THE MIXING SENSITIVITY OF POLYSULPHIDE GENERATION

by

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ABSTRACT

Increasing the yield of kraft pulping processes is desirable for both environmental and economic reasons. The addition of polysulphide to the cooking liquor is a solution, which has been shown to increase pulp yield by 1% or more. One economical approach used to generate polysulphide is the PAPRILOX™ process. In this process, sulphide in white liquor is oxidized to polysulphide in a sparged stirred tank reactor using lime mud and MnO_2 catalysts.

This thesis investigates the mixing-sensitivity of polysulphide generation in the PAPRILOX™ process, with the goal of determining the optimum generating conditions needed to maximize polysulphide yield and selectivity. Parameters affecting mixing and mass transfer, including impeller speed, gas flowrate, oxygen partial pressure, catalyst loading and catalyst type, were studied in two laboratory batch-operated reactors; one sparged (scale: 1:100 000 by volume, liquid volume 1.4 L, gas hold-up 2.4-28%, gas superficial velocity: 0.066-0.26 cm/s), at atmospheric pressure, and having low-intensity mixing and the other not sparged (liquid volume 1.25 L, gas fraction 20%), pressurized (1.8-20 psig), and having high-intensity mixing. In order to mimic the liquor conditions used in the PAPRILOX™ process the reactions were performed at 90 °C with white liquor compositions similar to those typically found in kraft pulp mills.

Polysulphide yield and selectivity increased during oxidation, reaching a maximum level in a time that depended on reaction parameters. In the sparged reactor, regardless of gas flowrate, oxygen partial pressure, catalyst type or catalyst loading, increasing the mixing intensity by increasing the impeller speed gave higher polysulphide yields, selectivities and initial rates of formation. Increasing the gas flowrate only impacted the initial polysulphide formation rate, whereas increasing the catalyst loading improved the yield, selectivity and initial rate of polysulphide formation. Reactions performed at higher oxygen partial pressures (sparging with O_2 instead of air) were faster, however the maximum polysulphide yield and selectivity reached were lower, 47 and 75% respectively at 2000 rpm, 2.0 g/L Fisher MnO_2 catalyst and 2.0 SLPM air versus 30 and 43% under the same conditions with 2.0 SLPM O_2 .

With the high-intensity reactor higher impeller speeds gave higher polysulphide yields regardless of the oxygen partial pressure. The initial rate of polysulphide formation increased with impeller speed up to 2000 rpm, after which the rate levelled off. Polysulphide selectivity was affected to the largest extent, in the high-intensity reactor, by O₂ partial pressure and was only minimally affected by mixing.

In the sparged reactor, with use of the Fisher MnO₂ catalyst, the maximum polysulphide yield and selectivity, 47% and 75% respectively, were obtained during 50 min of oxidation at an impeller speed of 2000 rpm and air flowrate of 2.0 SLPM. Results with oxygen sparging were only comparable when the concentration of the Fisher MnO₂ catalyst was 6.5 g/L or when the proprietary PAPRILOX™ catalyst was used. At a Fisher MnO₂ concentration of 6.5 g/L polysulphide formed in 39% yield and 69% selectivity in 9 min of oxidation at an impeller speed of 2000 rpm and oxygen flowrate of 2.0 SLPM. Under the same conditions, using the proprietary catalyst in a concentration of 2.0 g/L gave polysulphide in 46% yield and 85% selectivity after 8 min of oxidation.

With the high-intensity reactor reactions were much faster and polysulphide yield and selectivities of 43-45% and 66-76%, respectively, were obtained in 1.7-2.7 min of oxidation at oxygen partial pressures close to atmospheric. However, the energy required to reach these yields and selectivities in the high-intensity reactor was twice that of the sparged reactor.

In all of the cases studied lime mud settling was not adversely affected by the higher mixing intensities.

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INTRODUCTION

An Overview of the kraft Pulping Process

At present about 75-80% of U.S. virgin pulp is produced using the kraft pulping process. In this process wood chips are cooked in a sodium hydroxide and sodium sulphide solution ($\text{pH} > 12$) at 160-180 °C for 0.5-3 hours to dissolve and degrade most of the lignin contained in the wood fibres. Lignin is the name for the coloured phenolic polymers that act as the structural glue in wood and contribute to wood's brown colour. The sodium sulphide and sodium hydroxide solution, or white liquor, fed to this reactor, also called the digester, passes through a complex recovery cycle that regenerates the sulphide and hydroxide species before they are returned to the digester for reuse. Regeneration of the sulphide occurs in the recovery boiler with the reduction of the Na_2SO_4 left after digestion. In the same process unit, organic compounds extracted from the wood in the digester are combusted, with the heat generated being used to make the steam required throughout the rest of the pulp mill. Sodium hydroxide reforms in the causticizing system where Na_2CO_3 left after digestion reacts with CaO and water to form NaOH and CaCO_3 , or lime mud. Wood pulps recovered from the digester are washed then sent to the bleaching plant where further lignin removal and pulp brightening occurs [1].

Figure 1 gives an overview of the kraft process including the recovery system [2]. With the exception of the bleaching plant, the kraft process is mainly a closed cycle with the chemicals required for wood digestion being recovered and recycled. In the bleaching plant spent chemical solutions are collected, sent to biological treatment and discharged from the plant.

Figure 1: The kraft pulping process.

One of the disadvantages of kraft pulping is that the pulp produced is hard to bleach, requiring the use of chlorinated chemicals to achieve the desired pulp brightness. This use of chlorinated compounds has caused concern over the environmental impact of effluent from pulp mills [1]. During the past twenty years, both environmental and economic pressures have motivated the pulp and paper industry to reduce the quantity and improve the quality of effluent produced by kraft pulp mills. To reach these goals, mills must reduce the quantity of chemicals consumed in the bleach plant, the main source of mill effluent. This can be achieved by lowering the lignin content in the pulp before it reaches the bleaching stage. Modified cooking of the wood chips, O_2

delignification or the addition of oxidizing chemicals (anthraquinone and/or polysulphide) to the digester are some of the options used to achieve this result [3].

The use of modified cooking strategies or O₂ delignification causes the organic material, previously removed in the open bleaching stage, to be recycled through the recovery boiler putting greater strain on a system already running near capacity in many mills. Adding polysulphide to the digester protects wood polysaccharides, especially hemicelluloses, from degradation. This allows production of pulp at a higher yield for a given lignin content. Alternatively, the original pulp yield can be maintained at a lower lignin content, thus reducing the organic load to the recovery system [4]. In addition, pulps cooked in the presence of polysulphide have the same pulp strength and bleachability as conventional kraft pulps [5]. Adding polysulphide to the digester at an application of 0.8-1.1% sulphur on oven dried wood results in a 1.2-1.75% yield increase, on oven dried wood, in the screened pulp after cooking. Using anthraquinone (0.05% on oven dried wood) and polysulphide together produces a synergistic effect increasing the yield of screened pulp by 2.5-3.5% on oven dried wood over that from a conventional kraft cook [6,7,8,9].

Methods of Polysulphide Formation

Berthier, Peckman and May were among the first researchers to use polysulphide liquors, created through the addition of sulphur to the digester, in kraft pulping [10,11].

Unfortunately, polysulphide formed in this manner upset the sodium to sulphur balance in the mill, leading to increased gaseous sulphur emissions from the recovery system [12]. Several alternative methods, all involving some form of white liquor oxidation, have been developed to eliminate this problem and are discussed in further detail below.

Polysulphide yield and selectivity reported for each of the different methods are calculated as follows:

$$\text{Yield} = \frac{\text{polysulfide formed (g S}^{\circ}\text{/L)}}{\text{initial HS}^- \text{ (g S/L)}} \quad (1)$$

$$\text{Selectivity} = \frac{\text{polysulfide formed (g S}^{\circ}\text{/L)}}{\text{HS}^- \text{ consumed during oxidation (g S/L)}} \quad (2)$$

Polysulphide Production via Electrochemical White Liquor Oxidation

Electrochemical production of polysulphide is currently in the development stage, however the process is worth noting [13]. The electrochemical oxidation of white liquor occurs in a membrane cell using three-dimensional mesh electrodes. White liquor enters the anode compartment and oxidizes to form a polysulphide solution. Cations pass through the membrane and combine with hydroxide ions, formed from water reduction in the cathode compartment, producing a concentrated NaOH solution. Hydrogen gas, also evolved at the cathode, is collected and burned as an auxiliary fuel [14]. The separation of polysulphide and NaOH solutions offers a potential means to produce sulphide free alkali solutions for use in the bleach plant and allows for control of the sulphur to sodium ratio in the mill. Researchers from Nippon Paper Industries have recently implemented this electrochemical process for polysulphide generation during a pilot-scale trial at their Japanese mill. Analysis of the liquor formed in the anode compartment indicates that polysulphide forms in a maximum yield and selectivity of 64% and 88% respectively [15].

Polysulphide Production via Activated Carbon Catalyzed White Liquor Oxidation

The MOXY, or Mead Oxidation Process, first developed in 1965, forms polysulphide via white liquor oxidation in the presence of a granular activated-carbon catalyst using air as the oxidant [16]. The catalyst is wet-proofed to enhance gas-liquid-solid contact, improving the polysulphide yield during reaction. A diagram of the process is shown in Figure 2. White liquor passes through a series of pressure filters before being pumped to the reactors where the air and the liquor react in co-current downflow at typical pressures of 12-15 psig. Under normal operating conditions, when the catalyst is fresh, polysulphide yield and selectivity are 40-45% and 60-80% respectively. The use of polishing filters ahead of the reactor is essential to the MOXY process, as solid concentrations higher than 5 ppm in the white liquor stream lead to catalyst deactivation and plugging of the reactor column.

Figure 2: The MOXY Process for polysulphide formation [16].

A similar process developed by the Chiyoda Corporation in conjunction with the Mitsubishi Paper Mill uses a non-wetted porous activated-carbon extrudate as the catalyst [17,18]. Like the MOXY process, this system requires the use of a polishing filter to remove 95% of the incoming solids from the white liquor. Figure 3 highlights the main components of the process. The system produced polysulphide in 45% yield and 86% selectivity in commercial application with fresh catalyst.

Figure 3: Simplified flow diagram for polysulphide production developed by the Chiyoda Corporation and the Mitsubishi Paper Mill [17].

The sensitivity of both the MOXY and Chiyoda processes to solids in the white liquor feed is the main disadvantage for their application in a kraft pulp mill. The polishing filters used are expensive and require back-flushing every 24 hours to prevent clogging. In addition, despite the use of filters, catalyst deactivation due to solids deposition occurs easily requiring regeneration every two to three weeks with the MOXY process [16] and every three to four months with the Chiyoda process [17,18].

Polysulphide Production via White Liquor Oxidation in the Presence of MnO_2

Barker, of Union Camp Corporation, first patented the use of MnO_2 for polysulphide formation via white liquor oxidation in 1969 [19]. The reaction occurs in a stirred-tank reactor according to the following chemistry, using a near stoichiometric amount of MnO_2 .

The liquor and solid mixture then passes to a thickener, which removes the solids from the polysulphide solution with the help of a flocculant. Regeneration of the thickened MnO_2 slurry occurs in a kiln-type hot-air dryer prior to the recycle of the MnO_2 back to the reactor. The reactor operates at 80°C and produces polysulphide in 53% yield and 83% selectivity. A polishing filter is required to lower the MnO_2 levels back down to 2-4 ppm prior to introduction of the polysulphide liquor into the mill [20]. Figure 4 illustrates a flow diagram for the process.

Figure 4: Making polysulphide via white liquor oxidation with MnO_2 : the Union Camp Process [20].

Quantum Technologies Inc. uses a similar chemistry in their polysulphide production process, however only catalytic amounts of MnO_2 are required [4]. The process combines the reaction and MnO_2 regeneration into one stage in a pressurized reactor, using air as the oxidant. Figure 5 shows the flow diagram for the process in which white liquor pumped directly from the clarifier is combined with the MnO_2 catalyst in a mixing trough. The liquid and solid mixture then passes to the pressurized reactor where it is exposed to air at 35 psig, producing polysulphide in 1-2 min. After degassing, a centrifuge separates the solids from the liquor with the solids being recycled to the mixing trough while the polysulphide liquor is sent to storage. The process is capable of

producing polysulphide in 40-55% yield and 65-80% selectivity at a catalyst loading of 7-8 vol% in the white liquor.

Figure 5: Polysulphide formation in Quantum Technologies process [4].

Both the Union Camp and Quantum Technologies processes suffer from one major drawback, loss of MnO_2 to the mill system through carryover with the polysulphide liquor. Preventing this carryover requires the use of a polishing filter between the oxidation system and the mill. With the Union Camp process an additional disadvantage is the required use of near stoichiometric amounts of MnO_2 in the process.

All of the polysulphide production processes discussed so far require construction of a separate oxidation plant for the formation of polysulphide liquor, a fairly costly proposition. In an effort to reduce these costs and simplify the production process, Paprican researchers developed the PAPRILOXTM process, in which oxidation of white liquor to form polysulphide liquor occurs in a modified causticizer, essentially a sparged stirred-tank reactor, using lime mud and MnO_2 catalysts [12,21,22]. The process, diagrammed in Figure 6, is currently in full-scale trials and uses an air or O_2 oxidant to produce polysulphide in 37-48% yield and 68-78% selectivity. Use of an air oxidant gives the higher polysulphide yield and selectivity, but requires longer retention times

120 vs. 45 min. Levels of MnO_2 required in the process vary depending on the characteristics of the lime mud. Initial lab-scale studies indicated that addition of MnO_2 over 1-1.25 g/L did not further improve polysulphide yield [12], however in the full-scale trials increasing MnO_2 concentration up to 4 g/L continued to have a positive effect on the yield, selectivity and rate of polysulphide formation when using an O_2 oxidant [22].

Economic evaluation of the PAPRILOX™ process indicates that capital costs of \$1.75-\$2.75 million Canadian are expected with O_2 or air oxidation, respectively. These costs are approximately \$2.25-\$1.25 million dollars less than a typical packed-bed reactor installation, such as the MOXY or Chiyoda processes [23].

Figure 6: White liquor oxidation according to the PAPRILOX™ process [21].

Chemistry of Catalyzed Polysulphide Synthesis

The overall reactions thought to be involved in polysulphide formation via catalyzed sulphide oxidation are as follows [12,24,25]:

where $(1 \leq n \leq 4)$.

Compounds, such as MnO_2 or activated carbon, catalyze equation (6) favouring the formation of polysulphide over thiosulphate.

Complicating the process of polysulphide formation is the fact that various chain length polysulphides are formed during the oxidation reaction. Redistribution of these different chain length species subsequently occurs in an equilibrium process according to equation (7). Results from studies by Giggenbach [26,27], Teder [28] and Licht et al. [25] indicate that the equilibrium process is rapid, with a new equilibrium state being reached within 5 min. All of the authors conclude that the high speed at which the polysulphide species interchange validates the assumption that the relative proportions of different chain length polysulphide species stays constant provided the pH, temperature and sulphide concentration remain the same.

Using the equilibrium constants for polysulphide species redistribution determined by Licht et al. [25], and knowing the total amount of S^0 , OH^- and HS^- in solution, the average number of zero-valent sulphur atoms per polysulphide chain in oxidized white liquor can be calculated. For a typical polysulphide liquor, produced during mill trials of the PAPRILOX™ process [21], the number average length based on this calculation is 2.4 zero-valent sulphur atoms.[†] Other predictions, based on the changes in alkali concentration during polysulphide production, give values of 2.8-3.5 for typical polysulphide liquors produced from white liquor oxidation [29].

[†] The methodology and sample calculations used to determine this value are found in Appendix B.

Little is known on the exact mechanism of polysulphide formation through sulphide oxidation, probably due to the complexity of the system. What is known however, derives from studies performed on thiosulphate formation via sulphide oxidation. Studies on black liquor oxidation, performed by Morgan and Murray [30] indicate that the rate of thiosulphate formation, from sulphide oxidation, has a first-order dependence on oxygen concentration and a zero-order dependence on sulphide concentration at higher sulphide concentrations. These observations are supported by work completed by Fisher et al. [24,31] who also conclude that thiosulphate synthesis through sulphide oxidation requires the initial formation of polysulphide species. Subsequent degradation of the polysulphide gives the oxidized, thiosulphate, products with the rate-controlling step being the initial formation of the polysulphide species.

Analysis of Three-Phase Systems

Polysulphide formation through catalyzed white liquor oxidation occurs in a three-phase system using a packed-bed or slurry reactor. These systems are fairly complex and up to four different resistances can contribute to control of the reaction rate including gas-side mass transfer, gas-liquid mass transfer, liquid-solid mass transfer and reaction kinetics at the solid surface. In general gas-side mass transfer resistances are usually not rate controlling and are ignored, however any or all of the remaining three resistances may help limit the reaction rate. Determining which resistances contribute to the rate control is a complicated process. For agitated slurry reactors this process involves determining the effect of catalyst particle size, loading and agitation speed on the rate of reaction. In all cases the speed of agitation must be high enough to suspend all of the catalyst particles in solution [32].

If gas-liquid mass transfer forms the main resistance to reaction, then altering the catalyst loading or catalyst particle size will not affect the reaction rate. However, changes in impeller speed or gas flowrate, affecting the gas dispersion within the liquid will cause the rate of reaction to vary. If liquid-solid mass transfer or inherent reaction kinetics participate in controlling the reaction rate then changing either the catalyst loading or particle size should affect the reaction rate. An exception occurs when the system

operates in the turbulent regime, where the liquid-solid mass transfer coefficient, k_s , is no longer dependant on particle size but on the system hydrodynamics. In this case differentiation between liquid-solid mass transfer vs. surface chemical reaction control is possible through a study of the effect of temperature on the reaction, allowing determination of the reactions activation energy. If the activation energy is greater than ~ 40 kJ/mol then the surface reaction controls the reaction rate, else if it is less than ~ 20 kJ/mol then mass transfer to the solid particles is probably controlling [32]. Table 1 outlines the variables affecting the reaction rate for synthesis of a product C from a gaseous reactant A and an in-solution reactant B in a three-phase stirred-tank reactor.

Table 1: Effect of process variables on reaction rates under different controlling regimes in a three phase slurry reactor [32]. (A refers to the gas phase reagent whereas B refers to the liquid phase reagent.)

Controlling Resistance	Variables whose effect is:		
	Major	Minor	Negligible
Gas-Liquid Mass Transfer	-concentration of A at gas-liquid interface -type of impeller -impeller speed -gas sparging velocity	-temperature	-particle size -catalyst loading -concentration of B
Liquid-Solid Mass Transfer	-particle size -catalyst loading -concentration of A at gas-liquid interface -impeller speed	-temperature -gas velocity	-concentration of B
Surface Reaction (no pore diffusion)	-particle size -catalyst loading -concentration of A at gas-liquid interface [§] -concentration of B [§] -temperature		-type of impeller -impeller speed -gas velocity

[§] Assumes that the reaction kinetics are not zero order in A or B.

Researching the Mixing Sensitivity of Polysulphide Formation According to the PAPRILOX™ Process

Given that polysulphide is an intermediate in sulphide oxidation and that thiosulphate is an undesirable “dead-load” chemical that must be carried through the pulping liquor cycle, any method of polysulphide liquor production must optimize the polysulphide yield and selectivity. In order to do this, the rate of polysulphide formation relative to that of thiosulphate formation must be increased.

Initial data from pilot-plant studies of the PAPRILOX™ process shows that polysulphide selectivity may be increased by 20% simply by changing the type of impeller used in the reaction. (Use of a disc impeller in place of a straight blade turbine increased the selectivity for polysulphide formation from 25-35% to 50% [22].) The possibility that polysulphide generation might be mixing sensitive provides an opportunity for optimization of its generation in order to maximize its yield and selectivity. This thesis reports on a more detailed study of the formation of polysulphide in laboratory, batch-operated, stirred-tank reactors performed with the goals listed below. In order to mimic the liquor conditions typically found within a mill’s causticizing system, this study assumes that, prior to oxidation, the temperature of the white liquor is approximately 90 °C and the composition of the white liquor is similar to that found in the mill-scale studies of the PAPRILOX™ process [21].

Goals of this thesis:

- (1) To determine whether polysulphide generation in the PAPRILOX™ process is in fact sensitive to mixing.
- (2) To determine the affect of changing process variables, such as impeller speed, gas flowrate, oxygen partial pressure, catalyst loading and catalyst type on the yield, selectivity and initial rate of polysulphide formation.
- (3) To use information determined from the above study to attempt to isolate the factors controlling the rate of polysulphide formation: gas-liquid mass transfer, liquid-solid mass transfer or inherent reaction kinetics.

- (4) To use all of the information collected to determine the optimum generating conditions, including any required changes in the reactor design, needed to maximize the polysulphide yield and selectivity.

EXPERIMENTAL

Equipment

Polysulphide generation from white liquor oxidation in the presence of lime mud and MnO_2 was studied in two lab-scale stirred tank reactors. The first was a conventional sparged stirred-tank reactor (1:100000 scale). Tests were conducted in this reactor at atmospheric pressure and at power intensities from 0.37-28 W/kg ($N_p = 8.5$ under unsparged conditions). The other reactor was an unsparged, pressurized reactor. Tests conducted in this reactor occurred at power intensities from 17 to 3100 W/kg ($N_p = 4.5$ at a 20% gas fraction).

Sparged Reactor

The majority of the experiments were conducted in the sparged reactor diagrammed in Figure 7. The cylindrical reactor, 12.7 cm in diameter and 30 cm in depth, was constructed of SS316 and equipped with 6 baffles, 1 cm in width, extending 1.4 cm into the tank. Gas was sparged into the reaction mixture through a ring sparger located directly under the impeller blades that was 4 cm in diameter and formed from 1/8" SS316 tubing. Four holes, 1 mm in diameter, were drilled into the ring to allow gas to enter the reactor. The holes pointed towards the bottom of the reactor in order to limit solids plugging.

The reaction mixture was stirred using a 6-bladed turbine, 4.5 cm in diameter and composed of six 1.1 cm long by 0.9 cm wide blades mounted on a 3.5 cm disc. The impeller was located at a height of 4.5 cm from the bottom of the tank. A vertically mounted 0.25 kW variable speed DC motor, capable of reaching a maximum rotational speed of 2400 rpm, powered the mixer.

Torque measurements were taken using a shaft-mounted torque transducer and an optical digital tachometer (model# 08212, Cole Parmer). A silicon rubber coated heating tape (model# SRFG-618/5, OMEGA), covering the outside of the reactor and linked to a PID temperature controller (model# CN8501TC-R1, OMEGA) through a K-type SS316

thermocouple (model# TJ36-CASS-18G-12, OMEGA), raised and held the reaction temperature near 90°C. Gas flowrates into the reactor were monitored using a non-thermal differential pressure flowmeter (model# 32915-68, Cole Parmer). All gases flowing into the reactor were passed through a washing bottle containing water at 90°C to saturate the gas with water vapour to limit water loss from the reactor. Figure 8 shows the experimental set-up used in the sparged experiments, whereas Figure 9 illustrates the power curve characteristic of the reactor at different air flowrates.

Figure 7: Schematic diagram of the sparged reactor. Reactor characteristics: $N_p = 8.5$, $D = 12.7$ cm, $T = 11.9$ cm, $h = 11.1$ cm, $C = 4.5$ cm, $n_b = 6$, average sparged energy input of 0.37 to 28 W/kg.

Figure 8: Experimental set-up used in the sparged reactor studies.

Figure 9: Characteristic power curve for the sparged reactor. Conditions: 2.0 L of fluid, no gas entrainment, no gas sparging.

High-Intensity Reactor

Studies in the pressurized system were completed using a high-intensity mixer (Paprican P_{HT}, Pointe Claire, QC) with a modified 1.6 L reactor bowl, diagrammed in Figure 10. The cylindrical bowl, 15.0 cm in diameter and 11.1 cm in depth, contained six 0.79 cm wide baffles that protruded 1.6 cm into the bowl. Mixing was performed using a 6-bladed impeller, 10.2 cm in diameter that extended the full height of the bowl. The 2.4 cm long by 0.96 cm wide blades were welded onto a 5.4 cm diameter housing that fit over the motor shaft, which passed through a water lubricated mechanical seal at the bottom of the bowl.

The bowl was equipped with one sampling port located at a height of 6 cm from the base of the reactor. A 7.5 kW motor, capable of reaching a maximum impeller speed of 3000 rpm and mounted below the bowl, provided the mixing. Two electrical bands provided heating to the reactor bowl and were used to raise the bowl temperature to 90 °C prior to running an experiment. Cooling, required to maintain the bowl temperature at 90 °C while agitation of the reaction mixture occurred, was provided by continuously running cooling water through copper tubing wrapped around the outside of the bowl.

The reactor cover, containing two ports for pressurizing and venting the reactor bowl, was hydraulically controlled and allowed the pressure in the bowl to reach a maximum of 150 psig. The temperature, impeller speed and gas pressure for the system were computer controlled using (Mixer) software provided with the high-intensity mixer. Pressure readings were electrically monitored using a pressure sensor located in the bowl cover, while temperature readings were measured with an RTD probe located in the base of the reactor. Power measurements were recorded using a power meter that monitored the power drawn by the motor. Figure 11 shows the experimental set-up used in the high-intensity reactor studies and Figure 12 depicts the characteristic power curve for the high-intensity reactor.

Figure 10: Schematic of the high-intensity reactor. Reactor characteristics: $N_p = 4.5$, $D = 15.0$ cm, $T = 11.8$ cm, $h = 8.9$ cm, $n_b = 6$, average energy input of 17 to 3100 W/kg.

Figure 11: Experimental set-up used in the high-intensity reactor studies.

Figure 12: Characteristic power curve for the high-intensity reactor. Conditions: unpressurized, zero gas fraction.

Table 2 shows a comparison of the reactor characteristics and experimental conditions used in this study to those found used in the pilot- and mill-scale studies of the PAPRILOX™ process [12,21,22].

Table 2: Comparison of the dimensions and typical gas flowrates and impeller speeds for the current studies and the pilot- and full-scale studies of the PAPRILOX™ process.

Reactor Characteristic(s)	Lab-Scale Sparged Reactor	Lab-Scale High-Intensity Reactor	Pilot-Scale Sparged Reactor [22]	Mill-Scale Sparged Reactor [21,33]
Tank/Vessel Characteristics				
Diameter (m)	0.127	0.150	1.08	5.49
Height (m)	0.300	0.111	1.022	4.88
Volume (m ³)	0.0038	0.0020	0.94	116
# of Baffles	6	6	4	4
Baffle Width (m)	0.014	0.016	0.102	----
Height of Liquor (m)	0.111	0.089	0.65	4.0-4.3
Liquid Volume (m ³)	0.0014	0.00125	0.60	94-100
Impeller Characteristics				
Impeller Type	Turbine	Modified Turbine	Disc Turbine	Proprietary
Power Number (N _p)	8.5	4.5	5.0	----
Impeller Diameter (m)	0.045	0.102	0.2794	----
Disc Diameter (m)	0.035	0.054	0.1778	----
# of Blades	6	6	6	----
Blade Length (m)	0.011	0.024	0.06985	----
Blade Width (m)	0.009	0.0096	0.0508	----
Impeller Speed (rpm)	500-2000	500-3000	200-225	60-90
Sparging and Experimental Conditions				
Gas Flowrate (SLPM)	0.5-2.0	----	15-150	5950-17000
Superficial Gas Velocity (m/min)	0.039-0.16	----	0.016-0.16	0.25-0.62
Q/Nd _l ³ (x 10 ³)	2.7-11	----	3.1-31	7900-34000
MnO ₂ Catalyst	Fisher	Fisher	Proprietary	Proprietary
MnO ₂ Loading (g/L)	1.4-6.5	2.2	0-0.16	1.5-4.0
Reaction Times (min)	9-100	0.55-10	65-360	45-120
Power Dissipation				
Power Dissipated (W/kg)	0.37-28	17-3100	0.74-1.1	----
Power Dissipated (W/m ³) (assuming $\rho=1120 \text{ kg/m}^3$)	414-31400	19000- 3.5x10 ⁶	830-1230	----

Procedure for Studying Polysulphide Formation

Polysulphide was generated from air or oxygen oxidation of synthetic white liquor, using lime mud and MnO_2 as catalysts. Causticized synthetic green liquor acted as the source of the lime mud and white liquor mixture. Unless otherwise stated, chemicals used were obtained in the purity listed in Table 3. Praxair (Langley, BC) supplied the nitrogen and oxygen, and the building instrument air (after passing through a 50 μm filter) was used for air tests. HCl solutions of the desired concentration were made by dilution of the concentrate with distilled water in volumetric flasks. Similarly CoSO_4 solutions were formed by dilution of the desired amount of solid.

Table 3: Chemicals used during the oxidation reactions.

Chemical	Formula	Assay	Supplier	Cat. No.
Barium Chloride	BaCl ₂	10% w/v	LabChem	LC11600-1
Calcium Carbonate	CaCO ₃	Certified A.C.S. Powder (>99%)	Fisher	C64-500
Calcium Oxide	CaO	Technical (>98%)	Fisher	C114-3
Cobalt (II) Sulphate Hydrate	CoSO ₄ · xH ₂ O		Aldrich	23,093-3
EDTA		0.1 N	LabChem	LC13870-4
Formaldehyde	CH ₂ O	Certified A.C.S. 37% w/w	Fisher	F79-500
Hydrochloric Acid	HCl	NF/FCC Grade (36.5-38%)	Fisher	A481-212
Manganese Dioxide	MnO ₂	Certified A.C.S. (99%)	Fisher	M108-500
Sodium Carbonate	Na ₂ CO ₃	Certified A.C.S. Anhydrous (>99.5%)	Fisher	S263-10
Sodium Hydroxide	NaOH	Certified A.C.S. (>97%)	Fisher	S318-1
Sodium Sulphide Nonahydrate	Na ₂ S · 9H ₂ O	Certified Crystalline (>99.9%)	Fisher	S425-212
Sodium Sulphite	Na ₂ SO ₃	Certified A.C.S. Anhydrous (99.9%)	Fisher	S430-3
Sodium Tetrasulphide	Na ₂ S ₄	Technical 90+% Na ₂ S ₄ , 5% H ₂ O	Alfa Aesar	88697
Sodium Thiosulphate	Na ₂ S ₂ O ₃	Certified A.C.S. (>99.5%)	Fisher	S445-500

Sparged Reactor

In a typical experiment with the sparged reactor NaOH (25.8 g), Na₂CO₃ (148.4 g) and distilled water (1230 mL) were added to the reactor and degassed with N₂ (2.0 SLPM) for 20 min while the reactor mixture was heated and stirred (800 rpm). The N₂ flow (2.0 SLPM) was maintained during causticization to limit sulphide oxidation. At a solution temperature of ~ 70 °C, Na₂S· 9H₂O (228.7 g) was added to the reactor, followed by CaO (62.8 g) at a solution temperature of 85 °C. The temperature rose to 90 °C in the reactor as the CaO slaked and was maintained at this temperature during the 30-100 min causticizing time. (In initial studies the green liquors were causticized for 100 min, however subsequent studies indicated that the same liquor composition was reached during 30 min of causticizing. As a result subsequent studies were completed after allowing the green liquor to causticize for only 30 min).

Similar to the lab-scale studies of the PAPRILOX™ process [12], the CaO to Na₂CO₃ mole ratio was limited to 0.8 in the green liquor to ensure over liming did not occur. The Na₂S concentration in the green liquor was kept at 22 g S/L, the upper limit of the concentrations used in the lab-studies. Table 4 lists the typical liquor compositions after causticizing.

Table 4: Typical chemical composition of synthetic white liquors.

Chemical	White Liquor Composition [‡]	White Liquor Composition in PAPRILOX [™] Lab-Scale Studies [12]	White Liquor Composition in PAPRILOX [™] Mill-Scale Trials [21]	Typical Mill White Liquor Composition [34]
NaOH (g/L as Na ₂ O)	61.5		68.0	81-120
Na ₂ CO ₃ (g/L as Na ₂ O)	17.9	12.8-18.3 [§]	8.0	11-44
Na ₂ S (g/L as Na ₂ O)	39.1	42.5	34.0	30-40
Active Alkali (g/L as Na ₂ O)	101		102	111-160
Effective Alkali (g/L as Na ₂ O)	81.0		85.0	96-140
% Sulphidity on TTA	33.0		30.9	19.6-24.5

[‡] Based on results of ABC test for sample #1 (time zero) taken from white liquor prior to oxidation.

[§] Calculated assuming a 100-125 g/L lime mud concentration (assumed to be 100% CaCO₃) and a 0.80-0.82 mole ratio of CaO to Na₂CO₃ in the green liquor.

Once causticizing had completed, MnO₂ (2.76 g to give 2.0 g/L and 2.5 wt% on lime mud assuming complete conversion of CaO to CaCO₃) was added to the reactor and the impeller speed adjusted to the desired value. Five minutes later, using a syringe, a 30 mL sample of the mixture was removed from the reactor, placed in a 30 mL polypropylene bottle and capped with a septum so that there was no headspace in the bottle. The sample was then placed in a 70 °C oil bath until it could be analyzed. At this point the N₂ gas flow into the reactor was halted and either oxygen or air was sparged into the reactor. The start of the air or oxygen sparging was time zero for the reaction. Five more samples were taken from the reactor over regular time intervals in order to monitor the polysulphide and sulphide concentration profiles during the reaction. The shaft power input to the mixture under gassed conditions during the reaction was determined by subtracting the average power required to overcome the friction of the mixer bearings in the absence of the liquor from the average power drawn by the impeller over the reaction time. Torque measurements required in the power calculations were logged on a

throughout the reaction time. Each of the reactions was monitored over 100 min, or until the peak polysulphide concentration had been reached.

High-Intensity Reactor

White liquors required for polysulphide generation in the high-intensity reactor were synthesized according to the procedure for the sparged reactor studies. After causticizing was complete the white liquor and lime mud mixture (1400 g) was transferred to the preheated high-intensity reactor bowl at 90 °C. The reactor was purged with N₂ gas for 5 min with stirring (200 rpm), prior to the addition of MnO₂ (2.76 g to give 2.2 g/L and 2.8 wt% on lime mud assuming complete conversion of CaO to CaCO₃). This time period was also used to raise the mixture temperature back up to 90 °C. After 5 min the stirring was halted and the reactor purged with O₂ for 30 s, before being pressurized to the desired level. Using the sample port, 20 mL of the liquid-solid mixture were removed from the reactor and placed in a 20 mL glass vial leaving no headspace in the vial. Mixing then commenced, the start of mixing was time zero for the reaction. After the desired time interval, the motor was stopped and the reaction mixture was sampled. This procedure was repeated until the reaction was complete. Since the rate of sulphide oxidation was so rapid under these conditions, power input measurements for each of the conditions analyzed were determined in a separate experiment using a new batch of white liquor and lime mud mixture.

Experimental Design

Given the number of process variables involved in the study and the likelihood of non-linear interactions between the variables, especially between impeller speed and gas flowrate, an experimental strategy was necessary.

A simple 3² factorial design, illustrated in Table 5, was first completed in the sparged reactor in order to determine whether polysulphide formation was in fact mixing sensitive. In this initial design the catalyst loading and type were kept constant at 2.0 g/L of Fisher MnO₂.

Table 5: Initial 3^2 factorial experimental design for the sparged reactor; catalyst loading and type constant at 2.0 g/L Fisher MnO_2 .

Impeller Speed (rpm)	Gas Flowrate (SLPM)	Gas Composition
500	0.5	air
500	2.0	air
500	0.5	oxygen
500	2.0	oxygen
2000	0.5	air
2000	2.0	air
2000	0.5	oxygen
2000	0.5	oxygen

Having determined that polysulphide formation was indeed sensitive to mixing, the design was then expanded to incorporate intermediate and centre points to develop a better picture of the response surface. Since intermediate oxygen partial pressures in the sparged reactor could only be obtained by mixing the gases, the initial 3^2 factorial design was split into two 2^2 factorial designs. The intermediate and centre points were incorporated into each of these designs, see Table 6 for the designs. Each centre point experiment was repeated five times, with the error taken from these repeat reactions to be the error for all of the experiments with the design.

Table 6: Composite experimental designs incorporating intermediate and centre points into a base 2^2 factorial design for air and oxygen oxidation in the sparged reactor. The catalyst loading and type were kept constant at 2.0 g/L Fisher MnO_2 .

Impeller Speed (rpm)	Gas Flowrate (SLPM)
Air Oxidation	
500	0.5
500	2.0
800	0.8
800	1.8
1300	1.3
1300	1.3
1300	1.3
1300	1.3
1300	1.3
1800	0.8
1800	1.8
2000	0.5
2000	2.0
Oxygen Oxidation	
500	0.5
500	2.0
800	0.8
800	1.8
1300	1.3
1300	1.3
1300	1.3
1300	1.3
1300	1.3
1800	0.8
1800	1.8
2000	0.5
2000	2.0

Results from the above studies indicated that impeller speed had the largest affect on polysulphide yield and selectivity during the oxidation reactions in the sparged reactor and that the reaction could be followed to completion best with oxygen oxidation (see the Results and Discussion section). As a result investigations into the effect of catalyst loading on polysulphide formation were completed in a factorial design at high oxygen flowrates using the Fisher MnO_2 (Table 7). Studies completed in the first attempt to

determine k_{La} values for the sparged system, at 1300 rpm, 1.3 SLPM O_2 and various Fisher MnO_2 loadings, were also added to the design.

Table 7: Experimental design for studying the effect of catalyst loading on polysulphide formation in the sparged reactor using oxygen oxidation.

Impeller Speed (rpm)	Oxygen Flowrate (SLPM)	Fisher MnO_2 Loading (g/L)
500	2.0	1.06
500	2.0	4.25
500	2.0	6.54
1300	1.3	0.72
1300	1.3	1.08
1300	1.3	4.25
1300	1.3	6.54
2000	2.0	1.07
2000	2.0	4.26
2000	2.0	6.54

Finally, a brief analysis into the effect of catalyst type on polysulphide yield, selectivity and initial formation rate for reactions performed in the sparged tank reactor was completed by comparing the results of experiments run using 2.0 g/L of the proprietary PAPRILOX™ catalyst at 500 rpm and 2.0 SLPM O_2 , 1300 rpm and 1.3 SLPM O_2 , and 2000 rpm and 2.0 SLPM O_2 to those previously obtained with the Fisher MnO_2 catalyst.

Studies in the high-intensity reactor were limited to one experimental design due to the speed of reaction. Impeller speed and oxygen partial pressure were the only variables investigated, with the catalyst loading set at 2.2 g/L of Fisher MnO_2 . Table 8 illustrates the design used; experiments at 3000 rpm and 20 psig were not completed as the reaction was too fast.

Table 8: Experimental design used to study polysulphide formation in the high-intensity reactor. The catalyst loading and type were kept constant at 2.2 g/L of Fisher MnO_2 .

Impeller Speed (rpm)	O ₂ Pressure (psig)
500	2
500	20
2000	2
2000	10
2000	20
3000	2
3000	10

Sample Analyses

After allowing the lime mud particles to settle to the bottom of the sample bottles, 2 mL of the supernatant was removed via syringe under a N_2 atmosphere. This solution was passed through a 0.1 mm UV-vis transmission cell (cat# 14-385-933B, Fisher) and the absorbance of the solution over 190 to 800 nm was measured. Three isosbestic points exist in solution for the interconversion of the different polysulphide chains at 286, 330 and 460 nm [25]. The absorbance at these wavelengths is only a function of the total S^0 (in the form of polysulphides) concentration. As the typical absorbance of the polysulphide solutions did not exceed 2.0 at 286 nm, this wavelength was used. This data was compared with a calibration curve formed from the absorbances of polysulphide solutions created through the addition of Na_2S_4 to a N_2 degassed solution of NaOH, $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2S (see Appendix D for calibration solution concentrations). Using this calibration curve, shown in Figure 13, the concentration of S^0 in solution in the form of polysulphide was determined. Teder [35] and Danielsson *et al.* [36,37] have used similar methods to create calibration curves for spectroscopic analysis of polysulphide solutions.

Figure 13: Calibration curve, for polysulphide absorbance at 286 nm, used to determine the polysulphide concentration by UV-vis spectroscopy.

Gravimetric tests were also performed to verify the polysulphide concentration determined from UV-vis spectroscopy. A 5 mL volume of the supernatant removed from the sample bottles was analyzed for S⁰ content using a procedure developed by Dorris and Uloth [38]. The 5 mL sample was added to a 60 mL solution formed from 50 mL of distilled water and 10 mL of 0.1 N EDTA. The resulting solution was acidified to a pH of 7 with a 3 N HCl solution, and then acidified to a pH of 5-5.5 with a 1 N HCl solution. The precipitate (S⁰) that formed was filtered from solution using a Millipore filter assembly and 0.22 μ m, type GS, filter paper (Millipore). The solid residue was washed twice with distilled water (20 mL then 25 mL) and the filter paper removed and placed on a watch glass to dry. Once all six samples had been filtered the residue was further dried in an 80 °C oven for 20 min. The weight of the paper lost as water during the drying process was 0.0005 g on average, similar to that found by Dorris and Uloth [38]. As a result a correction factor of 0.0005 g was added to the weight of the solid residue. Based

on the weight of the solid residue the concentration of polysulphide in the sample was determined in terms of g S^o/L.[‡]

In order to directly measure the concentration of sulphide in solution, without resorting to dilution that might lead to oxidation of some of the sulphide, an ATR cell with a 3-reflection fused-silica optical element having an effective path length of 4.5 μm (Axiom Analytical Inc., Irvine, CA) was used. The extremely small path length of the ATR cell is achieved by passing a collimated beam of light through the fused-silica cylindrical probe. Light reflects from the surface of the probe several times before passing onto the spectrometer for measurement [39]. As the path length, and therefore signal strength, is affected by the refractive index of the solution the matrix of the calibration standards must match that of the sample solutions. The calibration curve for sulphide absorbance was therefore constructed based on solutions containing NaOH, Na₂CO₃, Na₂S, Na₂S₂O₃ and Na₂S₄. Each standard contained the same amount of NaOH, Na₂CO₃ and total sulphur as there was in the white liquor solutions. However, the concentrations of Na₂S, Na₂S₄ and Na₂S₂O₃ were varied to simulate oxidation of Na₂S over the course of an experiment. The actual concentration of Na₂S in solution was measured using the ABC method [40].[§] Absorbance of the sulphide species was extracted at 240 nm, the wavelength where there was the least amount of overlap from the other absorbing sulphur species, to form the calibration curve (Figure 14).

[‡] A sample calculation for the gravimetric determination of polysulphide concentration is shown in Appendix D.

[§] A sample calculation for the determination of sulphide concentration using the ABC test is shown in Appendix D.

Figure 14: Calibration curve for sulphide absorbance from UV-vis spectroscopy using the ATR cell. Absorbance data were abstracted at 240 nm.

About 6 mL of the supernatant solution from each sample was passed through the ATR cell and the absorbance of the solution was monitored from 190 to 800 nm. Absorbance data at 240 nm was extracted and compared with the calibration curve to obtain the concentration of S^{2-} in solution. In one experiment, the sulphide concentration predicted from ATR spectroscopy was compared with the values obtained by direct measurement of the sulphide concentration using the ABC test [40]. Figure 15 shows that there is a direct correlation between the two results, validating the concentration of sulphide determined from ATR spectroscopy. It should be noted that the spectroscopic method and ABC test used did not distinguish between free sulphide and the S^{2-} terminus to the polysulphide chains. Therefore the sulphide concentration represents the total amount S^{2-} in solution not just the free sulphide.

Figure 15: Comparison of the total sulphide concentrations obtained from UV-vis spectroscopy and the ABC test for one oxidation experiment. 2000 rpm, 2.0 SLPM air, 2.0 g/L Fisher MnO_2 .

Polysulphide yield and selectivity obtained during the oxidation reactions were calculated based on the sulphide concentration in sample #1 representing time zero for the oxidation reaction according to equations (1) and (2). Of note, because the yield is expressed in terms of the amount of elemental sulphur created and does not include the S^{2-} terminus of the polysulphide chains the theoretical maximum polysulphide yield will not reach 100%. Further, as the extent of reaction (sulphide conversion in oxidation reactions) differs from run to run (typically 58-90 % for the sparged reactor and 18-76% for the high-intensity reactor) yield and selectivity are not directly related.

Surface plots showing the data trends were created from the factorial experimental design data by gridding the data using a correlation (Kriging) method. Each figure was based on eight experimental data points at minimum (see Experimental Design section starting on page 26). This method creates a regular matrix from the data points by interpolating

between the data points included within a designated search radius [41]. Error in the yield, selectivity and initial rate data were taken as twice the standard deviation of the values obtained during five repeat experiments performed at 1300 rpm and 1.3 SLPM O_2 , representing a 99% confidence interval. The relative errors are 8, 10 and 20% respectively.

$k_L a$ Measurements

Experiments to determine the effects of the hydrodynamics on gas-liquid mass transfer, $k_L a$, were performed in the sparged reactor according to the sulphite oxidation method [42,43,44]. The stoichiometry for sulphite oxidation is:

The correct concentration of $CoSO_4$ must be determined such that there is a zero concentration of O_2 in the bulk liquid without chemical enhancement of the reaction rate. The required concentration of $CoSO_4$ was determined by monitoring the rate of Na_2SO_4 formation with varying catalyst concentrations. In a typical experiment distilled water (1400 mL) was added to the reactor and degassed with N_2 (2.0 SLPM) and stirring (800 rpm). After 10 min, Na_2SO_3 (123.45 g) was added to the reactor along with varying amounts of a $CoSO_4$ solution. The solution was mixed for 2 min under N_2 then the stirring was halted and a 10 mL sample was removed via syringe and placed in a vial with no headspace. Stirring was restarted at the same time that oxygen was sparged through the reactor at the desired flowrate. Samples (10 mL) were removed at 20-60 s time intervals to monitor Na_2SO_4 production with time.

The temperature of the reactor was maintained at 25-35°C during the course of the reaction. Samples were analyzed by FT-IR spectroscopy at 1100 cm^{-1} (absorption of Na_2SO_4) to determine the rate of Na_2SO_4 formation (or Na_2SO_3 consumption as the two values are equivalent). Figure 16 illustrates the absorption profile for one experiment with time; the isosbestic point indicates that clean conversion of sulphite to sulphate occurred. A plot of the rate of Na_2SO_3 consumption vs. $CoSO_4$ concentration, Figure 17,

indicates that the maximum CoSO_4 concentration that should be used is 10^{-6} M. This concentration was used in all other mass transfer studies.

Figure 16: FT-IR spectra illustrating Na_2SO_3 consumption (940 cm^{-1}) and Na_2SO_4 formation (1100 cm^{-1}) with time during mass transfer studies in the sparged reactor. Reaction conditions: impeller speed 1300 rpm, O_2 flowrate 1.3 SLPM, 30°C , 1 atm a.

Figure 17: Effect of CoSO_4 concentration on the rate of Na_2SO_3 consumption in the sparged reactor. Impeller speed: 1300 rpm, O_2 flowrate: 1.3 SLPM.

Experiments to determine $k_L a$ values under different impeller speeds and O_2 flowrates were performed as described above, with the exception that 10 mL of a 1.3×10^{-4} M solution of CoSO_4 were added with the Na_2SO_3 . The shaft power input to the mixture under gassed conditions during the reaction was determined by subtracting the average power required to overcome the friction of the bearings in the absence of the liquor from the average power drawn by the impeller over the reaction time. Torque measurements required in the power calculations were logged on a computer using "Xtalk" software throughout the reaction time.

Lime Mud Settling Tests

The lime mud and white liquor mixture was formed according to the procedure outlined above for the sparged reactor studies. MnO_2 was added to the mixture under N_2 at the end of the causticizing period. The mixture was then cooled to room temperature in a sealed bottle overnight. The entire liquor mixture was stirred briefly to suspend all of the particles before being transferred to a 10 cm diameter by 30 cm tall column and the height of the liquid-solid interface was monitored with time to determine the profile of lime mud settling. The entire liquor mixture was then transferred back to the reactor and stirred at 500 or 2000 rpm for ten or fifty minutes while N_2 was sparged through the reactor at 2.0 SLPM. The settling experiments were then repeated.

For the high-intensity reactor, 1400 g of the lime mud and white liquor mixture formed in the sparged reactor and cooled to room temperature was transferred to the high-intensity reactor bowl. The mixture was then stirred at an impeller speed of 2000 rpm for 1 or 2 min under an N_2 pressure of 10 psig. The contents of the reactor were transferred to the settling column and the height of the liquid-solid interface monitored with time.

RESULTS AND DISCUSSION

Liquid Flow Patterns

Sparged Reactor

Hydrodynamics of both reactors were characterized by visually examining the flow patterns of water in the reactor under different conditions. Figure 18-Figure 20 illustrate the dispersion and gas hold-up in the sparged reactor at an air flowrate of 2.0 SLPM and impeller speed of 500, 1300 or 2000 rpm. An examination of the pictures indicates that the gas circulation borders on complete circulation at 500 rpm. At higher speeds the gas becomes fully dispersed throughout the entire reactor and gas is engulfed from the surface of the liquid. Increasing the impeller speed also causes the size of the gas bubbles to decrease. Gas hold-up was determined at different conditions from the change in height of the liquid surface with stirring and air sparging; Table 9 lists the values.

Figure 18: Gas dispersion and liquid flow patterns in the sparged reactor at 500 rpm and 2.0 SLPM air. Plexiglas model of the sparged reactor contains 1.4 L of water at 20 °C.

Figure 19: Gas dispersion and liquid flow patterns in the sparged reactor at 1300 rpm and 2.0 SLPM of air. Plexiglas model of the sparged reactor contains 1.4 L of water at 20 °C.

Figure 20: Gas dispersion and liquid flow patterns in the sparged reactor at 2000 rpm and 2.0 SLPM of air. Plexiglas model of the sparged reactor contains 1.4 L of water at 20 °C.

Table 9: Gas hold-up measured at different impeller speeds and gas flowrates in the sparged reactor.

Impeller Speed (rpm)	Air Flowrate (SLPM)	Gas Hold-Up [§] (%)
500	0	2.4
500	2	2.4
1300	0	6.3
1300	2	15
2000	0	18
2000	2	28

[§] Gas hold-up is the ratio of the gas volume to the liquid volume with no gas.

High-Intensity Reactor

In the high-intensity reactor the gas fraction was maintained at 20%. The effect of impeller speed on the system hydrodynamics was examined at 500, 2000 and 3000 rpm using water, see Figure 21-Figure 23. In all cases the gas is well mixed with the liquid, however bubble sizes at 500 rpm are much larger than at 2000 and 3000 rpm.

Figure 21: The high-intensity reactor hydrodynamics at 500 rpm. The reactor contains 1.25 L of water at 20 °C and has a gas fraction of 20%.

Figure 22: The high-intensity reactor hydrodynamics at 2000 rpm. The reactor contains 1.25 L of water at 20 °C and has a gas fraction of 20%.

Figure 23: The high-intensity reactor hydrodynamics at 3000 rpm. The reactor contains 1.25 L of water at 20 °C and has a gas fraction of 20%.

Solids Suspension

Good dispersion of the solids throughout the reactors requires the use of a minimum impeller speed. At impeller speeds below this minimum the solids settle on the bottom of the reactor. Zweitering proposed a correlation, shown below, for determining the minimum impeller speed, based on the idea that a complete suspension of the solid occurs if none of the particles remain at the bottom of the reactor for longer than 1-2 s [45,46]

$$N_m = \frac{\beta_2 d_p^{0.2} \mu_L^{0.1} g^{0.45} (\rho_p - \rho_L)^{0.45} \left[\frac{w}{\rho_L} \right]^{0.13}}{\rho_L^{0.55} d_I^{0.55}}$$

where N_m = minimum impeller speed (rev/s)

d_p = particle diameter (cm)

μ_L = liquid viscosity (g/cm · s)

g = acceleration due to gravity (cm/s²)

ρ_L = liquid density (g/cm³)

ρ_p = solid density (g/cm³)

w = mass of catalyst per unit volume of slurry (g/cm³)

d_I = diameter of the impeller (cm)

d_T = diameter of the tank (cm)

$$\beta_2 = \left[\frac{d_T}{d_I} \right]^{1.33} \quad (\text{from Nienow's correlations})$$

The Fisher MnO₂ particles used had a diameter of 0.0149 cm (100 mesh) and a density of 5.062 g/cm³. The CaCO₃ particles were assumed to have a maximum particle diameter of 26 μm [47] and a density of 2.93 g/cm³ [48]. The density of the white liquor solution was 1.13 g/cm³ and the viscosity was 0.9 cP. As the lime mud particles were so small, suspension of the Fisher MnO₂ particles became the limiting factor requiring impeller speeds greater than 203 rpm for the sparged reactor and 52 rpm for the high-intensity reactor. Since impeller speeds for the polysulphide synthesis experiments exceeded these minimum values, it was assumed that a complete solid suspension existed under all conditions.

Monitoring the Reaction: Analysis for Polysulphides

Two methods, gravimetry and UV-vis spectroscopy were used to determine the concentration of polysulphide in solution. With synthetic liquors, formed by dissolving Na_2S_4 in a NaOH solution, the concentration of polysulphide determined from gravimetry and spectroscopy was the same, see Figure 24. However, a similar comparison for oxidized white liquors indicated a discrepancy between the two analysis methods. Figure 25 shows the correlation between polysulphide concentration determined gravimetrically and from UV-vis spectroscopy for a typical oxidized white liquor.

Figure 24: Correlation between gravimetric and UV-vis spectroscopic polysulphide concentrations for synthetic liquors.

Figure 25: Correlation between gravimetric and UV-vis spectroscopic polysulphide concentrations for an oxidized white liquor solution. Oxidizing conditions: 2000 rpm, 2.0 SLPM O₂, Fisher MnO₂ (2.0 g/L), 90 °C, 1 atm a.

The plot in Figure 25 highlights one of the problems found during polysulphide analysis, the fact that the concentrations determined gravimetrically were consistently higher than those obtained by UV-vis spectroscopy by about a factor of ~ 2 . At present, the reason for this discrepancy is unknown. Tench et al. have found similar discrepancies in their studies and reasons for this are currently being investigated [21]. The most probable explanation is that during white liquor oxidation polysulphide is not the only species created that contains elemental sulphur. The other S⁰ containing species could be colloidal sulphur or ring rather than straight chain polysulphide species. Since Paprican had expressed the polysulphide concentrations from their studies in terms of gravimetric S⁰ concentrations, I chose to do the same. The relative changes in polysulphide concentration found under different process conditions were the same regardless of whether UV-vis spectroscopy or gravimetry was used to determine the polysulphide concentration.

Sparged Reactor Studies

Initial studies undertaken in the sparged reactor, using air or oxygen as the oxidant, indicate that changes in mixing intensity, contributed by changes in impeller speed or gas flowrate, affect the yield, selectivity and initial rate of polysulphide formation. Data for these results were obtained by monitoring the concentrations of polysulphide and sulphide with time.

Figure 26 shows the typical polysulphide concentration profiles obtained during 100 min of O₂ oxidation. Under most of the conditions investigated the polysulphide concentration initially increased linearly with time before reaching a maximum point, after which the concentration rapidly dropped to zero. In these cases, the yield and selectivity for polysulphide formation were extracted at the time corresponding to the maximum measured polysulphide concentration. With O₂, at low impeller speeds (< 800 rpm), or with air oxidation (at impeller speeds < 2000 rpm) only the linear section of the growth in polysulphide concentration was captured in the 100 min test duration. As a result, yield and selectivity data quoted for these conditions correspond to the values reached at 100 min of oxidation. An oxidation period of 100 min was chosen as it represented a reasonable total residence time for green liquor in a mill's causticizing system [12]

Figure 26: Concentration profile for polysulphide formation measured as S⁰ by gravimetry under different mixing conditions over 100 min of O₂ oxidation with the Fisher MnO₂ catalyst (2.0 g/L). Reaction conditions: 90 °C, 1 atm a.

Figure 27: Concentration profile for polysulphide formation measured as S° by gravimetry under different mixing conditions over 100 min of air oxidation with the Fisher MnO_2 catalyst (2.0 g/L). Reaction conditions: 90 °C, 1 atm a.

Figure 28 depicts the corresponding changes in sulphide concentration during the oxygen oxidation reactions. Slight variations in sulphide concentration at zero time result from varying amounts of water lost from the system due to evaporation during causticizing (typically $1 \pm 5\%$ of the total water volume was lost). Sulphide consumption is linear over much of the reaction, exhibiting zero-order kinetics, similar to results found by Morgan and Murray [30] during black liquor oxidation studies. Only at concentrations below ~ 2.5 g S/L does the rate deviate from linearity. Therefore, the rate of polysulphide formation is independent of sulphide concentration for most of the reaction.

Figure 28: Concentration profile for sulphide consumption measured by UV-Vis spectroscopy under different mixing conditions over 100 min of O_2 oxidation with the Fisher MnO_2 catalyst (2.0 g/L). Reaction conditions: 90 °C, 1 atm a.

Effect of Changing Impeller Speed and Gas Flowrate for Air and O_2 Oxidation

The effects of mixing intensity, contributed by changes in impeller speed or gas flowrate, on the yield, selectivity and initial rate of polysulphide formation with O_2 sparging are more clearly depicted in Figure 29-Figure 31. Examination of these figures indicates that both gas flowrate and impeller speed are important process variables affecting the rate of polysulphide formation, especially at high impeller speeds. Only impeller speed, however, affects the yield and selectivity of the reaction. Changing the impeller speed from 500 rpm to 2000 rpm increases the polysulphide yield and selectivity from 6.2 to 34% and 11 to 53%, respectively. Increasing both the impeller speed and O_2 flowrate from 500 rpm and 0.5 SLPM to 2000 rpm and 2.0 SLPM increases the initial formation rate from 0.014 to 0.45 g S⁰/L·min. Similar effects on the polysulphide formation rate are seen with air sparging (Figure 32). Conclusive results for yield and selectivity data with air oxidation however were not obtained as under most of the conditions attempted (2000

rpm and 2.0 SLPM air being the exception) 100 min of air oxidation were not long enough to reach the maximum polysulphide concentration, see Figure 27. Of note, at 2000 rpm and 2.0 SLPM air, polysulphide forms in better yield and selectivity, 47% and 75% respectively, than found with O₂ sparging but at a much lower initial rate of 0.21 g S°/L min.

Figure 29: Effect of impeller speed and oxygen flowrate on the maximum polysulphide yield obtained in 100 min of oxidation with the Fisher MnO₂ catalyst (2.0 g/L). Reaction conditions: 90 °C, 1 atm a.

Figure 30: Effect of impeller speed and oxygen flowrate on the polysulphide selectivity at the maximum yield obtained in 100 min of oxidation with the Fisher MnO₂ catalyst (2.0 g/L). Reaction conditions: 90 °C, 1 atm a.

Figure 31: Effect of impeller speed and oxygen flowrate on the initial rate of polysulphide formation with the Fisher MnO₂ catalyst (2.0 g/L). Reaction conditions: 90 °C, 1 atm a.

Figure 32: Effect of impeller speed and air flowrate on the initial rate of polysulphide formation with the Fisher MnO_2 catalyst (2.0 g/l).^{**} Reaction conditions: 90 °C, 1 atm a.

Dorris [12], Tench et al. [21] and Uloth et al. [22] noted a similar effect of air vs. oxygen sparging on polysulphide yield and selectivity in all of their lab-, pilot- and mill-scale studies. As previously mentioned, published results from lab and pilot-scale studies indicated that the type of impeller used in white liquor oxidation in sparged tank reactors affected polysulphide yield and selectivity [12,22]. However, mill-scale studies indicated that changing the impeller speed had little impact on the rate of polysulphide formation, probably due to the limited range over which the impeller speed could be changed [21].

^{**} The rate of O_2 consumption in polysulphide and thiosulphate formation, determined from stoichiometry, was compared to the rate of O_2 supply through gas sparging. Under all of the conditions investigated there was an excess amount of O_2 supplied to the reactor. See Appendix F for more details and sample calculations.

The effects of gas flowrate and impeller speed on polysulphide formation can be summarized by examining the effect of the shaft power input under gassed conditions on yield, selectivity and rate of formation (Figure 33 and Figure 34).^{††} Given that the data in Figure 33 can be reasonably fitted using an empirical correlation, the expected polysulphide yield and selectivity may be determined if the shaft power input to the reactor under gassed conditions is known. Unfortunately, Figure 34 shows more scatter in the data, as a result a correlation between polysulphide formation rate and power input was not determined.

Figure 33: Effect of shaft power input under gassed conditions, contributed by changes in impeller speed and oxygen flowrate, on polysulphide yield and selectivity. Yields and selectivities were determined at the maximum polysulphide concentration obtained in 100 min of oxidation with pure oxygen. Reaction conditions: MnO_2 (Fisher, 2.0 g/L), 90 °C, 1 atm a.

^{††} Both impeller speed and gas flowrate contribute to the power input to a mixture in a sparged reactor. Increasing the impeller speed raises the power input to a mixture, raising the mixing intensity. Increasing the gas flowrate, however, can have two effects. Some power is input to the mixture through the increased flowrate of gas through the sparger (usually negligible compared to power input through the impeller for lab-scale reactors). More importantly, higher gas flowrates lead to a greater degree of gas engulfment around the impeller tip, lowering the fluid density near the impeller, and reducing the power input to the mixture. Therefore, keeping the impeller speed constant, while raising the gas flowrate may actually decrease the mixing intensity.

Figure 34: Effect of shaft power input under gassed conditions, contributed by changes in impeller speed and oxygen flowrate, on the initial rate of polysulphide formation. Reaction conditions: MnO_2 (Fisher, 2.0 g/L), 90 °C, 1 atm a.

The mixing sensitivity observed for polysulphide formation in the catalyzed oxidation of sodium sulphide may be due to a number of factors. Increased yield and selectivity means that the rate of polysulphide production is enhanced with mixing relative to the rate of thiosulphate formation. Inherent chemical kinetics and gas-liquid and liquid-solid mass transfer resistances may all affect polysulphide formation [4,8,12,16]. Thiosulphate formation does not require catalysis and only inherent chemical kinetics and gas-liquid mass transfer may affect its reaction rate [12,25]. Since the reaction occurs in the turbulent regime, changing impeller speeds will affect both gas-liquid and liquid-solid mass transfer resistances, should they be limiting the reaction rates [32]. Raising the gas flowrates however, will lead mainly to improved gas-liquid mass transfer by decreasing the gas bubble size and increasing the gas-liquid interfacial surface area [49].

Since the formation of polysulphide is zero order in sulphide over most of the reaction (Figure 28) and the rate of thiosulphate formation does not depend on polysulphide concentration,^{††} then the inherent chemical kinetics for both the initial rate of polysulphide and thiosulphate formation depend solely on the concentration of oxygen in solution. Further, at the highest impeller speeds and gas flowrates studied in the sparged reactor, switching from air to oxygen causes an approximate two-fold increase in the rate of polysulphide formation. However, using Henry's Law, the concentration of O₂ in water with oxygen sparging is about 4.8 times larger than that with air sparging, implying the rate of polysulphide formation has a fractional order dependence on oxygen concentration. In contrast Morgan and Murray [30] have shown that the rate of thiosulphate formation from sulphide oxidation, during black liquor oxidation, has a first-order dependence on oxygen concentration.

As both the polysulphide and thiosulphate formation rates depend only on oxygen concentration then, assuming perfect mixing occurs under each of the conditions investigated, the inherent reaction rate at the catalyst surface will not be affected by mixing. Therefore any changes incurred in the initial rate of polysulphide formation due to mixing result from changes to the mass-transfer resistances, either gas-liquid or liquid-solid. In addition, provided mass transfer resistances remain constant, increasing the oxygen concentration in solution will favour thiosulphate over polysulphide formation. This explains why air sparging produces polysulphide in greater selectivity but at a lower rate.

Figure 31 and Figure 32 indicate that increasing both the gas flowrate and impeller speed positively affect the initial rate of polysulphide formation, especially at high impeller speeds. At 2000 rpm increasing the gas flowrate from 0.5 to 2.0 SLPM increases the formation rate by a factor of 2.5, for air sparging, and by a factor of 1.8, for oxygen

^{††} The change in thiosulphate concentration (determined by performing a sulphur mass balance on the system) was linear over the same time period that the change in sulphide concentration was linear, indicating that the rate of thiosulphate formation did not depend on sulphide or polysulphide concentration.

sparging. This effect confirms that mass transfer contributes to the control of the reaction rate.

The fact that gas flowrate affects the formation rate indicates that gas-liquid mass transfer acts as one of the limiting resistances.^{§§} The effect of increased impeller speed however, could result from a change in either the gas-liquid or liquid-solid mass transfer resistance as the reactor operates within the turbulent regime. If gas-liquid mass transfer was the only resistance affecting the reaction rate, then increasing the mixing intensity should increase both the rates of polysulphide and thiosulphate formation, meaning that no effect on polysulphide yield or selectivity should be seen. However, Figure 29 and Figure 30 indicate that increasing impeller speed improves both polysulphide yield and selectivity with O₂ sparging. Therefore liquid-solid mass transfer must also contribute to control of the rate of polysulphide formation. The fact that increasing O₂ flowrate has no effect on yield or selectivity further supports this conclusion. At higher impeller speeds and gas flowrates both gas-liquid and liquid-solid mass transfer resistances decrease causing the relative rate of polysulphide vs. thiosulphate formation to increase giving improved polysulphide yields and selectivities.

In order to confirm the effects of liquid-solid mass transfer in limiting the reaction rate and to attempt to determine whether the inherent chemical reaction kinetics also limited the rate of polysulphide formation, studies in the oxygen-sparged reactor were completed with varying levels of MnO₂. Results indicate that catalyst loading also improves the yield, selectivity and formation rate for polysulphide synthesis.

^{§§} Gas-liquid interfacial area was affected to the greatest extent, in this study, by the gassed power input to the mixture (generated mainly by the torque on the impeller). At a constant impeller speed, the interfacial area increased with increasing gas velocity. In mill-scale studies, where a low impeller speed was used, gas-liquid interfacial surface area would be affected to a greater degree by the gas velocity through the reactor.

With the Fisher MnO_2 catalyst, increasing the concentration of MnO_2 in the oxygen sparged reactor from 1 g/L up to 6.5 g/L (at an impeller speed of 2000 rpm and gas flowrate of 1.3-2.0 SLPM) improved the polysulphide yield by a factor of 2.5, the selectivity by a factor of 3 and the rate of formation by a factor of 5.5. Similar trends were also noted at other impeller speeds, see Figure 35 - Figure 37. These results reflect the mill-scale results documented by Tench et al. [21], although they contrast with earlier lab-scale studies showing the effect of MnO_2 concentration levelling off at values above ~ 1 g/L (1 wt% MnO_2 on lime mud) [12]. The different results seen between our studies and those of Dorris [12] probably arise from different levels of lime purity used in the reactions. In this study pure CaO ($> 99\%$) was used as the lime source whereas Dorris [12] used lime supplied from a mill that was only 90% pure. The impure lime likely contained transition metals capable of catalyzing the formation of polysulphide.

Figure 35: Effect of impeller speed and Fisher MnO_2 loading on the maximum polysulphide yield obtained during O_2 oxidation. Reaction conditions: oxygen flowrate 1.3-2.0 SLPM (see Table 7), 90°C , 1 atm a.

Figure 36: Effect of impeller speed and Fisher MnO₂ loading on the polysulphide selectivity at the maximum yield obtained during O₂ oxidation. Reaction conditions: oxygen flowrate 1.3-2.0 SLPM (see Table 7), 90 °C, 1 atm a.

Figure 37: Effect of impeller speed and Fisher MnO₂ loading on the initial rate of polysulphide formation during O₂ oxidation. Reaction conditions: oxygen flowrate 1.3-2.0 SLPM (see Table 7), 90 °C, 1 atm a.

There are two possible explanations for the approximate five-fold increase in the polysulphide formation rate found with a 6.5 g/L vs. 1.0 g/L MnO_2 loading. The first, a decrease in the liquid-solid mass transfer resistance due to increased solid surface area and the second, an increase in the intrinsic chemical formation rate with exposure to a larger number of catalyst sites. The fact that catalyst loading does affect the reaction rate, in conjunction with the previously described affect of mixing on yield and selectivity at a given catalyst loading, confirms that liquid-solid mass transfer inhibits the rate of polysulphide formation. However, further studies must be completed in order to determine whether the inherent chemical reaction kinetics also contribute to control of the polysulphide formation rate. Of note, at an impeller speed of 2000 rpm and oxygen flowrate of 2.0 SLPM, use of a Fisher MnO_2 loading of 6.5 g/L gives yields and selectivities very close to those obtained with air (under identical mixing conditions with 2.0 g/L MnO_2) in approximately 20% of the reaction time.

The final factor investigated was the type of catalyst used in the oxidation reaction. Mill-scale studies performed by Tench et al. [21] obtained polysulphide in 36% yield and 68% selectivity, for sulphide oxidation with a proprietary catalyst, at power inputs similar to those found at 500 rpm in our lab-scale sparged reactor. In this work, oxidation with the Fisher MnO_2 catalyst performed under similar power inputs (at 500 rpm) gave polysulphide in only 6.2% yield and 11% selectivity.

The Fisher MnO_2 catalyst used in our studies was compared to the proprietary catalyst used by Tench et al. [21]. Our tests indicated that the proprietary catalyst gave better yields, selectivities and rates of polysulphide formation than the Fisher catalyst. Despite this, changes in mixing intensity affected polysulphide generation using both catalysts. Both catalysts showed higher polysulphide yield, selectivity and reaction rates at higher impeller speeds as shown in Table 10.

Table 10: Effect of catalyst type on the yield, selectivity and initial formation rate of polysulphide in the sparged reactor. Catalyst concentrations were 2.0 g/L in all cases and the reaction temperature and pressure were 90 °C and 1 atm a.

Catalyst	Impeller Speed (rpm)	O ₂ Flowrate (SLPM)	Polysulphide Yield (%)	Polysulphide Selectivity (%)	Initial Polysulphide Formation Rate (g S/L· min)
Fisher MnO ₂	500	2.0	6.2	11	0.013
Proprietary	500	2.0	34	43	0.13
Fisher MnO ₂	1300	1.3	26	34	0.19
Proprietary	1300	1.3	43	64	0.82
Fisher MnO ₂	2000	2.0	31	43	0.47
Proprietary	2000	2.0	46	85	1.3

At a catalyst loading of 2.0 g/L, an impeller speed of 2000 rpm and an oxygen flowrate of 2.0 SLPM, the proprietary catalyst produced polysulphide at a yield and selectivity of 1.5-1.9 times that of the Fisher catalyst. However, the greatest effect was on the rate of polysulphide formation, which increased by a factor of 3 under these conditions. At lower impeller speeds the magnitude of this effect increased, giving a 4 to 5 fold increase in polysulphide yield and selectivity and a 10-fold increase in the initial polysulphide formation rate when the proprietary catalyst was used. The discrepancy between polysulphide yield and selectivity obtained in the mill-scale studies [21] and this study result from differences in the activity of the MnO₂ catalyst.

Microscopic examination of both the Fisher MnO₂ and proprietary catalyst indicates that the MnO₂ particle sizes of the proprietary catalyst are much smaller than those of the Fisher MnO₂. Therefore, the increased reaction rate, yield and selectivity for polysulphide formation seen with the proprietary catalyst probably results from, at minimum, enhanced liquid-solid mass transfer. Given that increasing the solid surface area provides more sites for catalytic reaction, an enhancement of the reaction rate at the solid surface may also occur.

Approximating the Mass Transfer Effects

In an effort to verify that gas-liquid mass transfer resistance helped inhibit the rate of polysulphide formation, measurements of gas-liquid mass transfer in the sparged tank reactor were performed using the sulphite oxidation method. The actual $k_L a$ values for the particular system could not be determined from variations in catalyst weight as the plot of the inverse of the initial rate of O_2 uptake for polysulphide formation vs. the inverse of catalyst loading was non linear, see Figure 38. This non-linear relationship further supports the idea that polysulphide formation exhibits less than a first-order dependence on oxygen concentration.^{***} Of note, the rate of O_2 uptake for polysulphide formation was determined from the initial rate of polysulphide formation according to the following stoichiometry.

^{***} For the reaction of gaseous A and in-solution B to form product C in the presence of a solid catalyst, where the reaction is first order in A, it is possible to express the rate equation in the following terms:

$$\frac{[A^*]}{R'_A} = \frac{1}{k_L a} + \frac{1}{a_p} \left(\frac{1}{k_{SL}} + \frac{1}{k_R} \right)$$

where $[A^*]$ = concentration of A at the gas-liquid interface

R'_A = rate of consumption of A

k_L = gas-liquid mass transfer coefficient

k_{SL} = liquid-solid mass transfer coefficient

k_R = kinetic rate constant for reaction at catalyst surface

a = interfacial gas-liquid surface area

a_p = interfacial liquid-solid surface area

A plot of $[A^*]/R'_A$ vs. $1/w$, where w = catalyst loading and is directly proportional to a_p , should give a straight line with intercept $1/k_L a$. The fact that the plot is concave rather than linear confirms that polysulphide formation is not first-order in oxygen and prevents use of this relationship to determine $k_L a$ [32].

Figure 38: Attempt to determine k_La for system by determining the response of the polysulphide formation rate to changes in the catalyst loading in the sparged reactor at 1300 rpm, 1.3 SLPM O₂ and with the Fisher MnO₂ catalyst. Temperature 90 °C, pressure 1 atm a.

Using the sulphite oxidation method the effect of changing liquid hydrodynamics on the system was investigated. The studies assumed that the temperature and solid loading affected the k_La measurements to the same extent under all of the mixing conditions investigated. Figure 39 shows a comparison of the trend for changes in reaction rate and k_La with impeller speed. Predictions for k_La values based on correlations for sparged agitated-slurries, determined by Calderbank and Moo-Young as well as Yagi and Yoshida, are also shown [49]. Gas-liquid mass transfer values (k_La) determined experimentally agree with the correlated values, lying between the k_La values predicted by Calderbank and Moo-Young and by Yagi and Yoshida.

Figure 39: Trend for k_La values and initial polysulphide formation rate with changing impeller speed for white liquor oxidation in the sparged reactor with O_2 oxidation and the Fisher MnO_2 catalyst (2.0 g/L). k_La values based on correlations determined by Calderbank and Moo-Young as well as Yagi and Yoshida are also shown [49]. Reaction conditions: temperature 30-35 °C, pressure 1 atm a.

Examination of Figure 39 indicates that the changes in polysulphide formation rate follow the changes in k_La as the impeller speed increases, confirming gas-liquid mass transfer contributes to control of the initial rate of polysulphide formation. As a result, use of impellers designed to improve gas-liquid contact should improve the rate of polysulphide formation. Unfortunately, as previously mentioned, the initial rate of thiosulphate formation will also increase as k_La increases meaning that no improvements in yield and selectivity will be noted.

Effect of Lime Mud Composition

In an effort to determine whether $CaCO_3$ or residual CaO played a role in polysulphide formation from white liquor oxidation, a reaction was performed using pure $CaCO_3$ in the

place of causticized CaO. With the causticized CaO, polysulphide forms in $26 \pm 2\%$ yield, $34 \pm 3\%$ selectivity and at an initial rate of $0.19 \pm 0.04 \text{ g S}^\circ/\text{L} \cdot \text{min}$ in the sparged reactor at 1300 rpm and 1.3 SLPM O_2 . Using pure CaCO_3 increases the polysulphide formation rate by 50% to $0.30 \text{ g S}^\circ/\text{L} \cdot \text{min}$, however the yield and selectivity remain the same at 26% and 32% respectively. A probable explanation for these observations is that the smaller particle sizes of the pure CaCO_3 solid enhanced gas-liquid mass transfer causing the initial polysulphide formation rate to increase. Since enhanced gas-liquid mass transfer would also increase the rate of thiosulphate formation, no effect on polysulphide yield and selectivity would be noted. Schumpe et al. have previously noted the improved gas-liquid mass transfer in the presence of higher density, small particle solids [50].

Visual examination of the samples also reveals other differences. With the causticized systems, lime mud solids are green after causticizing. As the solution is oxidized the solids lose their colour until they eventually turn light brown when all of the sulphide has been oxidized. The polysulphide sample solutions removed during the reaction remain yellow in colour, only as long as the solution temperature remains above 70°C . If the temperature falls below this level, a black precipitate forms and the solution goes green in colour. In contrast, use of pure CaCO_3 causes the lime mud solids to remain white throughout the sulphide oxidation reaction. The polysulphide solutions formed are also yellow in colour, however this colour remains even when the solution temperature falls below 70°C and no precipitate formation is noted. Of interest, the ratio of UV-vis to gravimetric S° concentration is the same for the experiment run using pure CaCO_3 and the experiments run using lime mud formed through causticizing.

High-Intensity Reactor Studies

Sparged reactors can be inefficient in their gas-use as a large quantity of the gas can pass through the reactor without reacting. The solution to this problem is a closed, pressurized reactor where only the oxygen reacted needs to be replaced. The disadvantage is that increased oxygen pressure leads to higher concentrations of O_2 in solution that, due to the chemical kinetics of sulphide oxidation, leads to higher rates of thiosulphate formation,

an undesirable result.^{†††} Increased power dissipation can partially offset this disadvantage. For example, at an O₂ pressure of ~2 psig and impeller speed of 3000 rpm (power input of 3090 W/kg) the polysulphide yield and selectivity are similar to those found in the sparged reactor at 2.0 SLPM air and 2000 rpm (power input of 23 W/kg). The initial rate of polysulphide formation however, increased over 10 fold, with oxidation complete in less than 5 min.

Further tests in the high-intensity reactor showed that higher mixing intensities resulted in a better yield and a faster reaction but had little effect on the selectivity for polysulphide formation. Raising the O₂ pressure above atmospheric levels causes a decrease in the polysulphide yield and selectivity, but increases the initial rate of polysulphide formation. Figure 40 - Figure 42 depict the experimental results supporting these conclusions. The combination of high mixing intensities and near atmospheric pressures allows polysulphide formation in 45% yield and 77% selectivity, results comparable to those found with the air-sparged reaction.

The initial rate of polysulphide formation levels-off at an O₂ pressure of 10 psig and impeller speeds above 2000 rpm (Figure 8(c)). Since the power input at 3000 rpm (3100 W/kg) is ~ 2.5 times higher than that at 2000 rpm (1280 W/kg) the plateau probably indicates that gas-liquid and liquid-solid mass transfer no longer limit the polysulphide formation rate. Increasing the catalyst loading or changing the catalyst particle size, variables affecting the inherent chemical reaction rate on the catalyst surface, are now the only factors that may improve the polysulphide formation rate under these conditions. Further studies using higher catalyst loadings and the proprietary catalyst are required to verify these conclusions.

^{†††} Pure oxygen was used in the high-intensity reactor studies, rather than air, so that the O₂ pressure within the reactor could be kept constant. The reactor was hooked up to an oxygen cylinder allowing the oxygen consumed in the reaction to be replaced as required, keeping the total oxygen pressure constant in the reactor. Unfortunately this meant that the pressure of O₂ in the reactor was at minimum 1 atm a. After completion of the experiments it was suggested that the reaction at lower O₂ pressures could have been studied by initially padding the vessel with N₂. The addition of O₂ at a pressure higher than 1 atm a, achieved by connecting the reactor to the oxygen cylinder, would allow the oxygen utilized by the reaction to be replaced. This would keep the O₂ pressure in the reactor constant yet at a pressure lower than 1 atm a.

Figure 40: Effect of impeller speed and oxygen pressure on the maximum polysulphide yield obtained during oxidation with the Fisher MnO₂ catalyst (2.2 g/L) at 90 °C.

Figure 41: Effect of impeller speed and oxygen pressure on the polysulphide selectivity at the maximum polysulphide measured yield during oxidation with the Fisher MnO₂ catalyst (2.2 g/L) at 90 °C.

Figure 42: Effect of impeller speed and oxygen pressure on the initial rate of polysulphide formation during oxidation with the Fisher MnO₂ catalyst (2.2 g/L) at 90 °C.

Use of the high-intensity reactor also provided the chance to better investigate the effect of oxygen concentration on the initial rate of polysulphide formation and sulphide consumption. Similar to the results found with the sparged reactor the loss of sulphide is zero-order over much of the reaction. The initial polysulphide formation rate was also linear for reactions performed at low oxygen pressures (≤ 10 psig), however at higher pressures the initial formation rate had to be approximated from the first two data points as the reaction occurred so rapidly.

Interestingly, in contrast to the results found with the sparged reactor, the ratio of UV-vis to gravimetric S⁰ concentrations for the polysulphide solutions did not remain constant. At high pressures or low impeller speeds the polysulphide concentration predicted from UV-vis spectroscopy was approximately 1/10th that of the S⁰ concentration obtained from gravimetric testing. Table 11 illustrates the effect of different impeller speeds and O₂ pressures on the ratio. At present the reason for this change in the ratio is unknown,

however Dorris and Uloth reported a similar result for studies of white liquor oxidation in a pressurized pipeline reactor [38].

Table 11: Effect of impeller speed and O₂ pressure on the ratio of UV-vis to gravimetric S⁰ concentration in the high-intensity reactor. The reaction temperature was 90 °C.

Impeller Speed (rpm)	O ₂ Pressure (psig)	O ₂ Concentration [‡] (x 10 ⁻⁴ mol/L)	Ratio of UV-vis to gravimetric S ⁰ concentration
500	2	3.55	0.171
500	20	13.3	0.084
2000	2	3.55	0.456
2000	10	7.89	0.463
2000	20	13.3	0.099
3000	2	3.55	0.460
3000	10	7.89	0.468

[‡] Determined from Henry's Law.

Analysis of the initial polysulphide formation rate at 2000 rpm indicates that increasing the oxygen concentration by a factor of ~2.2, in going from 2 to 10 psig, causes the rate to increase by a factor of ~1.9. This result would seem to indicate that the initial rate of polysulphide formation has a first-order dependence on oxygen concentration, in conflict with the less than first-order dependence seen in the sparged-reactor and $k_L a$ studies (see pages 55 and 61 respectively). In order to establish the inherent chemical reaction kinetics for polysulphide formation further studies must be completed at impeller speeds greater than 2000 rpm at a range of O₂ pressures above 10 psig to eliminate mass transfer effects on polysulphide formation. These studies will require use of a continuous flow system as the reaction rate is too rapid to properly analyze in the batch mode.

Energy Requirements

The net rate of polysulphide generation is a function of the energy dissipation in the reactor. It is possible to generate polysulphide in minutes at comparable yields and selectivities to that obtained by the sparged reactor (power inputs of 0.37-28 W/kg) using a pressurized, high-intensity reactor (power inputs of 17-3100 W/kg). The total energy

required to do this, however is higher than that needed at the lower power dissipation levels, as shown in Table 12.

Table 12: A comparison of energy requirements for different reaction conditions providing high polysulphide yield and selectivity.

Entry #	Impeller Speed (rpm)	Gas Flowrate or Pressure	Catalyst	Polysulphide Yield (%)	Polysulphide Selectivity (%)	Time (min)	Energy Consumption (kJ/kg)
Sparged Reactor							
1	2000	air, 2.0 SLPM	Fisher MnO ₂ , 2.0 g/L	47	75	50	62.7
2	2000	O ₂ , 0.5 SLPM	Fisher MnO ₂ , 2.0 g/L	34	52	31	48.1
3	2000	O ₂ , 2.0 SLPM	Fisher MnO ₂ , 6.5 g/L	39	69	9	9.24
4	2000	O ₂ , 2.0 SLPM	Proprietary, 2.0 g/L	46	85	8	10.6
High-Intensity Reactor							
5	2000	O ₂ , 2.7 psig	Fisher MnO ₂ , 2.2 g/L	43	66	1.7	129
6	2000	O ₂ , 10.0 psig	Fisher MnO ₂ , 2.2 g/L	38	50	0.7	56.4
7	3000	O ₂ , 1.8 psig	Fisher MnO ₂ , 2.2 g/L	45	77	2.7	495
8	3000	O ₂ , 10.4 psig	Fisher MnO ₂ , 2.2 g/L	43	58	0.7	124

Comparison of entries 2 and 6 of Table 12 indicates that the mixing in the high-intensity reactor consumes similar amounts of energy as the oxygen sparged reactor using the same catalyst, giving similar polysulphide yield and selectivity. Higher polysulphide yield and selectivity, comparable to those obtained with air sparging, requires higher energy consumptions, at least twice those used in the air sparged reactor (compare entries

1, 5 and 7). The advantage of the high-intensity reactor is that polysulphide formation occurs in 0.7-2.7 min, depending on conditions, rather than in 30-50 min in the sparged reactor. This ability to create polysulphide with acceptable yields and selectivities in such a short period of time means that different process options exist for polysulphide synthesis, such as a high intensity inline mixer placed between the causticizers and the white liquor clarifier.

The choice of high (pressurized) vs. low (sparged) mixing intensity reactor will have to be determined based on the requirements of the mill, *i.e.* is the shorter reaction time in the high mixing intensity reactor worth the higher energy consumptions required to reach yields and selectivities of 45% and 75% respectively. Using the proprietary catalyst in place of the Fisher MnO_2 catalyst should reduce the energy requirements for polysulphide formation further while keeping the catalyst concentration constant (compare entries 1,2 and 4 of Table 12).

Lime Mud Settling

Another factor affecting the integration of polysulphide production in the white liquor cycle is the effect of input energy on the settling rate of lime mud. After polysulphide formation the lime mud and MnO_2 solids must be separated from the liquor prior to its use in the digester. White liquor clarifiers are commonly used to separate the lime mud solids from the liquor and typical settling rates are 2-4 cm/min at 95 °C [51]. Lime mud settling profiles obtained after causticizing and white liquor oxidation indicated that mixing in the sparged tank reactor, regardless of gas flowrate or impeller speed, had no adverse effect on lime settling. The change in height of the liquid-solid interface in the lime mud and white liquor mixture show the same profile for mixtures analyzed after causticizing and after mixing at 500 or 2000 rpm for 10 or 50 min with a 2.0 SLPM gas flowrate, see Figure 43 and Figure 44. (After mixing at 500 rpm for 50 min the solids settling rate was 0.404 cm/min at 23 °C vs. a settling rate determined after causticizing of 0.423 cm/min at 23 °C. After mixing at 2000 rpm for 50 min, the solid settling rate was 0.473 cm/min at 23 °C, the same as the rate determined after causticizing.) The average power input to the mixture at 500 and 2000 rpm was 0.44 and 21 W/kg respectively.

Over a 10 min mixing time these power inputs correspond to average energy inputs of 0.27 and 13 kJ/kg, whereas over 50 min of mixing they correspond to average energy inputs of 1.3 and 63 kJ/kg.

Figure 43: Lime mud settling profiles for sparged stirred slurries after mixing at 500 rpm for 10 and 50 min at an N_2 flowrate of 2.0 SLPM. H/H_0 is the ratio of the height of the liquid-solid interface at time t to the height of the interface at time $t = 0$. At 500 rpm and 2.0 SLPM the average power input to the mixture was 0.443 W/kg, corresponding to energy inputs of 0.266 and 1.33 kJ/kg over 10 and 50 min respectively.

Figure 44: Lime mud settling profiles for sparged stirred slurries after mixing at 2000 rpm for 10 and 50 min at an N_2 flowrate of 2.0 SLPM. H/H_o is the ratio of the height of the liquid-solid interface at time t to the height of the interface at time $t = 0$. At 2000 rpm and 2.0 SLPM the average power input to the mixture was 21.1 W/kg, corresponding to average energy inputs of 12.7 and 63.3 kJ/kg over 10 and 50 min respectively.

Interestingly, lime mud settling profiles for liquor mixed in the high-intensity reactor show that mixing actually improved both the rate of settling and the height of the compacted solids compared to the liquor analyzed just after causticizing. (After mixing at 2000 rpm for 130 s the solids settling rate was 0.652 cm/min at 23°C vs. a settling rate determined after causticizing of 0.510 cm/min at 23 °C.) These profiles disagree with the expected results of slower lime mud settling caused from particle attrition during mixing. A possible explanation is that the high-energy inputs caused agglomeration of the particles leading to faster settling rates[32]. At 2000 rpm the average power input to the mixture was 1280 W/kg, corresponding to an average energy input of 90 and 170 kJ/kg over 70 and 130 s of mixing, respectively. Also, synthetic liquors may not contain compounds that exist in mill liquors and which impair settling.

Figure 45: Lime mud settling profiles for slurries after mixing in the high-intensity reactor at 2000 rpm for 70 and 130 s at an N_2 pressure of 10 psig; gas fraction is 12%. H/H_0 is the ratio of the height of the liquid-solid interface at time t to the height of the interface at time $t = 0$. The average power input to the mixture at 2000 rpm was 1284 W/kg, corresponding to average energy inputs of 89.8 and 167 kJ/kg over 70 and 130 s respectively.

SUMMARY

Polysulphide formation via white liquor oxidation in a stirred-tank reactor is sensitive to several process conditions, including the mixing intensity, catalyst loading and type, and oxygen partial pressure. With the sparged reactor, regardless of gas type (O_2 or air), gas flowrate, catalyst type or catalyst loading, increasing the mixing intensity by raising the impeller speed gave higher polysulphide yields, selectivities and initial rates of formation.

With the high-intensity reactor, increased mixing intensity provided by increased impeller speed, increased the polysulphide yield regardless of O_2 pressure. The initial rate of polysulphide formation shows a similar dependence up to 2000 rpm. Above this value impeller speeds are high enough to overcome mass transfer effects, resulting in a levelling of the initial polysulphide formation rate. In the high-intensity reactor, mixing has a minimal effect on polysulphide selectivity and it is O_2 pressure that affects selectivity to the greatest degree.

Mass transfer resistances play a large role in controlling the initial rate of polysulphide formation. Both gas-liquid and liquid-solid mass transfer limit the initial rate of polysulphide formation. In addition, gas-liquid mass transfer resistance also limits the rate of thiosulphate formation. Preliminary kinetic data indicate that thiosulphate formation has a higher order dependence on oxygen concentration than polysulphide formation. Given these constraints, forming polysulphide in good yield and selectivity at a reasonable reaction rate requires good gas-liquid mass transfer, high catalyst particle surface areas and low oxygen concentrations, so that the rate of thiosulphate formation remains as low as possible.

Given the range of process variables affecting polysulphide formation, several different options may be used to synthesize polysulphide via white liquor oxidation in the presence of lime mud and MnO_2 in a sparged reactor with a turbine. With the Fisher MnO_2 catalyst, air sparging at high mixing intensity, 2000 rpm and 2.0 SLPM air, gave the

highest polysulphide yield of 47% and selectivity of 75% (9.6 g S⁰/L) in 50 min of oxidation. Results obtained with oxygen sparging only became comparable when the MnO₂ concentration was high, 6.5 g/L, giving polysulphide in 39% yield and 69% selectivity (8.5 g S⁰/L) in 9 min of oxidation at a 2000 rpm impeller speed and 2.0 SLPM O₂ flowrate. This dosage of MnO₂ is higher than that currently used in mill-scale studies (2.5 g/L) [21] due to the lower activity of the Fisher catalyst. Further, the lime used in this study did not contain transition metal impurities, which may also catalyze polysulphide formation.

It is possible to use an unsparged system to obtain similar polysulphide yields and selectivities. In a high-intensity reactor yields of 43-45% (5.6-5.9 g S⁰/L) and selectivities of 66-76% were obtained in much shorter times (1.7-2.7 min). This required very high mixing intensities and minimum O₂ pressures (close to atmospheric). Energy consumption for the pressurized reactions is twice that of the air-sparged reactions, 129 vs. 63 kJ/kg.

Oxygen sparging at a high MnO₂ concentration shows the lowest energy requirement of 9 kJ/kg. Use of the more active proprietary catalyst allows polysulphide generation in 46% yield and 85% selectivity (8.5 g S⁰/L) at an impeller speed of 2000 rpm, O₂ flowrate of 2.0 SLPM and a catalyst loading of 2.0 g/L. The total energy consumed to reach the maximum polysulphide yield using this catalyst is comparable to that with the Fisher MnO₂ catalyst at a 6.5 g/L loading. The results, obtained with the proprietary catalyst, are typical of those obtained during mill-scale trials of the PAPRILOXTM process [21].

Based on the results summarized above, polysulphide can be formed in good yield and selectivity in stirred-tank reactors in a much shorter time than previously described, provided mixing intensities are high. The results obtained depend strongly on the type of catalyst used, with the correct catalyst loading requiring determination for each different catalyst and lime mud mixture used. The sensitivity of polysulphide formation to the impeller speed is particularly important in continuous flow applications, where changes in impeller speed could be used to offset changes in the liquor residence time within the

reactor. Lime mud settling studies show that mixing in the sparged reactor has no effect on the settling profile, regardless of impeller speed or gas flowrate. Given the fact that settling studies with real mud samples from the mill have indicated that settling rates may be affected by mixing intensities, these results require verification larger scale conditions with mill samples.

Rapid formation of polysulphide on the order of 1-2 min is possible in unsparged systems, giving similar yields and selectivities to sparged systems, provided that mixing intensity is high. The energy consumption to reach a similar yield and selectivity in the high-intensity reactor was twice that required in the sparged reactor when the catalyst type and loading were the same. These results open an alternative pathway to polysulphide formation through the use of a high intensity mixer inline between the causticizer and white liquor oxidizer, provided the oxygen pressure in the system remains low. Further studies using the high-intensity reactor in a continuous mode are required to verify these predictions. Studies on lime mud settling indicate that high intensity mixing over 1-2 min does not negatively affect the rate of solid separation and the compactness of the solid bed.

FUTURE WORK

There are still several pieces of the polysulphide puzzle that require analysis. To start, an understanding of the reason behind the difference in predicted polysulphide concentrations between the gravimetric and UV-vis analysis methods is required. What exactly is responsible for the difference, is it colloidal sulphur or another type of sulphur chain? At present Paprican is attempting to find the answer to these questions, so hopefully an explanation will be available soon.

In addition, the role that the surface reaction plays in controlling the rate of polysulphide formation is unknown. Further studies should be undertaken at temperatures of 70 and 80 °C to determine the activation energy for polysulphide formation in order to complete the study of the reaction. With these results a more complete picture of polysulphide formation via catalyzed white liquor oxidation is possible.

A new set-up must be designed to analyze polysulphide formation under high-intensity mixing conditions. In the current study, preliminary investigations indicated that the polysulphide formation occurred too rapidly to be easily captured by a batch analysis. In order to verify the preliminary results and carryout more detailed kinetic studies (without the interference of mass transfer effects) a continuous flow system should be built. Using this system the concentration of polysulphide at the outlet to the reactor could be monitored with time as a function of temperature, pressure, residence time, catalyst loading and type, and impeller speed.

Finally in order to verify that similar results may be seen in mill-scale implementations, polysulphide formation using a mill's white liquor and lime mud mixture should be completed at the more optimum conditions for the different reactors.

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APPENDIX A: NOMENCLATURE

Symbol	Meaning
a	Gas-liquid interfacial surface area
a_p	Catalyst surface area
$[A^*]$	Oxygen concentration at the gas-liquid interface
ATR	Attenuated total reflectance
C	Clearance between the reactor bottom and the impeller
D	Stirred-tank diameter
d_i	Impeller diameter
h	Liquid height in the reactor
H	Height of solid-liquid interface at time t
H_0	Height of solid-liquid interface at time $t = 0$
k_L	Gas-liquid mass transfer coefficient
k_R	Inherent chemical kinetics rate coefficient
k_s	Liquid-solid mass transfer coefficient
N	Impeller rotational speed
n_b	Number of baffles
N_p	Power number = $P/\rho N^3 D^5$
N_{Re}	Reynolds number = $ND^2\rho/\mu$
P	Power input to reactor
Q	Gas volumetric flowrate
rpm	Revolutions per minute
ρ	Liquid density
SLPM	Standard litres per minute
T	Reactor height
TTA	Total titratable alkali
μ	Liquid viscosity

APPENDIX B: CALCULATING THE AVERAGE NUMBER OF ZERO-VALENT SULPHUR ATOMS PER POLYSULPHIDE CHAIN

The average number of zero-valent sulphur atoms per polysulphide chain can be determined, using the equilibrium constants for polysulphide species interconversion determined by Licht et al. [25], given the HO^- , HS^- and S^0 concentrations in solution.

The species in solution are related by the following equilibria and equations:

$$K_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$K_2 = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]}$$

$$K_w = [\text{H}^+][\text{HO}^-]$$

$$K_A = \frac{[\text{S}_2^{2-}]^2}{[\text{S}_3^{2-}][\text{HS}^-][\text{HO}^-]}$$

$$K_B = \frac{[\text{S}_3^{2-}]^3}{[\text{S}_4^{2-}]^2[\text{HS}^-][\text{HO}^-]}$$

$$K_C = \frac{[\text{S}_4^{2-}]^4}{[\text{S}_5^{2-}]^3[\text{HS}^-][\text{HO}^-]}$$

Values of the equilibrium constants determined by Licht et al. [25] are given in Table B-1. In order to perform the calculations I assumed that the activity coefficients for all of the species in solution were one.

Table B-1: Equilibrium constants for the aqueous polysulphide system [25] to be used with the equation $\log K = a/T - bT + c$ (T in Kelvin).

K	a	b	c
K_1	-2830.4	0.02083	8.7289
K_2	-28646.0	-0.26570	158.255
K_w	-3927.1	0.01223	2.8334
K_A	0	0	-4.18
K_B	0	0	-0.35
K_C	0	0	5.6

The equilibrium constants at 298 K calculated using the values from Table B-1 are listed in Table B-2.

Table B-2: Equilibrium constants calculated at 298 K for the aqueous polysulphide system.

K	Value
K_1	1.06×10^{-7}
K_2	8.98×10^{-18}
K_w	1.02×10^{-14}
K_A	6.61×10^{-5}
K_B	4.47×10^{-1}
K_C	3.98×10^5

The calculation requires an iterative solution of the following equations derived from the equilibrium expressions shown above.

$$[H^+] = \frac{K_w}{[HO^-]} \quad (B-1)$$

$$[H_2S] = \frac{[H^+][HS^-]}{K_1} \quad (B-2)$$

$$[S^{2-}] = \frac{K_2[HS^-]}{[H^+]} \quad (B-3)$$

$$[S_5^{2-}] = \left(\frac{[S_4^{2-}]^4 [H^+]}{K_C K_w [HS^-]} \right)^{1/3} \quad (B-4)$$

$$[S_3^{2-}] = \left(\frac{K_B K_w [HS^-] [S_4^{2-}]^2}{[H^+]} \right)^{1/3} \quad (B-5)$$

$$[S_2^{2-}] = \left(\frac{K_A K_w [HS^-] [S_3^{2-}]}{[H^+]} \right)^{1/2} \quad (B-6)$$

The value of $[HO^-]$ is kept constant at the given value measured for the liquor, while the initial value of $[HS^-]$ is approximated as the given value for the Na_2S concentration measured for the liquor. It is assumed that the measured Na_2S concentration represents the total amount of S^{2-} ions in solution in the form of H_2S , HS^- , S^{2-} and polysulphide chain ends. The initial value of $[S_4^{2-}]$ is approximated as the $[S^0]/3$. These initial values are plugged into the equations above (B-1 through B-6) to calculate the concentrations of the other species in solution. Improved estimations of the concentrations of HS^- and S_4^{2-} are then made by normalizing all of the species to satisfy the following mass constraints:

$$[HS^-]_{\text{measured}} = [H_2S] + [HS^-] + \sum_{i=1}^5 [S_i^{2-}] \quad (B-7)$$

$$[S]_{\text{measured}} = \sum_{i=2}^5 (i-1) [S_i^{2-}] \quad (B-8)$$

A sample calculation based on one of the polysulphide liquors produced during the mill-scale trials of the PAPRILOX™ process is shown below. The liquor composition was 87.4 g/L NaOH as Na_2O , 12.9 g/L Na_2S as Na_2O and 8.4 g/L S^0 [21].

$$[HO^-] = 87.4/(61.98 \times 2) = 2.82 \text{ mol/L}$$

$$[HS^-]_1 = 12.9/61.98 = 0.208 \text{ mol/L}$$

$$[S_4^{2-}]_1 = 8.4/(32.06 \times 3) = 0.0873 \text{ mol/L}$$

$$[H^+]_1 = (1.02 \times 10^{-14})/2.82 = 3.63 \times 10^{-15} \text{ mol/L}$$

$$[H_2S]_1 = (0.208)(3.63 \times 10^{-15})/(1.06 \times 10^{-7}) = 7.16 \times 10^{-9} \text{ mol/L}$$

$$[S^{2-}]_1 = (8.98 \times 10^{-18})(0.208)/(3.63 \times 10^{-15}) = 5.09 \times 10^{-4} \text{ mol/L}$$

$$[S_5^{2-}]_1 = \{(0.0873)^4(3.63 \times 10^{-15})/[(3.98 \times 10^5)(1.02 \times 10^{-14})(0.208)]\}^{1/3}$$

$$= 6.29 \times 10^{-4} \text{ mol/L}$$

$$[S_3^{2-}]_1 = [(4.47 \times 10^{-1})(1.02 \times 10^{-14})(0.208)(0.0873)^2/(3.63 \times 10^{-15})]^{1/3}$$

$$= 0.126 \text{ mol/L}$$

$$[S_2^{2-}]_1 = [(6.61 \times 10^{-5})(1.02 \times 10^{-14})(0.208)(0.126)/(3.63 \times 10^{-15})]^{1/2}$$

$$= 2.21 \times 10^{-3} \text{ mol/L}$$

$$[S^0]_1 = 4(6.29 \times 10^{-4}) + 3(0.0873) + 2(0.126) + 2.21 \times 10^{-3} = 0.519$$

$$[S_4^{2-}]_2 = [S_4^{2-}]_1/([S^0]_1/3) \cdot [S_4^{2-}]_1 = 0.0873/(0.519/3) \cdot 0.0873 = 0.0441 \text{ mol/L}$$

$$\text{total sulphide} = [H_2S]_1 + [HS^-]_1 + [S^{2-}]_1 + [S_2^{2-}]_1 + [S_3^{2-}]_1 + [S_4^{2-}]_1 + [S_5^{2-}]_1$$

$$= 7.16 \times 10^{-9} + 0.208 + 5.09 \times 10^{-4} + 2.21 \times 10^{-3} + 0.126 + 0.0873 + 6.29 \times 10^{-4}$$

$$= 0.424 \text{ mol/L}$$

$$[HS^-]_2 = [HS^-]_1/(\text{total sulphide}) \cdot [HS^-]_1 = 0.208/0.424 \cdot 0.208 = 0.102 \text{ mol/L}$$

Using the new values of $[HS^-]_2$ and $[S_4^{2-}]_2$ the calculations above are repeated until $[HS^-]_n = [HS^-]_{n+1}$ and $[S_4^{2-}]_n = [S_4^{2-}]_{n+1}$. At this point the mass balances for the system are satisfied and the polysulphide species distribution has been calculated. For the polysulphide liquor created via the PAPRILOX™ process [21] the polysulphide species distribution is as follows:

Table B-3: Polysulphide species distribution for the polysulphide liquor prepared using the PAPRILOX™ process [21].

Polysulphide Species	Concentration (mol/L)
S_2^{2-}	0.00108
S_3^{2-}	0.0629
S_4^{2-}	0.0446
S_5^{2-}	0.000329

From this distribution the average number of zero-valent sulphur atoms per chain is calculated as:

$$n = \frac{[S_2^{2-}] + 2[S_3^{2-}] + 3[S_4^{2-}] + 4[S_5^{2-}]}{[S_2^{2-}] + [S_3^{2-}] + [S_4^{2-}] + [S_5^{2-}]}$$

$$n = \frac{0.00108 + 2(0.0629) + 3(0.0446) + 4(0.000329)}{0.00108 + 0.0629 + 0.0446 + 0.000329}$$

$$n = 2.40$$

Therefore the average number of zero-valent sulphur atoms per polysulphide chain is 2.40 for a polysulphide liquor composition of 87.4 g/L NaOH as Na₂O, 12.9 g/L Na₂S as Na₂O and 8.4 g/L S⁰.

APPENDIX C: CHARACTERIZATION DATA FOR REACTORS

Sparged Reactor

Table C-1: Data for characterization of the sparged reactor at 21 °C.

Impeller Speed (rpm)	Solution Composition (wt % glycerol)	Torque Reading: no solution (Nm)	Torque Reading : 2 L of solution (Nm)	Reynolds Number	Power Number
500	0	4.988	5.101	51850	9.52
1300	0	5.004	5.854	19940	8.64
500	46	5.103	5.209	8184	8.36
1300	46	5.115	5.949	3148	7.15
500	70	5.096	5.193	2288	7.56
1300	70	5.111	5.910	880.1	6.20
500	100	4.957	5.184	38.58	8.23
1300	100	5.079	5.993	14.84	13.8

High-Intensity Reactor

Table C-2: Data for characterization of the high-intensity reactor.

Impeller Speed (rpm)	Liquid Composition (wt% glycerol)	Power Drawn: no Liquid (kW)	Power Drawn: filled with liquid (kW)	Temperature (°C)	Reynolds Number (x 10 ⁵)	Power Number
450	0	0.23	0.26	14	168200	4.45
745	0	0.30	0.38	14	111200	3.80
1127	0	0.38	0.69	14	67140	5.50
450	50	0.23	0.26	15	32670	4.19
745	50	0.30	0.39	15	21600	3.74
1127	50	0.38	0.71	15	13050	4.87
450	70	0.23	0.26	15	10020	4.50
745	70	0.30	0.41	15	6620	4.61
1127	70	0.38	0.76	15	3999	5.89
225	100	0.19	0.20	15	247.8	4.27
383	100	0.22	0.25	15	132.3	4.48
745	100	0.30	0.42	15	63.59	4.59
1127	100	0.38	0.78	17	32.69	8.43
1577	100	0.50	1.52	22	19.2	13.9

APPENDIX D: POLYSULPHIDE AND SULPHIDE SAMPLE ANALYSIS

Polysulphide Calibration Solutions for UV-vis Analysis

Table D-1: Polysulphide calibration solution compositions.

NaOH (g)	Na ₂ S ₄ (g) (90% pure)	Na ₂ S ₂ O ₃ (g)	Na ₂ S · 9H ₂ O (g)	H ₂ O (g)	Polysulphide Concentration (g S ⁰ /L) [§]	Absorbance (286 nm)
4.22	0.00	0.00	4.84	46.0	0.00	-0.0082
4.39	0.00	0.61	3.68	47.0	0.00	0.0108
4.38	0.074	0.46	3.67	47.0	0.767	0.3159
4.39	0.12	0.30	3.67	47.5	1.24	0.6382
4.36	0.19	0.14	3.70	47.5	1.96	0.9307
4.37	0.24	0.00	3.66	47.5	2.48	1.2852
4.62	0.00	1.24	2.48	48.0	0.00	0.0077
4.57	0.13	0.93	2.48	48.0	1.34	0.6286
4.60	0.23	0.60	2.46	48.0	2.37	1.1839
4.58	0.36	0.27	2.51	48.0	3.72	1.8832
4.63	0.48	0.00	2.47	48.5	4.93	2.3654
4.76	0.00	1.86	1.22	48.5	0.00	0.0124
4.78	0.18	1.37	1.27	48.5	1.85	0.8605
4.79	0.36	0.90	1.27	49.0	3.68	1.7621

[§] Based on a solution density of 1.16 g/mL.

Figure D-1: Absorbance spectra for polysulphide solutions measured using a 0.1 mm transmission cell.

Sulphide Calibration Solutions for UV-vis Analysis

Table D-2: Sulphide calibration solution compositions.

NaOH (g)	Na ₂ S ₂ O ₃ · 5H ₂ O (g)	Na ₂ S · 9H ₂ O (g)	H ₂ O (g)	Sulphide Concentration (g S/L) [§]	Absorbance (240 nm)
4.25	0.00	8.44	44.0	21.1	1.5748
4.46	0.62	7.36	45.0	18.2	1.3769
4.57	1.24	5.99	45.5	14.8	1.0553
4.80	1.88	4.80	46.0	11.8	0.8476
5.00	2.51	3.62	47.0	8.84	0.6366

[§] Measured using ABC test [32]

Figure D-2: Absorbance spectra for sulphide solutions measured using the ATR cell.

Validation of UV-vis Measurements with ABC Test and Gravimetric Analysis

Table D-3: Comparison data for sample sulphide concentrations analyzed by the ABC test [32] and by UV-vis spectroscopy. Oxidizing conditions: sparged reactor, 2000 rpm, 2.0 SLPM air, Fisher MnO_2 (2.0 g/L), 90 °C, 1 atm a.

Absorbance (240 nm)	Sulphide Concentration from UV-vis Spectroscopy (g S/L)	Acid Volume to First End Point (mL)	Acid Volume to Second End Point (mL)	Sulphide Concentration from ABC Test (g S/L)
1.5762	21.4	14.5	18.0	20.2
1.3525	18.3	14.5	17.5	17.3
1.1848	16.1	14.5	17.2	15.6
0.9817	13.3	14.8	17.0	13.0
0.7467	10.1	14.8	16.5	10.1
0.5259	7.13	14.8	16.0	7.23

Table D-4: Comparison of gravimetric polysulphide concentrations and polysulphide concentrations from UV-vis spectroscopy for synthetic polysulphide solutions.

Theoretical Polysulphide Concentration (g S ⁰ /L)	Polysulphide Concentration from UV-vis Spectroscopy (g S ⁰ /L)	Polysulphide Concentration from Gravimetric Analysis (g S ⁰ /L)
7.68	7.52	6.88
2.05	1.99	1.93
4.98	4.83	4.60
7.26	7.19	6.86

Table D-5: Comparison of gravimetric polysulphide concentrations and polysulphide concentrations from UV-vis spectroscopy for solutions sampled from an oxidized white liquor. Oxidizing conditions: sparged reactor, 2000 rpm, 2.0 SLPM Air, Fisher MnO₂ (2.0 g/L), 90 °C, 1 atm a.

Sample #	Polysulphide Concentration from UV-vis Spectroscopy (g S ⁰ /L)	Polysulphide Concentration from Gravimetric Analysis (g S ⁰ /L)
1	0.079	0.14
2	1.05	2.16
3	1.86	4.36
4	2.63	6.36
5	3.40	8.36
6	4.13	9.62

Sample Calculations

ABC Test

In the ABC test white liquor solutions are titrated with an acid solution to determine the concentration of sulphide in solution. The procedure for the test is as follows. A 5.00 mL volume of the sample solution was diluted with 50.0 mL of water, to which 10.0 mL of a 10 w/v% aqueous solution of BaCl₂ was added. The resulting mixture was then titrated to a pH of 9.3 with a 0.9017 M HCl solution (endpoint A). Formaldehyde (40 wt%, 10.0 mL) was then added to the solution and the mixture titrated again with the 0.9017 M HCl solution to a pH of 8.0 (endpoint B). Finally the solution was titrated to a pH of 4.0 to neutralize all of the hydroxyl ions produced by hydrolysis of the barium carbonate (endpoint C).

The first titration neutralizes the hydroxide ions in solution. Formaldehyde then reacts with the HS^- ions in solution causing the release of an equimolar amount of HO^- that is titrated to the second end point. The difference between the two end points gives the amount of acid required to titrate the HS^- in solution. The difference between the second and third end points gives the concentration of Na_2CO_3 in solution. In terms of effective and active alkali, the first endpoint gives the effective alkali, the second endpoint gives the active alkali and the third endpoint gives the total titratable alkali. Results from an ABC titration are shown below for sample #1 (time zero) of a white liquor prior to oxidizing. (Subsequent oxidizing conditions were 2000 rpm, 2.0 SLPM air, 2.0 g/L Fisher MnO_2 , 90 °C and 1 atm a.)

acid volume to first endpoint A = 14.5 mL

acid volume to second endpoint B = 18.0 mL

acid volume to third endpoint C = 21.2 mL

sample volume = 5.00 mL

acid concentration = 0.9017 M

$$\text{sulphide concentration} = \frac{18.0 - 14.5}{5.00} \times 0.9017 \times 32.06 = 20.2 \text{ g S/L}$$

$$\text{effective alkali} = \frac{14.5}{5.00} \times 0.9017 \times 61.98 \div 2 = 81.0 \text{ g Na}_2\text{O/L}$$

$$\text{active alkali} = \frac{18.0}{5.00} \times 0.9017 \times 61.98 \div 2 = 101 \text{ g Na}_2\text{O/L}$$

$$\text{total titratable alkali} = \frac{21.2}{5.00} \times 0.9017 \times 61.98 \div 2 = 118 \text{ g Na}_2\text{O/L}$$

Gravimetric Analysis

A description of the procedure used during gravimetric determination of the polysulphide concentration may be found in the experimental section of the text (page 31). The calculation of polysulphide concentration in terms of g S⁰/L is shown below for the oxidation of white liquor in the sparged reactor at 2000 rpm and 2.0 SLPM O_2 after 27 min of oxidation in the presence of 2.0 g/L Fisher MnO_2 . The reactor temperature and pressure were 90 °C and 1 atm a.

weight of filter paper = 0.0943 g

weight of filter paper and residue = 0.1284 g

weight of residue with 0.0005 g correction = 0.1289 g

volume of sample analyzed = 5.00

$$\text{polysulphide concentration} = \frac{0.1289 \text{ g} - 0.0943 \text{ g}}{0.00500 \text{ L}} = 6.92 \text{ g S}^{\circ}/\text{L}$$

**APPENDIX E: SUMMARY OF CONCENTRATION, YIELD, SELECTIVITY AND
INITIAL REACTION RATE RESULTS AND SAMPLE
CALCULATIONS FOR POLYSULPHIDE FORMATION**

Sparged Reactor:

Polysulphide and Sulphide Concentration Profile Data

Table E-1: Typical gravimetric polysulphide concentration profiles obtained during O₂ oxidation of white liquor with the Fisher MnO₂ catalyst (2.0 g/L) in the sparged reactor. Reaction conditions: 90 °C, 1 atm a.

Impeller Speed (rpm)	O ₂ Flowrate (SLPM)	Polysulphide Concentration (g S ⁰ /L) at [time (min)] for Sample No.					
		1	2	3	4	5	6
500	2.0	0.40 [0]	0.90 [20]	1.12 [40]	1.34 [60]	1.52 [80]	1.78 [100]
800	1.8	0.12 [0]	1.44 [20]	1.84 [40]	3.04 [60]	3.00 [80]	0.26 [95]
1300	1.3	0.12 [0]	1.60 [1.60]	2.74 [16]	4.28 [24]	5.54 [32]	2.28 [40]
1800	1.8	0.14 [0]	2.40 [8]	4.66 [15]	6.16 [20]	2.64 [28]	0.16 [31]
2000	2.0	0.20 [0]	1.18 [2]	2.38 [5]	4.54 [10]	6.92 [17]	2.22 [23]

Figure E-1: Absorbance profiles for polysulphide formation in the sparged reactor. Oxidation conditions: 2000 rpm, 2.0 SLPM O₂, Fisher MnO₂ (2.0 g/L), 90 °C, 1 atm a.

Table E-2: Gravimetric polysulphide concentration profiles obtained during air oxidation of white liquor with the Fisher MnO_2 catalyst (2.0 g/L) in the sparged reactor. Reaction conditions: 90 °C, 1 atm a.

Impeller Speed (rpm)	Air Flowrate (SLPM)	Polysulphide Concentration (g S ⁰ /L) at [time (min)] for Sample No.					
		1	2	3	4	5	6
500	0.5	0.00 [0]	0.28 [20]	0.44 [40]	0.75 [60]	0.94 [80]	1.16 [100]
500	2.0	0.13 [0]	0.31 [20]	0.72 [40]	1.07 [60]	1.44 [80]	1.81 [100]
800	0.8	0.22 [0]	0.88 [20]	1.74 [40]	2.58 [60]	3.32 [80]	4.04 [100]
800	1.8	0.14 [0]	0.88 [20]	1.84 [40]	2.92 [60]	3.84 [80]	4.81 [100]
1300 [§]	1.3	0.26 [0]	1.99 [20]	4.03 [40]	5.86 [60]	7.32 [80]	7.86 [100]
1800	0.8	0.24 [0]	2.22 [20]	4.32 [40]	6.24 [60]	7.32 [80]	7.56 [100]
1800	1.8	0.24 [0]	1.74 [10]	3.46 [20]	5.00 [30]	6.56 [40]	7.93 [50]
2000	0.5	0.24 [0]	2.06 [20]	3.80 [40]	5.06 [60]	5.82 [80]	6.15 [100]
2000	2.0	0.14 [0]	2.16 [10]	4.36 [20]	6.36 [30]	8.36 [40]	9.62 [50]

[§] Concentrations averaged over five repeat experiments.

Table E-3: Typical sulphide concentration profiles obtained during O_2 oxidation of white liquor with Fisher MnO_2 catalyst (2.0 g/L) in the sparged reactor. Reaction conditions: 90 °C, 1 atm a.

Impeller Speed (rpm)	O_2 Flowrate (SLPM)	Sulphide Concentration (g S/L) at [time (min)] for Sample No.					
		1	2	3	4	5	6
500	2.0	22.4 [0]	19.2 [20]	17.1 [40]	14.4 [60]	12.1 [80]	9.62 [100]
800	1.8	19.1 [0]	14.5 [20]	9.84 [40]	5.73 [60]	1.96 [80]	0.72 [95]
1300	1.3	21.8 [0]	17.4 [1.60]	13.0 [16]	8.90 [24]	5.06 [32]	1.93 [40]
1800	1.8	20.6 [0]	14.5 [8]	9.87 [15]	6.69 [20]	2.39 [28]	0.83 [31]
2000	2.0	23.4 [0]	21.0 [2]	18.0 [5]	13.3 [10]	6.91 [17]	2.46 [23]

Figure E-2: Absorbance profiles for sulphide consumption in the sparged reactor. Oxidation conditions: 2000 rpm, 2.0 SLPM O₂, Fisher MnO₂ (2.0 g/L), 90 °C, 1 atm a.

Table E-4: Comparison of polysulphide concentrations from UV-vis spectroscopic and gravimetric analysis for white liquors oxidized with air and the Fisher MnO_2 catalyst (2.0 g/L) in the sparged reactor. Reaction conditions: 90 °C, 1 atm a.

Impeller Speed (rpm)	Air Flow Rate (SLPM)	Power Input (W/kg)	UV-vis Polysulphide Conc. (g S ⁰ /L) [§]	Gravimetric Polysulphide Conc. (g S ⁰ /L) [§]	Ratio of UV-Vis to Gravimetric Conc. [‡]
500	0.5	0.320	0.65	1.16	0.564
500	2.0	0.441	0.88	1.81	0.484
800	0.8	2.16	1.62	4.04	0.402
800	1.8	1.12	1.93	4.81	0.400
1300	1.3	5.61	3.17	7.56	0.419
1300	1.3	5.86	3.24	7.56	0.429
1300	1.3	6.78	3.20	7.92	0.405
1300	1.3	5.90	3.56	8.42	0.423
1300	1.3	6.22	3.27	7.86	0.416
1800	0.8	20.0	3.28	7.56	0.434
1800	1.8	17.1	3.13	7.93	0.394
2000	0.5	28.1	2.70	6.15	0.439
2000	2.0	20.9	4.13	9.62	0.429

[§] Concentrations reported are the maximum concentrations found during the oxidation period analyzed.

[‡] Ratio of UV-vis spectroscopic and gravimetric concentrations quoted for these maximum values.

Table E-5: Comparison of polysulphide concentrations from UV-vis spectroscopic and gravimetric analysis for white liquor oxidized with O₂ and the Fisher MnO₂ catalyst (2.0 g/L) in the sparged reactor. Reaction conditions: 90 °C, 1 atm a.

Impeller Speed (rpm)	O ₂ Flow Rate (SLPM)	Power Input (W/kg)	UV-vis Polysulphide Conc. (g S ⁰ /L) [§]	Gravimetric Polysulphide Conc. (g S ⁰ /L) [§]	Ratio of UV-Vis to Gravimetric Conc. [¥]
500	0.5	1.29	0.63	1.68	0.373
500	2.0	0.446	0.58	1.78	0.326
800	0.8	2.12	2.22	4.78	0.464
800	1.8	0.834	2.09	4.90	0.427
800	1.8	2.60	1.46	3.00	0.488
1300	1.3	5.83	2.64	6.31	0.418
1300	1.3	5.32	2.57	6.10	0.421
1300	1.3	7.25	2.62	5.80	0.452
1300	1.3	4.46	2.24	5.54	0.403
1300	1.3	7.25	2.35	5.64	0.418
1800	0.8	14.7	2.72	6.20	0.439
1800	1.8	14.4	2.41	6.16	0.391
1800	1.8	19.6	2.52	6.18	0.408
2000	0.5	23.2	3.06	7.70	0.398
2000	0.5	28.5	3.21	7.80	0.411
2000	2.0	16.3	2.86	6.92	0.413
2000	2.0	26.1	2.93	6.84	0.428

[§] Concentrations reported are the maximum concentrations found during the oxidation period analyzed.

[¥] Ratio of UV-vis spectroscopic and gravimetric concentrations quoted for these maximum values.

Yield, Selectivity and Initial Reaction Rate Data for Polysulphide Formation via White Liquor Oxidation

Please note the following:

[§] Polysulphide concentration determined from gravimetry, initial formation rate calculated based on gravimetric concentrations.

[¥] Yield and selectivity data were taken at the maximum polysulphide concentration recorded during 100 min of oxidation. If maximum was not reached during 100 min then the yield and selectivity were calculated for the value at 100 min.

^κ Initial sulphide consumption rate determined from the linear section of the sulphide concentration vs. time plots.

Table E-6: Yield, selectivity and initial reaction rate data for polysulphide formation via O₂ oxidation of white liquor with the Fisher MnO₂ catalyst (2.0 g/L) in the sparged reactor. Reaction conditions: 90 °C, 1 atm a.

Impeller Speed (rpm)	O ₂ Flowrate (SLPM)	Sulphide Conc. at t = 0 (g S/L)	Polysulphide Conc. (g S ⁰ /L) [§]	Yield (%) ^κ	Selectivity (%) ^κ	Initial Polysulphide Formation Rate (x 10 ⁻² g S ⁰ /L· min) [§]	Initial Sulphide Consumption Rate (g S/L· min) ^κ
500	0.5	22.2	1.68	6.40	11.08	1.39	0.140
500	2.0	22.5	1.78	6.15	10.75	1.28	0.126
800	0.8	24.1	4.78	18.95	21.51	7.95	0.282
800	1.8	22.5	4.90	21.04	25.11	6.72	0.268
800	1.8	19.1	3.00	15.06	16.78	4.58	0.215
1300	1.3	22.4	6.31	27.18	35.30	17.6	0.471
1300	1.3	21.9	6.10	27.05	36.03	22.1	0.549
1300	1.3	21.4	5.80	26.58	32.43	21.7	0.549
1300	1.3	21.8	5.54	24.88	32.40	16.9	0.525
1300	1.3	22.0	5.64	25.05	32.51	18.8	0.528
1800	0.8	20.3	6.20	30.26	38.77	26.6	0.563
1800	1.8	20.6	6.16	29.15	43.13	30.1	0.657
1800	1.8	20.6	6.18	29.08	46.67	39.7	0.825
2000	0.5	22.0	7.70	33.33	55.45	26.2	0.547
2000	0.5	22.3	7.80	34.64	49.07	24.3	0.482
2000	2.0	23.4	6.92	28.68	40.66	39.5	0.911
2000	2.0	21.0	6.84	32.31	46.01	53.6	0.980

Table E-7: Yield, selectivity and initial reaction rate data for polysulphide formation via air oxidation of white liquor with the Fisher MnO_2 catalyst (2.0 g/L) in the sparged reactor. Reaction conditions: 90 °C, 1 atm a.

Impeller Speed (rpm)	Air Flowrate (SLPM)	Sulphide Conc. at t = 0 (g S/L)	Polysulphide Conc. (g S ⁰ /L) [§]	Yield (%) [‡]	Selectivity (%) [‡]	Initial Polysulphide Formation Rate (x 10 ⁻² g S ⁰ /L· min) [§]	Initial Sulphide Consumption Rate (g S/L· min) [‡]
500	0.5	19.8	1.16	5.85	11.8	1.16	0.0671
500	2.0	19.5	1.81	8.63	23.2	1.74	0.0753
800	0.8	20.5	4.04	18.6	32.4	3.89	0.100
800	1.8	19.7	4.81	23.8	45.6	4.76	0.106
1300	1.3	19.7	7.56	37.5	51.3	9.00	0.150
1300	1.3	19.7	7.56	37.4	48.0	9.19	0.159
1300	1.3	20.5	7.92	37.3	49.7	8.74	0.157
1300	1.3	20.6	8.42	39.2	52.5	9.47	0.162
1300	1.3	20.5	7.86	36.7	50.0	8.54	0.162
1800	0.8	19.5	7.56	37.6	50.7	10.1	0.165
1800	1.8	19.9	7.93	38.7	69.3	15.6	0.225
2000	0.5	19.6	6.15	30.1	43.7	8.10	0.136
2000	2.0	20.1	9.62	47.0	75.1	20.6	0.261

Table E-8: Yield, selectivity and initial reaction rate data for polysulphide formation via O₂ oxidation of white liquor in the sparged reactor with varying levels of Fisher MnO_2 catalyst. Reaction conditions: 90 °C, 1 atm a.

Impeller Speed (rpm)	O ₂ Flowrate (SLPM)	MnO ₂ Conc. (g/L)	Sulphide Conc. at t = 0 (g S/L)	Polysulphide Conc. (g S ⁰ /L) [§]	Yield (%) [‡]	Selectivity (%) [‡]	Initial Formation Rate (x 10 ⁻² g S ⁰ /L· min) [§]
500	2.0	1.06	17.1	1.32	7.12	14.1	1.00
500	2.0	4.25	20.3	3.90	18.5	28.0	3.78
500	2.0	6.54	18.1	3.90	20.9	29.0	5.24
1300	1.3	0.72	19.8	2.86	9.87	11.2	4.82
1300	1.3	1.08	19.4	3.70	14.7	17.1	9.58
1300	1.3	4.25	20.1	6.54	29.8	39.0	35.4
1300	1.3	6.54	18.2	7.44	37.9	54.3	39.0
2000	2.0	1.07	18.1	3.50	15.3	22.6	18.3
2000	2.0	4.26	19.8	8.22	38.6	60.3	86.5
2000	2.0	6.54	20.4	8.50	39.1	69.1	100

Sparged Reactor: Effect of Lime Mud Composition

Table E-9: Polysulphide and sulphide concentration profiles obtained during oxidation of white liquor in the sparged reactor with the Fisher MnO_2 catalyst (2.0 g/L) at 1300 rpm and 1.3 SLPM O_2 . Pure CaCO_3 was used in place of the lime mud formed from causticizing CaO . Reaction conditions: 90 °C, 1 atm a.

Sample #	UV-vis Polysulphide Conc. (g S° /L)	Gravimetric Polysulphide Conc. (g S° /L)	Sulphide Conc. (g S/L)
1	0.082	0.86	19.3
2	1.05	3.34	13.1
3	1.93	5.66	7.58
4	2.27	5.84	3.78
5	1.42	3.20	2.45
6	0.48	0.84	1.22

Under these conditions the yield and selectivity at the maximum gravimetric polysulphide concentration were 25.8 and 32.0% respectively. The ratio of polysulphide concentration for UV-vis spectroscopic to gravimetric analysis at this maximum was 0.388 and the initial polysulphide formation rate was 0.30 g S° /L· min.

High-Intensity Reactor:*Polysulphide and Sulphide Concentration Profiles*

Table E-10: Gravimetric polysulphide concentration profiles obtained during O₂ oxidation of white liquor with the Fisher MnO₂ catalyst (2.2 g/L) in the high-intensity reactor at 90 °C.

Impeller Speed (rpm)	O ₂ Pressure (psig)	Polysulphide Concentration (g S ⁰ /L) at [time (min)] for Sample No.					
		1	2	3	4	5	6
500	2.1	0.18 [0.00]	0.60 [1.66]	1.16 [3.00]	2.30 [5.00]	2.22 [10.0]	1.80 [15.0]
500	19.3	0.45 [0.00]	2.32 [1.00]	3.12 [3.00]	1.56 [5.00]	0.38 [6.00]	
2000	2.7	0.02 [0.00]	2.62 [0.67]	4.22 [1.17]	5.66 [1.67]	4.82 [2.00]	
2000	10.0	0.34 [0.00]	2.76 [0.33]	5.26 [0.73]	0.30 [1.00]		
2000	19.9	0.40 [0.00]	1.76 [0.08]	2.42 [0.17]	2.76 [0.30]	2.88 [0.55]	1.38 [0.78]
3000	1.8	0.10 [0.00]	1.25 [0.33]	2.62 [0.67]	3.24 [1.00]	4.17 [1.67]	5.91 [2.67]
3000	10.4	0.28 [0.00]	3.82 [0.33]	6.22 [0.67]	3.86 [1.00]	1.64 [1.33]	

Table E-11: Sulphide concentration profiles obtained during O₂ oxidation of white liquor with the Fisher MnO₂ catalyst (2.2 g/L) in the high-intensity reactor at 90 °C.

Impeller Speed (rpm)	O ₂ Pressure (psig)	Sulphide Concentration (g S/L) at [time (min)] for Sample No.					
		1	2	3	4	5	6
500	2.1	16.3 [0.00]	15.5 [1.66]	14.4 [3.00]	13.4 [5.00]	9.08 [10.0]	5.78 [15.0]
500	19.3	21.7 [0.00]	16.3 [1.00]	9.81 [3.00]	4.07 [5.00]	1.65 [6.00]	
2000	2.7	13.2 [0.00]	9.04 [0.67]	7.20 [1.17]	4.64 [1.67]	2.46 [2.00]	
2000	10.0	12.9 [0.00]	7.78 [0.33]	3.10 [0.73]	0.53 [1.00]		
2000	19.9	13.3 [0.00]	11.6 [0.08]	10.0 [0.17]	7.53 [0.30]	3.68 [0.55]	1.76 [0.78]
3000	1.8	13.0 [0.00]	10.7 [0.33]	9.41 [0.67]	8.71 [1.00]	7.70 [1.67]	5.44 [2.67]
3000	10.4	13.9 [0.00]	7.45 [0.33]	3.67 [0.67]	2.12 [1.00]	1.13 [1.33]	

Table E-12: Comparison of polysulphide concentrations from UV-vis spectroscopic and gravimetric analysis for experiments with the Fisher MnO₂ catalyst (2.2 g/L) in the high-intensity reactor at 90 °C.

Impeller Speed (rpm)	O ₂ Pressure (psig)	UV-vis Polysulphide Conc. (g S ^o /L) [§]	Gravimetric Polysulphide Conc. (g S ^o /L) [§]	Ratio of UV-Vis to Gravimetric Conc. [‡]
500	2.1	0.39	2.30	0.171
500	19.3	0.26	3.12	0.084
2000	2.7	2.58	5.66	0.456
2000	10.0	2.44	5.26	0.463
2000	19.9	0.29	2.88	0.099
3000	1.8	2.72	5.91	0.460
3000	10.4	2.91	6.22	0.468

[§] Concentrations reported are the maximum concentrations found during the oxidation period analyzed.

[‡] Ratio of UV-vis spectroscopic and gravimetric concentrations quoted for these maximum values.

Yield, Selectivity and Initial Reaction Rate Data for Polysulphide Formation via White Liquor Oxidation

Table E-13: Yield, selectivity and initial reaction rate data for polysulphide formation via oxidation of white liquor with the Fisher MnO₂ catalyst (2.2 g/L) in the high-intensity reactor at 90 °C.

Impeller Speed (rpm)	O ₂ Pressure (psig)	Power Input (W/kg)	Yield (%) [‡]	Selectivity (%) [‡]	Initial Formation Rate (g S ^o /L· min) [§]
500	2.1	16.7	13.0	72.8	0.427
500	19.3	17.4	12.3	22.4	1.87
2000	2.7	1286	42.6	65.6	3.38
2000	10.0	1282	38.2	50.3	6.69
2000	19.9	1283	18.7	25.9	16.3
3000	1.8	3091	44.6	76.5	2.54
3000	10.4	3095	42.8	58.2	8.91

[§] Polysulphide concentration determined from gravimetry, initial formation rate calculated based on gravimetric concentrations.

[‡] Yield and selectivity data were taken at the maximum polysulphide concentration recorded.

Sample Calculations

Sample calculation for polysulphide yield from white liquor oxidation after 20 min of oxidation at 2000 rpm and 2.0 SLPM air:

sulphide concentration at time zero (sample #1) = 20.1 g S/L

polysulphide concentration at time zero (sample #1) = 0.14 g S^o/L

polysulphide concentration after 20 min (sample #3) = 4.36 g S^o/L

$$\text{polysulphide yield after 20 min (sample \#3)} = \frac{4.36 - 0.14}{20.1} * 100 = 20.9 \%$$

Sample calculation for polysulphide selectivity from white liquor oxidation after 20 min of oxidation at 2000 rpm and 2.0 SLPM air:

sulphide concentration after 20 min (sample #3) = 15.0 g S/L

$$\text{polysulphide selectivity after 20 min (sample \#3)} = \frac{4.36 - 0.14}{20.1 - 15.0} * 100 = 82.0 \%$$

Sample calculation for the initial rate of polysulphide formation during white liquor oxidation at 2000 rpm and 2.0 SLPM air:

Figure E-3: Plot used to determine the initial rate of polysulphide formation. The slope of the linear regression over the linear section of polysulphide growth gives the initial polysulphide formation rate.

Sample calculation for determination of the amount of energy consumed during formation of the maximum polysulphide concentration at 2000 rpm and 2.0 SLPM air:

average power input to the reaction = 20.9 W/kg

time to reach maximum concentration = 50 min = 300 s

energy consumption = 20.9 W/kg * 300 s = 62.7 kJ/kg

APPENDIX F: DETERMINING THE AMOUNT OF OXYGEN CONSUMED DURING SULPHIDE OXIDATION

The rate of O₂ consumption during sulphide oxidation was compared to the rate of O₂ supplied through sparging in order to ensure that the sparging rate was not limiting the rate of sulphide oxidation. The rate of O₂ consumption was calculated based on the rate of O₂ consumption during polysulphide and thiosulphate formation according to the following equations.

The initial rate of polysulphide formation was determined as outlined above (Figure E-3) and the initial rate of thiosulphate formation was determined as the difference between the rate of sulphide consumption and the initial rate of polysulphide formation. The rate of sulphide consumption was taken as the slope of the line through the linear section of the sulphide concentration vs. time plot.

From equation F-1 and F-2 the total rate of oxygen consumption is:

$$\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{S}^0]}{dt} + \frac{d[\text{S}_2\text{O}_3^{2-}]}{dt} \quad (\text{F-3})$$

In units of mol/min the rate of O₂ consumption is:

$$\frac{dN_{\text{O}_2\text{consumed}}}{dt} = V \frac{d[\text{O}_2]}{dt}$$

where $N_{\text{O}_2\text{consumed}}$ = number of moles of oxygen
 V = the volume of solution ≈ 1.4 L

(F-4)

The gas flowrates were measured in terms of standard litres per minute, corresponding to the volumetric flow rate at 1 atm and 0 °C. Therefore the rate of O₂ supplied to the

reactor can be calculated, assuming ideal gas behaviour, in terms of mol/min according to the following equation:

$$\frac{dN_{O_2\text{supplied}}}{dt} = \frac{Pv}{RT}$$

where $N_{O_2\text{supplied}}$ = number of moles of oxygen supplied to the reactor

$P = 1 \text{ atm a}$

$R = 0.08206 \text{ atmL/mol} \cdot \text{K}$

$T = 273.15 \text{ K}$

$v = \text{oxygen flowrate in SLPM}$

(F-5)

Table F-1 displays the rate of O_2 consumption and supply calculated using equations F-3 to F-5 for polysulphide formation via white liquor oxidation in the sparged reactor. Since in all cases the rate of O_2 supplied to the reactor exceed the rate of O_2 consumption in the reaction it was assumed that the rate of O_2 supplied through sparging did not limit the initial rate of polysulphide formation.

Table F-1: A comparison of the rates of O₂ consumption and supply for polysulphide formation via white liquor oxidation with the Fisher MnO₂ catalyst (2.0 g/L) in the sparged reactor. Reaction conditions: 90 °C, 1 atm a.

Impeller Speed (rpm)	Gas Flow Rate (SLPM)	Gas Type	Total Rate of O ₂ Consumption (x 10 ⁻³ mol/min)	Rate of O ₂ Supplied by Sparging (x 10 ⁻³ mol/min)	% O ₂ Consumed
500	0.5	air	1.47	4.68	31.3
500	2.0	air	1.65	18.7	8.78
800	0.8	air	2.19	7.50	29.3
800	1.8	air	2.30	16.9	13.7
1300	1.3	air	3.28	12.2	26.9
1300	1.3	air	3.48	12.2	28.6
1300	1.3	air	3.42	12.2	28.1
1300	1.3	air	3.55	12.2	29.1
1300	1.3	air	3.54	12.2	29.0
1800	0.8	air	3.60	7.50	48.0
1800	1.8	air	4.91	16.9	29.1
2000	0.5	air	2.96	4.68	63.2
2000	2.0	air	5.71	18.7	30.5
500	0.5	O ₂	3.06	22.3	13.7
500	2.0	O ₂	2.75	89.2	3.08
800	0.8	O ₂	6.16	35.7	17.3
800	1.8	O ₂	5.85	80.3	7.29
800	1.8	O ₂	4.70	80.3	5.85
1300	1.3	O ₂	10.3	58.0	17.7
1300	1.3	O ₂	12.0	58.0	20.7
1300	1.3	O ₂	12.0	58.0	20.7
1300	1.3	O ₂	11.5	58.0	19.8
1300	1.3	O ₂	11.5	58.0	19.9
1800	0.8	O ₂	12.3	35.7	34.5
1800	1.8	O ₂	14.4	80.3	17.9
1800	1.8	O ₂	18.0	80.3	22.4
2000	0.5	O ₂	12.0	22.3	53.6
2000	0.5	O ₂	10.5	22.3	47.2
2000	2.0	O ₂	19.9	89.2	22.3
2000	2.0	O ₂	21.4	89.2	24.0

Sample calculations to determine the total rate of O_2 consumed through sulphide oxidation and the rate of O_2 supplied by sparging for polysulphide formation at 2000 rpm and 2.0 SLPM air are shown below. From Table E-7 the initial rate of polysulphide formation is $0.206 \text{ g S}^\circ/\text{L} \cdot \text{min}$ and the initial sulphide consumption rate is $0.261 \text{ g S/L} \cdot \text{min}$.

Therefore:

$$\begin{aligned}\frac{d[S^\circ]}{dt} &= \frac{0.206 \text{ g S}^\circ/\text{L} \cdot \text{min}}{32.06 \text{ g/mol}} \\ &= 0.00643 \text{ mol/L} \cdot \text{min} \\ \frac{d[S_2O_3^{2-}]}{dt} &= \frac{0.261 \text{ g S/L} \cdot \text{min} - 0.206 \text{ g S}^\circ/\text{L} \cdot \text{min}}{32.06 \text{ g/mol} * 2} \\ &= 0.000858 \text{ mol/L} \cdot \text{min} \\ \frac{dN_{O_2 \text{ consumed}}}{dt} &= (0.5 * 0.00643 + 0.000858) * 1.4 \\ &= 0.00571 \text{ mol/min} \\ \frac{dN_{O_2 \text{ supplied}}}{dt} &= \frac{2.0 \text{ SLPM} * 0.21 * 1 \text{ atm}}{0.08206 \text{ atm} \cdot \text{L/mol} \cdot \text{K} * 273.15 \text{ K}} = 0.0187 \text{ mol/min} \\ \% O_2 \text{ consumed} &= \frac{0.00571 \text{ mol/min}}{0.0187 \text{ mol/min}} * 100 = 30.5 \%\end{aligned}$$

APPENDIX G: K_LA MEASUREMENT DATA

The rate of oxygen mass transfer can be measured using either the change in sulphite or sulphate concentration with time and is given by the following equation [34]:

$$-\frac{dC_{O_2}}{dt} = k_L a (C_{O_2}^* - C_{O_2}^b) \quad (G-1)$$

where $C_{O_2}^* = O_2$ concentration at the gas - liquid interface

$C_{O_2}^b = O_2$ concentration in the bulk liquid

According to the reaction stoichiometry (equation 9):

$$-\frac{dC_{O_2}}{dt} = -\frac{1}{2} \frac{dC_{SO_3^{2-}}}{dt} = \frac{1}{2} \frac{dC_{SO_4^{2-}}}{dt} \quad (G-2)$$

$$\text{therefore } k_L a = \frac{\frac{1}{2} \frac{dC_{SO_4^{2-}}}{dt}}{C_{O_2}^*} \quad (G-3)$$

given that the oxidation conditions were chosen such that the oxygen concentration in the bulk liquid was zero.

In order to maintain a zero concentration of oxygen in the bulk liquid, a $CoSO_4$ catalyst is added to the reaction mixture. The correct $CoSO_4$ concentration is chosen such that the rate of sulphate production is not enhanced by the presence of the catalyst. Analysis at 1300 rpm, 1.3 SLPM O_2 and at varying levels of $CoSO_4$ concentration gave the following results.

Table G-1: Effect of $CoSO_4$ concentration on the rate of sulphate formation.

$[CoSO_4]$ (mol/L)	0	9.15×10^{-7}	1.38×10^{-5}	1.13×10^{-4}
$\frac{dNa_2SO_4}{dt}$ (mol/L·s)	9.78×10^{-4}	9.73×10^{-4}	1.10×10^{-3}	1.14×10^{-3}

Based on these results the concentration of CoSO_4 in solution was set at $9.15 \times 10^{-7} \text{ M}$ in order to ensure a bulk oxygen concentration of zero and no chemical enhancement of the oxygen mass transfer.

For the remainder of the mass transfer studies, $k_L a$ was calculated according to equation (G-3), where the O_2 concentration at the gas-liquid interface was determined following the correlation for oxygen solubility in sodium sulphate solutions developed by Linek and Vacek [36]:

$$\alpha = 5.909 \times 10^{-6} \exp \left\{ \frac{1602.1}{T} - \frac{0.9407 C_{\text{Na}_2\text{SO}_4}}{1 + 0.1933 C_{\text{Na}_2\text{SO}_4}} \right\}$$

$$C_{\text{O}_2}^* = \alpha P$$

where α = oxygen solubility in solution (M/atm) (G-4)

$C_{\text{Na}_2\text{SO}_4}$ = total concentration of Na_2SO_3 and Na_2SO_4 in solution (M)

P = pressure (atm)

T = temperature (K)

Oxygen concentrations for the different impeller and flowrate conditions studied are listed in the following table along with the corresponding $k_L a$ values.

Table G-2: Oxygen concentration and $k_L a$ values at different impeller speed and O_2 flowrates for the sparged reactor.

Impeller Speed (rpm)	O_2 Flowrate (SLPM)	Average Temperature ($^{\circ}\text{C}$)	$C_{\text{O}_2}^*$ ($\times 10^{-4} \text{ mol/L}$) [§]	$\frac{d\text{Na}_2\text{SO}_4}{dt}$ ($\times 10^{-5} \text{ mol/L} \cdot \text{s}$)	$k_L a$ (s^{-1})
500	2.0	26.8	7.73	6.40	0.041
800	1.8	27.9	7.58	41.1	0.271
1300	1.3	30.5	7.24	95.9	0.662
1800	1.8	31.4	7.12	127	0.888
2000	2.0	30.7	7.21	163	1.13

[§] All $k_L a$ measurements were taken at atmospheric pressure therefore $P = 1 \text{ atm}$. The concentration of Na_2SO_3 in all experiments was 0.554 M.

Sample calculation of $k_L a$ for 500 rpm and 2.0 SLPM O_2 :

$$\text{rate of Na}_2\text{SO}_4 \text{ formation} = 6.40 \times 10^{-5} \text{ mol/L} \cdot \text{s}$$

$$C_{O_2}^* = 5.909 \times 10^{-6} \exp \left\{ \frac{1602.1}{26.8 + 273} - \frac{0.9407 * 0.554}{1 + 0.1933 * 0.554} \right\} * 1$$

$$= 7.73 \times 10^{-4} \text{ M}$$

$$k_L a = 0.5 * \frac{6.40 \times 10^{-5}}{7.73 \times 10^{-4}}$$

$$= 0.041 \text{ s}^{-1}$$

APPENDIX H: LIME MUD SETTLING

Please note that H/H_0 refers to the ratio of the height of the solid-liquid interface at time t to the height of the solid-liquid interface at time $t = 0$.

Table H-1: Lime mud settling data for the sparged reactor taken at 500 rpm and 2.0 SLPM air. Temperature for settling studies: 20 °C.

Time (min)	H/H_0 After Causticizing	H/H_0 After 10 min	H/H_0 After 50 min
0	1	1	1
1	0.979	0.968	0.973
2	0.953	0.948	0.952
3	0.933	0.927	0.934
4	0.909	0.898	0.913
5	0.889	0.885	0.892
6	0.865	0.864	0.870
7	0.844	0.843	0.849
8	0.824	0.822	0.828
9	0.801	0.801	0.807
10	0.777	0.777	0.786
11	0.756	0.759	0.764
12	0.736	0.733	0.743
13	0.712	0.712	0.722
14	0.689	0.691	0.698
15	0.668	0.667	0.677
16	0.645	0.646	0.656
17	0.624	0.623	0.635
18	0.601	0.602	0.614
19	0.580	0.578	0.590
20	0.557	0.552	0.569
22	0.518	0.513	0.526
24	0.477	0.474	0.487
26	0.438	0.437	0.444
28	0.409	0.403	0.413
30	0.381	0.377	0.381
32	0.357	0.356	0.357
34	0.339	0.340	0.341
36	0.326	0.325	0.325
38	0.314	0.312	0.312
40	0.300	0.298	0.299
44	0.280	0.277	0.278
50	0.249	0.246	0.249

Table H-2: Lime mud settling data for the sparged reactor taken at 2000 rpm and 2.0 SLPM air. Temperature for settling studies: 20 °C.

Time (min)	H/H ₀ After Causticizing	H/H ₀ After 10 min	H/H ₀ After 50 min
0	1	1	1
1	0.972	0.969	0.972
2	0.949	0.949	0.950
3	0.926	0.926	0.925
4	0.903	0.903	0.900
5	0.880	0.879	0.877
6	0.855	0.856	0.851
7	0.829	0.831	0.828
8	0.806	0.808	0.805
9	0.783	0.782	0.779
10	0.758	0.759	0.753
11	0.735	0.736	0.728
12	0.709	0.710	0.704
13	0.684	0.685	0.679
14	0.661	0.662	0.656
15	0.635	0.636	0.632
16	0.612	0.613	0.607
17	0.587	0.587	0.581
18	0.561	0.564	0.558
19	0.538	0.538	0.532
20	0.513	0.515	0.509
22	0.467	0.469	0.463
24	0.426	0.426	0.424
26	0.390	0.387	0.388
28	0.362	0.356	0.362
30	0.342	0.333	0.342
32	0.324	0.315	0.324
34	0.309	0.300	0.308
36	0.296	0.287	0.296
38	0.283	0.274	0.270
40	0.273	0.264	0.242
44	0.250	0.244	
50	0.227	0.218	0.226

Table H-3: Lime mud settling data for the high-intensity reactor taken at 2000 rpm and an N₂ pressure of 10 psig. Temperature for settling studies: 20 °C.

Time (min)	H/H ₀ After Causticizing	Time (min)	H/H ₀ After 70 s	Time (min)	H/H ₀ After 130 s
0	1.000	0	1.000	0	1.000
1	0.970	1	0.955	1	0.948
2	0.945	2	0.919	2	0.908
3	0.920	3	0.884	3	0.866
4	0.896	4	0.845	4	0.824
5	0.871	5	0.806	5	0.781
6	0.846	6	0.771	6	0.739
7	0.821	7	0.735	7	0.696
8	0.796	8	0.697	8	0.650
9	0.771	9	0.655	9	0.608
10	0.746	10	0.619	10	0.565
11	0.721	11	0.581	11	0.523
12	0.697	13	0.503	12	0.484
13	0.667	14	0.468	13	0.438
14	0.642	15	0.432	14	0.399
15	0.617	16	0.400	15	0.359
16	0.592	17	0.368	16	0.324
17	0.565	18	0.342	17	0.291
18	0.540	19	0.319	18	0.265
19	0.515	20	0.303	19	0.248
20	0.490	22	0.277	20	0.239
22	0.445	24	0.258	23	0.209
24	0.403	26	0.242	25	0.196
26	0.371	30	0.213	30	0.170
28	0.346	35	0.187	34	0.150
30	0.326				
32	0.311				
34	0.296				
36	0.284				
38	0.274				
40	0.261				
44	0.241				
50	0.219				