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INDIGESTER BLACK LIQUOR OXIDATION FOR ODOR CONTROL IN KRAFT PULPING

by

W. T. McKean, Jr. and J. S. Gratzl

North Carolina State University
Department of Wood and Paper Science
Raleigh, North Carolina 27607

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EPA Project Officer: R. V. Hendriks

Control Systems Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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ABSTRACT

Laboratory studies have described the major reaction routes, key inhibition reactions and kinetics of methyl mercaptan and dimethyl disulfide during oxidation of black liquor. This provided the basis for helping to explain low oxidation efficiencies with respect to hydrogen sulfide, methyl mercaptan and dimethyl disulfide during black liquor oxidation at temperatures from 60 to 90°C and suggests that high temperature oxidation should be more efficient.

In small scale laboratory flow equipment softwood and hardwood black liquor was oxidized at temperatures between 80 and 170°C. Oxidation at temperatures above 100 to 120°C resulted in efficient oxidation of all three malodorous compounds with no liquor reversion during subsequent storage and distillation. Oxygen consumption was about 125% of theoretical below 140°C but increased to about 200% at 170°C. Application of this approach to batch and continuous digester systems is discussed.

Preliminary experiments show that injection of small amounts of oxygen into the liquor circulation line during the early stage of pulping could increase pulp yield by 1 to 3% depending on the final pulp kappa number. If this yield increase could be obtained in combination with indigester black liquor oxidation, the net costs for odor control in mills using batch digesters would be very attractive.

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CONTENTS

	Page
Abstract	ii
List of Figures	v
List of Tables	vii
Acknowledgements	viii
Sections	
Conclusions	I
Recommendations	3
Introduction	5
A. Background	5
B. Rationale for Indigester Oxidation	16
Objectives	17
Discussion	18
A. Reactions of Methyl Mercaptan and Dimethyl Disulfide in Sodium Hydroxide Solutions	18
1. Kinetics of oxidation of methyl mercaptan in aqueous alkaline solution with molecular oxygen	18
2. Hydrolysis of dimethyl disulfide	21
3. Kinetics of hydrolysis of dimethyl disulfide	23
4. Summary of methyl mercaptan and dimethyl disulfide reactions in aqueous, alkaline solutions	24
B. Reactions of Methyl Mercaptan and Dimethyl Disulfide in Simulated Black Liquor	28
1. Methyl mercaptan oxidation by models compounds featuring certain structures in kraft lignin	28
2. The effect of kraft lignin on the consumption of methyl mercaptan	33

Page

3. Effect of sodium sulfide on the oxidation of methyl mercaptan 40

4. Methyl mercaptan reactions during black liquor oxidation at temperatures below 100°C. 43

5. Methyl mercaptan reactions during black liquor oxidation at temperatures above 100°C 47

C. Summary of Methyl Mercaptan and Dimethyl Disulfide Oxidation Kinetics in Simulated Black Liquor 51

D. Odor Reduction by In-digester Oxidation of Kraft Black Liquor with Oxygen at Temperatures above 80°C 56

1. The influence of sodium sulfide throughout kraft pulping 56

2. In-digester oxidation: Influence on inorganic compounds 61

3. In-digester oxidation: Influence on methyl mercaptan, dimethyl sulfide and dimethyl disulfide 66

4. In-digester oxidation: Influence on pulp yield and pulp properties 70

5. In-digester BLO at variable temperatures 75

E. In-digester Oxidation of Hardwood Black Liquors 84

1. Influence of oxidation on methyl mercaptan, dimethyl sulfide and dimenthyl disulfide 84

2. Influence of Oxidation on Pulp Yield 84

F. Odor Control in Batch and Continuous Digesters 88

G. Possible Pulp Yield Increase in Combination with Odor Control by In-digester Oxidation 91

H. Cost Estimates and Effectiveness of Odor Control by Indigester BLO Compared to Other Control Methods 95

I. Experimental

1. Equipment and Materials 106

2. Procedures 108

FIGURES

		Page
1	Projection of Production of Chemical Pulps in the U. S.	6
2	Major Atmospheric Pollutants Lbs/T	7
3	Pulp Yield as a Function of Lignin Removed	8
4	Modifications of Pulp Mill for Odor Control	12
5	Oxidation of Methyl Mercaptan at Varying pH	20
6	Oxidation-hydrolysis Cycle for Conversion of Methyl Mercaptan to Nonvolatile Product	26
7	Methyl Mercaptan Consumption by Equimolar Amounts of Hydrogen Peroxide, Anthraquinone Beta Sulfonate, o-quinone and 10 psig Oxygen Respectively	31
8	Consumption of Methyl Mercaptan in Aqueous Alkaline Solution with Kraft Lignin Added	35
9	Formation of Dimethyl Disulfide in Alkaline Solution with Kraft Lignin Added	36
10	The Effect of Temperature on the Formation of Dimethyl Disulfide in the Presence of Kraft Lignin	39
11	Oxidation of Methyl Mercaptan with 5 g/ℓ Sodium Sulfide Added	41
12	Consumption of Methyl Mercaptan in Simulated Black Liquor	45
13	Consumption of Methyl Mercaptan in Simulated Black Liquor	48
14	Schematic Outline of Reactions of Methyl Mercaptan during Black Liquor Oxidation	52
15	Composition of Cooking Liquor as a Function of Cooking Time, and Temperature in Regular Kraft Cooking and Liquor Exchange Cooks of Loblolly Pine	58
16	Total Pulp Yield as a Function of Pulp Lignin Content	60
17	The Content of Sodium Sulfide in Black Liquor as a Function of the Amount of Oxygen Injected at a Rate of Injection of 5.3 g of O_2/min.	63

Page

18 Effective Alkali in Black Liquor in Regular Kraft Cooks and Cooks with Injection of Various Amounts of Oxygen at a Rate of 5.3 g of O_2/min. 65

19 Methyl Mercaptan Content in Black Liquor at Various Amounts of Injected Oxygen 68

20 Dimethyl Sulfide Content in Black Liquor at Various amounts of Injected Oxygen 71

21 Tear Factor Versus Breaking Length for Regular Kraft Pulps and Pulps Cooked with the Injection of Oxygen 74

22 Tensile Strength as a Function of Number of Revolutions in the PFI-mill for Regular Kraft Pulps and Pulps Cooked with the Injection of Oxygen 76

23 Representative Sodium Sulfide Oxidation Rates 81

24 Oxygen Consumption for Complete Oxidation of Sodium Sulfide in Black Liquor Oxidation 82

25 Methyl Mercaptan and Dimethyl Disulfide Concentration as a Function of Oxidation Time for Several Oxidation Temperatures 83

26 Methyl Mercaptan Content in Black Liquor from Pulping Red Gum 85

27 Total Pulp Yield as a Function of Kappa Number for Pulping Red Gum 87

28 Pulp Yield as a Function of Lignin Content for Reference Kraft Pulps and Kraft Pulps with Oxygen Pretreatment 94

TABLES

		Page
I	Air Pollutants from Kraft Pulp Mill with No Odor Control	10
II	Ambient Air Odor Thresholds (3)	15
III	Rate Constants for the Oxidation of Methyl Mercaptan	22
IV	Rate Constants for Dimethyl Disulfide Hydrolysis	25
V	Effect of Quantity of Oxygen Injected on the Methyl Mercaptan Content of Black Liquor	69
VI	Total Pulp Yields in Cooks with and without the Injection of Oxygen into the Digester at the End of the Cook	72
VII	Physical Properties of Regular Kraft Pulps and Pulps Produced with the Injection of Oxygen at the End of the Cook	77
VIII	Effect of Injection of Oxygen on Pulp Brightness	78
IX	Total Pulp Yield for Kraft Cooks of Red Gum with and without Oxygen Injection at the End of the Cook Liquor to Wood Ratio 3.6:1, 90 Minutes from 25°C to 170°C	86
X	Effectiveness and Costs for Odor Control in a 500 T/day Kraft Mill	97

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CONCLUSIONS

During black liquor oxidation (BLO) there are complex relationships between lignin, sodium sulfide, methyl mercaptan and dimethyl disulfide which can limit oxidation efficiencies. It is well known that at conventional oxidation temperatures (60-90°C) sodium sulfide in black liquor can be oxidized, but is regenerated during storage and evaporation of the oxidized liquor. The regeneration has been attributed to formation of elemental sulfur during oxidation which later is partially converted back to sulfide in alkaline liquors. The present studies suggest that another type of regeneration occurs. Sulfide reacts with lignin during oxidation and is slowly displaced from the lignin by hydroxide during storage and evaporation resulting in an apparent reversion.

At normal oxidation temperatures mercaptide anion reacts with lignin in an analogous manner and is later also displaced by hydroxide during evaporation. Furthermore, oxidation of mercaptan to dimethyl disulfide suffers an apparent inhibition in the presence of lignin or when the sulfide content of black liquor is greater than about 0.2 g/ℓ. Consequently, black liquor which has been oxidized at normal temperatures contains significant quantities of unoxidized methyl mercaptan and both mercaptan and sulfide are further regenerated during storage and evaporation of the oxidized liquors. Thus, the utility of BLO as an odor control measure at normal oxidation temperatures is limited by these relationships.

However, at temperatures greater than 100 to 120°C black liquor oxidation could be more effective as an odor control measure. Above these temperatures the rates of sulfide and mercaptan oxidation are greatly enhanced relative to rates during normal BLO. Furthermore, the inhibition of mercaptan oxidation by lignin and sulfide becomes negligible. Finally, no reformation of sulfide or mercaptan occurs during storage and evaporation of black liquors which have been

oxidized at temperatures above 120°C. Consequently, the potential for release of odorous substances would be greatly reduced by oxidation at elevated temperatures.

The configuration of a high temperature BLO system would depend on the type of digester. The results of the present work show that at oxidation temperatures of 130-140°C reaction rates are very rapid with oxygen consumption of about 125% of theoretical. Consequently, for continuous digesters the oxidation could be accomplished by direct injection of oxygen into the liquor extraction line before the first flash tank.

For circulation batch digesters redesign of the circulation system would be required to permit liquor circulation during the later stages of pulping. Injection of oxygen into the circulation line near the end of the cook would provide good odor control. In this case oxygen consumption would be somewhat greater because of side reactions which occur at digester temperatures (170°C). Results show that pulp yield and pulp quality are retained if the black liquor is oxidized during the last 30 to 45 minutes of a normal kraft cook producing bleachable grades.

Digester relief and blow gases would need to be combusted since dimethyl sulfide is not oxidized at temperatures below 170°C. Costs for collection and combustion of these low volume gas streams in the lime kiln are reasonable relative to other odor control costs.

Preliminary studies indicate that introduction of small amounts of oxygen into the circulation line of batch digesters early in the pulping cycle could result in some pulp yield increase. If such yield increase could be coupled with the efficient odor control obtained by high temperature BLO in the digester the economic incentive is very attractive. Similar yield increases may be obtained in continuous digesters, though further studies are required to define the operating limits of that system.

RECOMMENDATIONS

The present studies have shown the limitations of conventional black liquor oxidation (BLO) and the possible advantages of high temperature black liquor oxidation in the digester as a method of reducing odor from kraft pulping. These laboratory scale results suggest that high temperature BLO should be more effective than conventional systems at equal or lower cost. Confirmation of these results on a larger scale is required to provide the basis for firm cost estimates. The following work is recommended:

1. Continuous digesters

   High temperature oxidation could be accomplished by injection of oxygen into black liquor extraction lines before the flash tank. A field test should be made using a full scale continuous digester to confirm the extent of odor control and oxygen consumption. If oxidation is done at about 140°C the extraction system should be modified to have a residence time of 5 to 6 minutes between oxygen injection and the time that black liquor enters the first flash tank.

   The modification of extraction system should require a reasonable capital outlay and the major cost for a testing program would be for purchased oxygen. For testing period delivered oxygen could be used so no onsite generation and storage would be required. The total cost for a one month demonstration on a 500 T./day digester would probably be between $20,000 and $40,000 including digester modification, oxygen costs, gas controls, and testing for total reduced sulfur emissions from various sources in the pulp mill.

2. Batch digesters

   Similar field tests should be made using circulation batch digesters. The liquor strainers will probably require extensive modification to

avoid collection of fiber fines and pressure build-up which normally occurs to the later stages of pulping. Some type of wiper arrangement similar to continuous digesters may be required to maintain open strainers and permit adequate circulation rates to oxidize all the black liquor in the digester. Testing would provide confirmations of odor control, oxygen consumption and influence of indigester BLO on the pulp properties.

If odor control can be coupled with an increase in pulp yield, high temperature black liquor oxidation could be very economically attractive. Preliminary studies reported herein have shown that some yield increase can be obtained when small amounts of oxygen have been injected into the liquor circulation line during digester heatup. This yield increase may be the result of carbohydrate stabilization by oxidation of reducing end groups forming alkali stable aldonic acids. The oxidation may be by oxidation with oxygen or polysulfide formed from sodium sulfide in the liquor.

Stabilization will be influenced by the temperature, rate of liquor circulation, rate of oxygen injection, sulfidity and effective alkali of liquor and the rate of diffusion of oxygen or polysulfide into the wood chips. Laboratory studies should be made to determine the influence of these parameters on yield increases. This work would suggest the optimum conditions to obtain maximum yield increase.

INTRODUCTION

A. Background

The growing concern about odor emissions from kraft pulp mills is reflected in numerous studies published in this area over the last decade. This is a natural area for inquirv since the pulp and paper industry comprises a significant portion of total industrial output. Furthermore, of the nearly (250) pulp mills in the United States (126) are kraft mills. The dominant position is also illustrated in terms of production output in Figure 1 (1). Available projections indicate that this position will be maintained at least into the mid 1980's. Consequently, environmental difficulties with the process will be of continued concern and substantial efforts to develop methods for minimizing emissions are well justified.

As a basis for discussion a flow sheet for a "typical" southern kraft mill with minimal odor control is shown in Figure 2. Wood chips are treated with an aqueous solution of sodium hydroxide and sodium sulfide at 170°C for 2 to 4 hours. This treatment degrades and dissolves lignin and some carbohydrates so the recovered fiber amounts to about 45-55% of the original wood. While the pulp yield varies depending on species and pulping conditions, Figure 3 (2) indicates the extent of removal of the classes of wood components as a function of pulp lignin content. At the end of the cook residual pulping liquor is separated, and the pulp is washed.

PROJECTION OF PRODUCTION
OF CHEMICAL PULPS IN THE U. S.

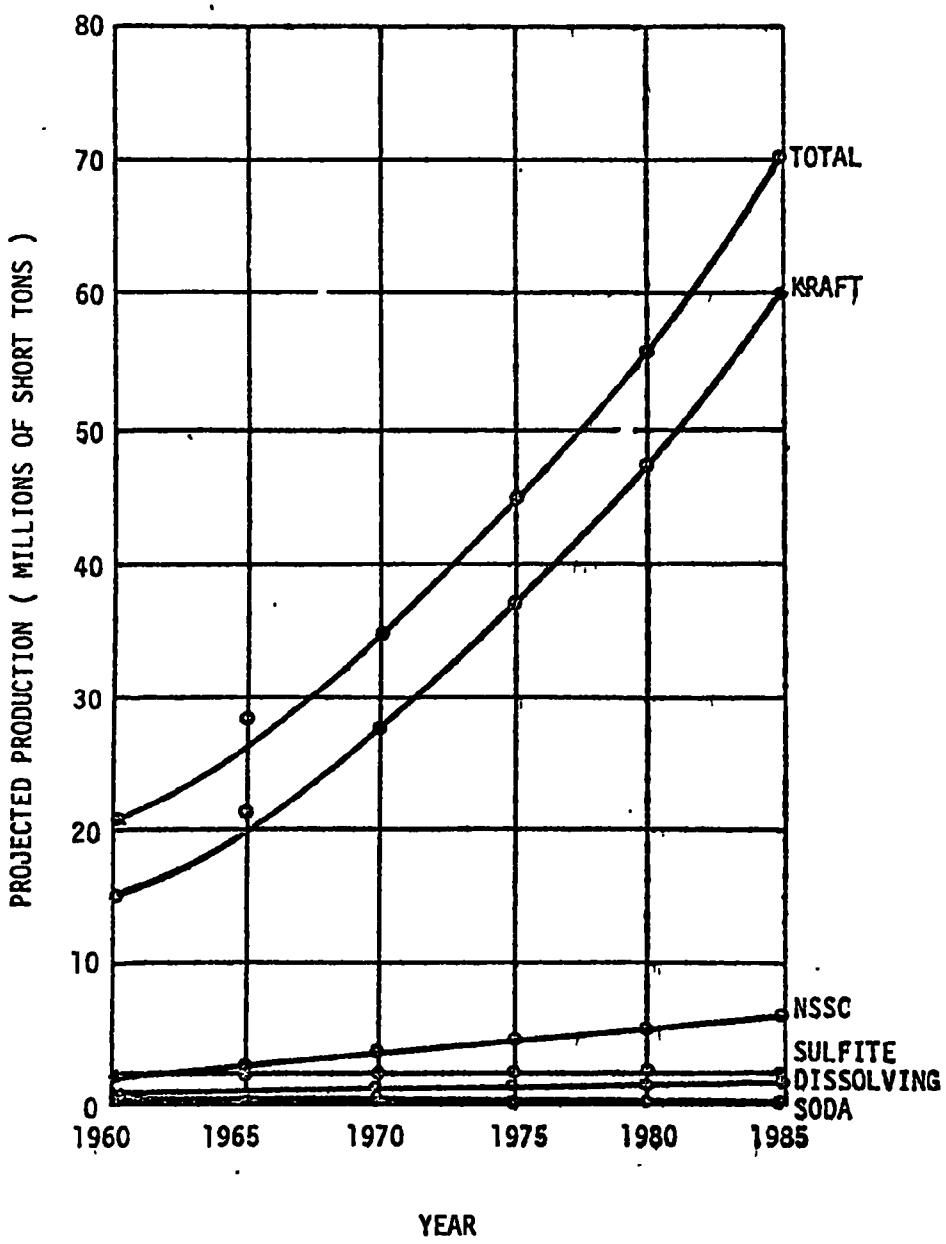


Figure 1

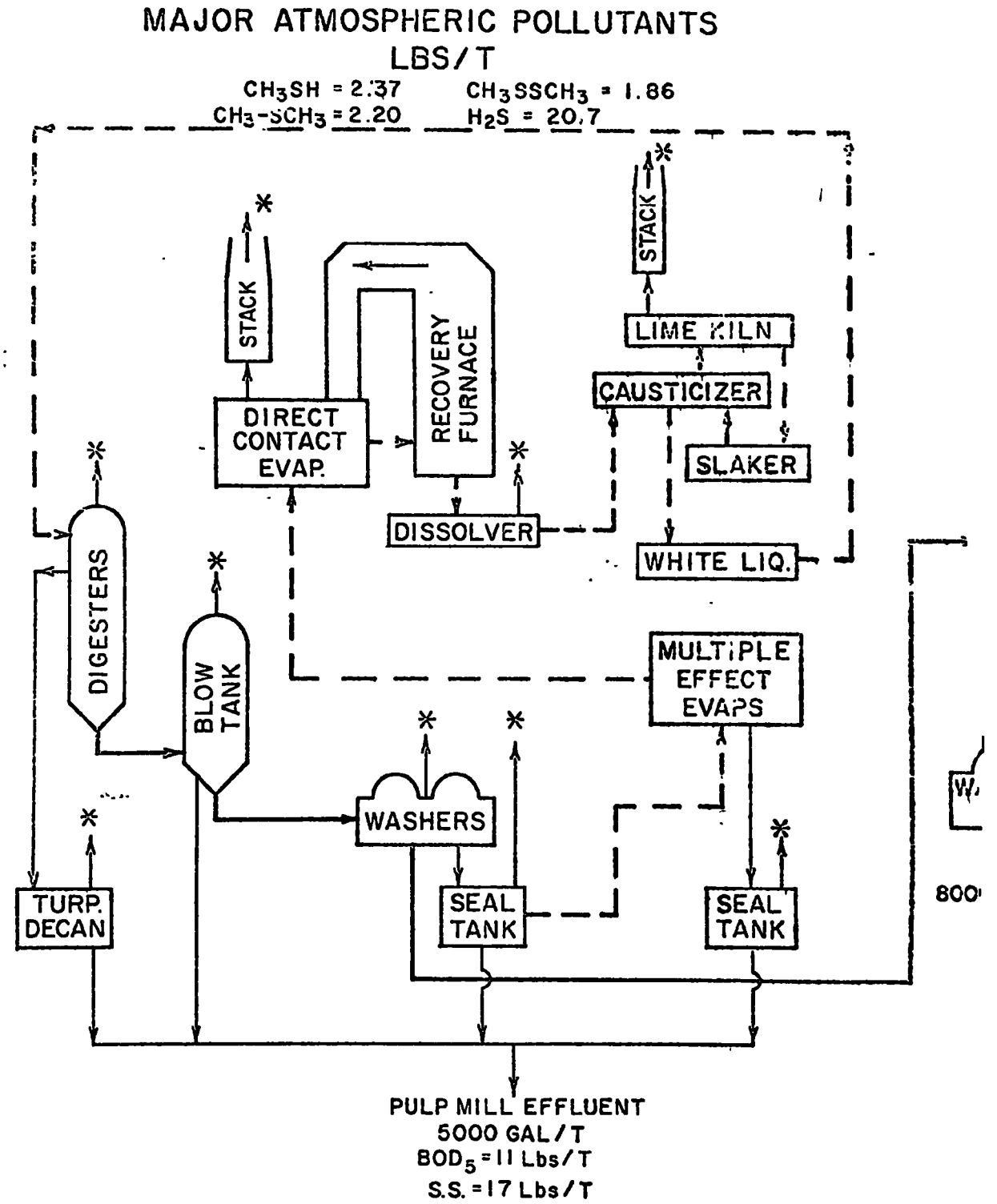

MAJOR ATMOSPHERIC POLLUTANTS
LBS/T
CH_3SH = 2.37
CH_3SSCH_3 = 1.86
CH_3-SCH_3 = 2.20
H_2S = 20.7
STACK
STACK
RECOVERY FURNACE
DIRECT CONTACT EVAP.
LIME KILN
CAUSTICIZER
SLAKER
DISSOLVER
WHITE LIQ.
DIGESTERS
BLOW TANK
MULTIPLE EFFECT EVAPS
WASHERS
TURP. DECAN
SEAL TANK
SEAL TANK
PULP MILL EFFLUENT
5000 GAL/T
BOD_5 = 11 Lbs/T
S.S. = 17 Lbs/T

Figure 2

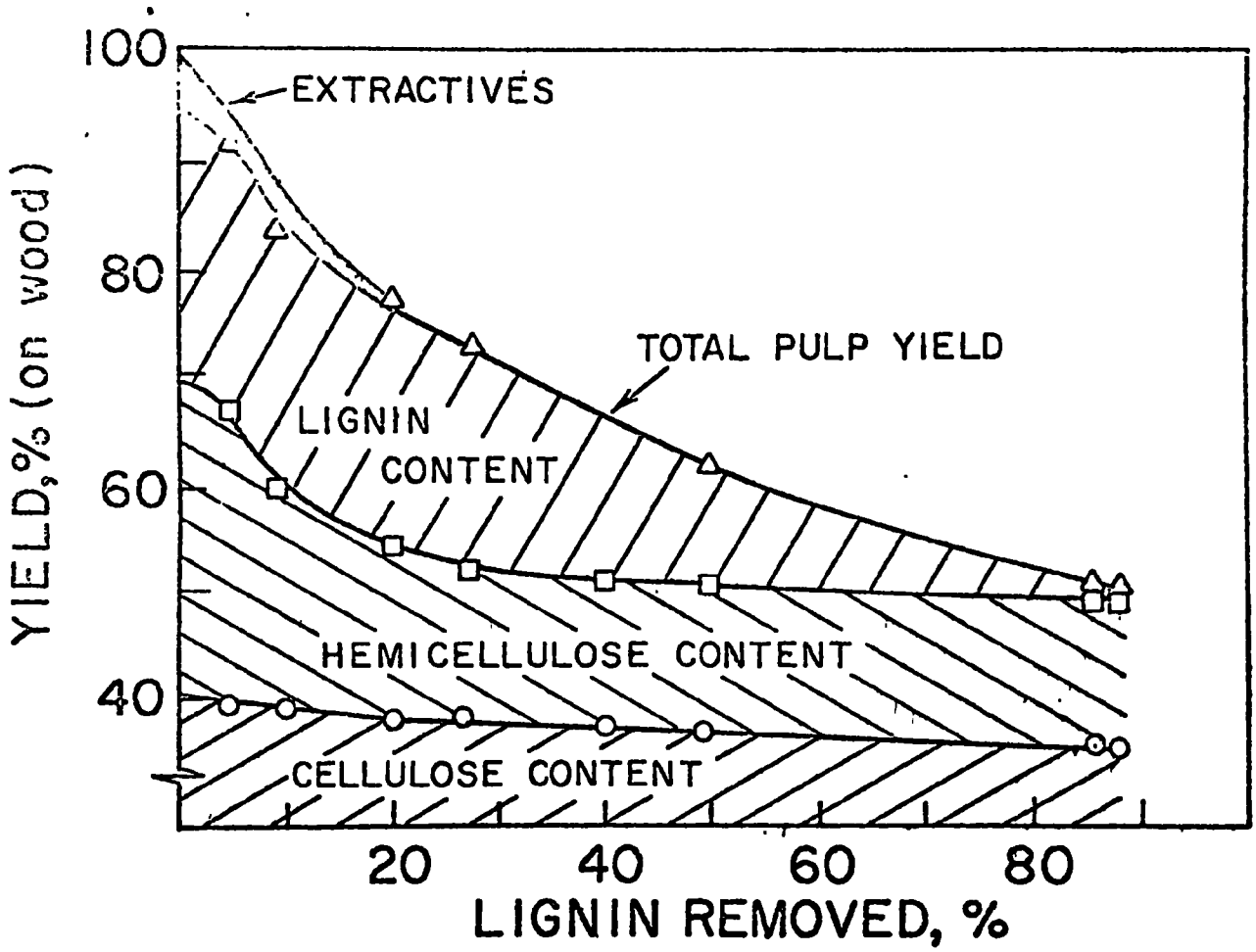


Figure 3. Pulp Yield as a Function of Lignin Removed

The remainder of unit operations shown in Figure 2 are intended to recover and reuse the inorganic pulping chemicals (NaOH and Na_2S) and to produce energy by burning organic material dissolved from the wood during pulping. The combined residual pulping liquor and pulp wash water called black liquor, normally has a solids content of 14-16% of which about 1/3 is lignin degradation products, 1/2 carbohydrate degradation products, 1/10 sodium sulfide and sodium hydroxide and less than 1% organic sulfur compounds. After concentration to about 60% solids in multiple effect evaporators, the resulting strong black liquor is further concentrated to 65 to 70% solids in a direct contact evaporator and fired to the recovery furnace. Combustion of the organic material provides hot water and steam for the pulp mill. The molten smelt issuing from the bottom of the furnace contains sodium carbonate and sodium sulfide. The smelt is dissolved in water and treated with lime in the causticizer to convert carbonate to sodium hydroxide. The resulting white liquor is recycled to pulp digesters. Lime is regenerated by heating the precipitated calcium carbonate in a lime kiln.

The major emission sources are identified in Figure 2 and typical quantities of sulfur containing malodorous substances emitted from these sources are shown in Table I. The volatile odorous substances of major concern to the kraft pulping industry are hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The total quantity of these four substances is termed Total Reduced Sulfur (TRS). Factors influencing the formation and release of these substances have been thoroughly reviewed (3). Hydrogen sulfide is

AIR POLLUTANTS FROM KRAFT PULP MILL WITH NO ODOR CONTROL

Table I

Source	Lbs/Ton A.D. Pulp			
	CH_3SH	CH_3SCH_3	CH_3SSCH_3	H_2S
1. Turpentine Decanter	0.02	0.40	0.03	≃0
2. Digester Blow Tank	0.45	1.40	1.50	0.05
3. Washer Hood Vent	0.15	0.05	0.05	0.05
4. Washer Seal Tank Vent	0.10	0.05	0.03	0.02
5. Evaporator Seal Tank	0.50	0.10	0.05	0.50
6. Direct Contact Evaporator & Recovery Furnace	1.10	0.20	0.20	20.0
7. Dissolver	0.03	0.01	≈0	0.03
8. Lime Kiln (with control)	0.05	0.05	0.05	0.10
TOTALS	2.37	2.20	1.86	20.70

derived from sodium sulfide which in alkaline liquors participates in the pH dependent hydrolyses shown in Equation 1. Sulfide and hydrosulfide anions are formed in kraft mill liquors at concentrations which are dependent on the ionization constants and on the amount of added sodium hydroxide. The dissociation constant K_1 has a value of

$$S^{=} + 2\,H^{+} \underset{}{\overset{K_2}{\rightleftharpoons}} HS^{-} + H^{+} \overset{K_1}{\rightleftharpoons} H_2S \qquad (1)$$

about 2×10^{-7} (4), so hydrogen sulfide will be released from alkaline liquors in a pulp mill only when the pH is reduced below a level of about 9 to 10. This occurs mainly in the direct contact evaporator where carbon dioxide in the flue gas neutralizes sodium hydroxide in the strong black liquor.

Since hydrogen sulfide comprises a substantial part of the total TRS, a major effort has been made by the pulp and paper industry to control its emission, particularly from the recovery furnace area. One approach has been to oxidize weak black liquor or strong black liquor (location of oxidation units is shown by dashed lines in Figure 4) with air or pure oxygen. The objective of black liquor oxidation (BLO) is to convert sodium sulfide to non volatile sodium thiosulfate as shown in Equation 2.

$$2\,S^{=} + 2O_2 + H_2O \longrightarrow S_2O_3^{=} + 2OH^{-} \qquad (2)$$

If this conversion can be successfully accomplished with high efficiency, little or no hydrogen sulfide is released from the recovery furnace stack.

MODIFICATIONS OF PULP MILL FOR ODOR CONTROL

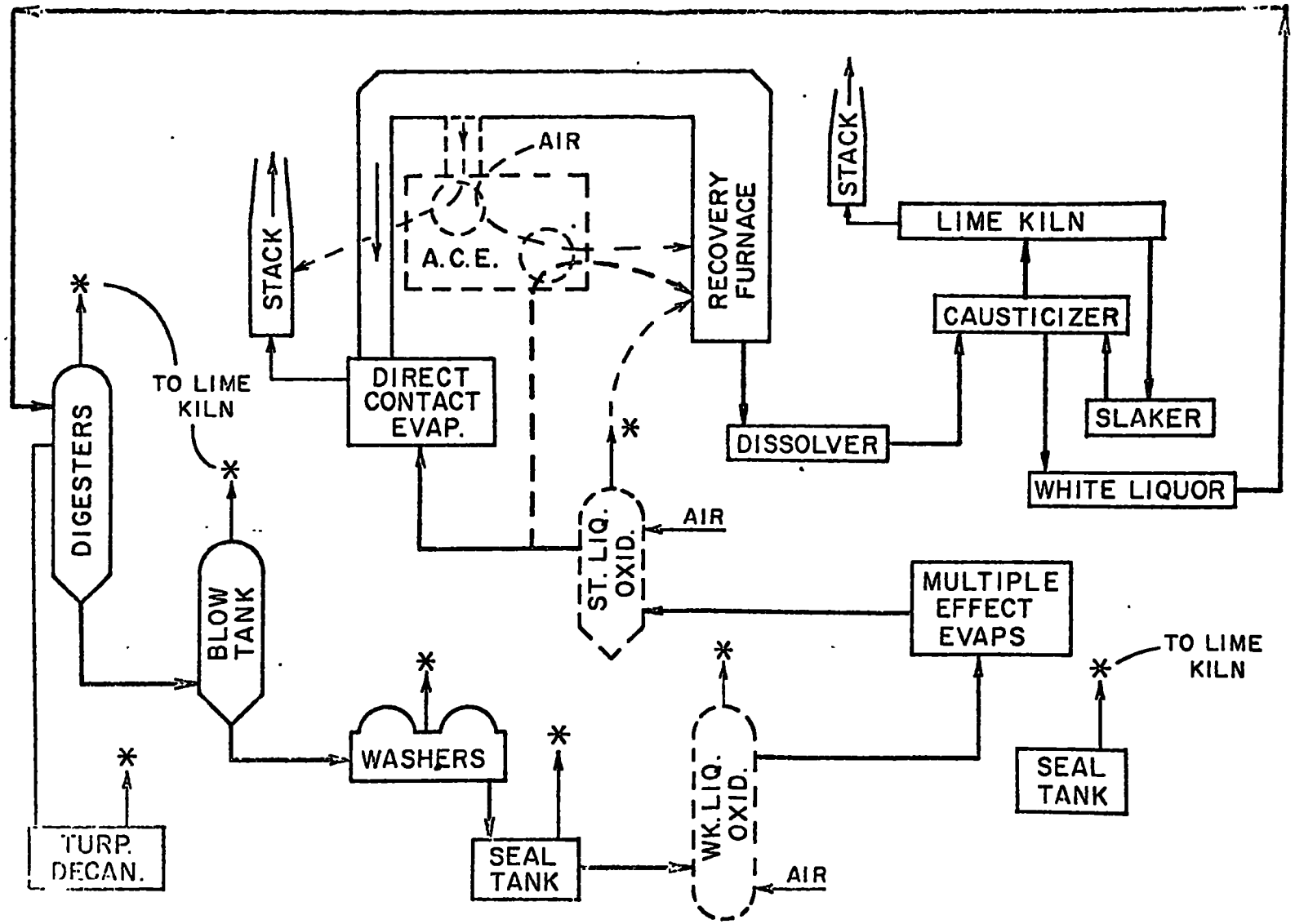


Figure 4

Obtaining a high, permanent conversion of sulfide to thiosulfate can be a difficult problem, however. Unless the oxidation temperature is maintained above about 70 to 80°C, elemental sulfur may form. This will slowly dissolve and later reform sulfide during evaporation and storage of the oxidized black liquor. The details of this liquor "reversion" have been discussed by Sarkanen (3) and Christie (5). In a second type of reversion methyl mercaptan present during black liquor evaporation may slowly disproportionate to reform sulfide ion (6).

A more recent approach to odor control has been to isolate the strong black liquor from direct contact with recovery furnace flue gas. Either strong black liquor (at 65-70% solids) is fired directly to the recovery furnace or black liquor (60% solids) is concentrated in an indirect heat exchanger (to 65 to 70% solids) by hot flue gas and then fed to the recovery furnace. This option is also identified in Figure 4 as the A.C.E. system. A variety of other control methods are discussed in reference 3.

Control of the malodorous organic sulfur compounds causes some difficulty since they are emitted from many sources in the mill as shown in Table I. Methyl mercaptan and dimethyl sulfide are formed <u>only</u> in the digester and released throughout the mill. Dimethyl sulfide is a neutral substance so is readily steam stripped from the alkaline liquors during digester relief and blow. Methyl mercaptan is a weak acid so it dissociates in aqueous solution according to Equation 3. The dissociation constant has a value of 4.3×10^{-11} (7) so free methyl mercaptan may be stripped from

black liquor at pH levels below 12 to 13. From Table I this clearly happens in several parts of the kraft mill.

$$CH_3SH \underset{}{\overset{K_3}{\rightleftharpoons}} CH_3S^- + H^+ \qquad (3)$$

Dimethyl disulfide is formed by air oxidation of methyl mercaptan after the digester has been relieved to atmospheric pressure. This neutral compound is also readily stripped out of black liquor and emitted to the atmosphere. Dimethyl disulfide may also be formed by oxidation of methyl mercaptan during black liquor oxidation. However, oxidation in black liquor and release of methyl mercaptan and dimethyl disulfide from black liquor during oxidation is much more complex than expected and is highly dependent on oxidation conditions. A detailed discussion of these effects is given in a later section of this report.

Because of the diversity in composition and flow rate, any single process modification can limit emissions of these odorous substances from only a part of the sources. Consequently, development of control measures has generally involved "add on" technology to limit emissions at each source. Significant progress has been made over the last two decades and the approaches are described in detail by Sarkanen, et al. (3). Installation of these types of collection and treatment systems involves a considerable capital outlay. Furthermore, the equipment must be operated at very high annual efficiencies to maintain the ambient air concentrations in the vicinity of the mills near or below the odor thresholds shown in Table II. Consequently, it may be useful to minimize emissions by destroying the odorous substances in the digester before blow down to atmospheric pressure.

Table II. Ambient Air Odor Thresholds (3)

Compound	Odor Threshold, ppb
H_2S	0.4-5
CH_3SH	2-3
CH_3SCH_3	$\sim$ 1.0
CH_3SSCH_3	1-5

B. Rationale for In-digester Oxidation

It is well known that essentially all methyl mercaptan (dimethyl disulfide) and dimethyl sulfide occuring during kraft pulping are formed in the digester and released thereafter from various places as described above. Consequently, a possible approach to odor control could be oxidation of all malodorous substances in the digester before the blowdown to atmospheric pressure. In-digester oxidation with oxygen is attractive for several reasons. This process may require limited changes in already existing mill equipment. Foaming problems are not expected since all gas injected will be consumed. The formation of elemental sulfur will be negligible at the high temperature in the digester. Consequently, reversion of the oxidized liquor may be less than in conventional oxidation systems. Furthermore, such a procedure may also lead to an in-digester oxidation of methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. In addition to the beneficial effects normally ascribed to conventional black liquor oxidation (BLO), the process should also reduce emissions of odorous compounds from digester relief, blow, and pulp washing operations which are presently not treated in many mills.

OBJECTIVES

The overall objective of this research project was to determine the feasibility of kraft mill odor control by oxidation of all malodorous sulfur compounds in the digester before blow down to atmospheric pressure. This method of black liquor oxidation (BLO) would permit oxidation of odorous substances at digester temperatures and pressures and eliminate emissions of hydrogen sulfide, methyl mercaptan and dimethyl disulfide from the digester, pulp washing and recovery furnace areas. If successful such a system would permit nearly odor free operation and eliminate the need for installation of equipment for collection, ducting and combustion of off gases from the numerous emission sources in a kraft mill.

The feasibility of this approach depends first on obtaining a high efficiency with respect to oxidation of the malodorous sulfur containing substances without excessive consumption of oxygen. In a first phase of work laboratory studies were made to determine the interaction of sulfur compounds, other black components and liquor during BLO and to study the influence of reaction variables on oxidation kinetics and oxidation efficiency.

Second, for indigester BLO to be acceptable, oxidation must be conducted in a way that pulp yield and physical properties are not adversely affected. Therefore, studies were required to determine:

a) At what stage of pulping oxygen could be injected without reducing pulp yield or affecting pulp physical and optical properties
b) The oxygen consumption and oxidation efficiency at conditions that did not result in unacceptable changes in yield or pulp properties.

These studies were made for pulping of a softwood (Loblolly Pine) and a hardwood (Red Gum) species.

Even if odor control could be successfully accomplished by this approach, some expense would be incurred for modification of digesters and for oxygen costs. However, if the modified digester could be operated in a way to obtain a pulp yield increase, the resulting increase revenue could be taken as a credit to offset the additional costs for odor control. Consequently, preliminary studies were made using a modified oxygen injection system on laboratory batch circulation digesters to determine if yield increases could be realized in combination with odor control.

DISCUSSION

A. Reactions of Methyl Mercaptan and Dimethyl Disulfide in Sodium Hydroxide Solutions

As a basis for studies on in-digester BLO, this section describes studies on the reactions of methyl mercaptan and dimethyl disulfide in sodium hydroxide solutions. The reactions of methyl mercaptan are highly influenced by other organic components present in the black liquor, so interpretation of reaction routes can be obscured by side reactions. Therefore, the oxidation of methyl mercaptan in water and sodium hydroxide solutions was studied. To this system components of black liquor were added in separate experiments, until a composition approaching commercial black liquor was reached.

The background information obtained from these experiments provides easier interpretation of results in actual BLO experiments.

1. Kinetics of the Oxidation of Methyl Mercaptan in Aqueous Alkaline Solution with Molecular Oxygen

Mercaptans are readily oxidized in an aqueous alkaline solution as reported by Oswald and Wallace (8). These detailed studies suggest that the active species in the oxidation of mercaptans involves mercaptide anions formed by the reaction of a base as shown in reaction 4.

$$RSH + HO^- \rightleftharpoons RS^- + H_2O \qquad (4)$$

Thus, the general kinetic expression for the oxidation of methyl mercaptan with molecular oxygen can be formulated as shown in Equation 5.

$$-\frac{d[MM]}{dt} = k[MM]^M[O_2]^N[HO^-]^P \qquad (5)$$

At a pH where all the methyl mercaptan is ionized, the reaction would become independent of base. For example, as illustrated in Figure 5, the rate of methyl mercaptan oxidation increases with increasing initial amounts of sodium hydroxide, until a pH between 12 and 13 is reached. At higher pH values the rate of oxidation is not further increased. Methyl mercaptan has a pKa value of approximately 10, so it is practically completely ionized at a pH between 12 and 13 and further addition of base apparently has no effect on its rate of oxidation.

For all practical conditions during black liquor oxidation the pH will be greater than about 12, thus Equation 5 simplifies to Equation 6, since P = 0 and $[HO^-]^0 = 1$.

$$-\frac{d[MM]}{dt} = k\,[MM]^M[O_2]^N \qquad (6)$$

The values of M and N were determined by the method of variation in ratio of reactants (9). The overall empirical expression for the oxidation of methyl mercaptan in sodium hydroxide solution is given by Equation 7.

$$-\frac{d[MM]}{dt} = k\,[MM]^{0.75}\ Po_2^{\,0.66} \qquad (7)$$

This form applies only at pH levels above 12 where all methyl mercaptan is ionized.

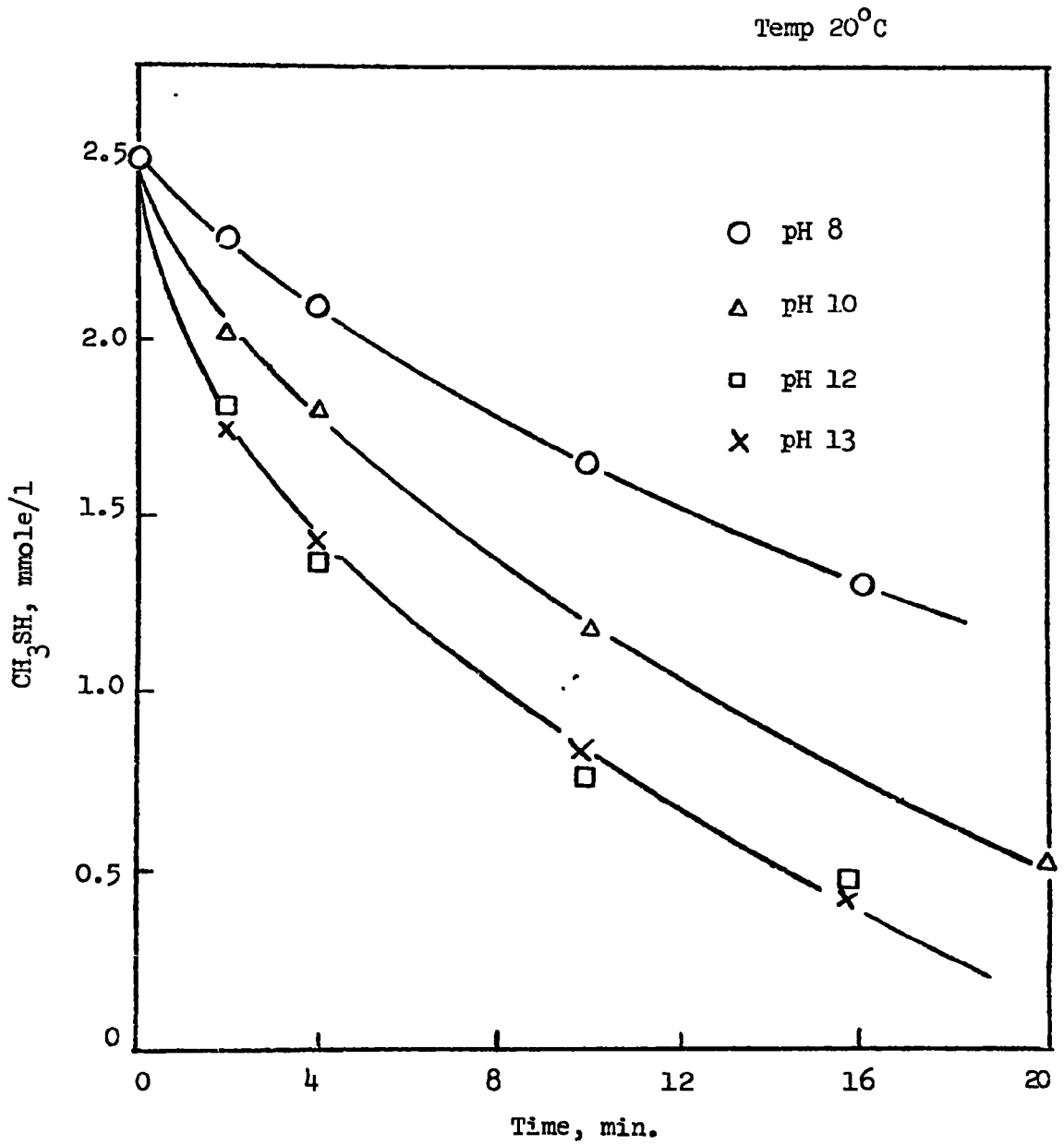


Figure 5 Oxidation of methyl mercaptan at varying pH.

The rate of oxidation is sufficiently fast that reliable kinetic studies could be made only at temperatures below about 25°C. The temperature dependence was determined by conducting reactions at 10, 15, 20 and 25°C. Oxygen pressure was maintained constant so Equation 7 reduced to Equation 8. The reaction followed the Arrhenius relationship

$$-\frac{d[MM]}{dt} = k' \quad Po_2^{0.75} \qquad \text{where } k' = k\ Po_2^{0.66} \qquad (8)$$

so integration of Equation 8 and appropriate graphing resulted in the rate constants and activation energy shown in Table III (9).

2. Hydrolysis of Dimethyl Disulfide

In the presence of base and molecular oxygen,methyl mercaptan is converted to dimethyl disulfide. Once formed, dimethyl disulfide does not oxidize at conditions employed during black liquor oxidation, but can undergo hydrolytic disproportionation (3). This hydrolysis of dimethyl disulfide has been studied in the present work for two reasons: first, dimethyl disulfide, is very volatile and has a very low odor threshold, so it contributes to the overall odor of kraft mills; second, when dimethyl disulfide hydrolyzes, significant amounts of methyl mercaptan are formed as one of the products.

In the study of this hydrolysis reaction, two approaches have been taken. First, the reaction products were determined by Nuclear Magnetic

Table III. Rate constants for the oxidation of methyl mercaptan.

Temp. °C	$k''' \frac{sec.}{mole^{1.75}}$	$t_{\frac{1}{2}}$ min.
10	1.01	12
15	1.47	8.5
20	2.06	6
25	3.25	4
ΔE	12.9 Kcal/mol	

Resonance (NMR) spectroscopy, and from the results the total hydrolysis stoichiometry was formulated. Studies on the hydrolysis of disulfides by sodium hydroxide have been reported (8, 10). It is generally suggested that the mechanism involves an initial nucleophilic displacement at the disulfide bond. From these studies it can be predicted that the major products of dimethyl disulfide hydrolysis may be methyl mercaptan, methane sulfinic acid and/or methane sulfonic acid. This was confirmed in the present work using the NMR technique. The reader is referred to reference (9) page 25 for a detailed discussion of the work.

The overall material balances for dimethyl disulfide hydrolysis by hydroxide and hydrosulfide anions are given in reactions 9 and 10 respectively.

$$2\ CH_3SSCH_3 \xrightarrow{OH^-} CH_3SO_2^- + 3\ CH_3S^- \qquad (9)$$

$$3\ CH_3SSCH_3 \xrightarrow{HS^-} 2\ CH_3SO_2^- + 4\ CH_3S^- \qquad (10)$$

3. Kinetics of the Hydrolysis of Dimethyl Disulfide

As described in the previous section, dimethyl disulfide is hydrolysed slowly by hydroxide and much more rapidly by hydrosulfide. Both components are present in the black liquor, so it is appropriate to study their effects on the hydrolysis of dimethyl disulfide in detail.

Since the rate limiting step involves nucleophilic attack of the anion at the disulfide bond, the simplest general kinetic expression for the disappearance of dimethyl disulfide by hydrolysis with sodium hydroxide and by sodium sulfide is shown in Equations 11 and 12 respectively. The powers M, N, P and Q, were determined to have the

$$-\frac{d[DMDS]}{dt} = k_1 [DMDS]^M [HO^-]^N \tag{11}$$

$$-\frac{[DMDS]}{dt} = k_2 [DMDS]^P [HS^-]^Q \tag{12}$$

value of 1.0 (9), supporting the suggestion that dimethyl disulfide hydrolysis is initiated by a nucleophilic, S_N2 substitution. The rate constants are summarized in Table IV.

Activation energies of 27.5 Kcal/mole were determined for hydrolysis by hydroxide anion (Equation 11) and 16.5 Kcal/mole for hydrolysis by hydrosulfide anion (Equation 12). This difference in temperature dependence has a significant effect on the optimum conditions for black liquor oxidation as will be discussed in a later section.

4. Summary of Methyl Mercaptan and Dimethyl Disulfide Reactions in Aqueous Alkaline Solution

The scheme shown in Figure 6 summarizes the reactions discussed in earlier sections. With a base and oxygen methyl mercaptan is readily oxidized to dimethyl disulfide which in turn hydrolyzes rapidly with

Table IV Rate constants for dimethyl disulfide hydrolysis.

Temperature	HO^- k_1 l/mole-min.	HS^- k_2 l/mole-min.
10	—	0.2
20	—	0.7
30	—	1.7
40	—	4.3
80	(0.0015)*	(78)*
128	0.02	—
146	0.1	—
160	3.6	—
ΔE	27.3 Kcal/mole	16.5 Kcal/mole

*Calculated from Arrhenius expression.

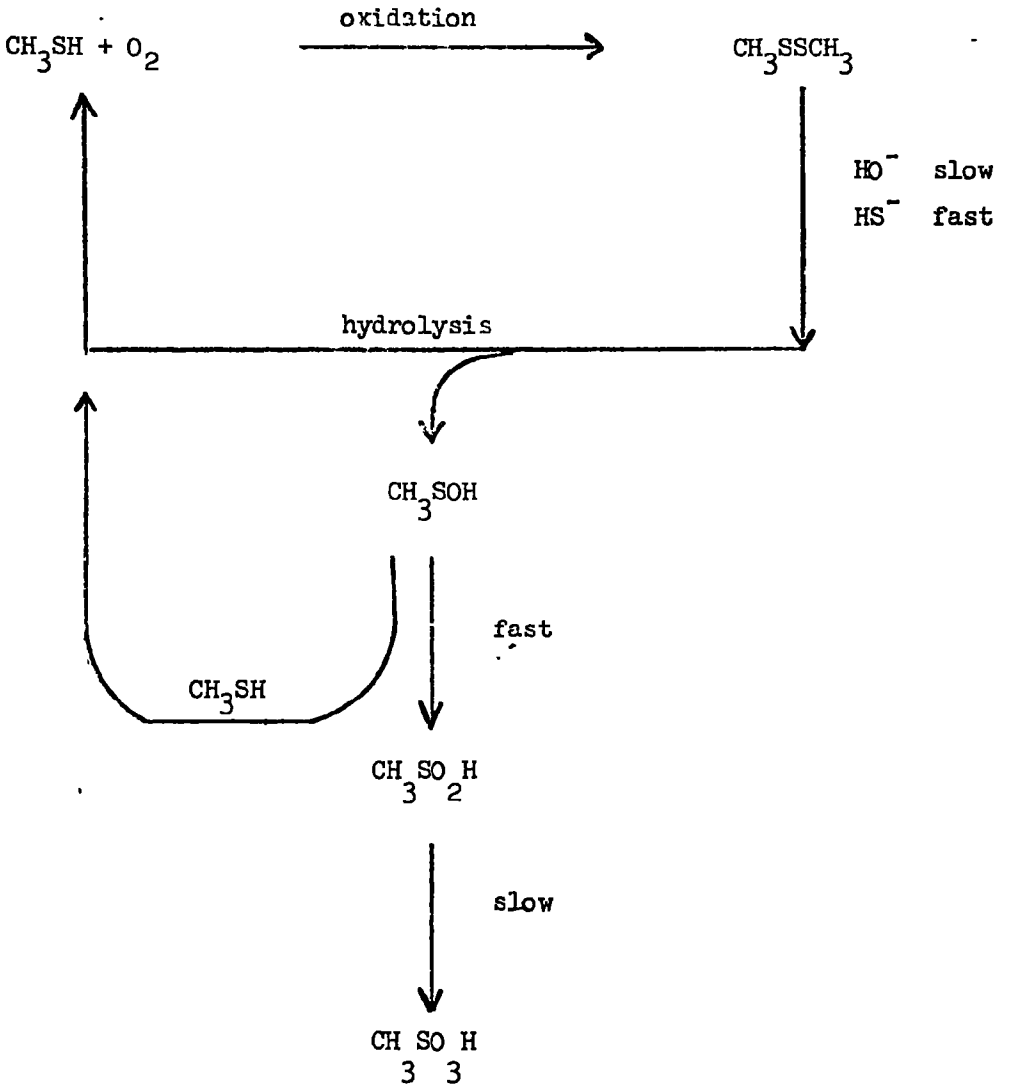


Figure 6 - Oxidation-hydrolysis cycle for conversion of methyl mercaptan to nonvolatile product.

hydrosulfide or more slowly with hydroxide forming methyl mercaptan and the non volatile methane sulfinic acid. From the overall equation for the hydrolysis of dimethyl disulfide by sodium hydroxide (reaction 9) it can be seen that 2 moles of dimethyl disulfide form 3 moles of methyl mercaptan. Thus, from the oxidation of 4 moles of methyl mercaptan, 3 moles are regenerated. Similarly, the overall equation for the hydrolysis of dimethyl disulfide with sodium sulfide (reaction 10) shows that 4 moles of methyl mercaptan are formed from 2 moles of dimethyl disulfide. While this oxidation-hydrolysis cycle permanently destroys some methyl mercaptan, the regeneration of substantial quantities makes inefficient use of oxygen and will be troublesome in black liquor oxidation.

The hydrolysis of dimethyl disulfide in this cycle could be the rate determining step depending on the conditions. At 50-90°C with sodium sulfide present the rate is quite high, but is very slow with only sodium hydroxide present. Thus, to complete the conversion of methyl mercaptan to its non-volatile product under practical conditions, sodium sulfide is required. However, under oxidizing conditions sodium sulfide will also rapidly oxidize to sodium thiosulfate by reaction 2 repeated here. While sodium sulfide oxidation is desired in black liquor oxidation, its consumption causes significant reduction in the rate of conversion of methyl mercaptan and dimethyl disulfide to non volatile products.

$$a\ Na_2S + 5/2\ O_2 \longrightarrow Na_2S_2O_3 + 2\ NaOH \qquad (2)$$

The activation energy for the hydrolysis reaction by hydroxide is quite high, consequently the rate is greatly effected by temperature changes. For instance by increasing the temperature to 125°C and above, the rate of hydrolysis by hydroxide will become quite high.

In summary, with oxygen and base present, the conversion of methyl mercaptan to the non volatile methane sulfinic acid, proceeds through a very inefficient oxidation -- hydrolysis cycle. The hydrolysis step in the sequence is possibly rate determining depending on the conditions. At lower temperatures, 50-90°C, the hydrolysis depends on the presence of sodium sulfide which, however, is also rapidly oxidized. At temperatures greater than about 125°C, the rate of hydrolysis by hydroxide becomes very rapid so the oxidation-hydrolysis cycle can be effectively completed even when the hydrosulfide concentration is very low.

Interpretations must be further modified to account for the influence of other compounds in black liquor. In the following sections the effects of other components in black liquor on the conversion of methyl mercaptan to its non-volatile product will be discussed.

B. Reactions of Methyl Mercaptan and Dimethyl Disulfide in Synthetic Black Liquor

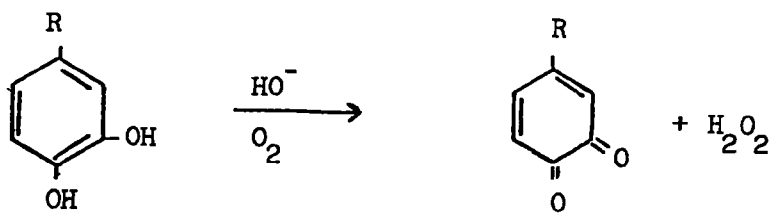
1. Methyl Mercaptan Oxidation by Model Compounds Featuring Certain Structures in Kraft Lignin

The reactions of methyl mercaptan are also influenced to a high degree by lignin present in the black liquor. Earlier investigators

(11, 12, 13) noticed that the consumption of methyl mercaptan was accelerated by organic material dissolved in black liquor. It is generally suggested that phenolic and catecholic structures in the lignin contribute to the increased rate of consumption of methyl mercaptan. Although no detailed studies have been made to describe the reactions under conditions employed during black liquor oxidation, results obtained by workers in the petrochemical field suggest possible mechanisms by which polyphenolic structures in lignin may interact with methyl mercaptan under oxidizing conditions.

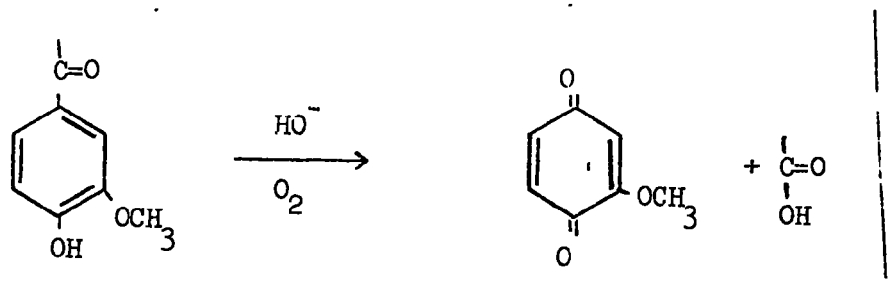
The chemical composition of black liquor is not accurately defined; for this reason, a discussion on the reactions of methyl mercaptan with model compounds featuring certain structures in lignin will be given first. Results derived from these studies will help to interprete observations made during oxidation of mixtures of methyl mercaptan and Kraft lignin in alkaline solutions.

As the result of demethoxylation reactions which occur during pulping, Kraft lignins contain about 0.3 moles of catechol structures per one thousand grams (14). In alkaline solution, these structures are readily oxidized by oxygen forming the corresponding quinones and hydrogen peroxide as shown in reaction 13. Furthermore, during oxidation of phenolic



(13)

structures some side chain elemination may take place with formation of p-quinonoid structures (15) as illustrated for moieties with α carbonyl sidechains.

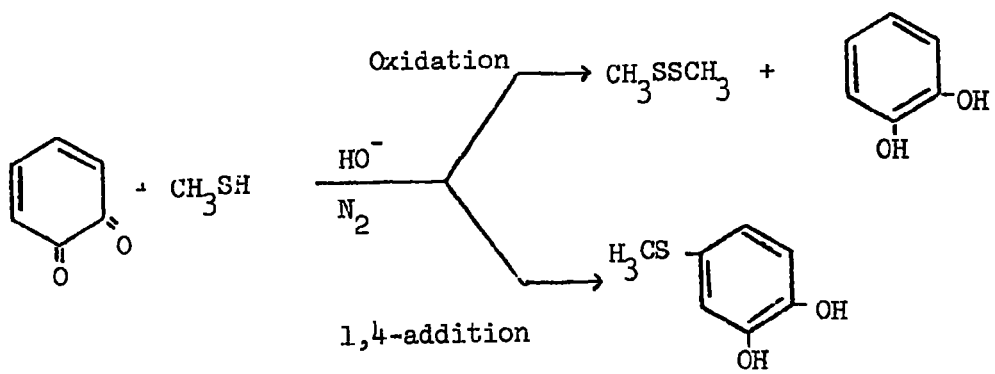


(14)

Meguerian (16) and Oswald (8) studied the catalytic effects of polyphenolic structures on the oxidation of a variety of mercaptans and suggested two possible reaction routes:

1. Oxidation of the mercaptan, by quinonoid structures, to the sulfide
2. Nucleophilic 1,4-addition of the mercaptide ion to the quinone.

To test these concepts, methyl mercaptan was oxidized by several oxidants under nitrogen atmosphere and the results are shown in Figure 7. As a reference one experiment at 10 psig oxygen was also included. The first oxidant chosen was o-quinone, since it most closely represents the quinonoid structure in the Kraft lignin. The following reactions may take place:



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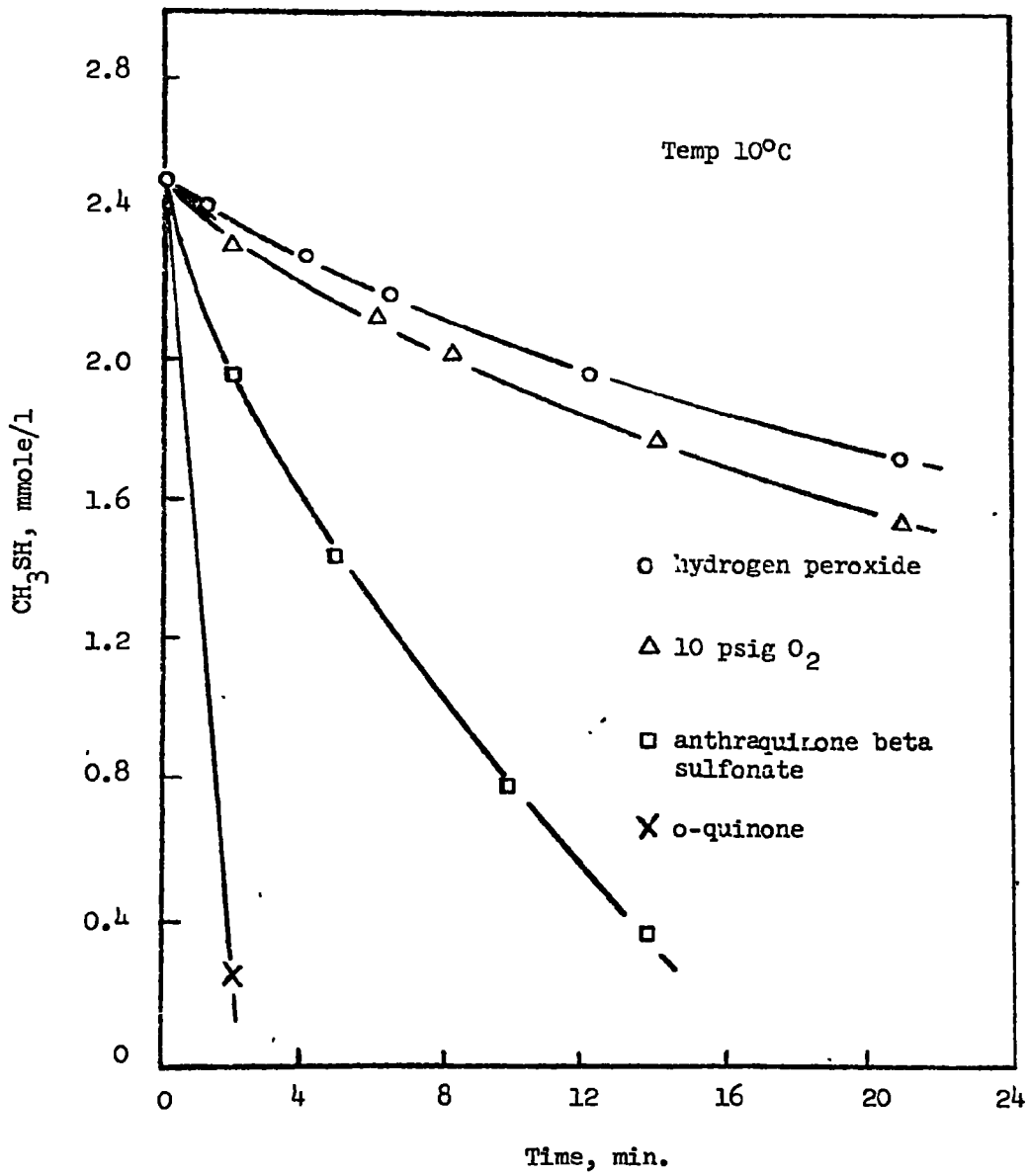
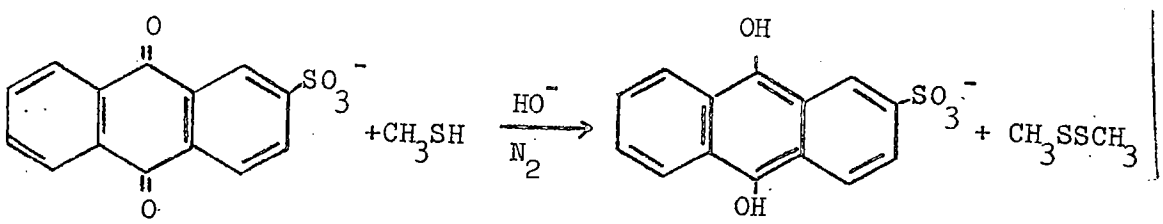


Figure 7 Methyl mercaptan consumption by equimolar amounts of hydrogen peroxide, anthraquinone beta sulfonate, o-quinone and 10 psig oxygen respectively.

Figure 7 shows the results of the experiment where equimolar amounts (2.5 mmole/l) of methyl mercaptan and o-quinone were mixed together at 10°C. Two general observations were made: first, methyl mercaptan was rapidly consumed; secondly, no dimethyl disulfide was detected. Tentatively, the following conclusion is drawn: methyl mercaptan reacts very rapidly with o-quinone in a nitrogen atmosphere apparently by nucleophilic 1,4-addition only.

To examine more closely the relative effects of the 1,4-addition and direct oxidation of methyl mercaptan by quinones, anthraquinone beta sulfonate was selected as the oxidant. Because of its condensed ring structures 1,4-addition cannot occur. Again equimolar amounts of methyl mercaptan and anthraquinone beta sulfonate (2.5 mmole/l) were mixed together at 10°C (Figure 7). The disappearance of methyl mercaptan was markedly slower compared to the experiment with o-quinone; but all methyl mercaptan consumed was converted to dimethyl disulfide. Thus, methyl mercaptan is readily oxidized by anthraquinone beta sulfonate in a nitrogen atmosphere, to dimethyl disulfide only. Furthermore, the nucleophilic 1,4-addition of the mercaptide ion to the quinone has a faster rate than the oxidation of methyl mercaptan to dimethyl disulfide by the quinone. The oxidation of methyl mercaptan by the anthraquinone derivative is shown in reaction (16).



(16)

When organic material present in black liquor is oxidized with molecular oxygen a variety of peroxide intermediates and hydrogen peroxide are formed (17) which could be responsible for the increased rate of consumption of methyl mercaptan. To test this hypothesis, an experiment with hydrogen peroxide under nitrogen gas was designed. The results presented in Figure 7 show that at 10°C the rate of methyl mercaptan disappearance is quite slow when compared to experiments with the quinones, and the methyl mercaptan consumed was all converted to dimethyl disulfide according to reaction 17. Further experiments with hydrogen peroxide at higher temperatures showed similar rates when compared to oxygen at these temperatures, and a stoichiometry as written for reaction 17.

$$2\ CH_3SH + H_2O_2 \longrightarrow CH_3SSCH_3 + 2H_2O \qquad (17)$$

From the results of these experiments the following order of the rate of disappearance of methyl mercaptan is proposed: o-quinone> anthraquinone beta sulfonate > oxygen~ hydrogen peroxide, and nucleophilic 1,4-addition >> oxidation by quinone to the disulfide.

2. The Effect of Kraft Lignin on the Consumption of Methyl Mercaptan

In the previous section, orienting studies with model compounds featuring certain lignin structures show the importance in reactions with methyl mercaptan. They are:

1. Nucleophilic 1,4-addition
2. Direct oxidation to the disulfide

Since the model compounds used feature only certain structures, it is necessary to work with Kraft lignin to verify the above observations.

Figures 8 and 9 show the results of experiments in which Kraft lignin was added to an alkaline solution containing methyl mercaptan at 10°C and 10 psig oxygen. It is shown that the addition of Kraft lignin results in a significant increase in the rate of methyl mercaptan disappearance accompanied by a simultaneous increase in the rate of dimethyl disulfide formation. Furthermore, the yield of dimethyl disulfide decreases with increasing amounts of lignin. Apparently in the presence of lignin, methyl mercaptan undergoes a reaction which leads to other products in addition to dimethyl disulfide.

These observations may be interpreted by assuming that initially the nucleophilic 1,4-addition takes place with the quinonoid structures present in the lignin. When all available addition sites are occupied, the remaining methyl mercaptan reacts with oxygen and/or quinones and peroxides to form dimethyl disulfide. This would explain the rapid disappearance of methyl mercaptan, and the formation of less dimethyl disulfide at a higher rate. The greater number of quinonoid structures available with greater quantities of lignin result in more methyl mercaptan addition and less dimethyl disulfide formation. Thus, with lignin and oxygen present the following reactions may occur. First, methyl mercaptan may be oxidized to dimethyl disulfide according to reaction 18:

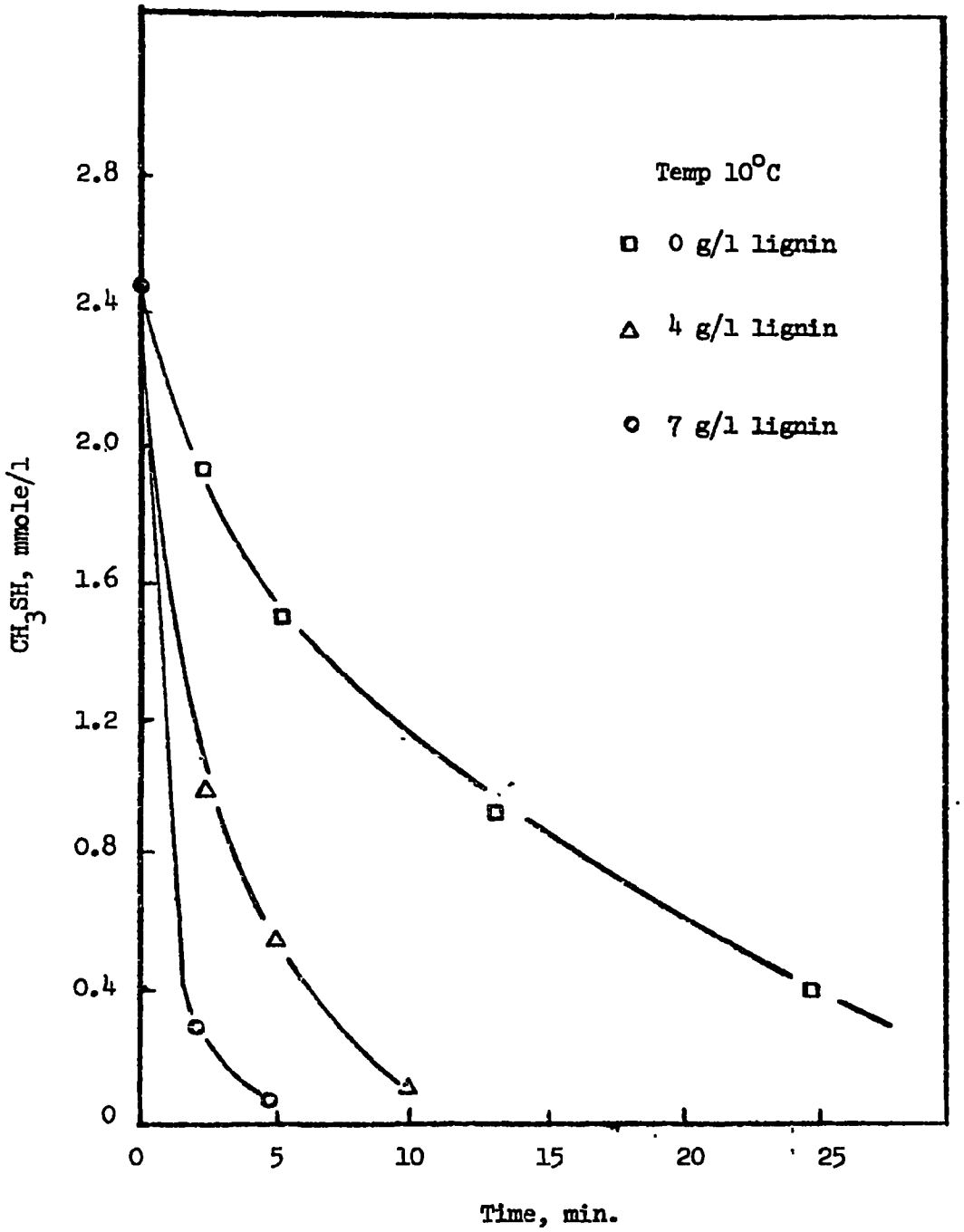


Figure 8 Consumption of methyl mercaptan in aqueous alkaline solution with Kraft lignin added.

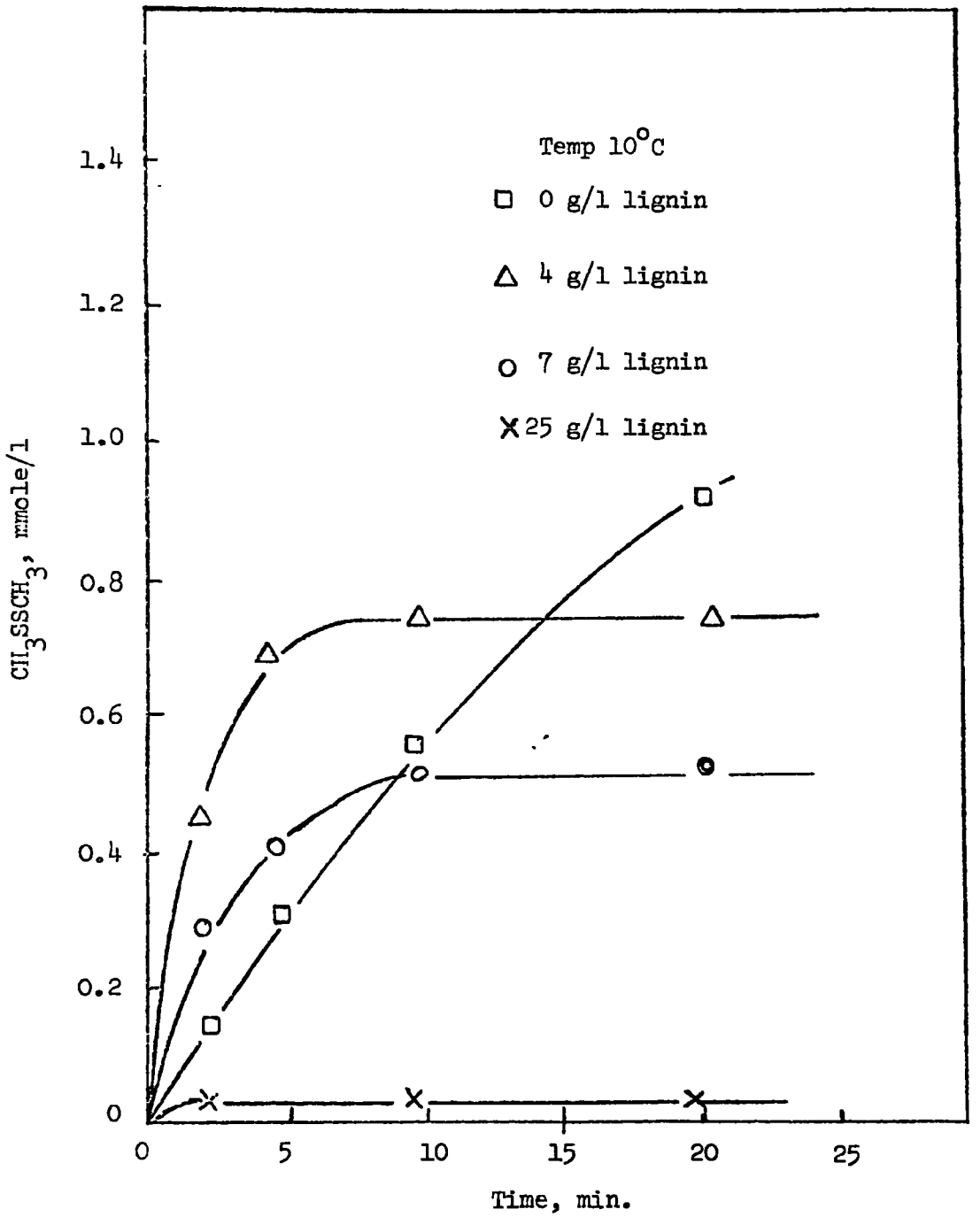
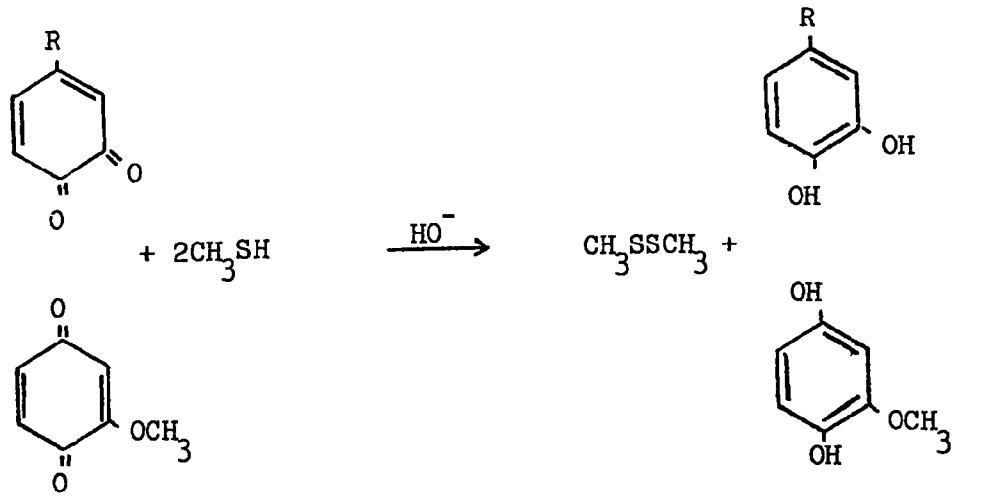


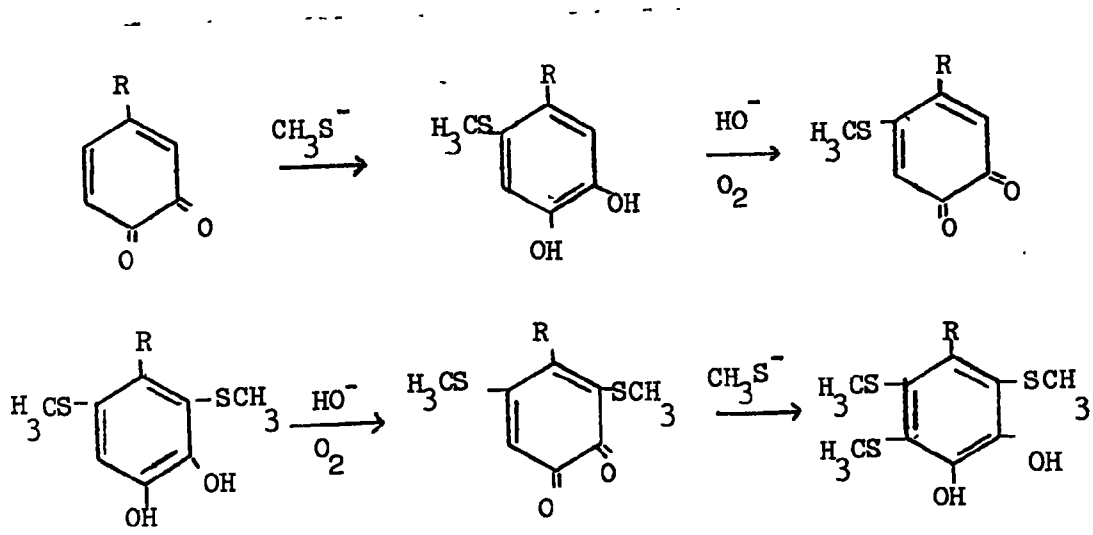
Figure 9 Formation of dimethyl disulfide in alkaline solution with Kraft lignin added.



(18)

With oxygen present and at temperatures below approximately 100°C the catechols formed may be reoxidized and are available for further mercaptan oxidation. Thus, small amounts of catechols present in lignin may oxidize large quantities of mercaptans by this redox cycle.

The second alternative is the nucleophilic addition of mercaptide anions to quinones to either mono-, di- and tri-thiopolyphenols by a series of successive steps of oxidation and nucleophilic addition as shown for the o-quinonoid structures in lignin as illustrated in reaction 19:



(19)

In addition, it has already been shown that reactions 20 and 21 occur:

$$2\ CH_3SH + 1/2\ O_2 \xrightarrow{HO^-} CH_3SSCH_2 + H_2O \qquad (20)$$

$$2\ CH_3SH + H_2O_2 \xrightarrow{HO^-} CH_3SSCH_3 + 2\ H_2O \qquad (21)$$

The rates of these reactions may be listed in the order 19 >18 >20~ 21. Thus, in alkaline solution, methyl mercaptan should be oxidized to the disulfide; but with Kraft lignin present, the major reaction is the 1,4-addition as shown in reaction 19, and less dimethyl disulfide is formed.

It was mentioned earlier that during the oxidation of black liquor side chain elimination of certain phenolic lignin structures could result in the formation of new (para) quinonoid moieties. Presumably, this formation increases with increasing temperatures. For instance, when methyl mercaptan in the presence of Kraft lignin was oxidized at 10, 50 and 75°C respectively, lesser amounts of dimethyl disulfide are formed at the higher temperatures (Figure 10). This could be due to the increase in quinonoid structures formed by side chain elimination. Furthermore, 5 g Kraft lignin/l which is approximately 10% of the amount actually present in black liquor, results in the formation of about 90% less disulfide from 5 mmole/l methyl mercaptan at 75°C. The concentration of methyl mercaptan and the temperature of 75°C are comparable to practical conditions of black liquor oxidation with approximately 50 g/ℓ of Kraft lignin, probably all methyl mercaptan is consumed by the nucleophilic 1-4 addition and very little is oxidized to the dimethyl disulfide at between 50 and 90°C.

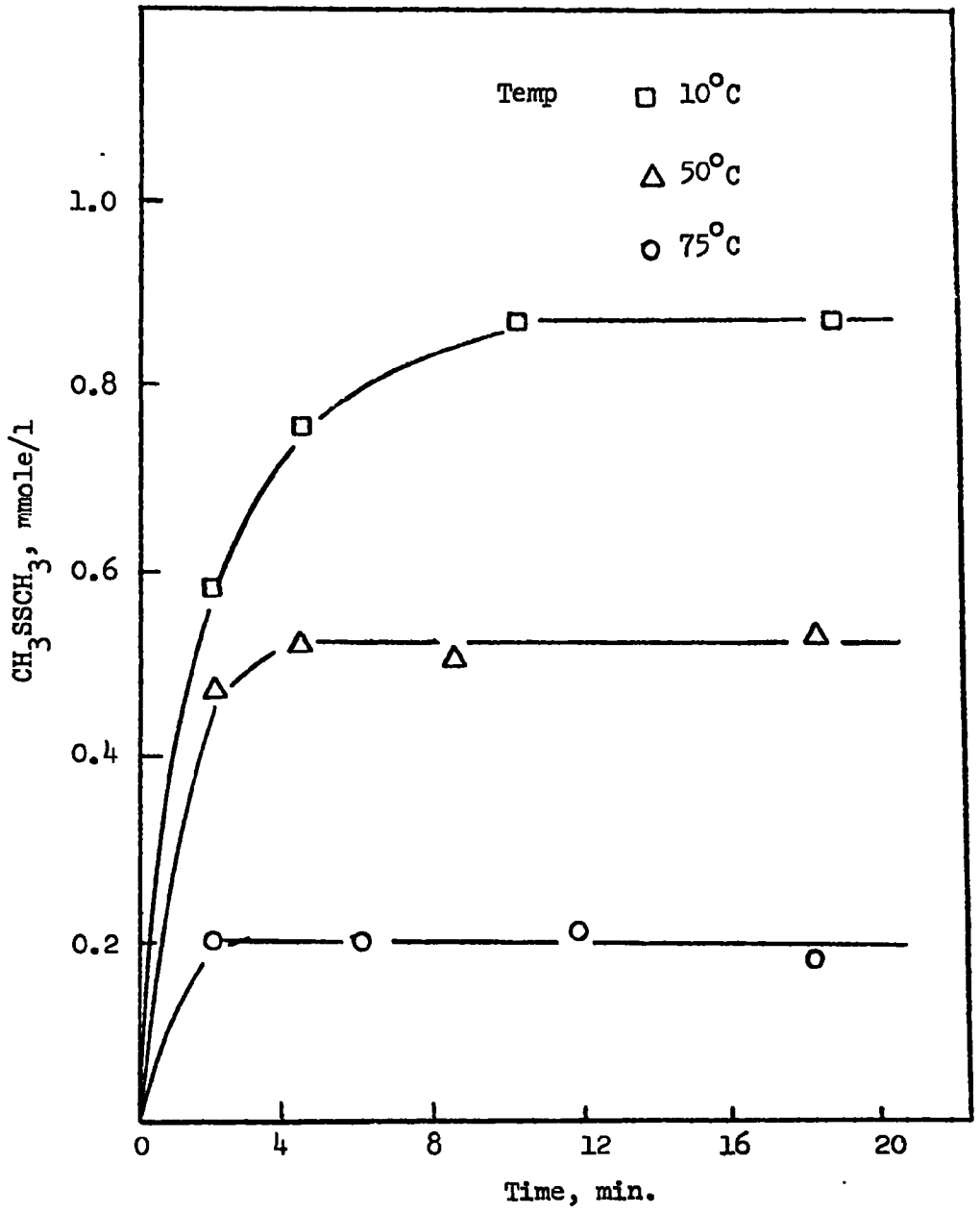


Figure 10 The effect of temperature on the formation of dimethyl disulfide in the presence of Kraft lignin.

3. Effect of Sodium Sulfide on the Oxidation of Methyl Mercaptan

Sodium sulfide has two effects on the oxidation of methyl mercaptan which highly influence the efficiency of reactions during black liquor oxidation. The first is an apparent inhibition which is dependent on temperature and sodium sulfide concentration.

For example, when 5 g/l sodium sulfide is added to an aqueous alkaline solution containing 2.5 mmole/l methyl mercaptan the methyl mercaptan consumption depends on the reaction temperature as shown in Figure 11. Throughout this experiment the pH of the reaction mixture remained between 12 to 13 and the oxygen pressure at 2.5 psig. The results in Figure 11 suggest an apparent inhibition of the oxidation of methyl mercaptan of at least 60 minutes at 60°C and approximately 15 minutes at 100°C. Analysis showed that sodium sulfide was oxidized to sodium thiosulfate, and when the methyl mercaptan finally started to react only very small amounts of sodium sulfide remained in solution (approx. 0.2 g/l). Thus, it seems apparent that the presence of sodium sulfide inhibits the oxidation of methyl mercaptan. The results of the experiment at 150°C are different and will be discussed later in this section.

To explain the above observations the following is suggested. The oxidation of both methyl mercaptan and sodium sulfide seems to involve radical mechanisms (18, 8, 19). Results of a study on the photodecomposition of acetaldehyde catalysed by thiols (20) provides a possible explanation for the sulfur inhibition in systems involving radical

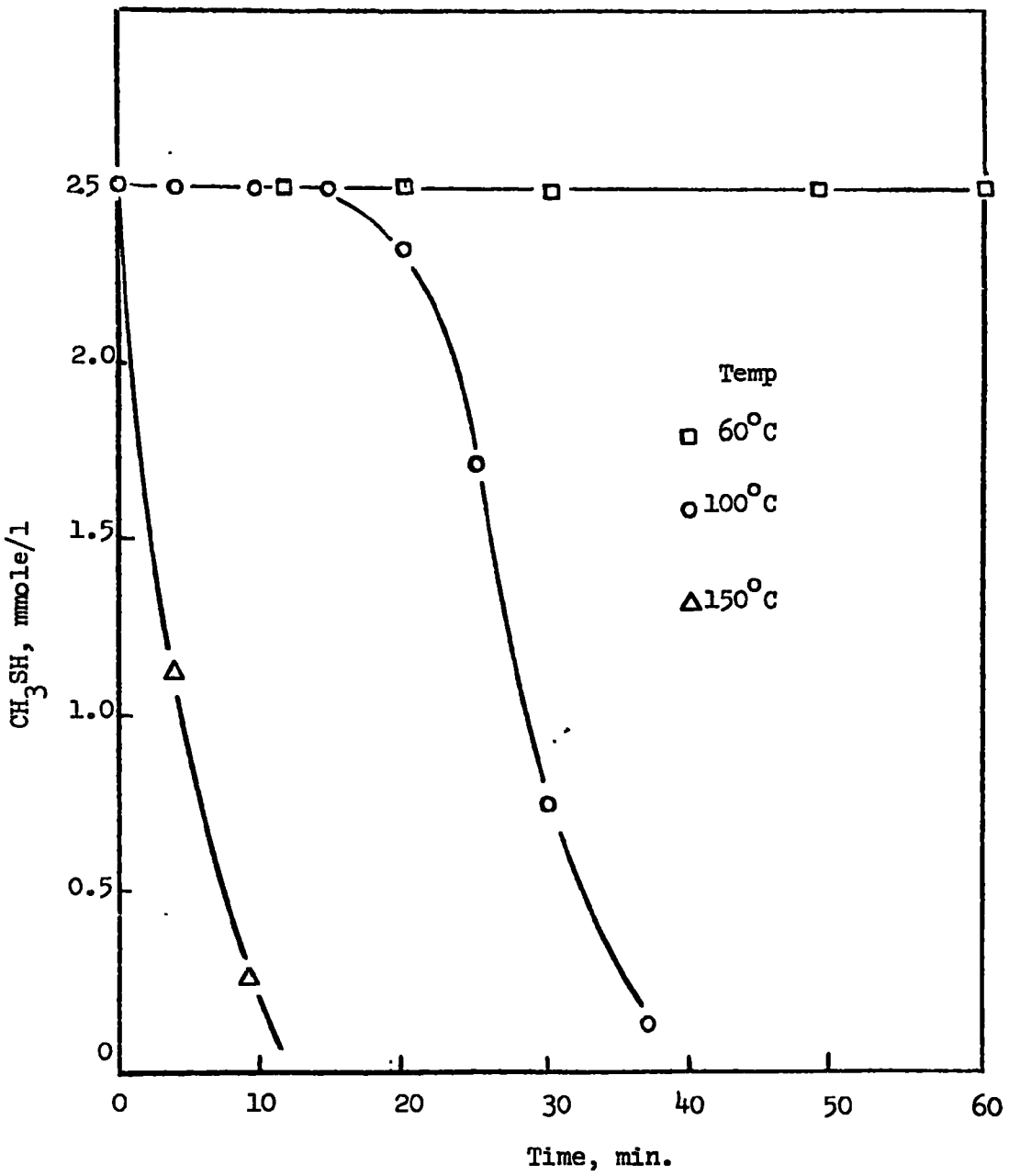
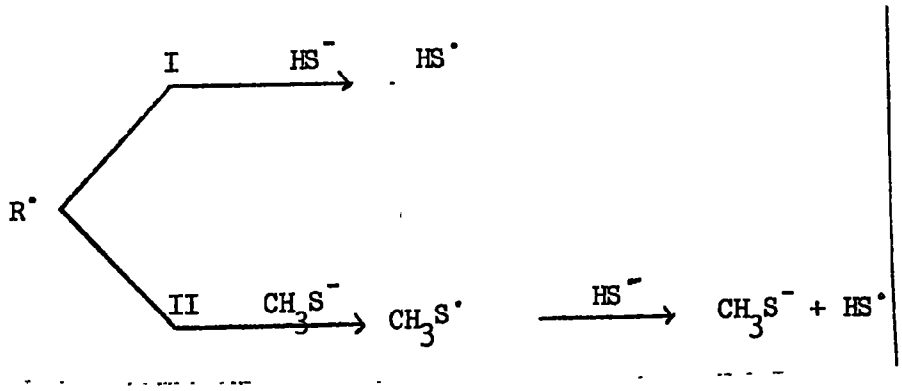


Figure 11 Oxidation of methyl mercaptan with 5 g/l sodium sulfide added.

mechanisms. From this study, the apparent order of stability of thivl radicals was determined: $HS^{\cdot} > CH_3S^{\cdot} > C_2H_5S^{\cdot}$. Thus, it appears that the following competing reactions may occur;



(22)

Where $R^{\cdot}$ could be any radical present, e.g. hydroxyl-,perhydroxy-radical or the biradical oxygen. Since $HS^{\cdot}$ is more stable than $CH_3S^{\cdot}$, route I should be preferred. If route II occurs the rate of $CH_3S^{\cdot}$ formation should be slower than $HS^{\cdot}$ formation. Furthermore, transfer of an electron would form the more stable CH_3S^{-} ion and $HS^{\cdot}$ radical. Thus, if hydrosulfide is abundant, the concentration of $CH_3S^{\cdot}$ is too small or its life time too short to undergo further reactions which would lead to the disulfide.

However, the experiment conducted at 150°C (Figure 11) does not show any inhibition for methyl mercaptan oxidation. An analysis at the point where approximately 25% of methyl mercaptan had been converted showed the presence of significant amounts of sodium sulfide. Thus, apparently under these conditions methyl mercaptan oxidation was not inhibited by the presence of sodium sulfide. Birrell (20)

has reported a change in relative stability of $HS^{\cdot}$ and $CH_3S^{\cdot}$ radicals with temperature. For instance it was suggested that at temperatures between 125 and 150°C the $HS^{\cdot}$ and $CH_3S^{\cdot}$ radicals have about equal stability. Thus, at 150°C route I and II are equally possible and reaction (23) should not be important.

$$CH_3S^{\cdot} + HS^{-} \longrightarrow CH_3S^{-} + HS^{\cdot} \qquad (23)$$

It has been shown that the presence of sodium sulfide is required for the hydrolysis of dimethyl disulfide, and thus for permanent conversion of methyl mercaptan to nonvolatile methane sulfinic acid. At the same time, at temperatures below 100°C the concentration of sodium sulfide must be below about 0.2 g/l to permit oxidation of methyl mercaptan to dimethyl disulfide. Thus, efficient oxidation of methyl mercaptan will be very difficult to achieve under practical black liquor oxidation conditions. On the other hand, at higher temperatures methyl mercaptan oxidation is not retarded by sodium sulfide, and dimethyl disulfide hydrolysis by sodium hydroxide is rapid. As a consequence high temperature black liquor oxidation should be more efficient for odor control.

The second effect of sodium sulfide is discussed in the following section.

4. Methyl Mercaptan Reactions During Black liquor Oxidation at Temperatures Below 100°C

In the following experiment sodium sulfide, Kraft lignin and methyl mercaptan were added to an alkaline solution of pH of 13 and 75°C to simulate

black liquor and the results are shown in Figure 12. As expected from earlier discussions methyl mercaptan rapidly disappeared. Apparently all methyl mercaptan was consumed by rapid 1,4-addition to the quinonoid structures in lignin since no dimethyl disulfide could be detected. Surprisingly, methyl mercaptan was slowly regenerated following its initial rapid consumption. This rapid consumption followed by slow regeneration may be explained in terms of the nucleophilicity of ionic species in black liquor and their relative concentration at different stages of the oxidation.

Turunen (21) and Goheen (22) have shown that the nucleophilic strength of anions is in the following order; $CH_3S^- > HS^- > HO^-$. Thus, the methyl mercaptide anion should compete most effectively for quinonoid structures and be rapidly consumed by nucleophilic 1-4 addition. In early stages of oxidation when methyl mercaptan concentration is relatively large the weaker hydrosulfide nucleophile competes ineffectively with mercaptide for the quinone structures. However, when the mercaptide concentration becomes depleted (for example after about 2 minutes in Figure 12 the ratio of hydrosulfide to mercaptide is much greater than at zero time. Thus, although hydrosulfide is a weaker nucleophile, as a result of its much higher concentration a slow displacement of the mercaptide may occur according to reaction 24.

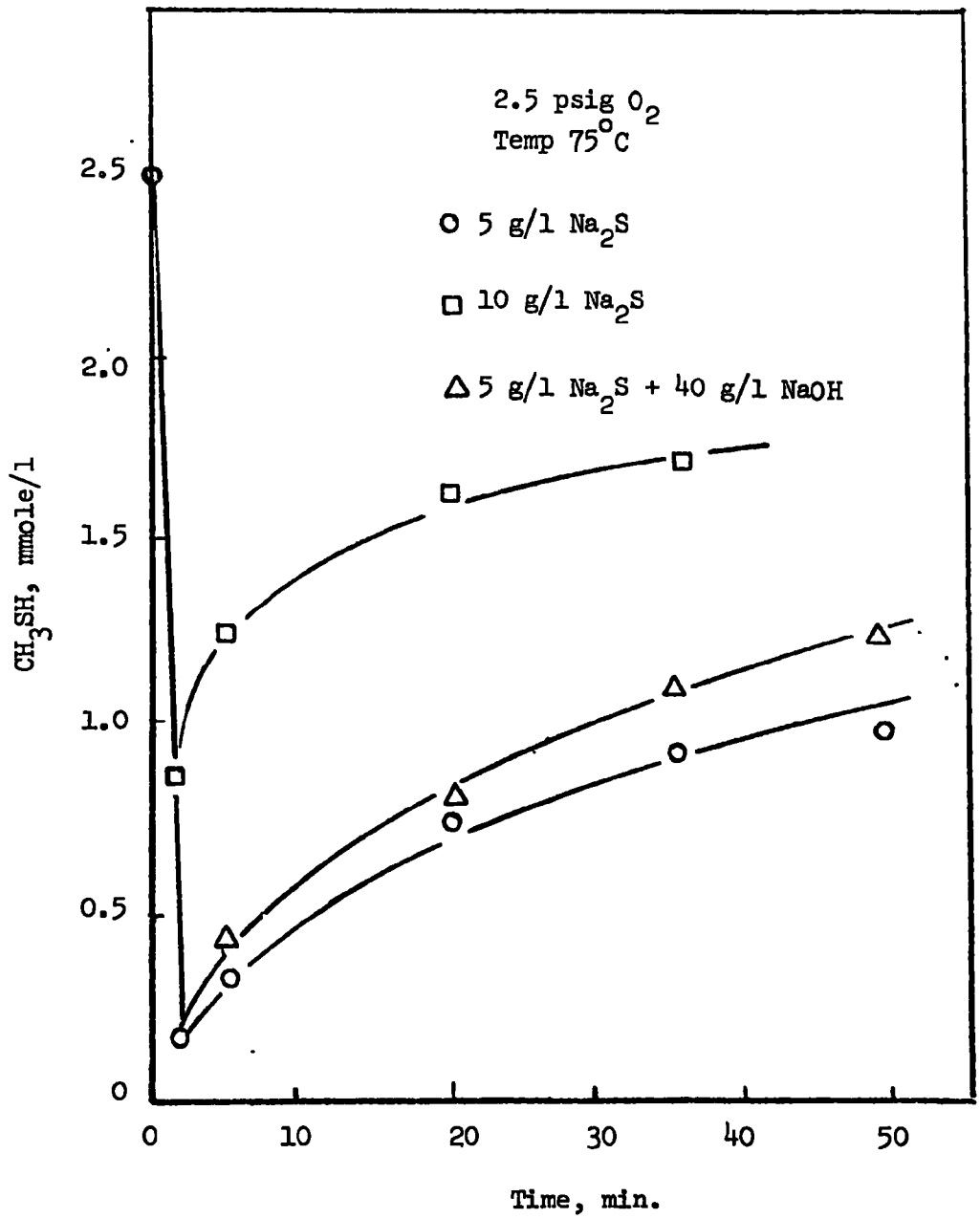
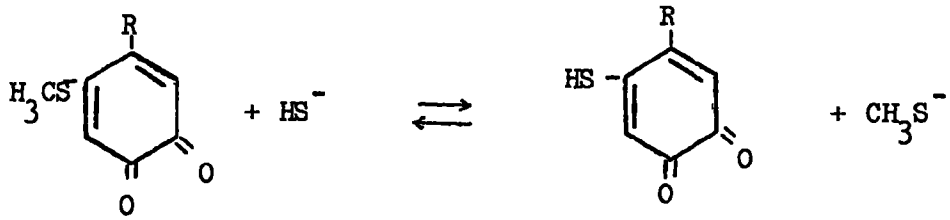
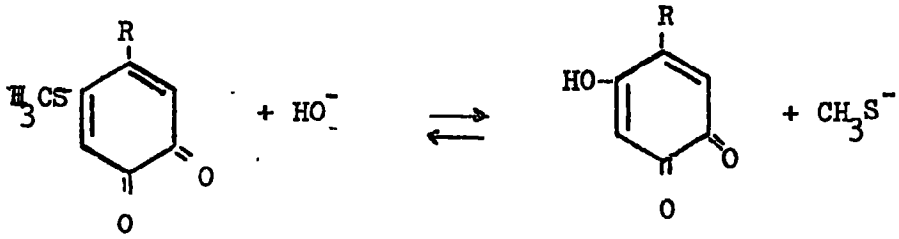


Figure 12 Consumption of methyl mercaptan in simulated black liquor.



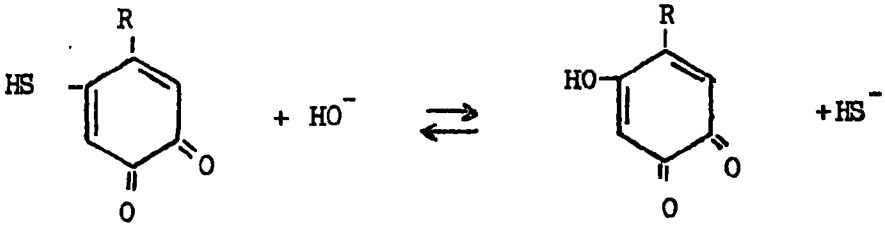
(24)

When the concentration of sodium sulfide was increased to 10 g/l significantly more methyl mercaptan was reformed as is shown in Figure 12. Large amounts of the weaker hydroxide nucleophile should also displace the mercaptide ion as shown in reaction 25.



(25)

Indeed, this was found and is shown in Figure 12. If the conditions are appropriate, reaction (26) could possibly also take place.



(26)

Although no detailed experimental studies were made, a slow displacement of hydrosulfide from lignin by the hydroxide ion during storage and evaporation of oxidized black liquor could partially account for sulfide "reversion" reported by numerous Kraft mills.

Methyl mercaptan in an aqueous alkaline solution will be oxidized by molecular oxygen, but in these experiments the regenerated methyl mercaptan did not oxidize. It has been shown that even small amounts of sodium sulfide could effectively inhibit the oxidation of methyl mercaptan. Analysis after 50 minutes (see Figure 12) revealed that there was still sufficient sodium sulfide left to inhibit methyl mercaptan oxidation. This suggests that the stability of methyl mercaptan in this simulated black liquor oxidation results from inhibiting effects similar to those earlier discussed.

In summary, methyl mercaptan oxidized under simulated practical conditions with molecular oxygen, is rapidly consumed without formation of dimethyl disulfide. It has been proposed that almost all methyl mercaptan undergoes an initial rapid 1,4-addition with the quinonoid structures present in lignin. However, methyl mercaptan can be slowly displaced from the 1,4-addition product by hydrosulfide or hydroxide at rates dependent on relative concentrations of the three anions. At higher temperatures and longer times the hydrosulfide should be slowly displaced by the hydroxide ion which is present in black liquor at concentrations of about 0.1 to 0.5 mole/l.

5. Methyl Mercaptan Reactions During Black Liquor Oxidation at Temperatures Above 100°C

Figure 13 illustrates the fate of methyl mercaptan when 2.5 mmole/l was oxidized with 10 psig oxygen in a solution containing 5 g/l Kraft

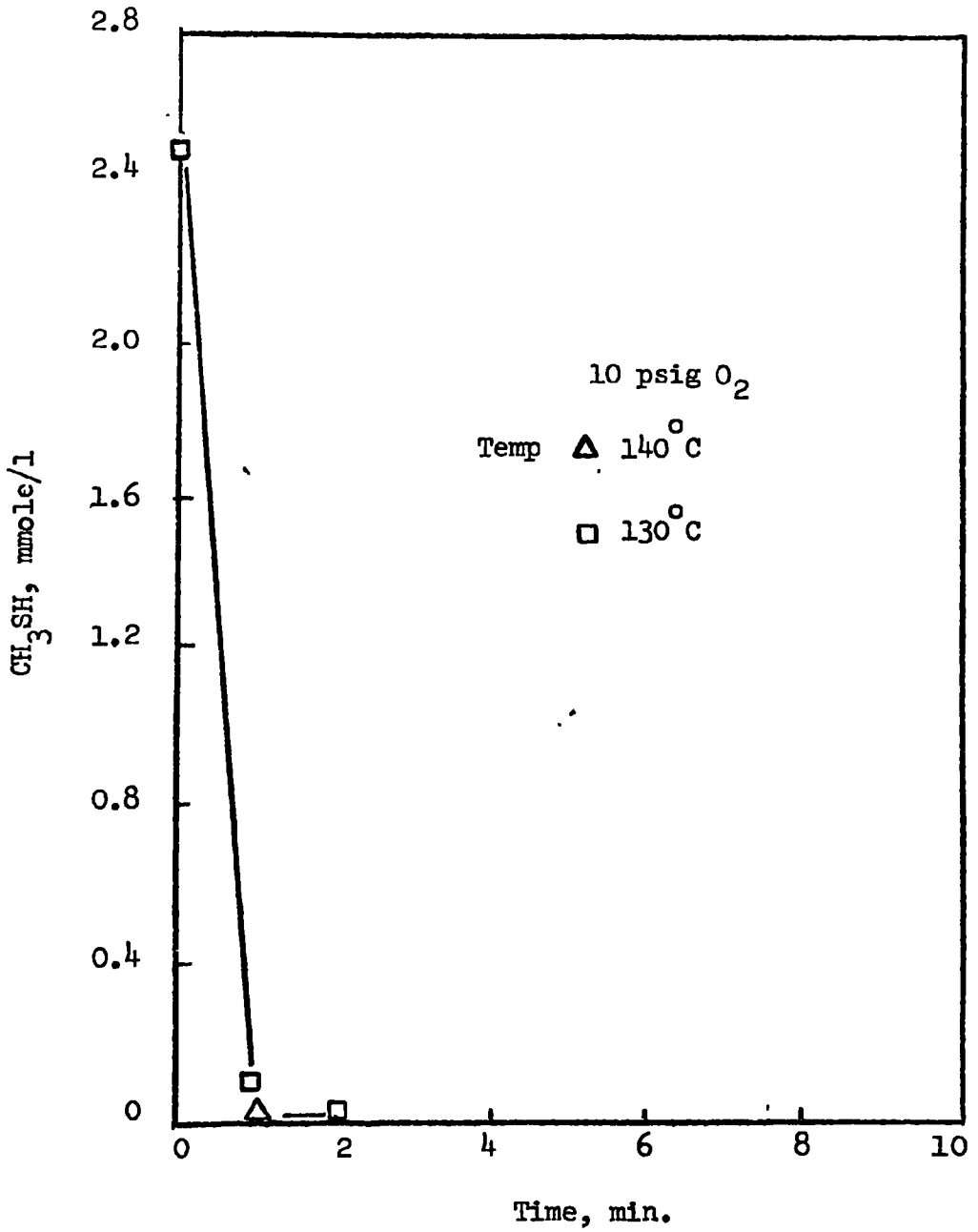
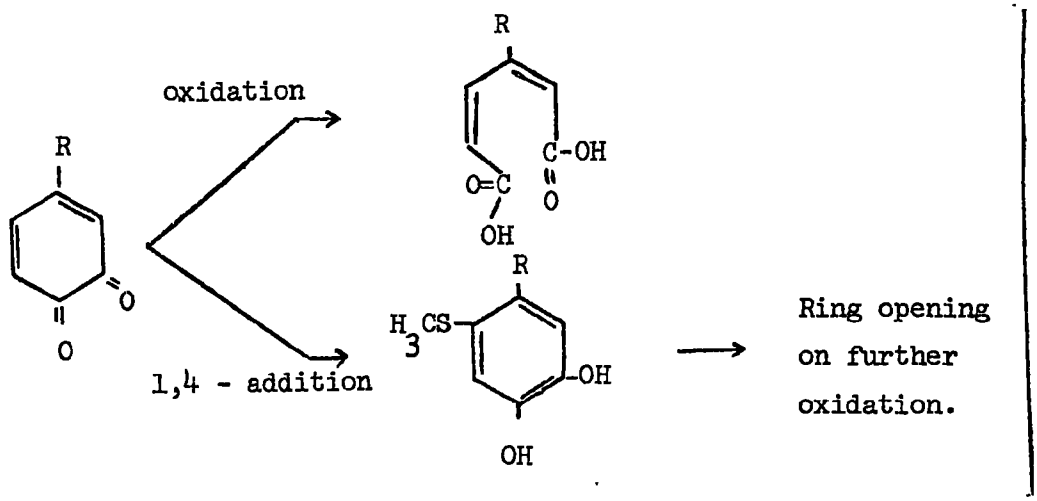


Figure 13 Consumption of methyl mercaptan in simulated black liquor.

lignin and 5 g/l sodium sulfide at 130 and 140°C respectively. Methyl mercaptan was rapidly consumed with no detectable amounts of dimethyl disulfide at any time during the oxidation. Furthermore, no methyl mercaptan was regenerated. The following two events may occur:

1. The fact that methyl mercaptan is not regenerated suggests the absence of the 1,4-addition products.

It is well known that lignin related quinonoid structures are rapidly oxidized to a variety of aliphatic acids at temperatures above 100°C (23). Thus, quinonoid structures generated at these high temperatures could react by two general routes as shown in equation 27.



(27)

Further oxidation of the quinonoid structures with or without thiomethyl group (s) in the ring will result in opening of the ring (16). It is suggested that the thiomethyl group cannot be displaced from these further oxidized (muconic acid) structures.

2. Apparently, at these high temperatures sodium sulfide does not inhibit the oxidation of methyl mercaptan.

While studying the inhibition effect of sodium sulfide in a pure system, the oxidation of methyl mercaptan appeared to be no longer affected by sodium sulfide at 150°C. Since the inhibition was observed in the presence and absence of lignin, it is suggested that results obtained in a pure system may be used to interprete results obtained when lignin was present. Thus, it is possible that at high temperatures methyl mercaptan is oxidized very rapidly to dimethyl disulfide even in presence of sodium sulfide.

The activation energy for the hydrolysis of dimethyl disulfide by hydroxide was found to be quite high (27.3 Kcal/mole), indicating a significant temperature effect. In fact, at 130 to 140°C the rate of hydrolysis of dimethyl disulfide was found high enough to keep the concentration of the disulfide at an undetectable level.

It can be concluded that methyl mercaptan when oxidized in a system resembling black liquor at temperatures of 130-140°C is consumed rapidly and no regeneration takes place. Thus,oxidation at high temperatures resultsin efficient destruction of methyl mercaptan and dimethyl disulfide.

C. Summary of Methyl Mercaptan and Dimethyl Disulfide Oxidation Kinetics in Simulated Black Liquor

The reactions of methyl mercaptan during black liquor oxidation have been described. From the available information a general scheme outlined in Figure 14 describes the reactions for the conversion of methyl mercaptan to its non-volatile products. The temperature at which black liquor oxidation is carried out is the single most important variable. Above about 70°C sodium sulfide may be oxidized completely to sodium thiosulfate (3,5). But a below 90-100°C, a complete and permanent conversion of methyl mercaptan to non-volatile products does not seem possible. However, at above about 125°C the reactions taking place are significantly different, resulting in a complete and permanent conversion of methyl mercaptan.

When black liquor containing methyl mercaptan is oxidized at 60-90°C with oxygen the first reaction to take place is the oxidation of the polyphenolic structures in the lignin to quinonoid structures followed by a very rapid 1,4-addition with methyl mercaptide anion. This results in the formation of mono, di- and tri-thiopolyphenols by a series of successive steps of oxidation and addition. However, under these low temperature conditions, methyl mercaptan is regenerated under the influence of hydrosulfide and hydroxide. With an excess of sodium sulfide practically all methyl mercaptan initially present could be regenerated, suggesting that possibly all methyl mercaptan undergoes the

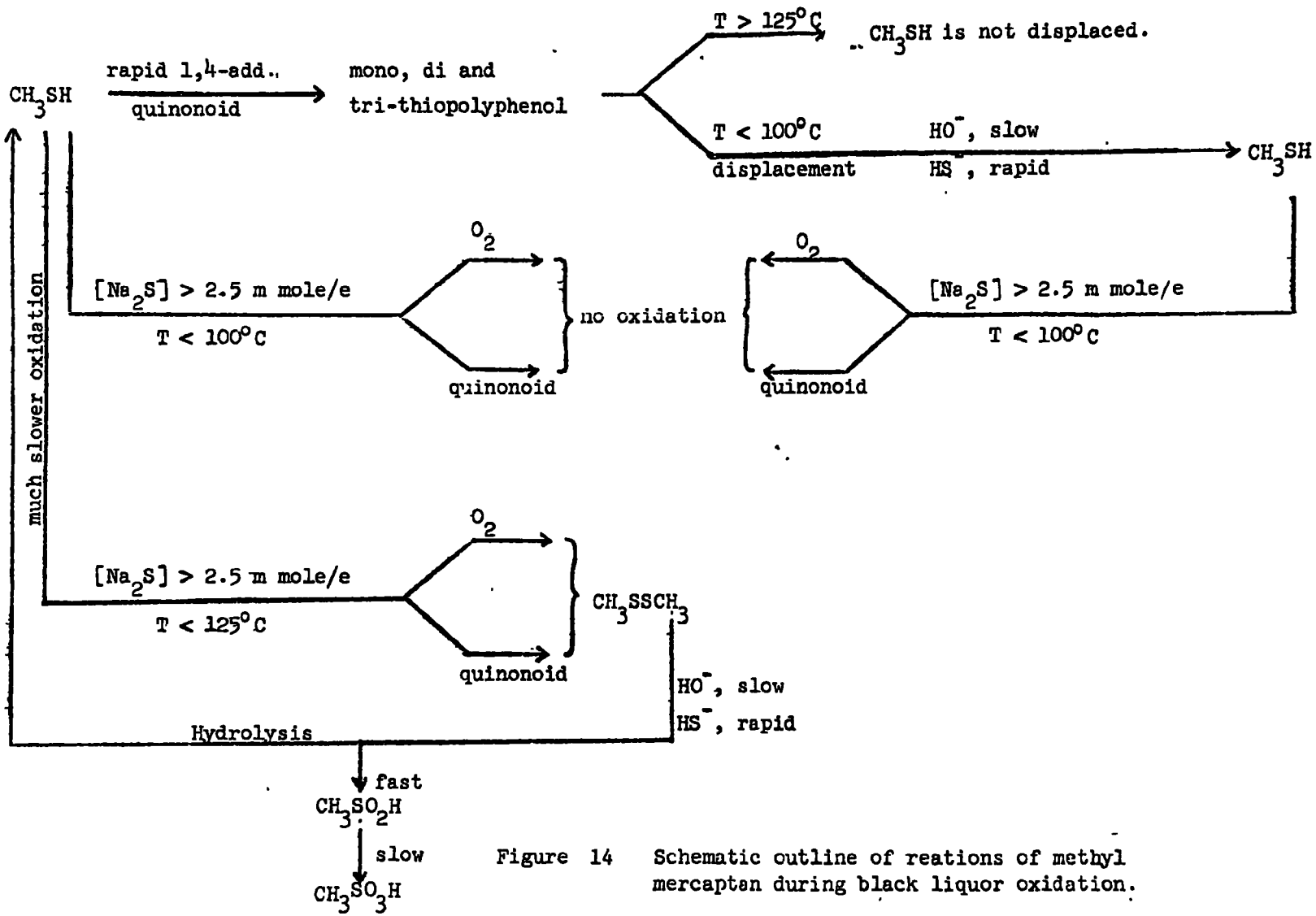


Figure 14 Schematic outline of reations of methyl mercaptan during black liquor oxidation.

1,4-addition with the quinonoid and the direct oxidation to dimethyl disulfide either by oxygen or the quinonoid is negligible. In the presence of sodium sulfide, the oxidation of methyl mercaptan is inhibited, until the sodium sulfide has diminished by approximately 95-98%. This is usually the condition at which black liquor oxidation is stopped in practice. Thus, when the oxidation is terminated the regenerated methyl mercaptan is left in the black liquor while the remainder is in the form of mono, di-or tri-thiopolyphenol. If one desires total oxidation of methyl mercaptan, the oxidation should be continued. With prolonged time methyl mercaptan oxidation follows a continuous oxidation-hydrolysis cycle with dimethyl disulfide intermediate in which one cycle converts four moles of mercaptan to one mole methane sulfinic acid and with regeneration of three moles methyl mercaptan. A sufficient number of cycles will lead ultimately to complete conversion of methyl mercaptan and dimethyl disulfide to the non-volatile methane sulfinic acid. The completion of this oxidation-hydrolysis cycle, however, will be very difficult to obtain. Because of the very low concentration of hydrosulfide the intermediate dimethyl disulfide must be hydrolysed by hydroxyl. Unfortunately, the rate of this reaction is very slow at these low temperature conditions. Moreover, methyl mercaptan is continuously, slowly displaced from its addition product by hydroxyl. These results suggest how substantial quantities of methyl mercaptan and dimethyl disulfide could survive a conventional black liquor oxidation.

The emissions of methyl mercaptan and dimethyl disulfide from the recovery area of a mill could be minimized by several means. Black liquor oxidation systems employing pure oxygen do not require venting so methyl mercaptan and dimethyl disulfide will not be stripped from the oxidizer. Reduced "hold up" time between the black liquor oxidizer, direct contact evaporator and recovery furnace would minimize the time for slow release of methyl mercaptan from its addition product. The best system employing conventional conditions would appear to be strong black liquor oxidation with direct feed into the direct contact evaporator.

Alternatively oxidation at higher temperatures would offer improved efficiency for several reasons. First, at temperatures above approximately 125°C the quinonoid structures are quite easily further oxidized to aliphatic products. It is not known at this time whether, under these conditions, the life time of the quinonoid is long enough to undergo nucleophilic 1,4-addition with the mercaptide ion. However, if 1,4-addition should take place the resulting thiopolyphenol should be rapidly unstable at these conditions. Further oxidation to aliphatic products should rapidly follow and displacement of methyl mercaptan from these oxidized products should not occur.

Second, the oxidation of methyl mercaptan is no longer inhibited by the presence of sodium sulfide at temperatures above 125°C. As a result, methyl mercaptan should also be oxidized in the early stages of [illegible] oxidation over which [illegible] sodium sulfide remain. Sodium sulfide will be available to promote the important dimethyl [illegible] hydrolysis.

Finally, the activation energy of hydrolysis by hydroxide is about 28 Kcal/mole while that by hydrosulfide is 16 Kcal/mole. Therefore, above 125°C the rate of hydrolysis by hydroxide becomes quite significant because of the high specific rate constant at those temperatures and the constant high concentration of hydroxide.

The following sections describe laboratory studies of an in-digester black liquor oxidation to confirm the results predicted by the earlier sections of this report.

D. Odor Reduction by In-Digester Oxidation of Kraft Black Liquor with Oxygen at Temperatures above 80°C

This section reports on investigations to study the feasibility of in-digester BLO with oxygen as the oxidant. The following specific questions are addressed: a) At what stage of pulping should oxygen be injected into the digester? b) What is the oxygen consumption and utilization efficiency with respect to the oxidation of sodium sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide? and c) What is the influence of the oxygen injection on the pulp yield and the physical and optical properties of the pulp?

1. The Influence of Sodium Sulfide Throughout Kraft Pulping

The mechanisms involved in the formation of methyl mercaptan and dimethyl sulfide during a kraft cook has been well established (3). In a first step, hydrosulfide ions react with lignin methoxyl groups to form methyl mercaptan. The latter dissolves in the cooking liquor forming methyl mercaptide ions. These react further with lignin methoxyl groups to yield dimethyl sulfide. In the kraft pulping of softwood, the major portions of methyl mercaptan and dimethyl sulfide are formed after a temperature of 170°C has been reached (3). If the sulfide ion is partly or fully removed by oxidation with oxygen at this stage, the formation of methyl mercaptan and dimethyl sulfide may also be reduced or prevented.

A preliminary series of cooks were studied to determine if reduction or removal of sodium sulfide after 170°C has been reached will influence the rate of delignification and the obtainable pulp yield. This may not necessarily be so, since Gierer and Smedman have shown that considerable amounts of thiol groups are already introduced in the lignin molecule at 150°C (24).

Loblolly pine (Pinus taeda L.) chips were pulped in 2.8-liter autoclaves as described in the experimental section. Autoclaves were removed at different time intervals, and the pulping was arrested by cooling the autoclave in cold water. Figure 15 shows the content of effective alkali and sodium sulfide in the liquor, as a function of cooking time and temperature, in regular kraft pulping of this wood species. From an oxidation point of view, it is important to note that the content of sodium sulfide decreases by about 50% throughout the pulping and that about 80% of this decrease apparently occurs before the maximum temperature has been reached. Since only a slight increase in the content of sodium thiosulfate and no significant changes in the contents of sodium sulfite and polysulfide were measured, the decrease in the content of sodium sulfide may be largely the result of early introduction of sulfur into the lignin in accordance with Gierer and Smedman's results.

Figure 15 illustrates the approach used to study the influence of a reduction or removal of sodium sulfide during the latter part of the pulping on the rate of delignification and the pulp yield. Regular kraft cooks were interrupted as soon as the maximum temperature of 170°C was

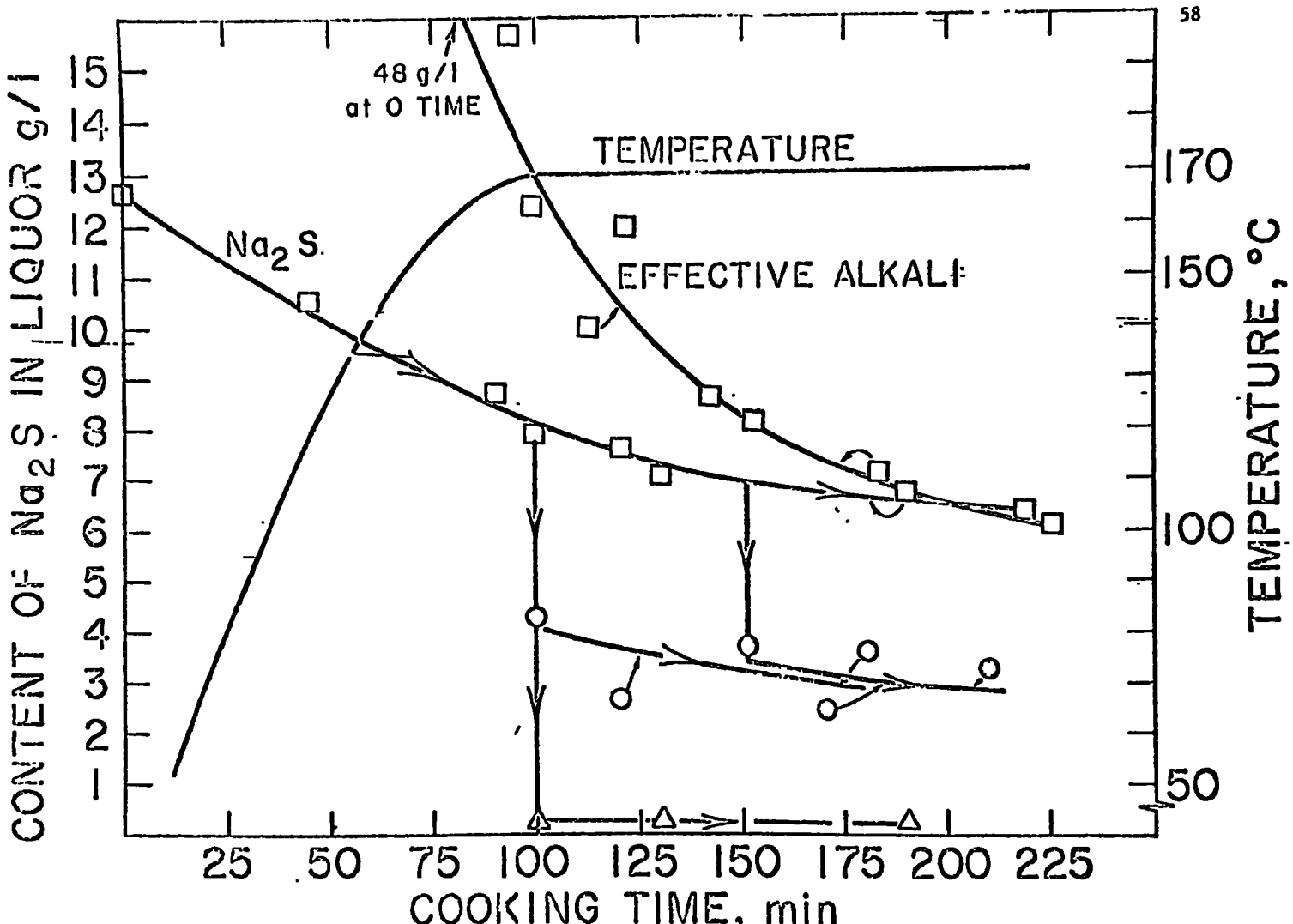


Figure 15. Composition of cooking liquor as a function of cooking time, and temperature in regular kraft cooking and liquor exchange cooks of loblolly pine. Cooking conditions: effective alkali 18.5% (NaOH), sulfidity 25% liquor to wood ration 4:1 □ Regular kraft cooks. △ Liquor exchange cooks with 0% sulfidity in second stage liquor. ● ○ liquor exchange cooks with 50% liquor replacement in second stage.

reached (100 min.) and rapidly cooled to room temperature. In some cooks, 50% of the total volume of black liquor was replaced by sodium hydroxide solution with a content of effective alkali equivalent to the effective alkali content of the withdrawn black liquor. Subsequently, the autoclaves were rapidly reheated to 170°C to complete the pulping. The content of sodium sulfide in the second stage was approximately 50% of the sodium sulfide content of the regular cook (Figure 15). In other cooks,the total volume of black liquor was removed from the partly cooked chips by washing with water. Again, a sodium hydroxide solution was added yielding a content of effective alkali equivalent to the effective alkali of the removed black liquor. In a third series, regular kraft cooks were interrupted after 150 minutes, cooking time, 50% of the black liquor was replaced by sodium hydroxide solution, and the pulping was then completed. Regular kraft cooks which had been cooled and reheated at the same stages as the two-stage cooks served as control.

The relationship between total pulp yield and lignin content of regular kraft pulps and two-stage pulps is shown in Figure 16. All of the two-stage cooks with 50% or 0% of original sodium sulfide in the second-stage liquor have lower pulp yields compared at equal lignin contents. The yield difference seems to be of the same magnitude for both 50% and 0% sodium sulfide and may vary from about 0.5% (on wood) at intermediate yield levels to about 2% at low levels.

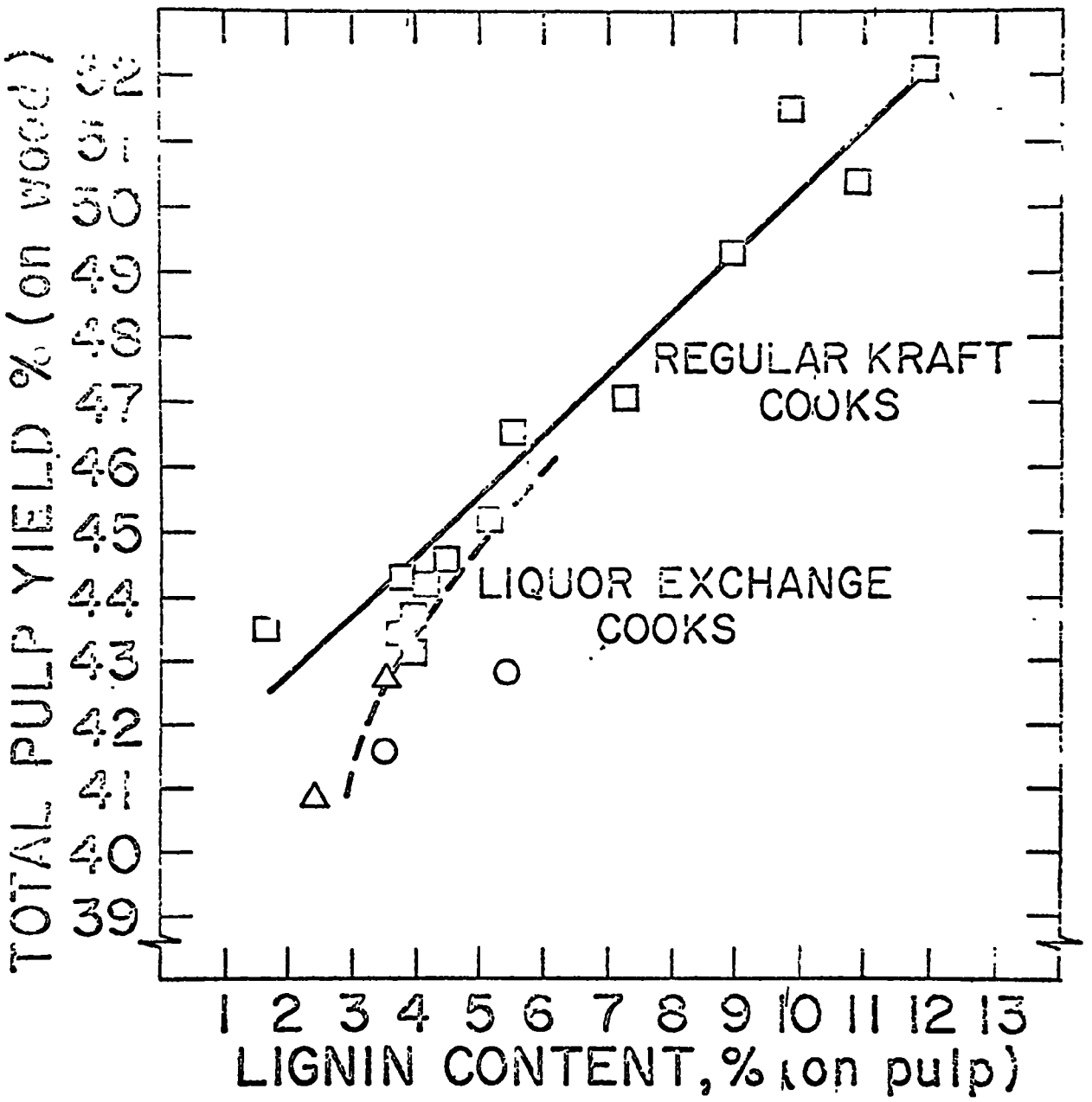


Figure 16

Total pulp yield as a function of pulp lignin content.

Although, surprisingly, no significant differences in the rate of delignification were found between regular kraft cooks and liquor exchange cooks, the early sulfidation of lignin did not prevent the loss in carbohydrate yield that was observed under two-stage cooking conditions. Hartler, Andersson, and Bergstrom studied two stage cooks with liquor exchange at 155°C and reduced sulfidity in the second stage (25). These authors also found a loss in total pulp yield in such cooks.

These results, therefore, suggest that injection of oxygen into the digester to oxidize sodium sulfide should be carried out as late in the cook as possible.

2. In-Digester Oxidation: Influence on Inorganic Components

Various amounts of oxygen were injected into the circulation line of a laboratory batch digester from 2 to 30 minutes before blowing the digester. The black liquor was analyzed for sodium sulfide, thiosulfate, and effective alkali before and after oxygen injection. The oxidation of sodium sulfide should result in thiosulfate formation following the overall reaction 1 repeated here.

$$2\ S^{=} + 2O_2 + H_2O \longrightarrow S_2O_3^{=} + 2\ OH^- \qquad (1)$$

The sodium sulfite and polysulfide contents were determined on selected cooks, but only negligible quantities were detected. Thus, sulfur material balances showed that disappearance of sulfide corresponded with almost stoichiometric formation of thiosulfate as predicted by reaction (2). Since polysulfide and free sulfur were not formed in detectable quantities, the resulting oxidized black liquor should not be subject to reversion with subsequent formation of sulfide anion. This is presently being studied in more detail.

Oxygen requirements at various sodium sulfide oxidation efficiencies for one series of cooks are shown in Figure 17. For example, 90% oxidation of liquor containing approximately 8 g/liter sodium sulfide requires about 70 g when using an oxygen injection rate of 5.3 g/min. under the present conditions. Proportionally, higher amounts of oxygen were required to achieve a higher degree of sodium sulfide oxidation.

The consumption of 70 g of oxygen is equivalent to two moles of oxygen per mole of oxidized sodium sulfide or 2.3% (calc.) based on wood or 4.5-5% based on pulp. The stoichiometric amount of oxygen required is one mole per mole of sodium sulfide according to reaction (2). Therefore, other oxygen consuming reactions must also proceed under the present conditions of oxidation. Since sulfur balances show only sodium sulfide and thiosulfate as major components in the liquor, reactions which cause oxygen consumption in excess of requirements for sodium sulfide oxidation very likely involve the oxidation of lignin and/or polysaccharide degradation products dissolved in the black liquor. Grangaard has shown that in such reactions, various carboxylic acids are formed in high yields (26).

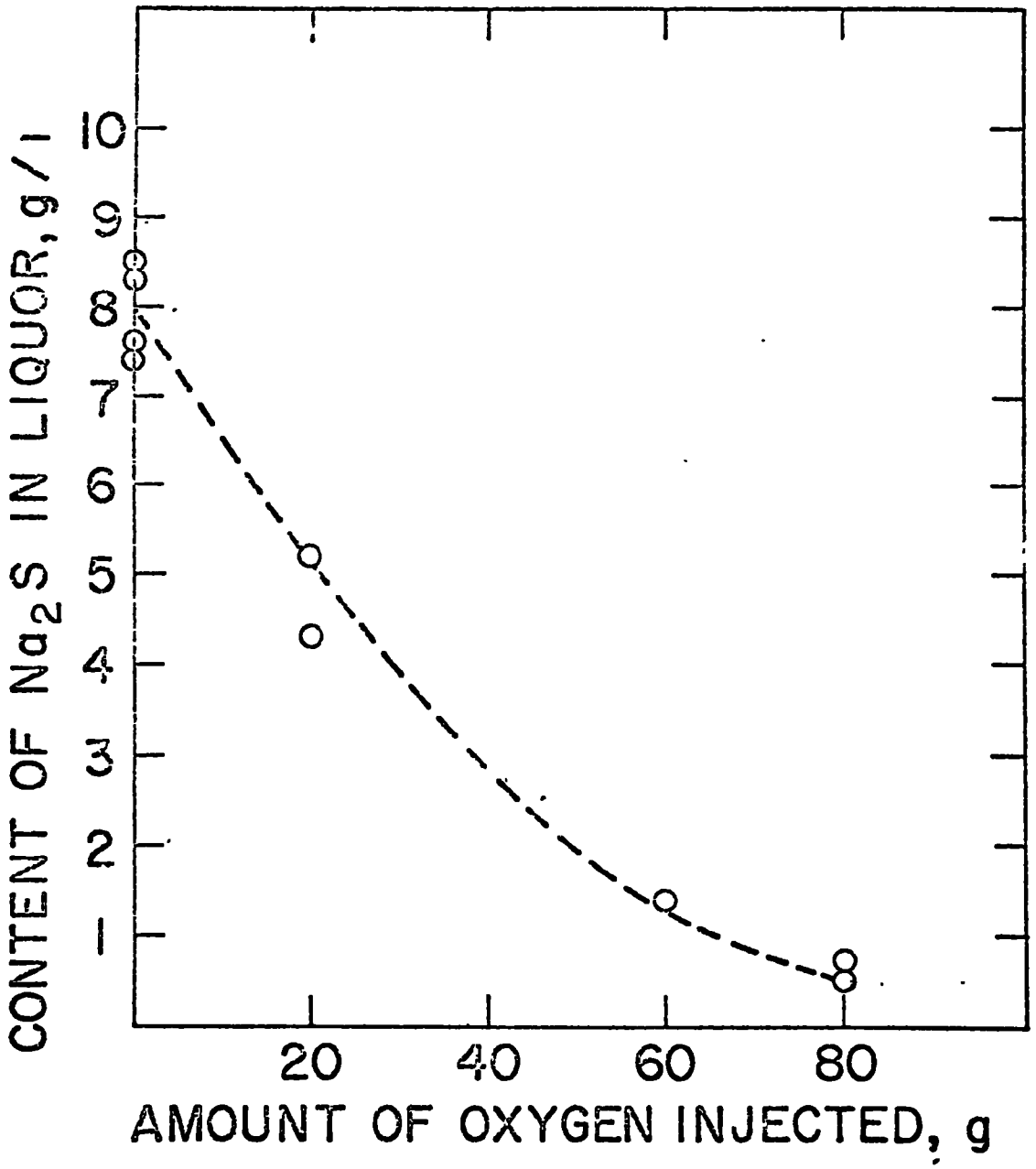


Figure 17
The content of sodium sulfide in black liquor as a function of the amount of oxygen injected at a rate of injection of 5.3 g of O_2/min. Total amount of liquor = 12 liter.

The formation of acidic groups is also reflected by a decrease in effective alkali. The consumption of effective alkali is significantly increased in oxygen injection cooks as compared to the composite average for several reference cooks (Figure 18). Removal of sodium sulfide should cause an apparent loss in effective alkali since one mole of sodium sulfide contributes 1/2 mole to effective alkali of the liquor. However, this is compensated for by a new formation of alkali in the oxidation reaction 2 described above. Thus, the reduction in effective alkali shown in Figure 18 is not explained by sodium sulfide oxidation.

The present studies employed injection rates of 5-100 g/min., the lower rates tending to require higher oxygen consumption to reach the same sulfide oxidation efficiency. In their studies Fones and Sapp (27) recorded oxygen requirements of about 4.5 moles of oxygen per mole of oxidized sodium sulfide which are significantly higher than the present work. This low oxygen utilization efficiency may have been caused by the very low injection rates and poor mixing used in that study.

In most cases black liquor samples were withdrawn from the digester approximately 2 minutes after the injection of oxygen. In some separate cooks, the pulping was continued for periods of up to 60 minutes after the oxygen injection was completed. Analysis of the black liquor showed no increase in the content of sodium sulfide during the continuation of the pulping indicating that analyses represented the total amount of black liquor present in the digester, including the portion penetrating the chips.

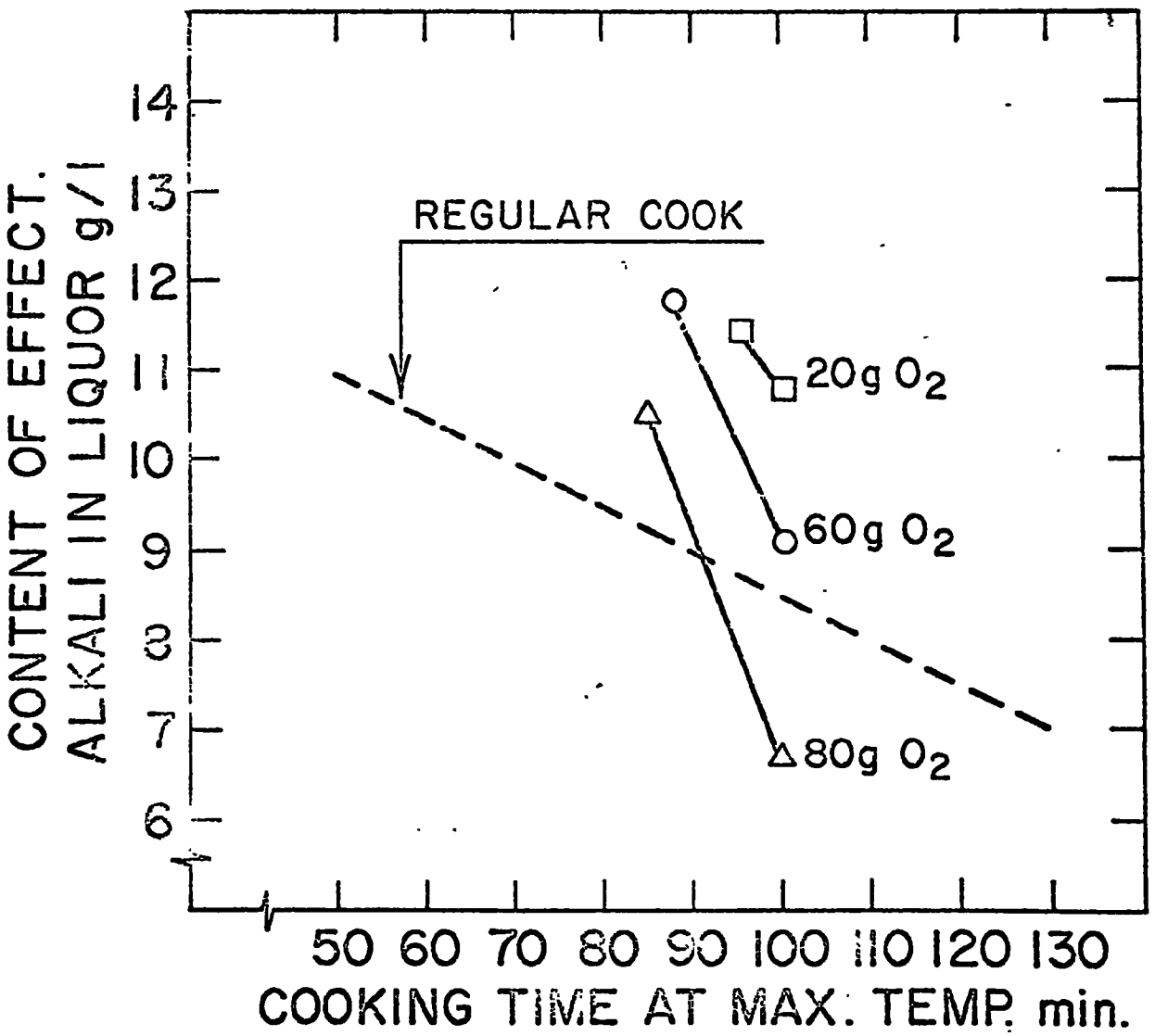


Figure 18

Effective alkali in black liquor in regular kraft cooks and cooks with injection of various amounts of oxygen at a rate of 5.3 g of O_2/min. Total amount of liquor = 12 liter.

In preliminary studies, the temperature in the digester increased about 4°C with the injection of 80 g of oxygen. In most cooks this was compensated for by reducing the supply of heating steam, and no increase in the digester pressure was found during the injection of oxygen. This indicates that the injected oxygen is consumed rapidly by the black liquor at digester conditions.

3. In-Digester Oxidation: Influence on Methyl Mercaptan, Dimethyl Sulfide, and Dimethyl Disulfide

Black liquor samples taken before and after oxygen injection were analyzed to determine the content of the malodorous sulfur compounds, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Samples were withdrawn from the circulation system through the liquor sampling valve.

In these cooks the amounts of methyl mercaptan and dimethyl sulfide generated during the heating up and constant temperature period prior to oxygen injection were consistent with other pulping studies (3). In all cooks the digester was evacuated before liquor injection to remove air and to facilitate impregnation of the wood chips by the liquor. Consequently, oxygen was absent from the digester during the heating up and constant temperature period of the cook so that methyl mercaptan oxidation was negligible and only trace amounts of dimethyl disulfide were found prior to oxygen injection.

At the end of the normal cooking time, various amounts of oxygen were injected to study the efficiency of oxidation of sulfur compounds. The results for methyl mercaptan oxidation are shown in Table V. The efficiency of oxidation is increased profoundly with increase of injected oxygen. Injection of 60 g of oxygen will destroy over 99.8% of the methyl mercaptan present at the end of a kraft cook.

After oxygen injection, pulping was continued for 45 minutes with black liquor samples analyzed at 15-minute intervals. Figure 19 shows that injection of 80 and 100 g of oxygen will cause almost total permanent methyl mercaptan removal. Injection of 20, 40, and 60 g of oxygen result in an initial drop in methyl mercaptan content of black liquor which is then followed by renewed formation. Injection of these lower amounts of oxygen does not totally destroy the sodium sulfide content of the black liquor. Consequently, methyl mercaptan formation can continue during the prolonged cooks by further demethylation of lignin.

The oxidation of methyl mercaptan involves conversion to dimethyl disulfide, and at conditions of conventional black liquor oxidation, substantial amounts of dimethyl disulfide are formed as follows:

$$4\ CH_3SNa + 2H_2O + O_2 \longrightarrow 2\ CH_3SSCH_3 + 4\ NaOH \qquad (28)$$

At the higher pulping temperatures, only trace amounts of dimethyl disulfide were measured following injection of oxygen. Regardless of the

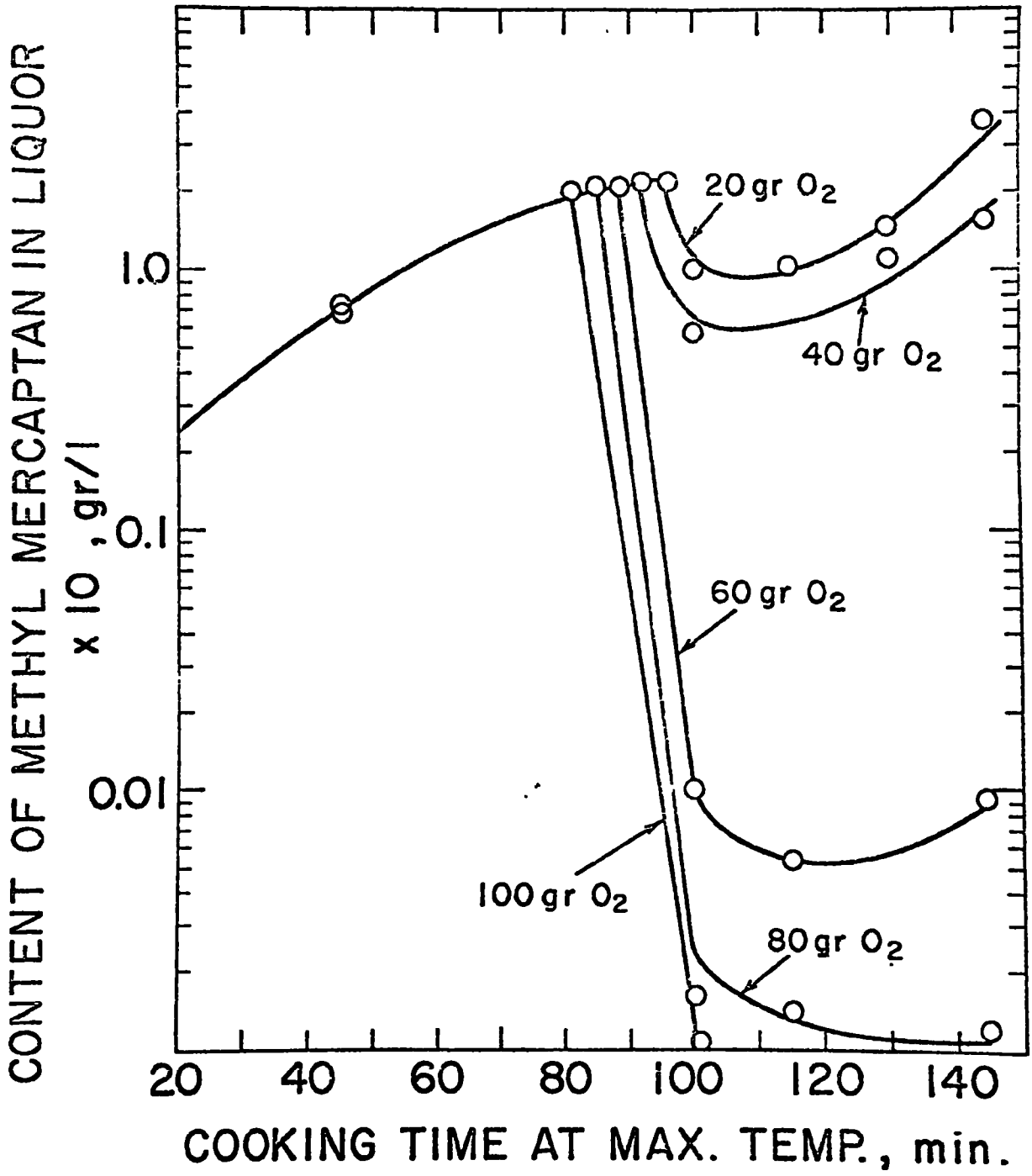


Figure 19

Methyl mercaptan content in black liquor at various amounts of injected oxygen. Total amount of liquor = 12 liter.

Quantity of Oxygen Injected, g	Methyl Mercaptan Concentration at End of Normal Cooking, g/ℓ	Methyl Mercaptan Concentration at End of Oxygen Injection, g/ℓ	Final Concentration / Initial Concentration
20	2.14×10^{-1}	1.01×10^{-1}	0.47
40	2.16×10^{-1}	0.85×10^{-1}	0.27
60	2.24×10^{-1}	0.01×10^{-1}	0.005
80	2.15×10^{-1}	0.001×10^{-1}	0.0005
100	2.31×10^{-1}	trace	0

Table V: Effect of quantity of oxygen injected on the methyl mercaptan content of black liquor.

amount of oxygen injected, no accumulation of dimethyl disulfide occurred. Consequently, in-digester oxidation by injection of oxygen near the end of technical kraft pulping provides a possible method for odor reduction by destruction of both methyl mercaptan and dimethyl disulfide.

Conversely, in-digester oxidation has much less influence on the content of dimethyl sulfide as shown in Figure 20. At low levels of oxygen injection, the formation of dimethyl sulfide is temporarily interrupted by the partial destruction of methyl mercaptan shown in Figure 19. Injection of 80 and 100 g of oxygen totally oxidizes the sodium sulfide and methyl mercaptan content of the black liquor, effectively halting further demethylation to form malodorous sulfur species. Under these conditions dimethyl sulfide content of black liquor decreased only slightly, indicating a mild oxidation of this substance.

4. In-Digester Oxidation: Influence on Pulp Yield and Pulp Properties

Table VI and Figure 16 show total pulp yields versus the lignin content of pulps obtained in regular kraft cooks and in cooks where 80 or more grams of oxygen were injected at the end of the cook with injection rates varying from 2.7 to 20 g/min. Under the present conditions the injection of oxygen does not noticeably influence the pulp yield when compared at equal lignin contents (Figure 16). Similar results were obtained in cooks with lower amounts of oxygen injected. Also, no significant differences were found between regular and oxygen injection cooks with regard to screened yields and the rate of delignification.

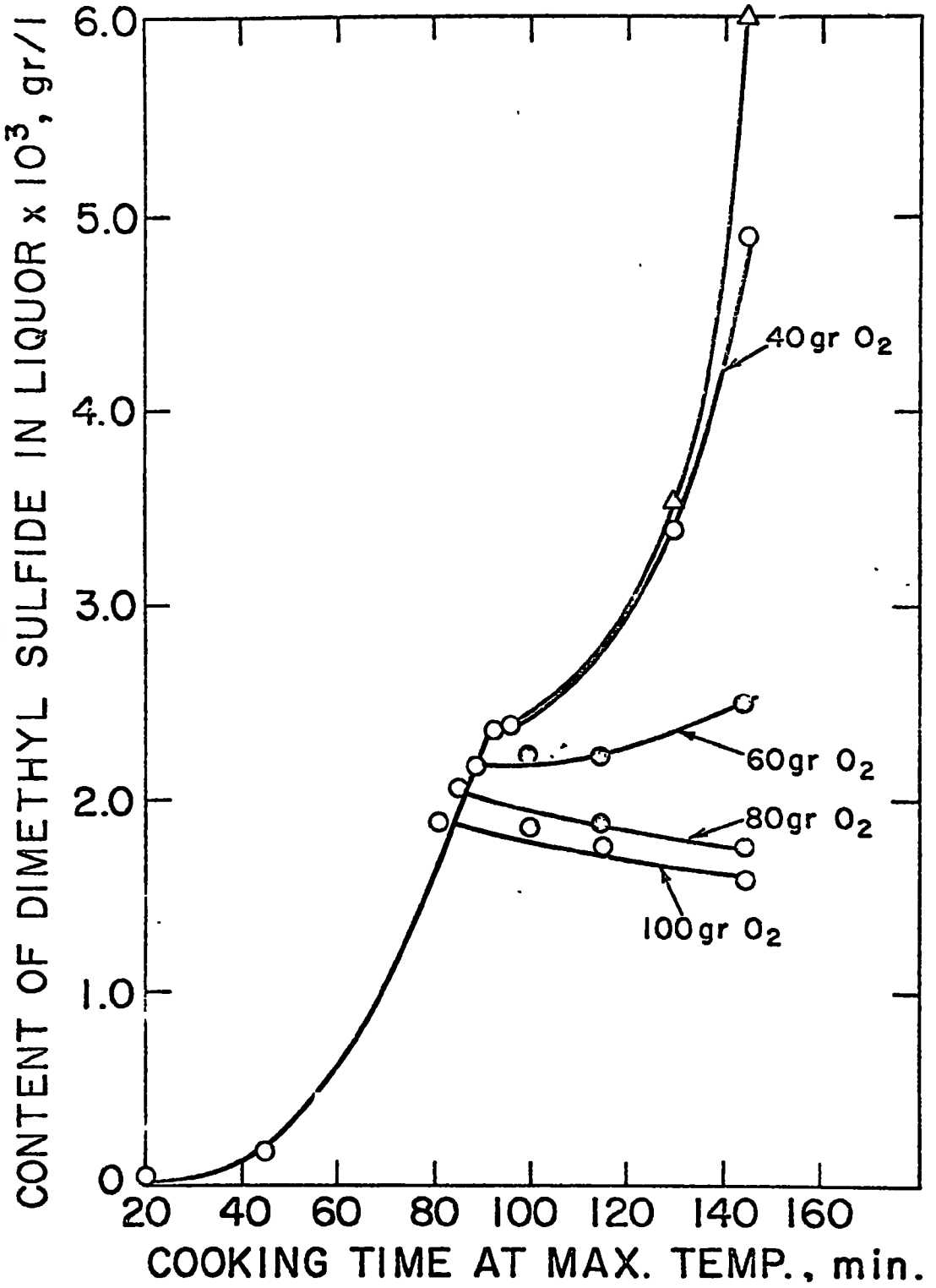


Figure 20. Dimethyl sulfide content in black liquor at various amounts of injected oxygen. Total amount of liquor=12 liter

Cook time at max. temp. min.	Eff. alkali in white liquor g/ℓ	Na_2S in white liquor g/ℓ	O_2 inj. g	Inj. rate g/min	Total pulp yield %	Lignin cont. %	Kappa No
80	47.5	13.1	0	--	48.7	7.8	--
80	45.8	12.4	0	--	50.3	8.1	60
90	48.2	13.3	0	--	48.3	7.4	53
90	46.5	12.6	0	--	49.1	7.6	52
100	47.2	13.0	0	--	48.6	7.0	48
130	46.8	12.5	0	--	46.0	4.8	36
150	43.7	12.8	0	--	45.6	4.9	32
60	49.2	12.3	80	5.3	51.1	9.1	--
80	49.8	10.9	80	5.3	48.6	7.3	--
90	48.2	12.6	96	9.6	51.4	7.7	53
100	45.5	13.1	80	20.0	47.9	6.5	46
100	45.0	12.8	80	2.7	47.4	6.5	47

Table VI: Total pulp yields in cooks with and without the injection of oxygen into the digester at the end of the cook. Liquor to wood ratio 4:1, 90 minutes from 25° - 170°C.

Burst, fold, tensile, and tear strength of 3 regular kraft pulps and 4 pulps which had been pulped with the injection of 77-96 g of oxygen were compared to study the influence of the oxygen injection on the physical properties of the pulp. All pulps had a lignin content between 6.7 and 8% (Kappa numbers from 48 to 58). In Figure 21 the injection of oxygen has no significant effect on the tear-tensile strength relationship of the pulps. The data in Table VII show that tear-burst relationship and folding endurance are compared to values obtained from normal kraft cooking. (Altogether more than 100 cooks were made in this study and data points are averages from replicated cooks.

Retention of strength characteristics do not agree with the conclusion made by Fones and Sapp who showed that the addition of oxygen at the end of a kraft cook significantly reduces pulp strength (27). However, these authors based their conclusion primarily on the significant strength losses observed in experiments in which unbleached, regular kraft pulps, buffered in a sodium carbonate solution, were pulped in an oxygen atmosphere. It is a moot question if such conditions may be considered as fully representative for the conditions existing at the end of a kraft cook. In the latter case sodium sulfide, lignin, and carbohydrate degradation products dissolved in the black liquor appear to favorably compete with the pulp in consuming the injected oxygen, thereby preventing strength losses.

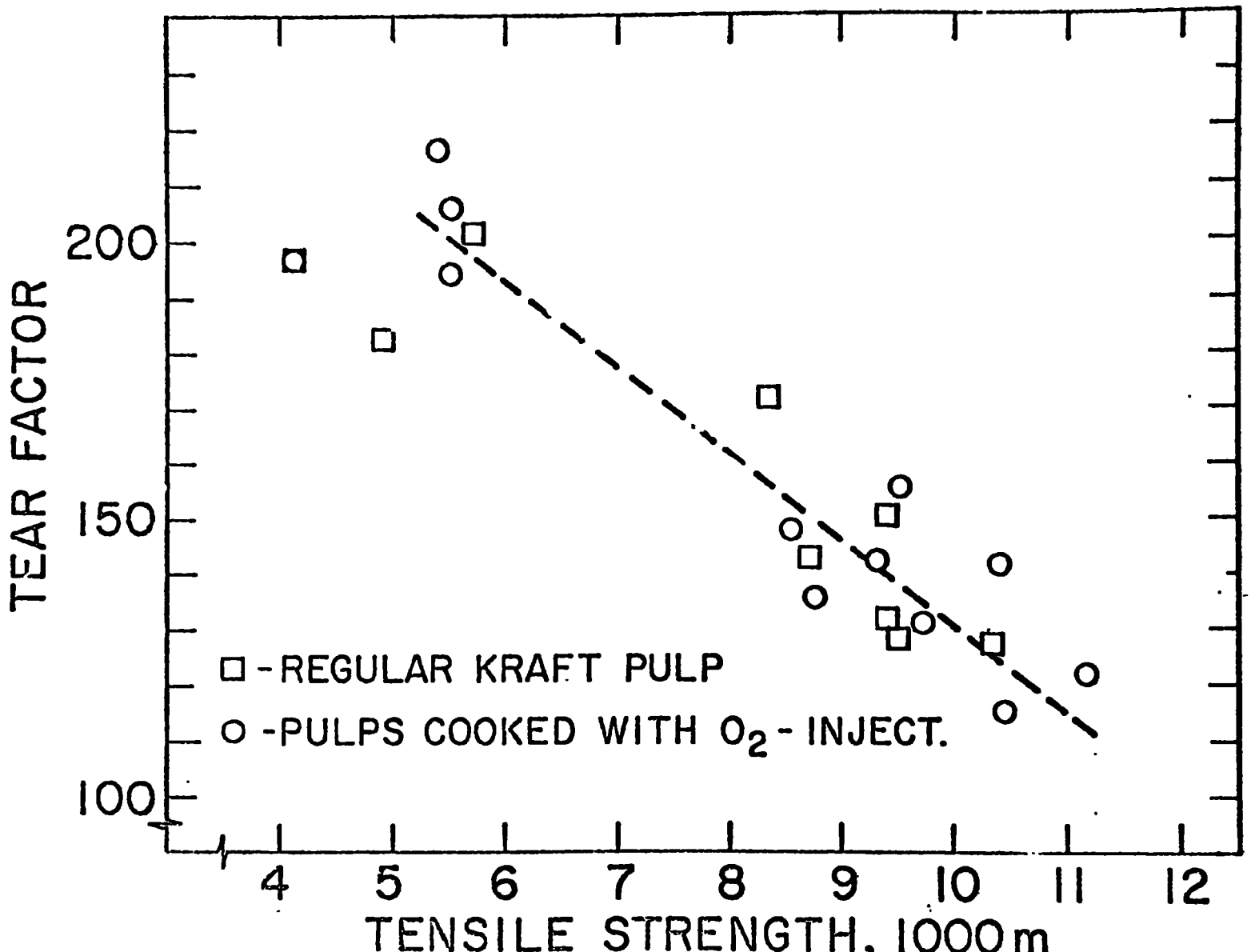


Figure 21. Tear factor versus breaking length for regular kraft pulps and pulps cooked with the injection of oxygen.

In accordance with Fones and Sapp's results, the present investigations indicated that the pulps with oxygen injection were somewhat easier to beat to a given tensile strength (Table VII and Figure 22). Table VII additionally indicates that, at equal tensile strength, the oxygen injection pulps have a higher freeness.

Also, in agreement with the latter authors, a decrease in the pulp brightness varying from 0.5-2 units was found as a consequence of the injection of oxygen (Table VIII). This decrease is, however, much lower than previously reported.

5. In-Digester BLO at Variable Temperatures

While high temperature BLO should be more efficient at odor control, it is important to know the influence of oxidation temperature upon the oxygen consumption. Experience shows that in conventional BLO systems (60-80°C) oxygen consumption often amounts to a 5 to 10% excess over the stoichiometric requirements for reaction (2). At high temperatures (170°C) about 100% excess oxygen was required as discussed in the last section. While an increase in oxidation temperature may cause increased oxygen consumption by reaction with lignin, the critical temperatures have not been established. This section describes experiments made between 80 and 150°C to determine oxygen consumption and oxidation efficiency with respect to sodium sulfide, methyl mercaptan and dimethyl disulfide.

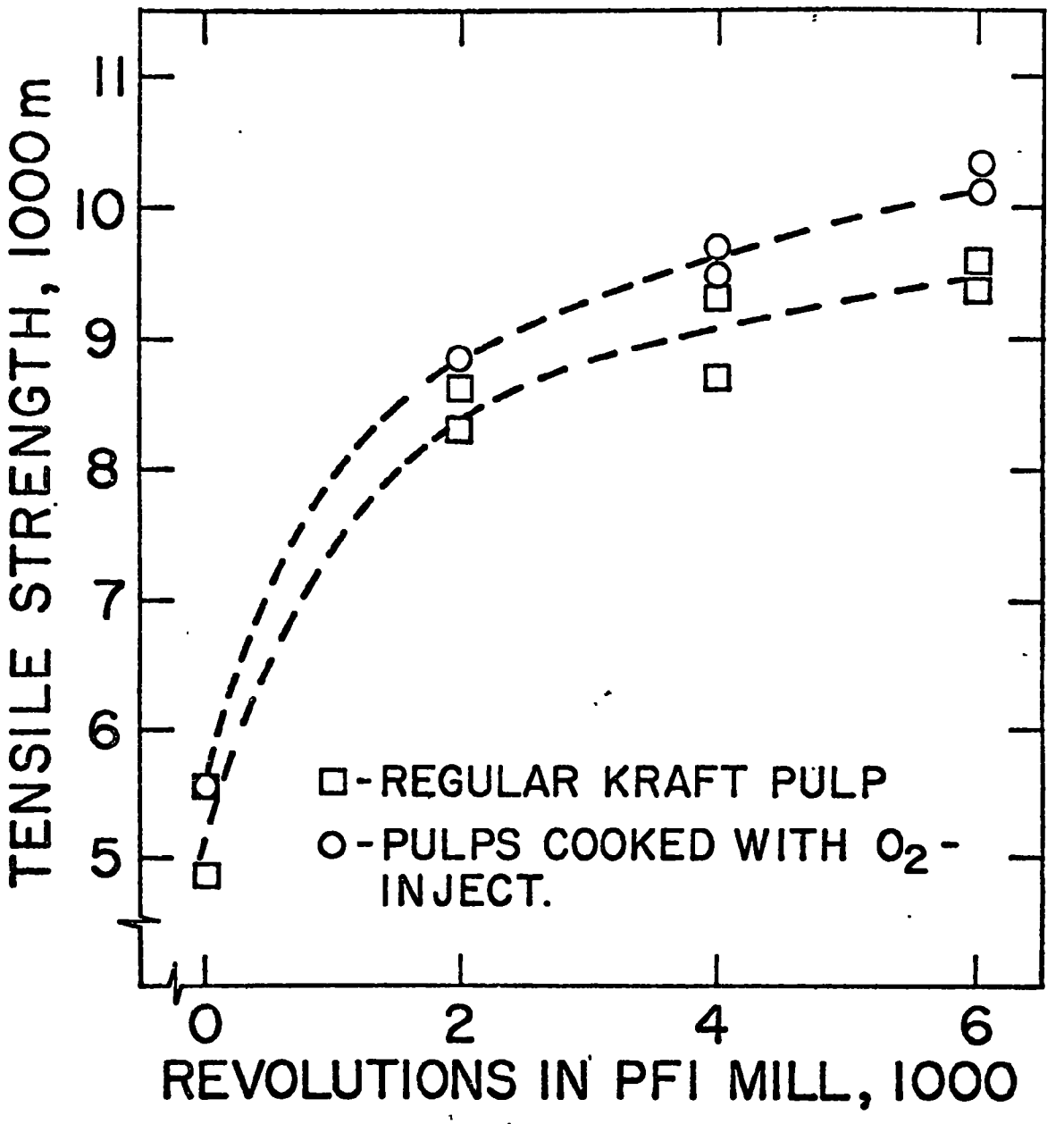


Figure 22. Tensile strength as a function of number of revolutions in the PFI-mill for regular kraft pulps and pulps cooked with the injection of oxygen.

Total Yield %	Lignin Cont. %	O_2 inj. g	Beating PFI-mill Revolutions	Freeness mℓ	Tensile Strength km	Burst Factor	Tear Factor	Fold
48.3	7.4	0	0	--	4.1	20	197	30
			2000	--	8.3	57	172	760
			4000	--	9.4	63	150	1050
			6000	274	10.3	71	128	2850
48.6	7.0	0	0	710	5.6	37	202	340
			2000	630	8.7	65	144	1280
			4000	352	9.4	70	--	1860
			6000	240	9.6	70	129	2200
49.1	7.6	0	0	700	4.9	38	182	240
			2000	631	8.3	63	130	1240
			4000	380	8.7	67	--	1750
			6000	252	9.4	72	132	2750
47.6	7.1	80	0	722	5.5	37	206	400
			2000	642	8.6	60	148	860
			4000	457	9.7	69	131	1500
			6000	223	10.4	74	115	2600
47.9	6.5	80	0	710	5.6	38	196	330
			2000	628	8.8	65	135	1400
			4000	331	9.4	68	120	1900
			6000	--	10.2	73	112	2000
48.9	8.0	77	0	710	5.4	35	217	280
			2000	665	9.5	62	155	900
			4000	503	10.4	68	143	1100
			6000	345	10.7	73	139	1350
51.4	7.7	96	0	--	4.1	20	198	50
			2000	650	9.3	62	142	900
			4000	--	10.2	65	157	1020
			6000	220	11.2	75	123	1700

Table VII: Physical properties of regular kraft pulps and pulps produced with the injection of oxygen at the end of the cook. Liquor to wood ratio 4:1.

Table VIII. Effect of Injection of Oxygen on Pulp Brightness

O_2 inj., g	Inj. Rate, g/min	Brightness, % Elrepho
0	---	23.4
96	9.6	22.0
77	25.9	22.5
0	---	21.7
80	5.3	19.8

Black liquor was generated by a conventional kraft cook in a one cubic foot laboratory digester. At the end of the cook the digester and its contained pulp and black liquor were cooled to the desired oxidation temperature. Oxygen was injected at the outlet side of the circulation pump, so the circulation line acted as a flow reactor similar to the equipment employed by Cooper (28) and Galeano (29). The system behaved similar to a back mix flow reactor since the liquor charge was 12ℓ and the circulation rate was about 36ℓ per minute. Black liquor samples were taken at about two minute intervals and analyzed for sodium sulfide, methyl mercaptan and dimethyl disulfide. Analysis of selected samples showed nearly quantitative conversion of sodium sulfide to sodium thiosulfate with no detectable quantities of polysulfide or elemental sulfur and only small amounts of sodium sulfate. Sodium sulfide content of the black liquor was between 7 and 8 g/ℓ. In this work the circulation rate was not controlled, so the Reynolds number varied from about 150,000 at 170°C to 45,000 at 80°C and was always above the critical values reported by Cooper (28) for efficient oxygen absorption.

The rate of sodium sulfide consumption is shown in Figure 23 for oxidation at 100°C and 140°C with oxygen supply rates of 10 and 8.2 g/min. respectively. The amount of oxygen required to totally oxidize sodium sulfide may be calculated and is shown in Figure 24 for various temperatures. With 12ℓ of liquor at 7.8 g/ℓ sodium sulfide the theoretical oxygen required is shown as 1.2 moles. Thus, at temperatures below about 140°C

the sodium sulfide could be totally oxidized with about 20% excess oxygen consumption by side reactions. Above that temperature large quantities of oxygen are consumed presumably by lignin oxidation reactions.

Figure 25 shows the efficiency of methyl mercaptan and dimethyl disulfide oxidation at various oxidation temperatures. When oxidizing at 130 to 140°C the methyl mercaptan was about 95% consumed by the time sodium sulfide had been reduced to undetectable levels. No dimethyl disulfide could be detected at any time during oxidation at these temperatures. At 80 and 100°C less than 50% of the mercaptan was consumed when sodium sulfide was at undetectable level. Dimethyl disulfide was present throughout the oxidation period. Prolonged oxidation could reduce the mercaptan and disulfide to lower levels, but at the expense of greater oxygen consumption.

Oxidation at higher temperatures results in greater destruction of the odorous organic sulfur compounds than conventional BLO at the expense of slightly higher oxygen consumption. It's practical application would involve substantial changes from existing black liquor oxidation systems. At higher temperatures a closed oxidation system would be required and the system would probably be best used in a flow reactor configuration with molecular oxygen. The oxidation efficiency is high for all sulfur compounds and no "reversion" of hydrosulfide or methyl mercaptan occurs. Thus, oxidation of black liquor before pressure release from the digester system should result in less emission of TRS substances from all sources between the digester and the direct contact evaporator.

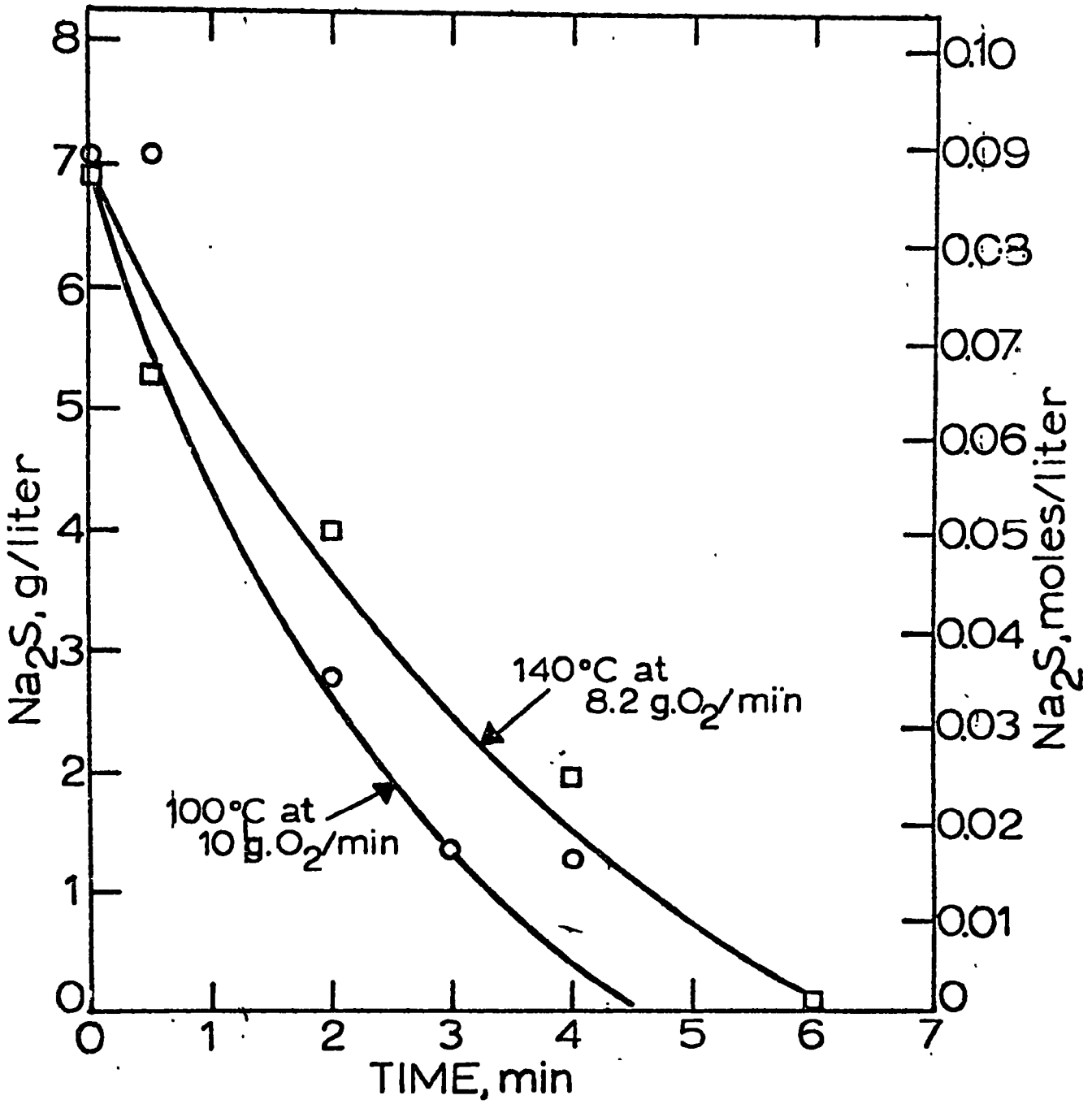


Fig. 23 Representative sodium sulfide oxidation rates.

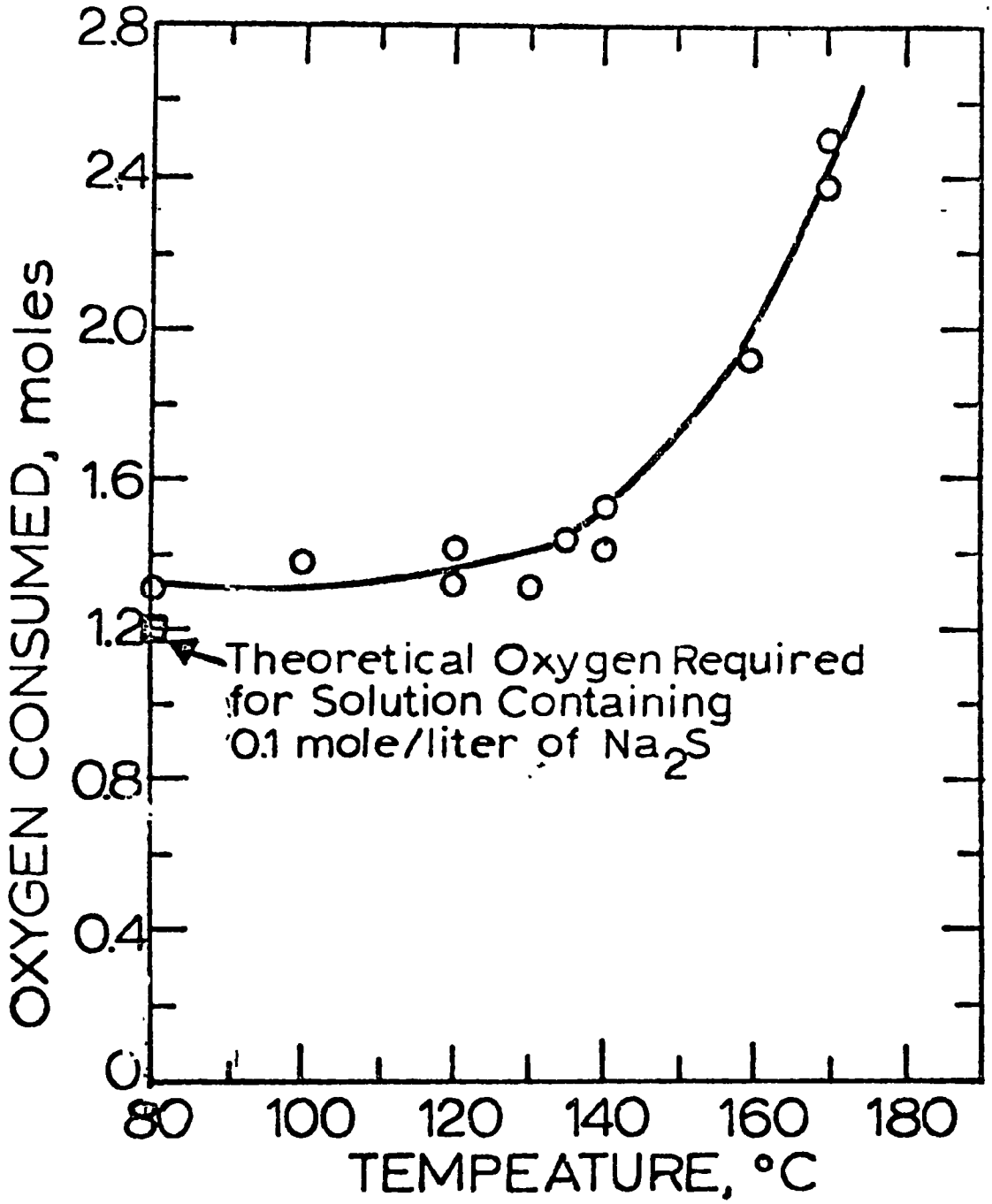


Fig. 24 Oxygen consumption for complete oxidation of sodium sulfide in black liquor oxidation

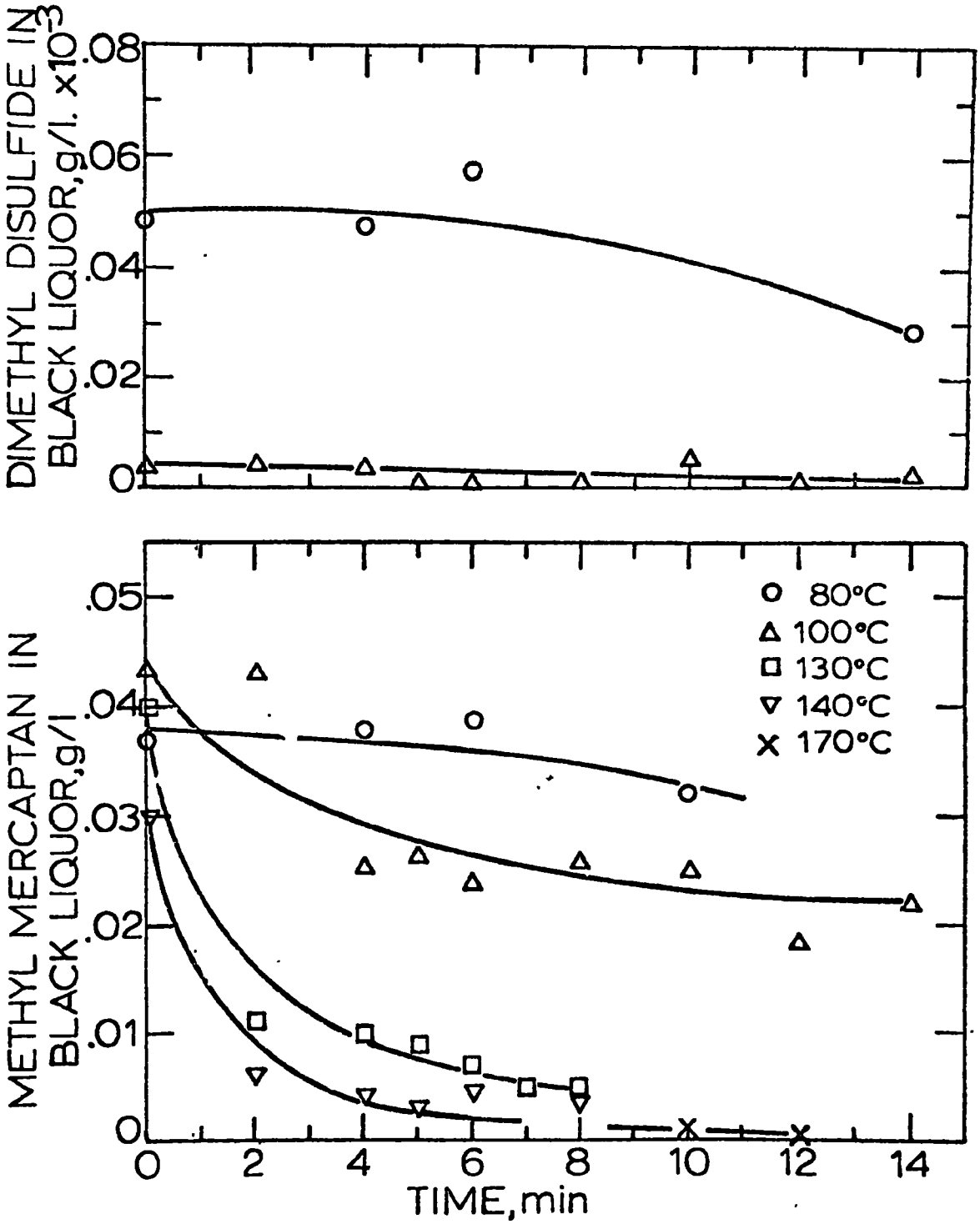


Fig. 25 Methyl mercaptan and dimethyl disulfide concentration as a function of oxidation time for several oxidation temperatures

E. Indigester Oxidation of Hardwood (Red Gum) Black Liquor

A hardwood species (Red Gum, Liquadambar styraciflua) was pulped and oxygen was injected into the digester in the latter stages of pulping to determine the effectiveness for odor control and the influence on pulp yield. In these studies the rates of oxidation of sodium sulfide were nearly identical to those discussed earlier for softwood species.

1. Influence of oxidation on methyl mercaptan, dimethyl sulfide and dimethyl disulfide

The formation of methyl mercaptan and its rate of oxidation by oxygen injection is shown in Figure 26. The amount of mercaptan formed during kraft pulping of the hardwood species is somewhat greater than softwood species (3). Injection of 80 g of oxygen was adequate to essentially destroy all methyl mercaptan. No dimethyl disulfide was detected in the oxidized black liquor. Essentially no dimethyl sulfide oxidation was observed in agreement with the soft-wood results.

2. Influence of oxidation on pulp yield

Table IX and Figure 27 summarize the results from reference kraft cooks and oxygen injections cooks of Red Gum. The results confirm the conclusion given earlier for softwoods that oxygen injection in the latter stages of a cook does not change the pulp yield, kappa number relationship which applies to normal kraft cooks.

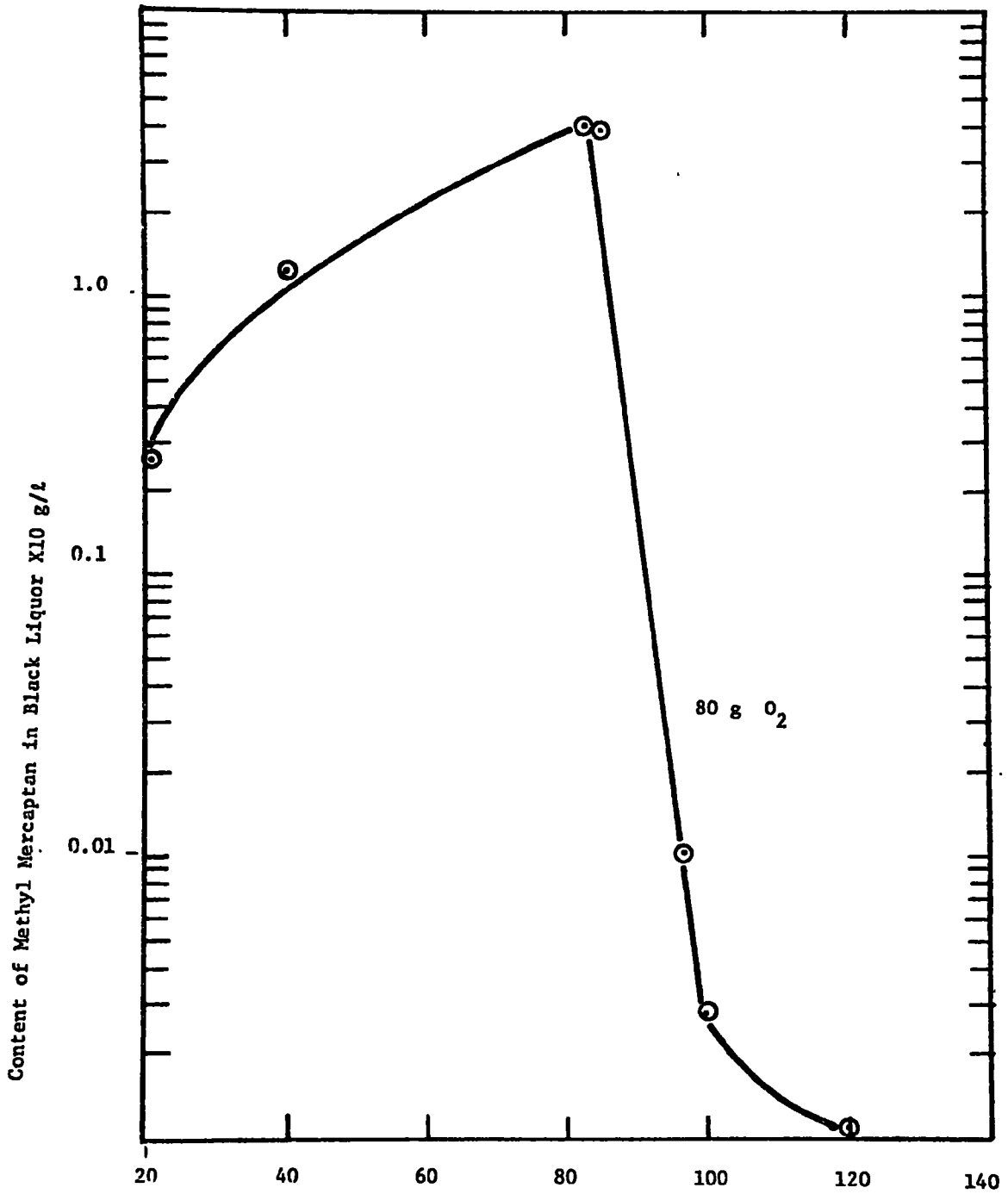


Figure 26. Methyl Mercaptan content in Black Liquor from Pulping Red Gum

White Liquor Eff. Alk. g/ℓ	Na_2S in White Liq. g/ℓ	O_2 Inj. Rate	Total O_2 g	Total Pulp Yield %	Kappa No.
33.1	12.3	0	0	62	50.7
43.5	12.6	0	0	42	40.2
35.0	12.5	0	0	44.2	16.9
30.0	10.7	0	0	46.0	19.0
30.5	21	0	0	45.2	13.3
36.7	11.0	0	0	45.7	28.4
40.3	11.2	0	0	47.6	20.9
41.2	11.9	0	0	43.3	20.9
35.3	11.8	5.3	80	56.5	46.7
40.2	10.4	5.3	80	56.2	43.0
37.0	10.6	5.3	80	48.0	22.0
39.6	11.2	5.3	80	45.8	22.4
39.9	10.9	5.3	80	47.4	23.7

Table IX. Total Pulp Yield for Kraft Cooks of Red Gum with and without Oxygen Injection at the end of the Cook Liquor to Wood Ratio 3.6:1, 90 minutes from 25°C to 170°C.

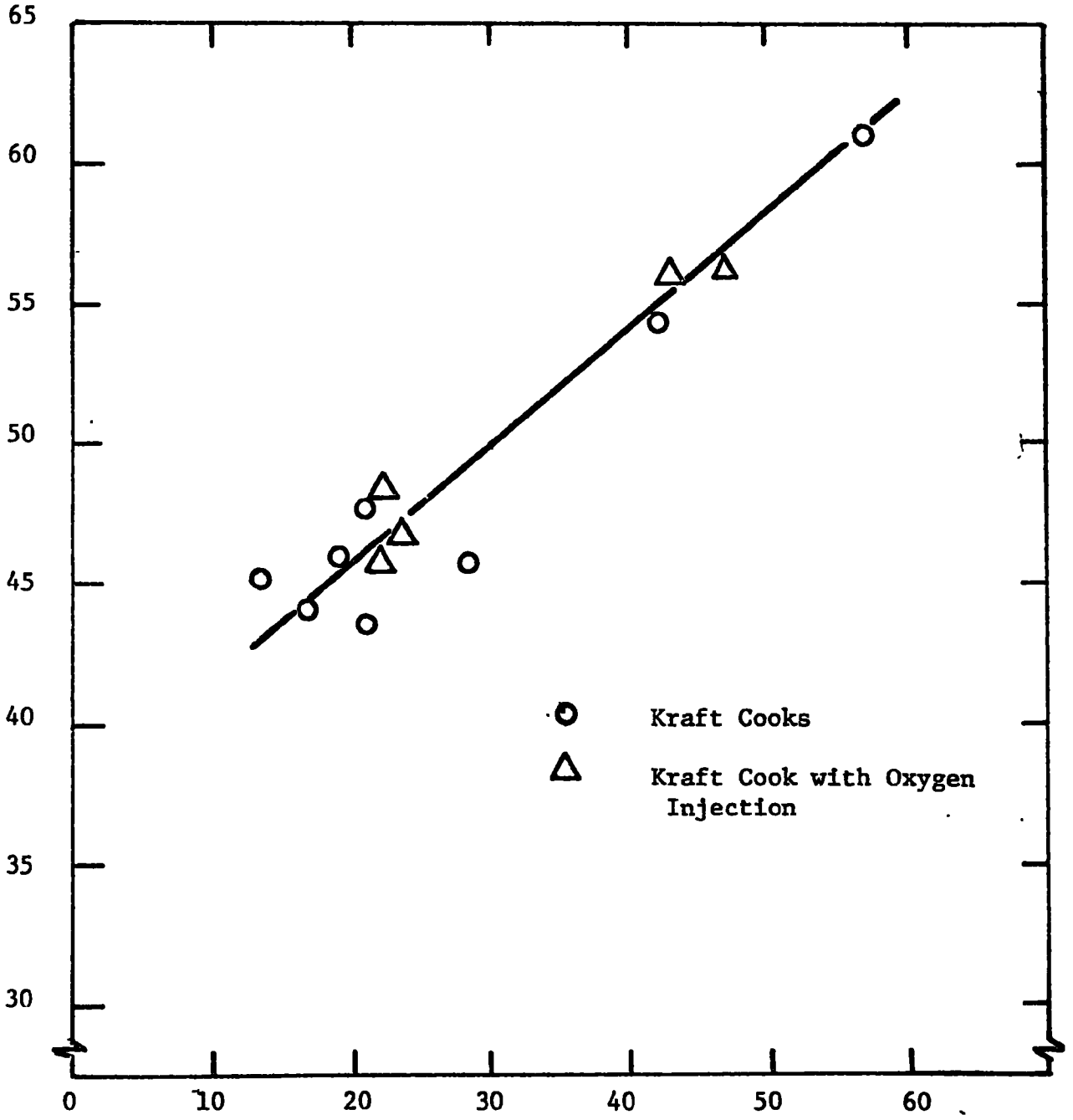


Figure 27. Total Pulp Yield as a Function of Kappa Number for Pulping Red Gum

F. Odor Control in Batch and Continuous Digesters

1. Odor Control in Batch Digesters

The results given in this report were obtained using 1 cu. ft. batch circulation digesters which were operated somewhat differently than normal industrial digesters. Black liquor was circulated throughout the heat up and cooking cycle. This was necessary to avoid temperature drop in the uninsulated digester during cooking. The liquor charge was 12ℓ (4:1 liquor wood ratio) and liquor was pumped at 10ℓ/min. so the "turn over" time was less than two minutes. The digester and circulation line could then be treated as a backmix reactor. By slow injection of oxygen (total time of 2 to 40 minutes) into the circulation line the oxygen was uniformily distributed in the black liquor. Commercial sized batch reactors are classed as direct or indirect steam heated. In the first case steam enters the bottom of the closed digester through a special nozzle. The major amount of steam is injected during heat up with only small amounts being required during cooking since heat losses from the insulated digesters is small. Uniform heating of the wood chips results from convective circulation of heated liquor.

In indirect heated digesters liquor removal is through strainers in the digester walls, pumped through a steam-liquor heat exchanger and returned to the digester top and bottom. Liquor circulation rates are high during heat up, but are reduced during the cooking cycle since little heat loss occurs from the insulated digester. Circulation rates are limited in the later stages of cooking by accumulation of fiber fines on the strainers with resultant pressure build-up across the strainer.

Black liquor oxidation in the direct heated type of digester would be accomplished by either direct injection of oxygen into the digester shell or injection of oxygen into the blow line during the blow. Neither digester shell would probably not result in uniform oxygen distribution. That portion of pulp mass exposed to oxygen would likely suffer oxidative damage and the resulting pulp would be weaker as reported by Fones and Sapp (27). Furthermore, with poor oxygen distribution portions of the black liquor would remain unoxidized with resultant low oxidation efficiencies with respect to the sulfur compounds.

Injection of oxygen into the blow line would provide adequate mixing. However, resident times of the liquor and oxygen in the blow line would be from 5 to 10 seconds which is too short for oxidation of the sulfur substances. This alternative was not studied in the present work because of inadequate facilities to simulate conditions in the blow line.

Indirect heated batch digesters offer more promise for odor control, oxygen may be injected into the circulation line where it is normally consumed before black liquor enters the digester. Distribution can be controlled by black liquor circulation rate and oxygen injection rate. The strainer system would have to be redesigned to permit high liquor pumping rates near the end of the cook so all liquor in the digester could be circulated at least once within the last 30 to 45 minutes of the cook. Odor control by this type of indigester BLO would probably be accomplished at the conventional digester temperatures ($\approx$170°C). At these temperatures, oxygen consumption would be approximately 200% of theoretical (cf. page 75).

2. Odor Control in Continuous Digesters

High temperature black liquor oxidation could be employed as an odor control measure in mills using continuous digesters. Liquor extraction lines could be modified between the extraction point and the first flash tank for injection of oxygen. This type of arrangement would permit more flexibility than in the case of batch digesters. Normally liquor temperatures are in the range 120 to 120°C at which oxidation rates are more rapid for all malodorous sulfur compounds. At the same time excessive oxygen consumption would not occur (Figure 24).

G. Yield Increase in Combination with Odor Control

If the concept of indigester BLO is accepted as a feasible approach for odor control, some modification of existing batch digesters would be required to permit introduction of oxygen into the liquor recirculation system. With this modification it may be possible to obtain increased pulp yields by introduction of small amounts of oxygen into the liquor during the heating up of the digester. Preliminary studies were made to determine the magnitude of yield increase that could be obtained.

When oxygen is introduced into the circulating liquor during heat up, at least two categories of reactions will take place. First the sulfide content of the liquor may be partially converted to polysulfide which can react to stabilize wood carbohydrates against alkaline induced peeling. This should result in a yield increase.

1. Sodium sulfide in the circulating liquor will be oxidized in several reactions. Sulfide may be converted to polysulfide as shown in reaction (29).

$$4\ Na_2S + O_2 + 2\ H_2O \longrightarrow 2\ Na_2S_2 + 4\ NaOH \qquad (29)$$

Simultaneously polysulfide may be converted to sodium thiosulfate according to reaction 30 and sodium sulfide may

$$2\ Na_2S_2 + 3O_2 \longrightarrow 2\ Na_2S_2O_3 \qquad (30)$$

be partially oxidized to sodium sulfite according to reaction 31.

$$Na_2S + O_2 \longrightarrow Na_2SO_3 \qquad (31)$$

Once formed polysulfide is subject to two types of reactions. At low temperatures polysulfide solutions are relatively stable (in the absence of sulfite, see below discussion), but at elevated temperatures and alkalinity decompose to thiosulfate as shown in reaction (32).

$$S_2^{=} + OH^- + 3/4\ H_2O \longrightarrow 1/2\ HS^- + 1/4\ S_2O_3^{=} \qquad (32)$$

In the presence of sulfite polysulfide is decomposed forming sulfide and thiosulfate as shown in reaction (33)

$$SO_3^{=} + S_2^{=} \rightleftharpoons S_2O_3^{=} + S^{=} \qquad (33)$$

The rates of these reactions, of course, depend on reaction conditions, but in general at elevated temperatures and alkalinity and after extended periods substantial amounts of the generated polysulfide are lost by decomposition (30, 31). Consequently, a system where the polysulfide is generated in the digester where it may diffuse quickly to the reaction sites and stabilize reducing end groups (reaction 34) before decomposition occurs has some attraction.

$$2\ RCHO + Na_2S_2 + 4\ NaOH \longrightarrow 2\ RCOONa + 2\ Na_2S + 4\ H_2O \qquad (34)$$

2. If some oxygen is carried unreacted with the liquor into the digester, a second type of carbohydrate stabilization may occur. It is known that even at low temperature (32) carbohydrate reducing end groups will be oxidized to aldonic acids.

Formation of aldonic acid end groups by oxidation of carbonyl reducing end groups by either polysulfide or oxygen should result in less peeling and greater pulp yields. A series of experiments was made to test if introduction of oxygen into the liquor circulation line would indeed result in improved yield. The results shown in Figure 28 illustrate that a yield increase of from 1 to 3% may be obtained by introduction into the digester. In these experiments oxygen was injected into the circulating liquor at 35°C and a rate of 3 g/min for 7 minutes. This amount of oxygen corresponds to about 1.25% on pulp. The 12ℓ of unoxidized white liquor contained 13 g/ℓ of sodium sulfide and 48 g/ℓ effective alkali, so the amount of oxygen introduced corresponded to approximately a 20% consumption of the available sodium sulfide.

Recently a U. S. patent has been issued to R. G. Barker (33) in which these results have been confirmed. No further work has been completed on this project to date, but the approach is very encouraging and should receive further study.

In principle this approach may also be used on continuous digesters. The application would require some modification of digester internals to provide for adequate control of the oxygen with white liquor into the impregnation zone. Of course, odor control as described in the previous section would be an independent oxygen injection system. No studies were done.

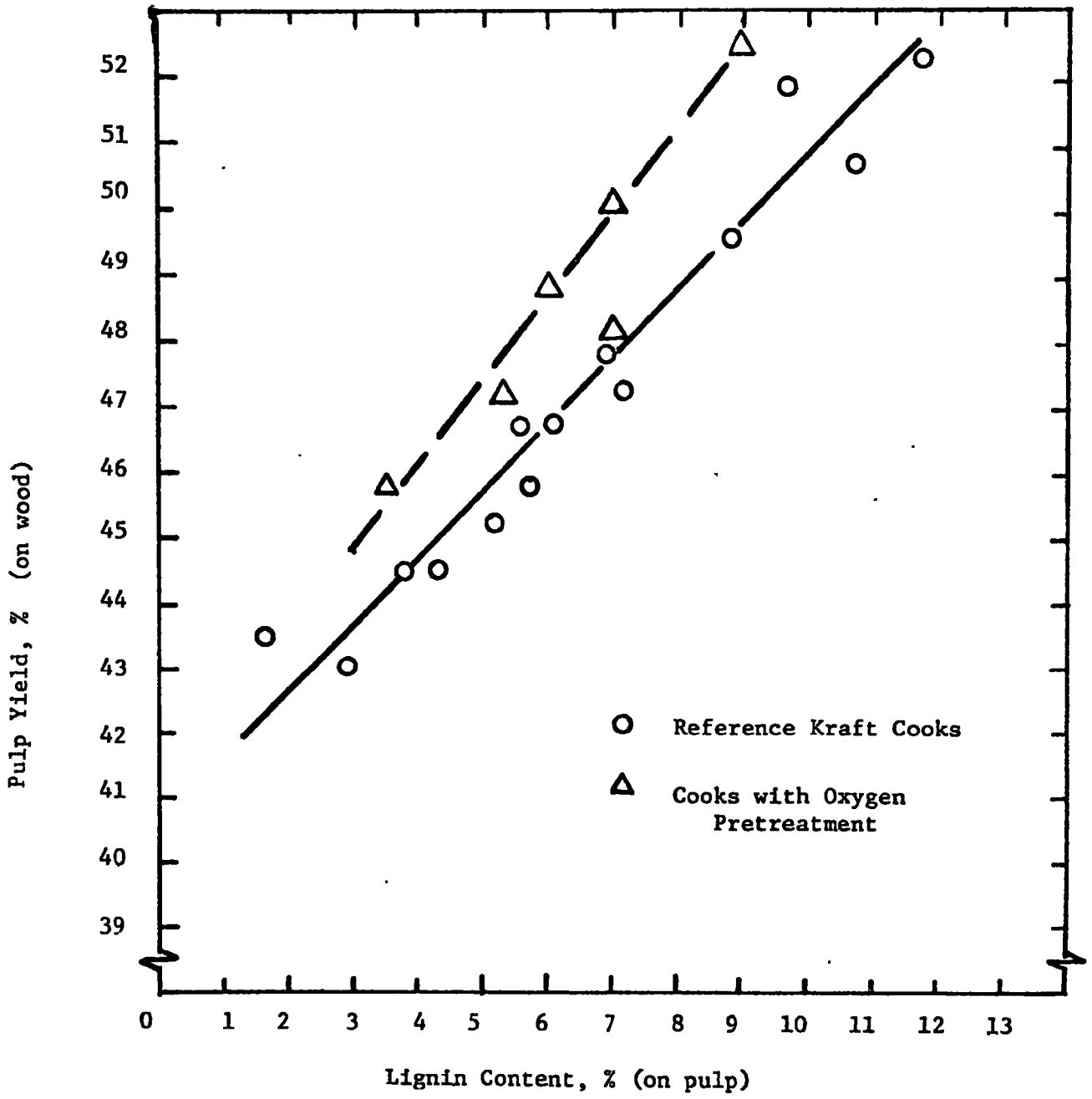


Figure 28. Pulp Yield as a Function of Lignin Content for Reference Kraft Pulps and Kraft Pulps with Oxygen Pretreatment. 4:1 liquor to wood ratio

H. Estimates for Cost and Effectiveness of Odor Control by Indigester BLO Compared to other Control Methods

In this section preliminary estimates of cost and effectiveness are given for odor control. The effectiveness of various odor control systems are based on well run systems in non overload. The basis for calculations draws heavily on the data provided by Hendrickson, et. al. (1). The calculations are made based on a 500 T/day kraft mill with total TRS emissions of 27 #/T with no odor control (see Table I). Oxygen costs assume that other uses such as oxygen bleaching or waste water treatment will bring the total usage to about 50 T/day.

Values for recovery furnace emissions are based upon optimum operating parameters. The NAPCA report (1) indicates that the value of this emission can vary between 0.16 and 2.55 lbs. TRS/ton of pulp, with a mean value of 0.50 lbs./ton. Because studies have shown that 0.30 lb./ton should be achievable with moderate controls, that figure will be used in this paper.

Values for lime kiln operation are based on the use of fresh water for causticizing and installation of a 99% efficient particulate scrubber on the discharge of the stack gases. Use of condensate instead of fresh water could add an additional 0.25 lbs. TRS/ton pulp, while use of an 80% efficient particulate scrubber will add another 0.30 lbs. TRS/ton pulp. If no particulate scrubber of any kind is installed, and condensate is used

for causticizing, the lime kiln emissions are used because it is desirable to see how low the emissions can be reduced using practical and economical equipment.

Calculations are made for the cases listed in Table X. Annual operating cost and effectiveness are given with each case. A more detailed development of the figures is given on pages 99 to 105 of this section. The cost and effectiveness of these alternatives for odor control are summarized in Table X. The following comments can be made at this preliminary stage:

1. Assuming no yield increase the cost of indigester oxidation is comparable to other systems at equal or better effectiveness.

2. Assuming a 1% yield increase by low temperature pretreatment with oxygen the resulting credits make the annual cost of indigester oxidation in batch digesters about zero.

3. The high effectiveness in control of odors by in-digester oxidation results from elimination of all emissions except dimethyl sulfide in the digester blow and this low volume stream can be treated in the lime kiln. Furthermore, liquor which has been oxidized at high temperature in the digester does not undergo reversion during evaporation and storage.

Table X. Effectiveness and Cost of Odor Control in a 500 T/D Kraft Mill

Case	Annual Cost	Unit Cost	Remaining Emission Lbs./T
1. Indigester Oxidation	$142,000-Batch Digesters	0.78	0.3 Rec.Fur. & DCE 0.3 lime kiln
	96,000-Continuous	0.52	0.5 Dig. Relief 1.1
2. Indigester Oxidation (assuming 1% yield increase)	$0 - Batch	0	Same as Above
	96,000-Continuous	0.52	
3. Indigester Oxidation with lime kiln combustion of digester relief and blow	$172,000-Batch	0.94	0.3 Rec. Fur. & DCE
	110,000-Continuous	0.60	0.3 lime kiln 0.6
4. Weak BLO with Oxygen	$120,000-Batch		0.3 Rec. Fur. & DCE 0.3 Washers 0.2 Multiple Effect. Evap. 3.5 Digester Blow 0.5 Digester Relief 0.3 Lime Kiln 5.1
5. Case 4 with lime kiln Combustion of digester Blow and Relief Gases	$150,000-Batch		0.3 Rec.Furn & DCE 0.3 Washers 0.2 MEE 0.3 Lime Kiln 1.1
6. Weak BLO with air	$ 90,000-Batch	0.49	0.3 Rec. Fur. & DCE 0.3 Washers 0.2 Multiple Effect Evap. 3.5 Digester Blow 0.5 Digester Relief 0.3 Lime Kiln 5.1

Table X - Continued -

Case	Annual Cost	Unit Cost	Remaining Emission Lbs./T.
7. Case 6 with lime kiln combustion of digester relief and blow gases. MEE and WK BLO off gas combustion in Rec. Furnace	$136,000	0.74	0.3 Rec. Furnace & DCE 0.3 Washers 0.3 Lime Kiln 0.9
8. Strong BLO with air	$ 78,000	0.42	0.3 Rec. Furn. & DCE 0.4 SBLO Oxidation tower 0.3 Washers 0.9 MEE 3.5 Blow gases 0.5 Relief gases 0.3 Lime Kiln 6.2
9. Case 8 with lime kiln combustion of digester relief and blow gases. MEE and SBLO off gas combustion in Rec. Furn.	$126,000-Batch 115,000-Continuous	0.69 0.63	0.3 Rec. Furn. 0.3 Washers 0.3 Lime Kiln 0.9
10. Air Contact Evaporator with same incineration as Case 7	400,000*	2.20	1.0-1.5*

*Estimate

4. In-digester oxidation should be applicable to:

   a. Older mills with no odor control systems.

   b. Mills with black liquor oxidation systems already installed, but operating at overload. The capital investment is very low so incremental costs to help unload an existing BLO unit will be low.

   c. New mills which will probably have continuous digesters can use in-digester oxidation. This may be the best application since the liquor could be oxidized at the best conditions for high oxidation efficiency at the lowest possible oxygen consumption. However, oxidation in this case would probably be carried out in the liquor extraction line upstream from the flask tank.Consequently no increase in yield could be realized.

The following section gives a more detailed discussion of the basis for cost and emission estimates.

1. Digester Relief - .50 lbs TRS/ton pulp - 35 cf gas/ton @ 120°F

   During the cooking process, it is necessary to relieve the gases that form in the digester. These gases are, in part, air and stream that have been trapped in the woodchip during the pretreatment stage, and also reduced sulfur gases that form during the cooking process. And since the cook is carried out under pressure, it is sometimes necessary to vary that pressure to control the cook. The relief gases from this pressure control plus a partial pressure relief at the end of the cook add to those relief gases mentioned above. Because the cook is carried out at a high pH, most of the H_2S and

RSH stay in solution. The primary TRS gases are, therefore, RSR and RSSR. The gas stream is a low volume/high concentration stream.

2. Digester Blow - 3.45 lbs TRS/ton pulp - 300 cf gas/ton @ 120°F
   At the end of the cook, the contents of the digester are blown into a blow tank to relieve the remaining pressure and to break up the chips. Here again, due to the high pH, the H_2S and RSH stay in solution, and the major TRS compounds are RSR and RSSR. This gas stream, like the digester relief, is a low volume/ high concentration stream.
3. Washers and Screens - .30 lbs TRS/ton pulp - 95,000 cf gas/ton @ 120°F
   The next step in the process is the washing of the pulp to remove the cooking liquor. The typical washer is a vacuum droplet type, which pulls air from the atmosphere as well as TRS gases in the process. Here, however, the major TRS compound is RSH which leaves the solution as the pH is lowered by the diluting effect of the water. The emission stream from this source, however, is a high volume/low concentration stream. It is, therefore, difficult to treat.
4. Multiple Effect Evaporators- .90 lbs/ton pulp - 35 cf/ton @ 120°C
   Emissions from operations following the washer stage are all concerned with the recovery of the chemicals. The first step in the recovery of the cooking chemicals is the evaporation of water from the diluted wash liquors to a 50% solids concentration. The process is primarily a boiling process, and in the process TRS gases are stripped from solution. Most of the TRS gases are H_2S and RSH, since the RSR and RSSR have been removed in the preceding operations. Some RSR does form, however, probably due to a decomposition of RSH. As with the blow and

relief gases, this is a low volume/high concentration stream.

5. Direct Contact Evaporator/Recovery Furnace- 12.5 lbs TRS/ton pulp - 470,000 cf @ 325°F.

The direct contact evaporator concentrates the liquor from 50% solids to about 65% solids by direct contact of the hot flue gases of the recovery furnace with the liquor from the multiple effect evaporation stage. This operation has long been recognized as the major source of reduced sulfur; of the total of 17.5 lbs TRS/ton pulp, better than 12 lbs is emitted from the recovery furnace and direct contact evaporator. Theoretically, if the recovery furnace itself is operated at less than 130% of rated capacity, the amount of reduced sulfur leaving the top of the furnace should be insignificant. The major source of the reduced sulfur emissions, therefore, is the direct contact evaporator. It is here that the CO_2 generated in combustion goes into solution, lowering the pH and causing the evolution of H_2S and RSH. Some mass transferring also occurs due to a concentration graduant. The generation of TRS gases can, however, be almost completely eliminated by oxidizing the black liquor prior to entry into the direct contact evaporator. The NAPCA report estimates that the total evaporator emissions from a furnace operating at proper levels with 99.9+% oxidation of the black liquor, should be about .5 lbs/ton pulp. Two independent tests run by a recovery furnace supplier and by a pulp mill indicate that this figure can be as low as .3 lbs/ton.

Obviously, this emission source is an extremely high volume stream. Treatment by any means other than, say, catalytic oxidation would seem impractical.

6. Lime Kiln with 99% efficient scrubber - .30 lbs. TRS/ton pulp

The source of this sulfur gas is the sulfur normally present in the oil burned in the lime kiln, and reduced sulfur in the lime mud. As stated in the summary, the reduced sulfur that would be added from use of evaporator condensate in the causticizing operation can be eliminated by using fresh water. This stream of gases is, again, primarily H_2S and RSH, and it is a high volume/low concentration stream.

Costs of Various Systems for 500 T/D Pulp Mill

1. Indigester Oxidation

A. Oxygen Costs -

1. The Batch digester present study as well as independent tests run by paper companies indicate that the oxygen consumption would be about 5% based on pulp production. A 500 T/D pulp plant would use, therefore, 500 T/D x 5% = 25 T/D O_2. At a minimum oxygen cost of $15/ton, annual oxygen costs would be $25 \frac{\text{tons}}{\text{day}} \times \frac{\$15}{\text{ton}} \times 365 \frac{\text{days}}{\text{year}} = 137{,}000/\text{yr}$.

2. Continuous Digester

If oxidation is done in the extraction line at 130°C, oxygen consumption will be about 2.5% on pulp. 2.5 x 500 = 12.5 T/day. At $20/T (for the reduced capacity) annual oxygen costs will be $12.5 \frac{T}{\text{day}} \times \frac{\$20}{T} \times 365 \frac{\text{day}}{\text{year}} = \$91{,}000/\text{yr}$.

B. Oxygen system costs

The cost of equipment will vary with the total number of digesters in the plant. For the sake of discussion it will be assumed that a total of about 10 digesters (continuous + batch) are in use. If it is also assumed that a total of 3000 ft. of oxygen piping @ $2/ft., and individual controls and associated wiring of $1000/digester are required, equipment costs could easily run as high as $2 (3000) + 10 ($1000) = $16,000. Using the figures generated in the NAPCA report, i.e. annual costs of about 35% based on capital costs, annual costs for equipment would be 35% x $16,000) = $5000/yr. Total annual costs, therefore, for indigester oxidation would be about $137,000/yr. + $5000/yr. = $142,000/yr.

2. Indigester Oxidation Assuming a 1% yield Increase Resulting from Oxygen Pretreatment

A. Assuming a 1% yield increase, at a value of $100/T the credits from additional pulp would be $5\ T \times \frac{\$100}{T} \times 365\ \frac{days}{year} = \$182,500.$
Against this must be charged the additional cost of oxygen for pre-treatment amounting to about 1.25% on pulp.

$$1.25 \times 500\ \frac{T}{day} \times \frac{\$15}{T} \times 365\ \frac{day}{year} = \$34,200/year.$$

Thus, a total profit of about $142,000 + 34,200 - 182,500 = $6,300 may be realized.

3. Strong Black Liquor Oxidation with Air

From the NAPCA report, the new annual costs for operation of a strong black liquor oxidation system in a 500 T/D pulp plant would be about $78,000/year. This figure is in agreement with the Owens Illinois figures for breakeven costs between weak black liquor oxidation with oxygen and

and strong black liquor oxidation with air. Although O-I stated breakeven oxygen costs of 14/ton - $18/ton, a careful review indicated that if the questionable improvement in tall oil recovery and evaporator life are neglected, the breakeven oxygen cost would be about $10/ton. At 4% oxygen utilization based on pulp weight, this gives an annual breakeven cost for the oxygen system of $10/ton O_2 x 4% x 500 TID x 365 days/year = $73,000/year. This is also, then the cost of a comparable SBLO system and compares with the NAPCA figure of $78,000/year.

4. Weak Black Liquor Oxidation with Oxygen

A. Oxygen Costs - As stated above, the oxygen consumption for WBLO with oxygen was confirmed in the O-I test to be 4%. At $15/ton O_2, the annual oxygen costs would be $15 x 20 ton O_2 x 365 days = $110,000/yr.

B. System Costs - O-I estimated system costs at $30,000. Again using the NAPCA report's average annual cost of 35% of capital cost, the annual system costs would be 35% x $30,000 = $10,500/year.

Total cost for the WBLO system using oxygen would be $110,000/yr. + $10,500/yr. = $120,500/yr.

5. Lime Kiln Incineration of Emissions from Digester Blow, Digester Relief, and MEE.

The NAPCA study shows that the total annual cost for the incineration of batch digester relief gases, blow gases, and MEE noncondensible from a 500 T/D plant is about $30,000/year. The cost for incineration of continuous

digester TRS emissions is only $14,000/yr. the difference being the flexible surge chamber required in batch operation to "even out" the gas flow to the lime kiln. Since many companies have both continuous and batch digesters, and would, therefore, require a surge chamber, the $30,000/yr. figure will be used.

6. Incineration of SBLO Oxidation Gases in Power Boiler.

A. Incineration Cost

The gases from the oxidation tower are emitted at a temperature of 150°F. It is assumed that the BTU's provided by the incineration of the TRS compounds is negligible, and that the energy required to incinerate this gas stream is merely the BTU's required to rasie the temperature from 150°F to 350°F. This is certainly not absolutely accurate, since the SBLO gases are about 12% oxygen and would provide some oxygen for combustion. For the purposes of this calculation however, it is assumed that this might be offset by a reduction in boiler efficiency. A rough annual cost for incinerating the oxidation tower gases is, therefore,

$$.25 \frac{\text{BTU}}{\text{lb°F}} \times \frac{900 \text{ lbs gas}}{\text{ton pulp}} \times \frac{500 \text{ tons pulp}}{\text{day}} \times \frac{365 \text{ days}}{\text{year}} \times (350°\text{F} - 150°\text{F}) \times \frac{\$.65}{1{,}000{,}000 \text{ BTU}} = \$5400/\text{year}$$

B. Piping Costs

The piping would be about 17" diameter piping. Assuming a length of 1000 feet, and a cost/ft of $30.00, the total capital cost would be $30,000. At 35% annual charges based on capital costs, the annual cost would be $10,500/year.

Total annual cost, therefore, for the incineration of the SBLO oxidation gases in the lime kiln would be $5400/year + $10,500/year = $16,000/year.

I. Experimental

1. Equipment and Materials

A. Laboratory Reactor

All reactions were carried out in a 1000 cc T316 stainless steel, high pressure reactor. (Parr Instrument Company, 211 Fifty Third Street, Moline, Ill., Cat. No. 4521). The reactor was equipped with a pressure gauge, gas inlet valve, liquid sampling valve and gas tight stirring shaft. Modifications were made to enable rapid injection of reactants by means of a syringe. The liquid sampling valve was fitted with a syringe needle so rapid (approximately 3 seconds) sampling with exclusion of oxygen was possible. To maintain constant temperature the reactor was placed in a constant temperature bath which could be controlled within limits of $\pm$ 0.1°C. By changing pulleys on the stirring shaft between 200 and 1000 revolutions per minute could be obtained.

Gas Chromatograph

In laboratory kinetic studies discussed under sections A and B analysis of methyl mercaptan and dimethyl disulfide was carried out using a Perkin Elmer Model 990 gas chromatograph equipped with a flame ionization detector. Analytical data were recorded using a Servo/riter II Potentiometric recorder from Texas Instruments Incorp., Houston, Texas 77066.

For quantitative work, the column packing was prepared by depositing 20% by weight of Carbowax 20M on acid washed chromosorb 80-100 mesh.

This material was packed into stainless steel tubing 10 feet long and 1/4 inch OD. Operating conditions were 100°C and 75cc per minute nitrogen carrier gas.

A. In pulping studies the methyl mercaptan, dimethyl sulfide and dimethyl disulfide content of black liquor samples was determined as follows: The samples for gas chromatographic analyses were collected using the technique described by Andersson (35). Carbon tetrachloride extracts were analyzed with a Perkin Elmer 990 gas chromatograph equipped with a flame photometer detector (Meloy Laboratories, Inc. Model 100 AT) which provided specific response for compounds containing sulfur. The 28 ft by 1/8 in. o.d. teflon column was packed with 60-80 mesh Haloport F coated with 10% diisodecylphthalate. The oven was operated at 100°C with a 75 ml/min nitrogen carrier. Helium and oxygen flow to the detector were 75 and 16 ml/min, respectively. Retention times of hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide were 0.6, 1.2, 2.0, and 8.5 min, respectively. The sulfur specificity of this detector avoided interference by other substances extracted from black liquor by the carbon tetrachloride.

Calibration was done by iterative addition of measured amounts of the sulfur compounds to sample vials containing carbon tetrachloride and the buffered black liquor sample. The carbon tetrachloride phase was analyzed following each addition.

B. Materials

Methyl mercaptan was obtained from Air Products and Chemical Inc., dimethyl disulfide and methane sulfonic acid from Sigma Chemical Company.

Methane sulfinic acid was synthesized according to the procedure used by Claesson (36). Sodium hydroxide, sodium sulfide and organic solvents used were reagent grade purchased from Fisher Scientific and were used without further purification. The 1,4-dioxane was distilled over sodium borohydride immediately before use. Kraft lignin (Indulin ATR RXL 3340;4) was obtained from Westvaco.

2. Procedures

A. Preparation of Solutions

Freshly distilled water was stored under nitrogen and oxygen was excluded during preparation of solutions to prevent undesired oxidation of sulfur compounds in the reaction mixture.

Alkaline solutions of sodium methyl mercaptide were prepared daily by absorbing the appropriate weight of methyl mercaptan gas into a 1N sodium hydroxide solution.

B. Sampling from Laboratory Reactor

The sampling valve of the 1ℓ. laboratory reactor was equipped with a hypodermic needle. By placing this needle through the rubber septum of the sampling bottle and opening the sampling valve, very rapid sampling was possible from the pressurized reactor.

For sampling, a 35 ml vial was prepared by filling it with 10 ml carbon tetrachloride and 10 ml 0.75 N sulfuric acid. The vials were closed by an airtight rubber septum and aluminum cap and part of the air was removed by vacuum. The purpose of removing the air from the vial was to facilitate the accommodation of an approximately 5 gram sample taken from the reactor. Accurate determination of samples taken was obtained by measurement of weight differences.

Sulfuric acid was added to quench the base catalysed reactions by neutralizing the base.

C. Liquor Exchange Pulping

Freshly cut loblolly pine wood was chipped in an Appleton laboratory chipper, air dried, and screened. The fraction passing a 1 1/4 inch mesh screen and retained by a 1/2 inch screen was used for pulping experiments.

The cooks were carried out in 2.8 liter stainless steel autoclaves. Autoclaves and chips (400 g o.d.) were evacuated for 30 min. at about 23 mm Hg to facilitate liquor impregnation (18% effective alkali, 25% sulfidity at 4:1 liquor to wood ratio). Temperature was raised from 25°C to the maximum cooking temperature of 170°C in 100 min by a hot air heating unit providing rotating motion to the autoclaves.

D. Oxygen Injection Pulping

Commercially produced chips of loblolly pine were used for the oxygen injection cooks. Charges of 3000 g (calc. o.d.) were vacuum impregnated and cooked in a 28-liter circulation digester equipped for liquid and gas sampling. Oxygen (prepurified grade) was injected at 130 psi at the outlet of the circulation pump. Reynolds numbers were estimated at 100,000 (34) providing adequate oxygen mixing. The oxygen flow was regulated with a needle valve and measured quantitatively by a calibrated flowmeter (Flowrator Meter, Model 10A356A, manufactured by Fisher and Porter, Warminster, Pa.).

E. Pulping Testing

A PFI-mill was used for pulp beating. Physical properties, lignin contents, and kappa numbers of the pulps were determined according to TAPPI standard methods. The brightness was measured according to SCAN-C11:62 using the Elrepho Reflectance Photometer.

F. Black Liquor Analysis

The contents of sodium sulfide, thiosulfate, polysulfide, and sulfide in white and black liquors were determined by potentiometric titration using the methods developed by Danielsen, Johnsen, and Landmark (37).

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15. Supplementary Notes

16. Abstracts

The report gives results of laboratory studies describing the major reaction routes, key inhibition reactions, and kinetics of methyl mercaptan (CH3SH) and dimethyl disulfide (CH3SSCH3) during oxidation of black liquor. The studies help explain low oxidation efficiencies with respect to hydrogen sulfide, CH3SH, and CH3SSCH3 during black liquor oxidation at 60-90°C and suggest that high-temperature oxidation should be more efficient. Softwood and hardwood black liquor was oxidized at 80-170°C. Oxidation at above 100-120°C resulted in efficient oxidation of all three malodorous compounds with no liquor reversion during subsequent storage and distillation. Oxygen consumption was about 125% of theoretical below 140°C, but increased to about 200% at 170°C. Application of this approach to batch and continuous digester systems is discussed. Preliminary work shows that injecting small amounts of oxygen into the liquor circulation line during the early stage of pulping could increase pulp yield by 1-3%, depending on the final pulp kappa number. If this yield increase could be obtained in combination with indigester black liquor oxidation, the net costs for odor control in mills using batch digesters would be very attractive.

17. Key Words and Document Analysis. 17a. Descriptors

Air Pollution
Sulfate Pulping
Black Liquors
Odor Control
Oxidation
Kinetics
Cost Estimates

17b. Identifiers/Open-Ended Terms

Air Pollution Control
Stationary Sources
Indigester Black Liquor Oxidation
Oxygen Injection
Reduced Sulfur Compounds
Laboratory Scale

17c. COSATI Field/Group 07A, 07D, 13B

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