9	19.25	3.25
17.3	1.0	19.4	3.5
17.6	1.1	19.5	3.75
17.75	1.2	19.5	4.0
17.75	1.3		
17.75	1.4		
18.1	1.5		

Liquor Batch No. 1, Trial No. 57

PR = 114.7	PBARO = 739.7	PWR = 39.3
TR = 726	PH2O = 23.2	Q = 2
TWGM = 536	VTOT = 4	TOD = 139.8

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.6	1.6
7.75	0.1	17.75	1.7
11.2	0.2	17.75	1.8
12.0	0.3	17.9	1.9
13.1	0.4	18.0	2.0
13.75	0.5	18.1	2.25
14.8	0.6	18.25	2.5
15.3	0.7	18.5	2.75
16.1	0.8	18.6	3.0
16.5	0.9	18.7	3.25
16.8	1.0	18.75	3.5
17.0	1.1	19.1	3.75
17.25	1.2	19.25	4.0
17.3	1.3		
17.5	1.4		
17.5	1.5		



Liquor Batch No. 1, Trial No. 65

PR = 214.7	PBARO = 749.6	PWR = 69
TR = 762	PH2O = 25.5	Q = 2
TWGM = 539	VTOT = 6	TOD = 137

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	15.6	1.6
4.75	0.1	15.6	1.7
7.2	0.2	15.7	1.8
9.4	0.3	15.7	1.9
11.1	0.4	15.8	2.0
12.2	0.5	15.8	2.25
13.25	0.6	15.9	2.5
14.0	0.7	15.9	2.75
14.6	0.8	16.0	3.0
14.9	0.9	16.0	3.25
15.1	1.0	16.1	3.5
15.3	1.1	16.25	3.75
15.4	1.2	16.5	4.0
15.5	1.3	16.75	4.25
15.5	1.4		
15.5	1.5		
16.8	4.5		
17.0	4.75		
17.1	5.0		
17.2	5.25		
17.25	5.5		
17.25	5.75		
17.25	6.0		

Liquor Batch No. 1, Trial No. 69

PR = 114.7	PBARO = 743.6	PWR = 39.3
TR = 726	PH2O = 22.5	Q = 2
TWGM = 535	VTOT = 5	TOD = 144.4

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.3	1.6
8.0	0.1	17.4	1.7
10.4	0.2	17.5	1.8
11.4	0.3	17.6	1.9
12.3	0.4	17.7	2.0
13.3	0.5	17.9	2.25
14.0	0.6	18.0	2.5
14.3	0.7	18.0	2.75
14.8	0.8	18.1	3.0
15.1	0.9	18.25	3.25
15.6	1.0	18.4	3.5
16.1	1.1	18.5	3.75
16.5	1.2	18.5	4.0
16.7	1.3	18.7	4.25
17.0	1.4		
17.1	1.5		
18.75	4.5		
18.9	4.75		
19.1	5.0		

Liquor Batch No. 1, Trial No. 70

PR = 114.7	PBARO = 744.9	PWR = 39.3
TR = 726	PH2O = 21.0	Q = 2
TWGM = 533	VTOT = 5.0	TOD = 144.4

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	17.1	1.6
8.5	0.1	17.2	1.7
11.0	0.2	17.3	1.8
12.2	0.3	17.4	1.9
12.8	0.4	17.5	2.0
13.3	0.5	17.7	2.25
13.9	0.6	17.9	2.5
14.4	0.7	18.0	2.75
14.9	0.8	18.1	3.0
15.4	0.9	18.25	3.25
15.7	1.0	18.4	3.5
16.0	1.1	18.5	3.75
16.4	1.2	18.6	4.0
16.7	1.3	18.7	4.25
16.8	1.4		
16.9	1.5		
18.75	4.5		
18.8	4.75		
18.9	5.0		

Liquor Batch No. 2, Trial No. 5

PR	=	214.7	PBARO	=	736.6	PWR	=	67
TR	=	762	PH2O	=	23.2	Q	=	2
TWGM	=	536	VTOT	=	6	TOD	=	136.4

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	16.3	1.6
2.1	0.1	16.4	1.7
2.4	0.2	16.6	1.8
2.6	0.3	16.6	1.9
3.2	0.4	16.6	2.0
4.4	0.5	16.7	2.25
7.3	0.6	16.75	2.5
8.4	0.7	16.9	2.75
10.4	0.8	17.1	3.0
12.3	0.9	17.25	3.25
13.25	1.0	17.5	3.5
14.0	1.1	18.0	3.75
14.6	1.2	18.2	4.0
15.3	1.3	18.3	4.25
16.1	1.4		
16.2	1.5		
18.5	4.5		
18.5	4.75		
18.5	5.0		
18.6	5.25		
18.6	5.5		
18.6	5.75		
18.6	6.0		

Liquor Batch No. 2, Trial No. 7

PR = 214.7	PBARO = 743.1	PWR = 67
TR = 762	PH2O = 21.8	Q = 2
TWGM = 534	VTOT = 5	TOD = 143.7

Percent Oxygen	VWGM	Percent Oxygen	VWGM
0	0	15.5	1.6
1.8	0.1	15.75	1.7
2.1	0.2	16.0	1.8
2.2	0.3	16.1	1.9
2.8	0.4	16.5	2.0
4.25	0.5	16.75	2.25
5.25	0.6	16.9	2.5
7.1	0.7	17.25	2.75
9.25	0.8	17.4	3.0
11.0	0.9	17.5	3.25
12.25	1.0	17.6	3.5
12.75	1.1	17.75	3.75
14.1	1.2	17.9	4.0
14.5	1.3	18.0	4.25
14.8	1.4		
15.1	1.5		
18.25	4.5		
18.4	4.75		
18.5	5.0		

#### APPENDIX IV

##### TEMPERATURE-TOD REDUCTION LIMITS

Given the previously described asymptotic approach of the outlet gas oxygen concentration toward 21%, it was not possible to run HIBLOX trials aimed at determining temperature-TOD limits to completion, since the time requirement became excessive. Also, the possible error in the oxygen concentration measurement (a maximum of 0.25% oxygen at 25% oxygen full scale) became significant as the outlet gas oxygen concentration neared 21%. To overcome these limitations an alternative manner of estimating the maximum TOD reduction possible as a function of temperature was developed.

For the temperature-TOD reduction limit trials the gas flow rate was set at the minimum possible value the experimental system would allow. This value was 2 cubic feet/hour, the minimum flow rate recommended for the oxygen analyzer by the manufacturer. With the gas flow minimized, the "leveling off" of the oxygen concentration occurred near 10% during the trials. Given this constraint the trials were terminated when the oxygen concentration of the outlet stream reached 20% (at this point the rate of oxygen consumption had slowed to 12.9, 10.5, and 9.6% of its initial value at 100, 130, and 150°C, respectively). The TOD reductions generated in this manner represent conservative estimates, since slightly more oxygen could have been consumed by the liquor given infinite time.

## APPENDIX V

### EFFECT OF REACTION PARAMETERS ON HIBLOX REACTION RATE

In addition to the parameters which significantly affected the HIBLOX reaction rate (liquor solids and sulfide content, reactor temperature and agitator rpm's) many experimental parameters were examined which did not substantially alter the reaction rate. The graphs of this appendix illustrate the fact that a number of parameters, including reactor pressure and surface area, air flow rate, and initial liquor active alkali and trace metal content, did not exert a detectable influence on reaction rate within the ranges examined. In each graph all reaction conditions were constant except those specified.

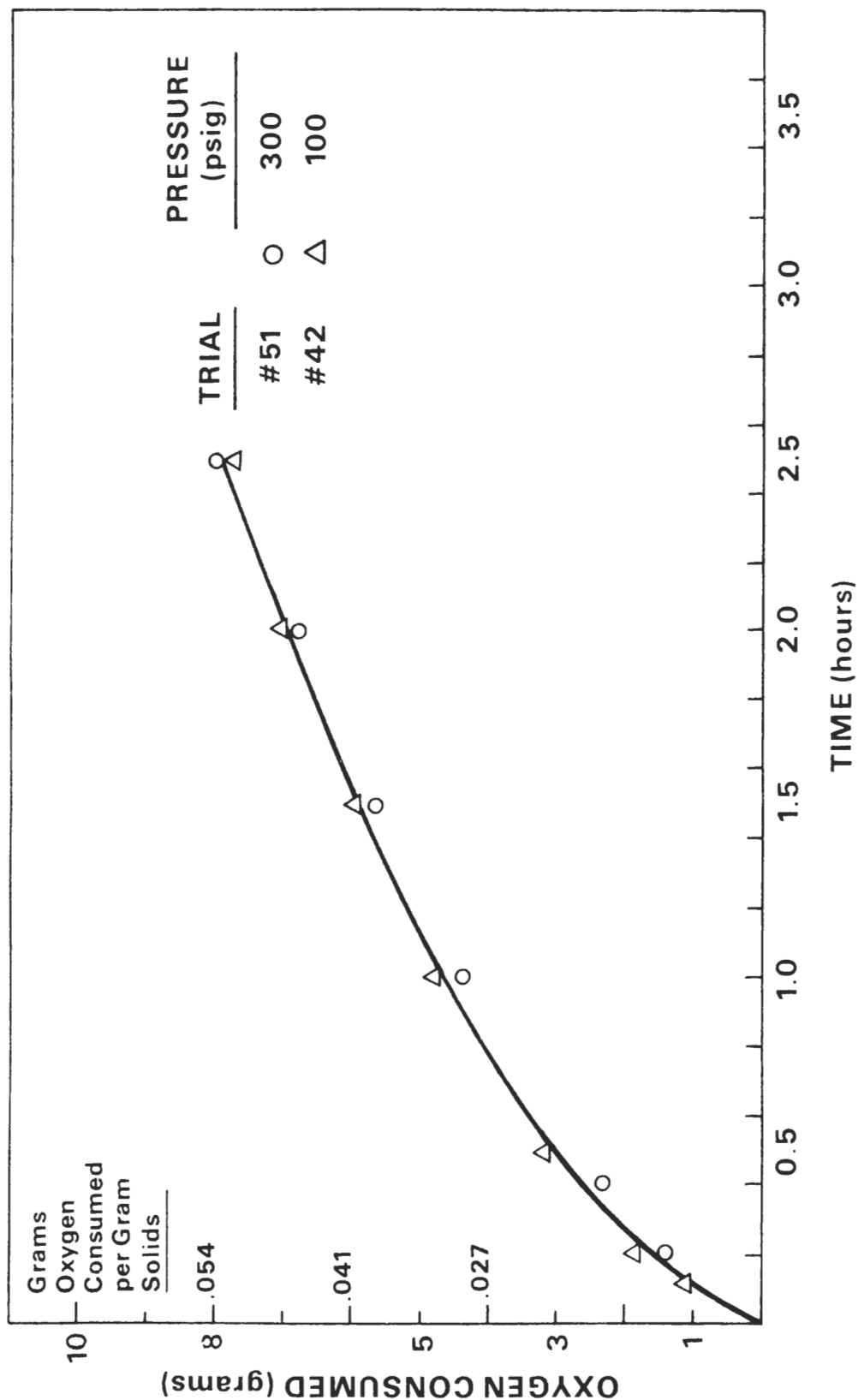


Figure 33. Effect of reactor pressure on oxygen consumption.

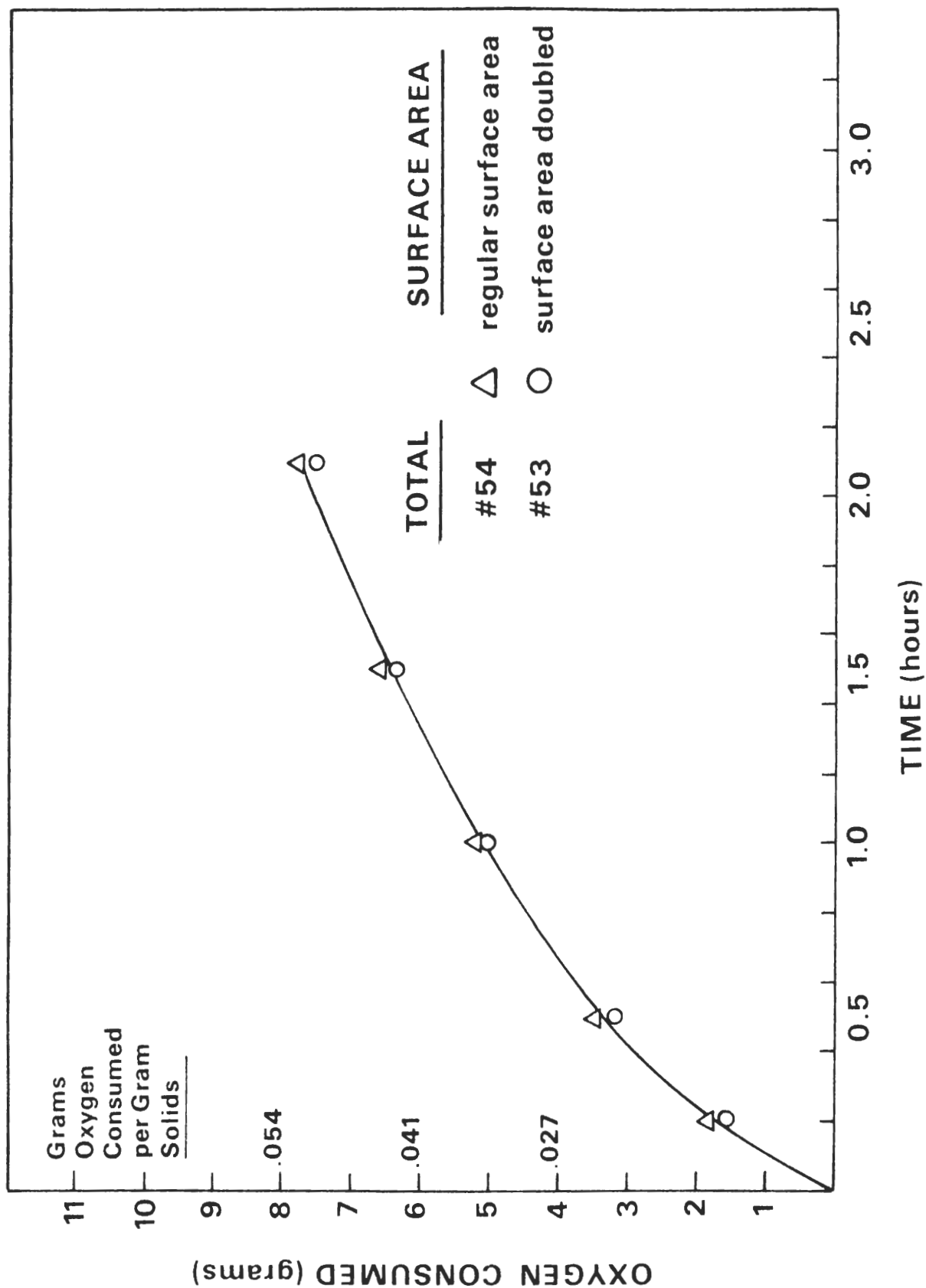


Figure 34. Effect of reactor surface area on oxygen consumption.



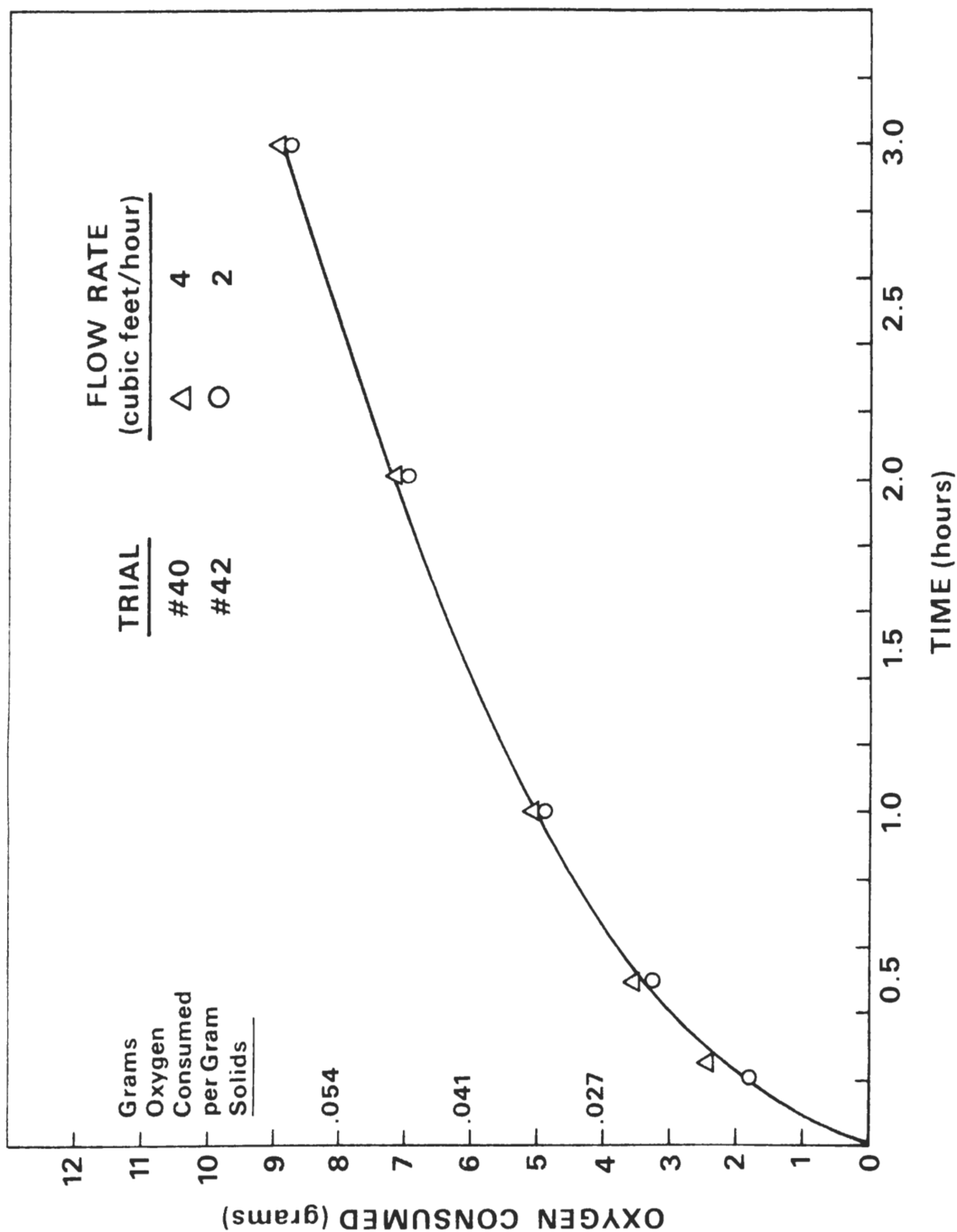


Figure 35. Effect of gas flow rate on oxygen consumption.

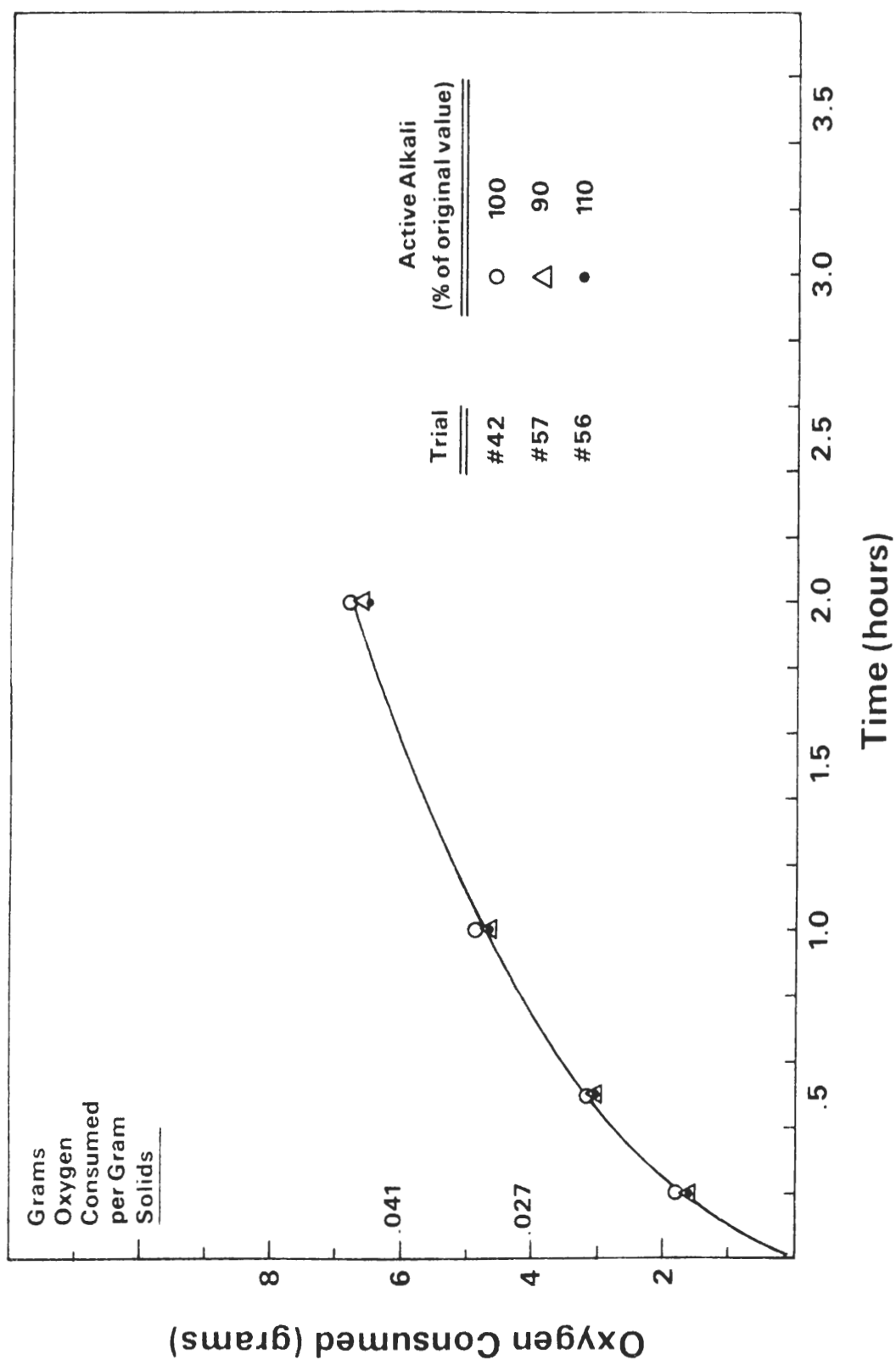


Figure 36. Effect of initial active alkali level on oxygen consumption.

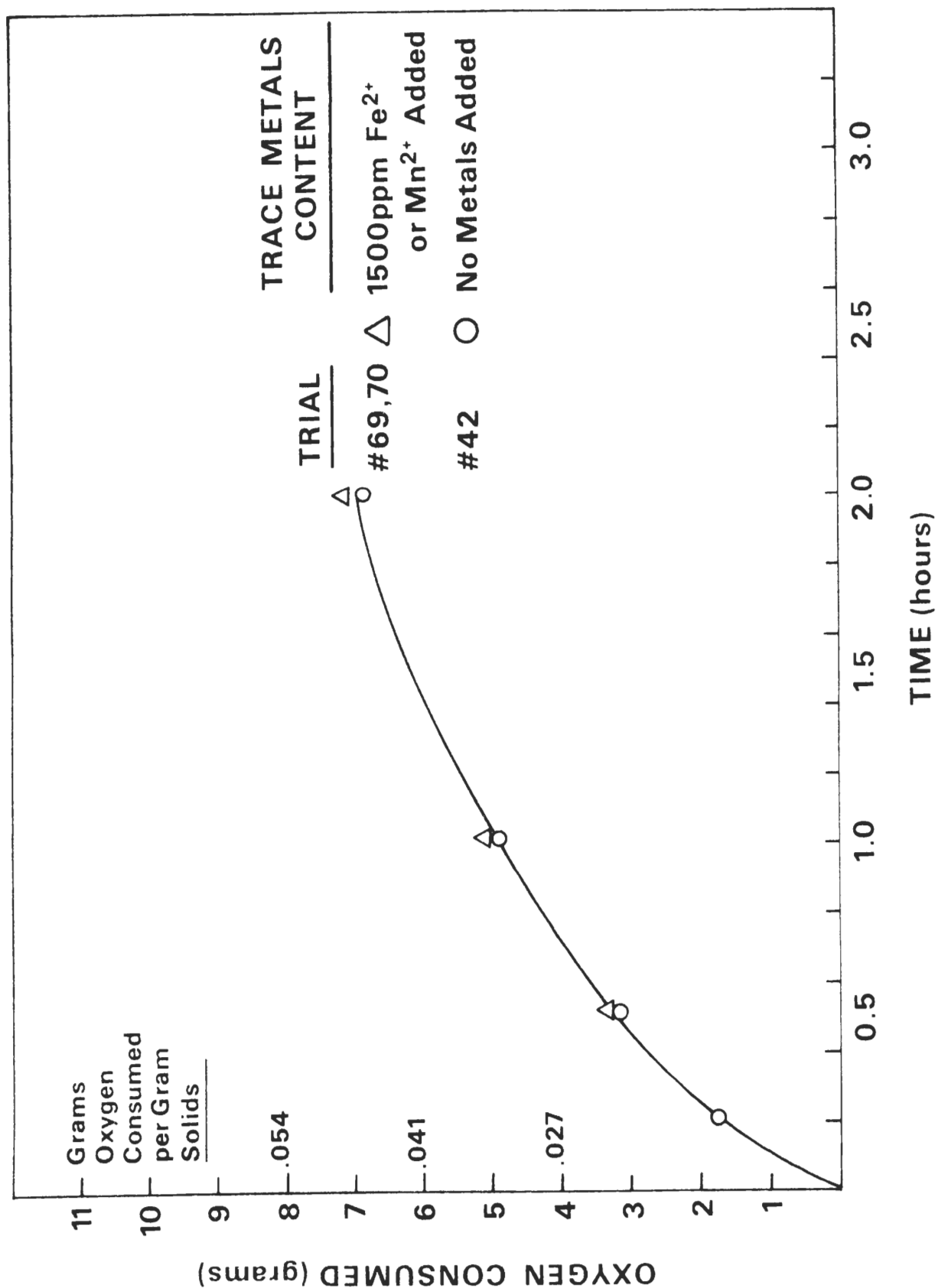


Figure 37. Effect of trace metals content on oxygen consumption.

# APPENDIX VI

## RATE EXPRESSIONS FOR KINETIC ANALYSIS

First order reactions are usually represented mathematically as follows:

$$-\frac{dc}{dt} = kc \quad (6)$$

c = molar concentration of reactant

k = reaction rate constant, units of reciprocal time

With concentration in grams TOD/liter rather than the conventional moles/liter and k in (hours<sup>-1</sup>) it is apparent that the equation remained dimensionally correct, each side being in grams TOD/liter-hour. Upon rearrangement and integration:

$$k = -2.303 \frac{(\log \text{TOD})_2 - \log (\text{TOD})_1}{t_2 - t_1}$$

The reaction rate constants were then determined from a plot of log TOD vs. time using the standard technique and the suitable times for each rate constant. k<sub>1</sub> values were calculated for TOD reductions up to the point at which a substantial decline in the rate of oxygen consumption became apparent. k\* and k\*\* values were determined from the first and second data points recorded, at times 0.2 and 0.4 hour. k<sub>2</sub> was calculated beginning at the time at which the transition to the slower reaction rate was complete.

The apparent activation energies of the reactions were then calculated from the rate constants. From the Arrhenius Equation:

$$k = k_0 e \{ -E_A/RT \} \quad (8)$$

$k$  = reaction rate constant at a given temperature

$k_0$  = reaction rate constant at base temperature

$E_A$  = activation energy in calories/gram mole

$T$  = temperature in  $^{\circ}\text{K}$

$R$  = universal gas constant.

A plot of  $\ln k$  as a function of temperature has a slope of  $-E/R$  and provided a means of determining the activation energy.

# APPENDIX VII

## METHOD FOR CALCULATION OF UNKNOWN ACIDS IN HIBLOX LIQUOR

The unknown acids (those not detectable by ion chromatography) produced during HIBLOX were determined by an indirect method. Equal amounts (100 mL at 10% solids after dilution) of unoxidized and oxidized liquors were acid titrated using 1N HCl, and the acid consumption due to known constituents as a function of pH was subtracted from the titration curve. The titration curves after subtraction of consumption due to known species were essentially the same until a pH of 7.0 was reached. At pH's below 7, the oxidized liquors consumed more acid, apparently due to acid salts formed during HIBLOX, which accepted protons at the lower pH's.

The consumption due to each species as a function of pH was determined using the equations which govern acid-base equilibria and the pertinent Ka's for each species. The Ka's used for each species are shown in Table 36. For species of sufficient concentration and suitable Ka's, the normal simplifying assumptions were made while the more precise equations were applied where dilute concentrations would result in appreciable error.

Table 36. Acid dissociation constants for titrations.

Species	K <sub>1</sub>	K <sub>2</sub>
Sulfate	Strong	1.2 x 10 <sup>-2</sup>
Thiosulfate	3.5 x 10 <sup>-1</sup>	2.8 x 10 <sup>-2</sup>
Sulfide	5.7 x 10 <sup>-8</sup>	1.2 x 10 <sup>-15</sup>
Sulfite	2.73 x 10 <sup>-2</sup>	6.2 x 10 <sup>-8</sup>
Carbonate	4.6 x 10 <sup>-7</sup>	4.4 x 10 <sup>-11</sup>
Lactate	1.38 x 10 <sup>-4</sup>	--
Formate	2.7 x 10 <sup>-4</sup>	--
Acetate	2.75 x 10 <sup>-5</sup>	--
Oxalate	6.2 x 10 <sup>-2</sup>	6.1 x 10 <sup>-5</sup>

The moles of unknown acids present were considered to be equal to the unaccountable excess moles of HCl required for titration. The additional acids could be formed by breaking phenolic rings in the lignin, formation of acid groups on the C<sub>3</sub> branch of the phenyl propane type units of the lignin, or from the oxidation of the carbohydrates. In any case, the resulting acids would most likely have pK<sub>a</sub>'s in the range of 4-5 and could be expected to accept protons over the pH range of 2-7.

The mechanics of calculating the unknown acids formed during HIBLOX is shown in this appendix for the liquor depicted in Table 19. The total acid consumption as a function of pH for the starting material and the HIBLOX liquor are shown in Fig. 38. The acid consumption after subtraction of the portion attributable to known constituents is shown in Fig. 39. The amount of acid consumption attributable to each species for both liquors is shown in Tables 37 and 38. The manner in which the consumption for each species was derived is shown on the ensuing pages.

The net difference in consumption, 4.6 millimoles, was the increase in unknown acids in 42.54 mL of liquor, since 42.54 mL were necessary to produce 100 mL at 10%. Multiplication of the 4.6 millimoles by the total liquor volume, 600 mL, and division by 42.54 mL yielded the 64.9 total millimoles of unknown acids produced during the trial. This value was reported in the mass balance.

Following the charts showing the method used for calculating the unknown acids in Trial No. 40 is Table 39, which shows the key data used to determine the millimoles of unknown acids in the mass balances for the other trials discussed in the thesis. The total millimoles of acid needed for titration, the consumption due to known species, and the resulting millimoles of unknown acids for each

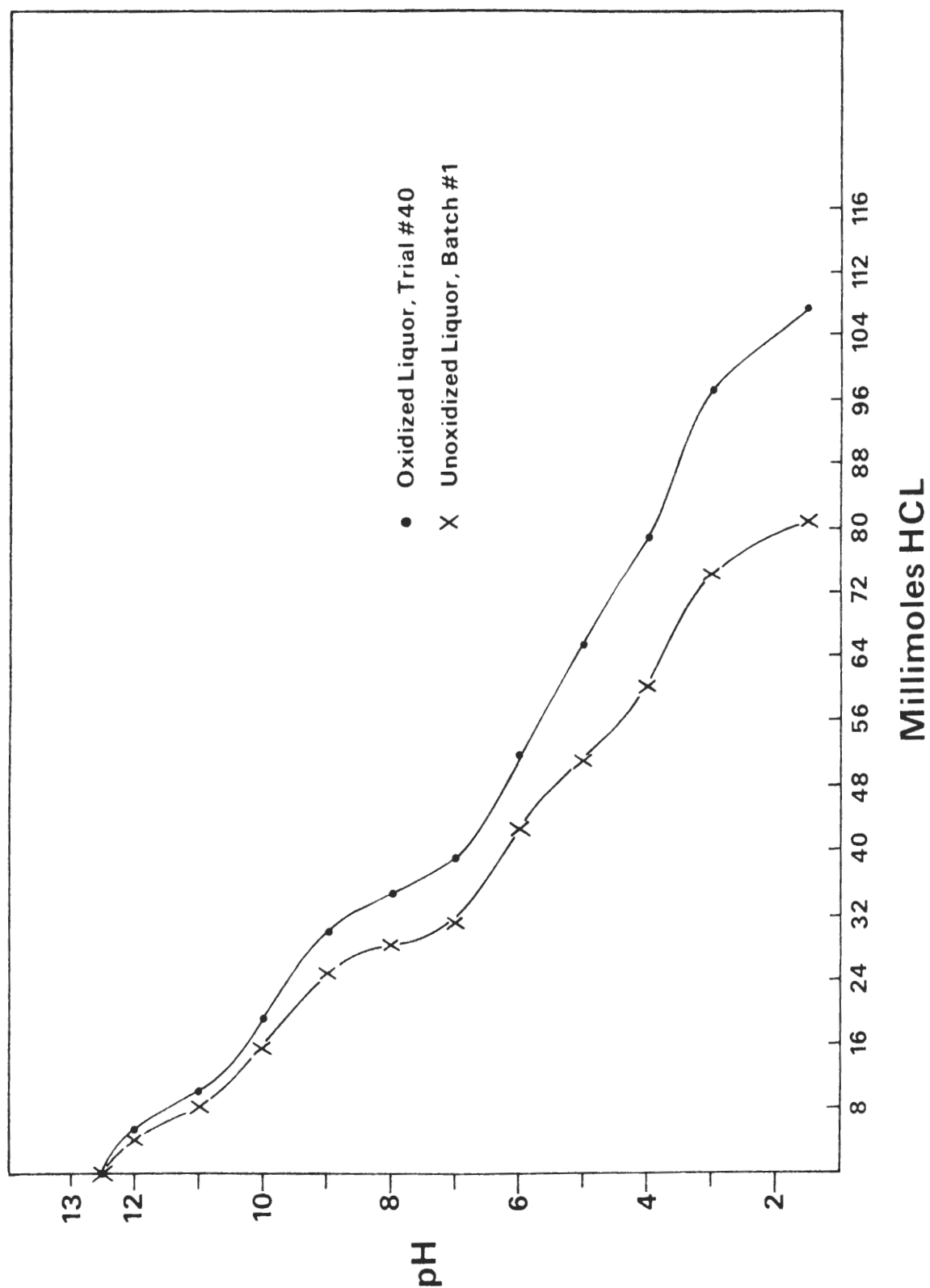


Figure 38. Acid titration of unoxidized and HIBLOX liquors.



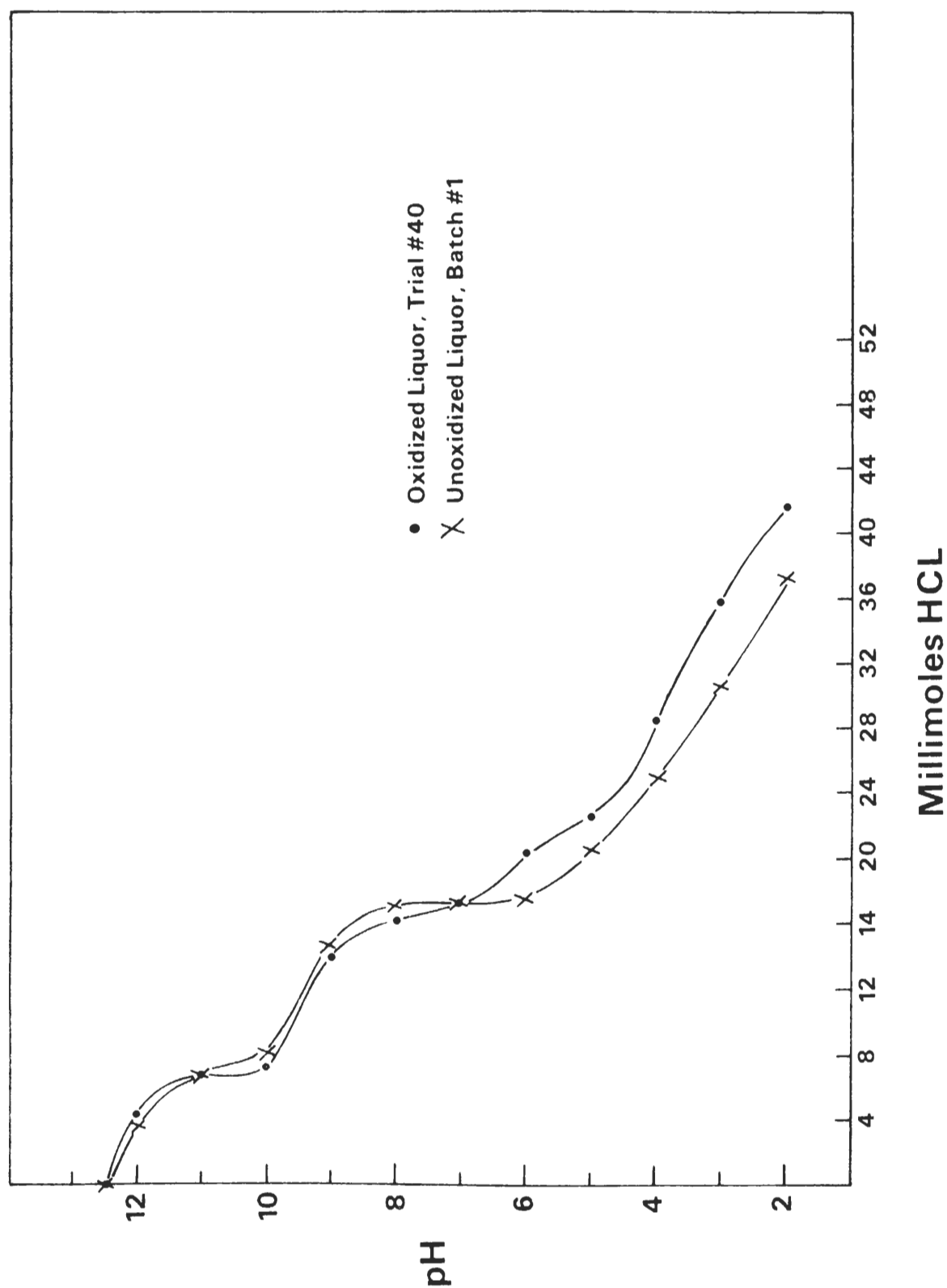


Figure 39. Acid titration of unoxidized and HIBLOX liquors after subtraction of known species.

liquor are shown. These numbers were derived using the previously discussed procedure and were used to generate the unknown acids reported in each mass balance.

Table 37. Acid consumption by known species for unoxidized liquor.

pH	Oxalate	Sulfide	Sulfite	Thiosulfate	Formate
12	0	0	0	0	0
11	0	0	0	0	0
10	0	0	0	0	0
9	0	0	0	0	0
8	0	0.2	0	0	0
7	0	0.8	0.1	0	0
6	0	1.2	0.2	0	0
5	0	1.3	0.2	0	0.4
4	0.2	1.3	0.2	0	2.7
3	0.4	1.3	0.2	0.1	6.2
2	0.5	1.3	0.3	0.9	7.1

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pH	Sulfate	Carbonate	Lactate	Acetate	Total
12	0	0.2	0	0	0.2
11	0	2.1	0	0	2.1
10	0	7.7	0	0	7.7
9	0	10.6	0	0	10.6
8	0	11.3	0	0	11.5
7	0	13.1	0	0	14.0
6	0	18.7	0	0.4	20.5
5	0	21.7	0.3	2.9	26.9
4	0	22.1	1.8	6.9	35.2
3	0.1	22.2	3.8	8.0	42.3
2	0.7	22.2	4.2	8.1	45.3

Table 37 (Continued). Acid consumption by known species for unoxidized liquor.

pH	$\text{Na}_2\text{C}_2\text{O}_4$	$\text{NaHC}_2\text{O}_4$	$\text{H}_2\text{C}_2\text{O}_4$	Millimoles HCl
12	0.4	0	0	0
11	0.4	0	0	0
10	0.4	0	0	0
9	0.4	0	0	0
8	0.4	0	0	0
7	0.4	0	0	0
6	0.4	0	0	0
5	0.3	0.1	0	0.1
4	0.2	0.2	0	0.2
3	0	0.4	0	0.4
2	0	0.5	0.1	0.5

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pH	$\text{Na}_2\text{S}$	$\text{NaHS}$	$\text{H}_2\text{S}$	Millimoles HCl
12	0	1.3	0	0
11	0	1.3	0	0
10	0	1.3	0	0
9	0	1.3	0	0
8	0	1.1	0.2	0.2
7	0	0.5	0.8	0.8
6	0	0.1	1.2	1.2
5	0	0	1.3	1.3
4	0	0	1.3	1.3
3	0	0	1.3	1.3
2	0	0	1.3	1.3

Table 37 (Continued). Acid consumption by known species for unoxidized liquor.

pH	Na <sub>2</sub> SO <sub>3</sub>	NaHSO <sub>3</sub>	H <sub>2</sub> SO <sub>3</sub>	Millimoles HCl
12	0.2	0	0	0
11	0.2	0	0	0
10	0.2	0	0	0
9	0.2	0	0	0
8	0.2	0	0	0
7	0.1	0.1	0	0.1
6	0	0.2	0	0.2
5	0	0.2	0	0.2
4	0	0.2	0	0.2
3	0	0.2	0	0.2
2	0	0.1	0.1	0.3

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pH	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	NaHS <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Millimoles HCl
12	3.6	0	0	0
11	3.6	0	0	0
10	3.6	0	0	0
9	3.6	0	0	0
8	3.6	0	0	0
7	3.6	0	0	0
6	3.6	0	0	0
5	3.6	0	0	0
4	3.6	0	0	0
3	3.5	0.1	0	0.1
2	2.7	0.9	0	0.9

Table 37 (Continued). Acid consumption by known species for unoxidized liquor.

pH	Na <sub>2</sub> SO <sub>4</sub>	NaHSO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	Millimoles HCl
12	1.5	0	0	0
11	1.5	0	0	0
10	1.5	0	0	0
9	1.5	0	0	0
8	1.5	0	0	0
7	1.5	0	0	0
6	1.5	0	0	0
5	1.5	0	0	0
4	1.5	0	0	0
3	1.4	0.1	0	0.1
2	0.8	0.7	0	0.7

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pH	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>	H <sub>2</sub> CO <sub>3</sub>	Millimoles HCl
12	10.9	0.2	0	0.2
11	9.0	2.1	0	2.1
10	3.4	7.7	0	7.7
9	0.5	10.6	0	10.6
8	0	10.9	0.2	11.3
7	0	9.1	2.0	13.1
6	0	3.5	7.6	18.7
5	0	0.5	10.6	21.7
4	0	0.1	11.0	22.1
3	0	0	11.1	22.2
2	0	0	11.1	22.2

Table 37 (Continued). Acid consumption by known species for unoxidized liquor.

pH	Sodium Lactate	Lactic Acid	HCl Consumed
12	4.3	0	0
11	4.3	0	0
10	4.3	0	0
9	4.3	0	0
8	4.3	0	0
7	4.3	0	0
6	4.3	0	0
5	4.0	0.3	0.3
4	2.5	1.8	1.8
3	0.5	3.8	3.8
2	0.1	4.2	4.2

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pH	Sodium Acetate	Acetic Acid	HCl Consumed
12	8.1	0	0
11	8.1	0	0
10	8.1	0	0
9	8.1	0	0
8	8.1	0	0
7	8.1	0	0
6	7.7	0.4	0.4
5	5.2	2.9	2.9
4	1.2	6.9	6.9
3	0.1	8.0	8.0
2	0	8.1	8.1

Table 37 (Continued). Acid consumption by known species for unoxidized liquor.

pH	Sodium Formate	Formic Acid	HCl Consumed
12	7.2	0	0
11	7.2	0	0
10	7.2	0	0
9	7.2	0	0
8	7.2	0	0
7	7.2	0	0
6	7.2	0	0
5	6.8	0.4	0.4
4	4.5	2.7	2.7
3	1.0	6.2	6.2
2	0.1	7.1	7.1

Table 38. Acid consumption by known species for oxidized liquor.

pH	Oxalate	Sulfide	Sulfite	Thiosulfate	Formate
12	0	0	0	0	0
11	0	0	0	0	0
10	0	0	0	0	0
9	0	0	0	0	0
8	0	0	0	0	0
7	0	0	0	0	0
6	0	0	0.1	0	0.1
5	0.1	0	0.2	0	0.6
4	0.6	0	0.2	0	3.8
3	0.8	0	0.2	0.1	8.8
2	1.0	0	0.3	0.4	10.1

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pH	Sulfate	Carbonate	Lactate	Acetate	Total
12	0	0.4	0	0	0.4
11	0	3.3	0	0	3.3
10	0	12.3	0	0	12.3
9	0	17.0	0	0	17.0
8	0	18.1	0	0	18.1
7	0	20.9	0	0.1	21.0
6	0	29.8	0	0.6	30.6
5	0	34.6	0.3	3.8	39.6
4	0	35.3	2.1	8.9	50.9
3	0.4	35.4	4.3	10.3	60.3
2	2.6	35.4	4.8	10.5	65.1



Table 38 (Continued). Acid consumption by known species for oxidized liquor.

pH	$\text{Na}_2\text{C}_2\text{O}_4$	$\text{NaHC}_2\text{O}_4$	$\text{H}_2\text{C}_2\text{O}_4$	HCl Consumed
12	0.9	0	0	0
11	0.9	0	0	0
10	0.9	0	0	0
9	0.9	0	0	0
8	0.9	0	0	0
7	0.9	0	0	0
6	0.9	0	0	0
5	0.8	0.1	0	0.1
4	0.3	0.6	0	0.6
3	0.1	0.8	0	0.9
2	0	0.8	0.1	1.0

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pH	$\text{Na}_2\text{SO}_3$	$\text{NaHSO}_3$	$\text{H}_2\text{SO}_3$	Millimoles HCl
12	0.2	0	0	0
11	0.2	0	0	0
10	0.2	0	0	0
9	0.2	0	0	0
8	0.2	0	0	0
7	0.1	0.1	0	0.1
6	0	0.2	0	0.1
5	0	0.2	0	0.2
4	0	0.2	0	0.2
3	0	0.2	0	0.2
2	0	0.1	0.1	0.3

Table 38 (Continued). Acid consumption by known species for oxidized liquor.

pH	$\text{Na}_2\text{S}_2\text{O}_3$	$\text{NaHS}_2\text{O}_3$	$\text{H}_2\text{S}_2\text{O}_3$	Millimoles HCl
12	1.6	0	0	0
11	1.6	0	0	0
10	1.6	0	0	0
9	1.6	0	0	0
8	1.6	0	0	0
7	1.6	0	0	0
6	1.6	0	0	0
5	1.6	0	0	0
4	1.6	0	0	0
3	1.5	0.1	0	0.1
2	1.2	0.4	0	0.4

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pH	$\text{Na}_2\text{SO}_4$	$\text{NaHSO}_4$	$\text{H}_2\text{SO}_4$	Millimoles HCl
12	0	0	0	0
11	0	0	0	0
10	0	0	0	0
9	0	0	0	0
8	0	0	0	0
7	0	0	0	0
6	0	0	0	0
5	0	0	0	0
4	5.8	0	0	0
3	5.4	0.4	0	0.4
2	3.2	2.6	0	2.6

Table 38 (Continued). Acid consumption by known species for oxidized liquor.

pH	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>	H <sub>2</sub> CO <sub>3</sub>	Millimoles HCl
12	17.3	0.4	0	0.4
11	14.4	3.3	0	3.3
10	5.4	12.3	0	12.3
9	0.7	17.0	0	17.0
8	0	17.3	0.4	18.1
7	0	14.5	3.2	20.9
6	0	5.6	12.1	29.8
5	0	0.8	16.9	34.6
4	0	0.1	17.6	35.3
3	0	0	17.7	35.4
2	0	0	17.7	35.4

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pH	Sodium Lactate	Lactic Acid	HCl Consumed
12	0	0	0
11	0	0	0
10	0	0	0
9	0	0	0
8	0	0	0
7	0	0	0
6	4.9	0	0
5	4.6	0.3	0.3
4	2.8	2.1	2.1
3	0.6	4.3	4.3
2	0.1	4.8	4.8

Table 38 (Continued). Acid consumption by known species for oxidized liquor.

pH	Sodium Acetate	Acetic Acid	HCl Consumed
12	10.5	0	0
11	10.5	0	0
10	10.5	0	0
9	10.5	0	0
8	10.5	0	0
7	10.4	0.1	0.1
6	9.9	0.6	0.6
5	6.7	3.8	3.8
4	1.6	8.9	8.9
3	0.2	10.3	10.3
2	0	10.5	10.5

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pH	Sodium Formate	Formic Acid	HCl Consumed
12	10.3	0	0
11	10.3	0	0
10	10.3	0	0
9	10.3	0	0
8	10.3	0	0
7	10.3	0	0
6	10.2	0.1	0.1
5	9.7	0.6	0.6
4	6.5	3.8	3.8
3	1.5	8.8	8.8
2	0.2	10.1	10.1

Table 39. Titration data for mass balances.

Liquor Batch/Trial	Total mL of Acid for Titration	Consumption Due to Known Species	Total Unknown Acids
1/40	106.9	65.1	41.8
1/44	101.0	61.4	39.6
1/47	112.6	68.7	43.9
1/Unoxidized	82.5	45.3	37.2
2/1	87.2	62.2	25.0
2/2	88.7	62.7	26.0
2/3	88.1	61.1	27.0
2/4	82.0	57.1	24.9
2/5	95.1	65.8	29.3
2/6	81.6	56.6	25.0
2/7	96.5	68.0	28.5
2/Unoxidized	76.0	51.5	24.5