Study on Reaction Between H_2S and Sulfuric Acid For H_2 Production From a H_2S Splitting Cycle

A Thesis Submitted to the College of Graduate Studies and Research
in Partial Fulfillment of the Requirements for the
Degree of Master of Science
in the Department of Chemical and Biological Engineering
University of Saskatchewan
Saskatoon

By

Patricia da Silva Nuncio

December, 2010

COPYRIGHT

The Head
Department of Chemical Engineering
University of Saskatchewan
105 Maintenance Road
Saskatoon, Saskatchewan
S7N 5C5 Canada

ABSTRACT

Because of the high demand for hydrogen in the oil industries, new technologies for hydrogen production are being investigated. The thermochemical splitting cycle is one of them. Among the cycles that have been investigated, sulfur-iodine (S-I) water splitting is the most studied. In the S-I cycle, there are three reactions: H_2SO_4 decomposition, Bunsen reaction and HI decomposition. A new thermochemical cycle has been developed based on the S-I cycle, which is a H_2S splitting cycle. In the H_2S cycle, there are also three reactions. The only difference between S-I and H_2S cycle is that the H_2SO_4 decomposition reaction is replaced by a reaction between hydrogen sulfide and sulfuric acid which produces sulfur dioxide, elemental sulfur and water. Research on this reaction has been done for many years, studying thermodynamic, kinetics and mass transfer. This reaction produces sulfur, sulfur dioxide and water. The SO_2 produced is the used in the second reaction in the H_2S cycle; the Bunsen reaction.

The main objective of this research was to find an operating condition to increase the production of SO_2 from the reaction between H_2S and H_2SO_4. This study investigated different conditions such as temperature, stirring rate and sulfuric acid concentration to maximize the production of SO_2. The temperature and stirring rate range used in the reaction were from 120 to 160°C and from 0 to 400 rpm, respectively. The sulfuric acid concentrations were between 90 and 96 wt%. The results showed that increasing the temperature and the acid concentration in the reaction between H_2S and H_2SO_4, the SO_2 produced from this reaction will increase. There is no need to apply stirring in the reaction, because the stirring will increase the surface area which allows the produced sulfur dioxide in the gas phase to be dissolved more in sulfuric acid solution, which favors the unwanted side-reaction between SO_2 and H_2S. A model that was developed to predict the partial pressure change of SO_2 in closed reactor. This model was used to compare the data between experimental and simulation through Matlab software. The simulated data was compared to the experimental data and the results indicated that the model fits the data satisfactorily.

Additionally, study on the separation between the remaining sulfuric acid and produced elemental sulfur from the reaction between H_2S and H_2SO_4 were performed. The mixture was placed in an oven at140°C of temperature for two hours. It was found that all small droplets of sulfur produced during the reaction between hydrogen sulfide and sulfuric acid agglomerated and the sulfuric acid solution became clearer.

ACKNOWLEDGEMENT

I would like to acknowledge many people for their encouragement and comments during my research. First, I would like to thank my supervisor, Dr. Hui Wang for his support, invaluable guidance and time spent in helping me to complete my work that is shown in this thesis. I am grateful for his patience and knowledge which were a great importance to the direction of my work.

Secondly, I would like to express my deep gratitude to the member of my advisory committee, Dr. Richard Evitts and Dr. Catherine Niu. for their revision, encouragement and important suggestions which greatly improved my work.

Richard Blondin, Heli, Rlee Prokopishyn and Dragan Cekie for being always helpful and giving a good support in the experimental difficulties.

My friends Morgan and Majak for giving me their advice and their constant support.

Finally, my endless gratitude goes to my precious Canadian family, especially Blaine and Colleen. Their patience, support, endless love throughout these years that I have been in Saskatoon, gave me extra strength and motivation. I deeply thank you.

DEDICATION

Dedicated to

My parents

For all love, support and belief in me

TABLES OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

A_0	Preexponential factor	mol s^{-1} m^{-2} Pa^{-1}
a	Surface area	m^2
E_a	Activation energy	kJ mol^{-1}
K	Constant	
k	Reaction rate constant	mol m^2 s^1 Pa^{-1}
P	Pressure	Pa
R	Gas constant	J mol^{-1}
r	Reaction rate	mol s^{-1}
T	Temperature	K
t	time	s
V	Volume of gas phase	m^3
x	Variable	
[SO2]	Concentration of SO_2	mol L^{-1}

Subscripts

G	Gas
p	Pressure
total	Total pressure
1	Referred as to reaction 1
2	Referred as to reaction 2

Chapter 1

Introduction

Fossil fuels are still the main energy source worldwide. Among fossil fuels, oil is the most important energy supply. About 36 % of the global primary energy comes from oil (WEO, 2009).

Canada's oil resources have one of the largest reserves of crude oil in the world. Canada has the second largest proven oil reserve in the world, just behind Saudi Arabia (CAPP, 2009). The Canadian oil sand, tar sand, is a mixture of sand, water and bitumen. The bitumen can be classified as crude bitumen or extra-heavy crude oil (CAPP, 2009). According to the Alberta Chamber of Resources (2004), the Canadian oil sand industry is an important energy source in North America. In 2007, Canadian production averaged 2.8 million barrels per day of crude oil and it is predicted that by 2030 the Canadian oil production will reach 4.15 million barrels per day of oil (NEB, 2008).

Canadian oil industries have high dependency on natural gas. Expanding Canadian oil production brings some concerns such as the high consumption of natural gas (Yildiz and Kazimi, 2006; Söderbergh, *et al.* 2007). In 2007, the average of natural gas required for oil sands operations in Canada was 32 million m^3/day at standard temperature and pressure (NEB, 2008). The dependency of oil on natural gas will continue to increase until 2030 (Schindler and Zittel, 2007). Natural gas is the main source for the production of hydrogen which is used for the upgrading and refining processes of oil (Balat, 2008). According to the Alberta

Chamber of Resources (2004), the hydrogen used from natural gas in the oil sand industries is 11 cubic meters (400 ft^3) per barrel (Figure1.1). Moreover, natural gas is used in the bitumen extraction process to produce heat to generate steam and to produce electricity to be used in the operations. Two methods are applied to extract bitumen from oil sand: in-situ and mining recovery process. For in-situ process, the demand of natural gas is 28 cubic meters (1000 ft^3) per barrel and for mining, is 7 cubic meters (250 ft^3) per barrel respectively (Figure1.1). In-situ extraction process separates the bitumen from oil sand that is underground by using steam to heat it which allows the bitumen be pumped by a well to the surface. On the other hand, in the mining process, the oil sand is mined from the surface by using trucks and shovels (Lee *et al*., 2007 and Levi, 2009).

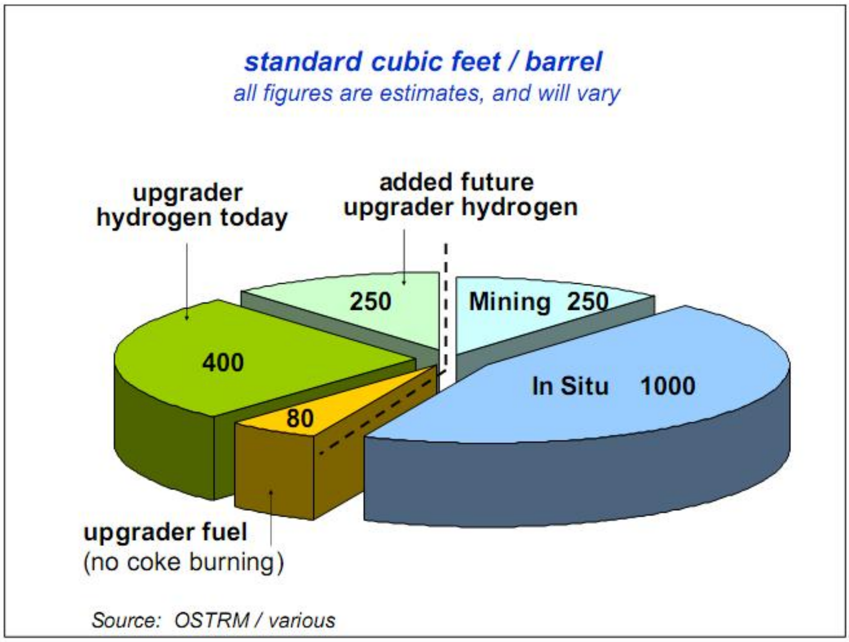


Figure 1.1 Distribution of natural gas use in oil sands recovery and upgrading (Alberta Chamber of Resources, 2004).

In the oil upgrading process, one of the main objectives of the use of hydrogen is to remove impurities such as the sulfur (Salary *et al*. 2008). The sulfur content in the Canadian bitumen is 4.8 wt% (Lee *et al*., 2007 and Soderberg, 2005). The sulfur removal is achieved through the hydrodesulfurization process (HDS) which is a catalytic process that is the reaction between different sulfur compounds such as mercaptans (RSH) and hydrogen to produce hydrocarbons and hydrogen (Eq.1.1) (Speight, 1990; Kabe, 1999).

$$RSH + H_2 \rightarrow RH + H_2S \tag{1.1}$$

The demand of hydrogen is expected to increase in oil operations, not only because of environmental regulations, which include lowering fractions of sulfur content in the fuel decreasing pollutant gas emission, but also for having a high quality of oil (Granovskii *et al*., 2006; Kothari *et al*., 2008). The supply of natural gas for hydrogen production is considered insufficient to support the increase of oil production from oil sand (NEB, 2008; Fanchi, 2005). Due to the high demand of hydrogen, one of the important challenges of oil industry is to find other sources for the production of hydrogen. Efforts are underway to reduce the dependency of oil sand industry on natural gas. A new technology, H_2S thermochemical splitting cycle, has been developed with objective of producing hydrogen by decomposing hydrogen sulfide. For this reason, his study focuses on enhancing SO_2 production. SO_2 is needed in the cycle to be used in the Bunsen reaction which produces HI. The HI then is decomposed into H_2 and I_2.

1.1 Organization of the thesis

This thesis is organized in five chapters. Chapter 1, Introduction, gives an overview about the Canadian oil sand, and the consumption of natural gas for the oil sand extraction methods and the dependency of natural gas for hydrogen production. Chapter 2, Literature Review, reviews the technologies for hydrogen production from natural gas and thermochemical splitting cycle. In addition, the knowledge gap and the objectives of this research are presented. Chapter 3, Experimental Methods, describes the experimental procedure to conduct the reaction between H_2S and H_2SO_4 for analyzing the SO_2 production through the final partial pressure and also describes the experimental procedure for the separation between sulfuric acid and elemental sulfur. Chapter 4, Results and Discussion, presents the effects of changing the operating conditions on the reaction between H_2S and H_2SO_4 for the SO_2 production, the mathematical model that was used to predict the partial pressure change of SO_2 and shows the results about the separation between the H_2SO_4 and elemental sulfur. Chapter 5, Conclusions and Recommendations, summarizes conclusions made from the discussion and present some suggestions for further development.

Chapter 2

Literature Review

This chapter presents a review on the technologies for hydrogen production from natural gas and thermochemical splitting cycles. In addition, it presents a review on the H_2S recovery process and on the H_2S splitting cycle. After describing the H_2S cycle which is composed of three main reactions (H_2S oxidation, Bunsen reaction and HI decomposition), a review is given on the studies on the H_2S oxidation reaction: reaction between hydrogen sulfide and sulfuric acid. Elemental sulfur, sulfur dioxide and water are the products of this reaction. A description about the properties of elemental sulfur is also included.

2.1 Hydrogen production from natural gas

2.1.1 Steam methane reforming

Forty eight percent of hydrogen production comes from natural gas. Coal and petroleum are also other sources hydrogen production and produce 30 and 18% respectively (Figure 2.1). Steam methane reforming is the process that produces hydrogen by reacting steam and methane at high temperature (800ºC). Methane is the main composition of natural gas.(Gary and Handwerk, 2001).

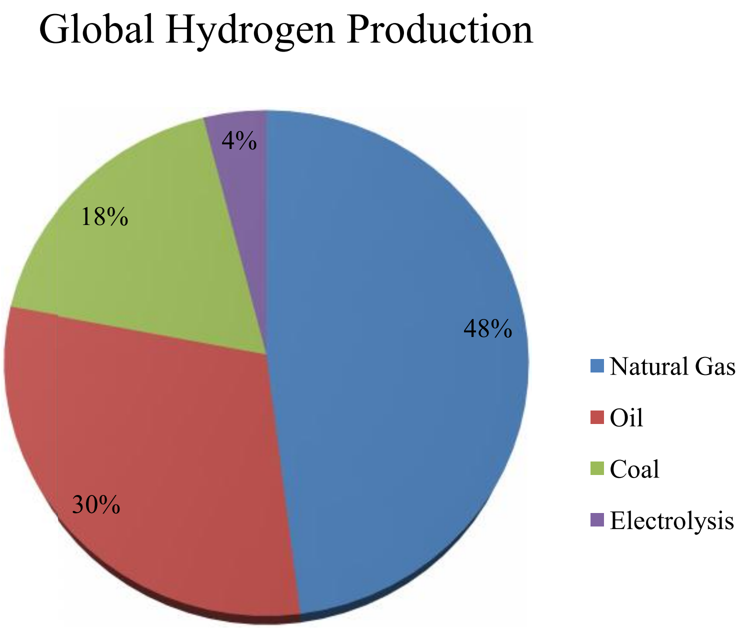


Figure 2.1 Annual global hydrogen production share by source (Balat, 2008).

Hydrogen production from methane by the steam reforming involves two reactions: the steam reforming reaction and the water-gas shift reaction. In the steam reforming reaction, methane reacts with steam at high temperature, between 760 and 816ºC, producing carbon monoxide and hydrogen Eq. (2.1).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (2.1)$$

In the water-gas shift reaction, carbon monoxide reacts with steam at lower temperatures (343-371ºC) compared to the steam reforming reaction producing carbon dioxide and hydrogen as shown in Eq. (2.2) (Baade *et al*. 2001).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2.2)$$

Thus, the overall reaction for the hydrogen production from steam reforming is

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (2.3)$$

2.2 Hydrogen production from thermochemical splitting cycles

There has been research on the production of hydrogen from renewable sources such as thermochemical water splitting cycle in which the water is decomposed into hydrogen and oxygen by using intermediate elements such as Cu, Cl, and S, through chemical reactions (Naterer *et al*., 2009). The energy source in a thermochemical cycle is usually thermal energy produced by a nuclear reactor (Vitart *et al*., 2006). Cycles involving the sulfur family, including the sulfur-iodine thermochemical cycle (S-I), have been extensively studied because it is one of the promising method in long term for large-scale production of hydrogen, because of the prospect of a lack of fossil fuel resources (Kane and Revankar, 2008; Vitart *et al.*,2006).

2.2.1 S-I water splitting cycle

The S-I water splitting process has been investigated by General Atomics (GA), who originally proposed it, Japan Atomic Energy Agency (JAEA) and the French Atomic Energy Commission (CEA). In this cycle, there are three main reactions involving sulfuric and hydriodic acid as intermediates (Huang and T-Raissi 2005). The three reactions are:

H_2SO_4 decomposition

$H_2SO_{4(g)} \rightarrow H_2O_{(l)} + SO_{2(g)} + \frac{1}{2}O_{2(g)}$ $\Delta H_{(298.15K)} = 174.264$ kJ (2.4)

The sulfuric acid decomposition reaction is highly endothermic and requires a temperature between 850 and 1000ºC. Because the reaction requires a lot of heat, normally the primary heat source is a nuclear reactor. The products of the sulfuric acid decomposition are water, sulfur dioxide and oxygen.

The Bunsen reaction, which is composed of water, sulfur dioxide and iodine, produces two aqueous immiscible acidic phases: sulfuric acid (upper phase) and hydroiodic acid (lower phase). This reaction operates at 120ºC. The Bunsen reaction is not spontaneous and requires an excess of water to make the reaction thermodynamically favorable. In addition, excess iodine is also required to help the process to separate the mixture into two phases.

$2H_2O_{(l)} + SO_{2(g)} + I_{2(l)} \rightarrow H_2SO_{4(aq)} + 2HI_{aq}$ $\Delta H_{(298.15K)} = -\ 143.846$ kJ (2.5)

After hydrogen iodide is extracted from hydroiodic acid solution, it goes to be decomposed into hydrogen and iodine. The decomposition of hydrogen iodide is also an endothermic reaction which requires a large amount of heat.

$2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$ $\Delta H_{(298.15K)} = -52.\ 718$ kJ (2.6)

The overall reaction is:

$H_2O \rightarrow H_2 + \frac{1}{2}O_2$ (2.7)

Sulfuric acid decomposition is a more endothermic reaction than hydrogen iodide decomposition (Wang, 2007). Therefore, there is research into more energy efficient technologies for hydrogen production.

2.2.2 H_2S recovery and H_2S splitting cycle

Research into finding components that can be used in alternative methods of producing hydrogen with low cost has been extensive. Hydrogen sulfide is one of the compounds that has been investigated for hydrogen production through electrochemical, thermal decomposition and thermochemical processes. H_2S is produced in large quantities during hydrodesulfurization in oil production and is an undesired by-product in the petroleum industry that needs to be removed.

H_2S is removed from the hydrocarbon gas stream by passing through the amine treating unit that includes an absorber (contactor) and a regenerator (stripper) (Figure 2.2). In the absorber, the sour gas which contains H_2S passes through an amine solution to produce a sweetened gas stream (free of hydrogen sulfide) and acid gas. From the top of the absorber the purified sweetened gas is produced. From the bottom of absorber the rich amine solution (amine solution and H_2S acid gas) is sent to the regenerator after heating with a heat exchanger by hot lean amine that comes from the bottom of regenerator. In the regenerator, from the top, the acid gas is separated from the amine solution and is sent to the processing unit: Claus process (Figure 2.2) (Clark, 2006; Kohl, 1997).

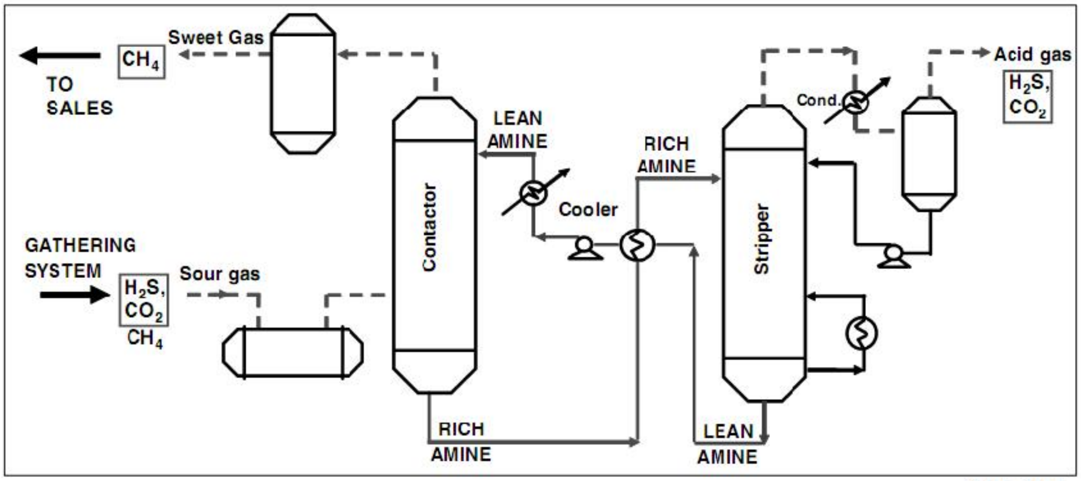


Figure 2.2 Flow diagram shows the process of removing H_2S and CO_2 from the gas streams by using amine solutions (Clark, 2006).

The Claus process is a widely used technique to recover elemental sulfur from H_2S (Kohl, 1997). There are three main chemical reactions in the Claus process which are:

$$H_2S + \tfrac{1}{2}O_2 \rightarrow H_2O + S \tag{2.8}$$

$$H_2S + \tfrac{3}{2}O_2 \rightarrow H_2O + SO_2 \tag{2.9}$$

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S \tag{2.10}$$

The reactions occur in two stages: thermal and catalytic stages. Reaction (2.8) and (2.9) take place in the thermal stage (reaction furnace). Reaction (2.10) takes place in the catalytic stage (catalytic converters).

During the thermal stage, the acid gas that comes from the amine regenerator goes through a reaction furnace where the acid gas is burned at temperatures between 1300 and 2000ºC. Sulfur dioxide and elemental sulfur are formed in the thermal stage. Between 60 and 70% of elemental sulfur is produced in this stage. The elemental sulfur goes to a condenser and then is sent to a container.

In the catalytic stage, the remaining hydrogen sulfide reacts with sulfur dioxide produced in the thermal stage which produces more elemental sulfur. The sulfur is condensed in the same manner as the thermal stage. Usually, more than one catalytic stage is used to maximize the efficiency of hydrogen sulfide conversion. The final step of sulfur separation involves the incineration of effluent gas or another treating unit, such as tail-gas treating, where the gas is prepared to be exhausted to the atmosphere (Gary and Handwerk, 2007).

Considering that hydrogen sulfide is a waste, a new process for hydrogen production was proposed: H_2S thermochemical water splitting cycle.

The H_2S splitting cycle is based on the S-I themochemical cycle. The difference is that the H_2SO_4 decomposition reaction from S-I cycle is replaced by the reaction between hydrogen sulfide and sulfuric acid in the H_2S splitting cycle, which is also called H_2S oxidation reaction. The H_2S cycle is composed of three main reactions which convert hydrogen sulfide into hydrogen and sulfur through chemical reactions (Wang, 2007):

H_2S oxidation

$$H_2S + H_2SO_4 \rightarrow S + SO_2 + 2H_2O \qquad \Delta H_{(298.15K)} = -59.636\ \text{kJ} \qquad (2.11)$$

Bunsen reaction

$$2H_2O + I_2 + SO_2 \rightarrow H_2SO_4 + 2HI \qquad \Delta H_{(298.15K)} = -143.846\ \text{kJ} \qquad (2.5)$$

HI decomposition

$2HI \rightarrow H_2 + I_2$ $\Delta H_{(298.15K)} = - -52.718$ kJ (2.6)

The overall reaction:

$H_2S \rightarrow H_2 + S$ (2.12)

The reaction between hydrogen sulfide and sulfuric acid produces elemental sulfur, sulfur dioxide and water. SO_2 produced by this reaction, can also react with H_2S to form sulfur and water in a second reaction (Wang, 2007):

$2H_2S + SO_2 \rightarrow 3S + 2H_2O$ (2.13)

Because sulfur dioxide is needed for the Bunsen reaction, the reaction between hydrogen sulfide and sulfur dioxide is undesirable for the H_2S cycle. To avoid this reaction, the sulfuric acid solution in the H_2S oxidation reaction must be at a high concentration, between 90 and 96 wt%, because by increasing the acid concentration, the solubility of SO_2 in the sulfuric acid solution will decrease (Zhang et al., 1998). In addition, to avoid the reaction between H_2S and SO_2, the temperature of H_2S oxidation reaction has to be between 120 and 150ºC. A schematic representation of the H_2S –splitting cycle is shown below (Wang, 2007):

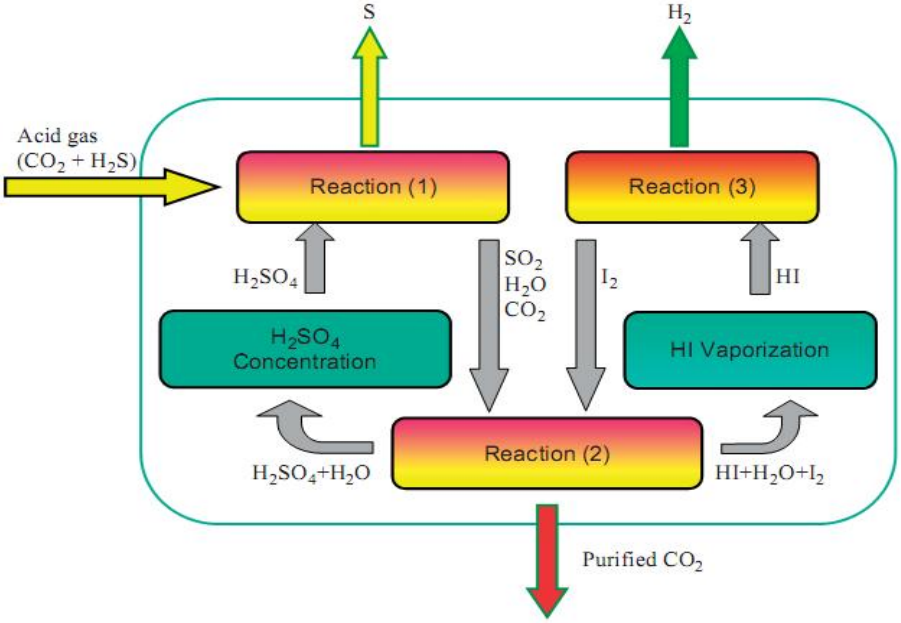


Figure 2.3 Schematic representation of H_2S-splitting cycle (Wang, 2007).

The reaction between H_2S and H_2SO_4 in the H_2S splitting cycle requires lower temperature comparing to the H_2SO_4 decomposition reaction in the S-I cycle. In addition, the S-I cycle uses the nuclear reactor as energy source for the heat needed in the reactions. This cycle is considered promising in a long term because of the prospect that the nuclear energy, in the future, will be one of the main energy sources. On the other hand, H_2S splitting cycle is based on the large quantity of waste of hydrogen sulfide is produced nowadays in the upgrading process of oil production. Therefore, the hydrogen produced in this cycle is a good alternative to be used in the upgrading and refining processes in oil production in a short term.

The H_2S cycle is a new area to be studied. The study of the reaction between hydrogen sulfide and sulfuric acid has been studied for a long time. In the next section, a review on the kinetics and mass transfer studies on the reaction between H_2S and H_2SO_4 will be shown.

2.3 Studies on the reaction between hydrogen sulfide and sulfuric acid

As mentioned in Section 2.2.2, the reaction between hydrogen sulfide and sulfuric acid produces three products: elemental sulfur, sulfur dioxide and water.

Early studies (Zhang *et al.*, 2000) have investigated possible reaction pathways for the reaction of hydrogen sulfide with sulfuric acid. After conducting thermodynamic analysis, such as determination of the heat of reaction, ΔH_{rxn}, and the Gibbs free energy change, ΔG_{rxn}, it was concluded that the probable reaction pathways when H_2S reacts with concentrated sulfuric acid are:

$$H_2S_{(g)} + H_2SO_{4(l)} \rightarrow S_{(s)} + SO_{2(g)} + 2H_2O_{(l)} \qquad (2.11)$$

$$2H_2S_{(g)} + SO_{2(g)} \rightarrow 3S_{(s)} + 2H_2O_{(l)} \qquad (2.13)$$

After studying the possible reactions that occur when hydrogen sulfide reacts with concentrated sulfuric acid solutions, the kinetic studies of these two reactions (reaction (2.11) and reaction (2.13)) were investigated. It was determined that the reaction between hydrogen sulfide and sulfuric acid (reaction 2.11) takes place at the gas-liquid interface. According to Wang *et al* (2002a) , the reaction rate can be determined in terms of the partial pressure (P_{H_2S}) in a constant volume reactor (Eq.2.14). In this equation, k_{p1} is the rate constant of the reaction between H_2S and H_2SO_4, a represents the surface area between the gas and liquid.

$$r_{H_2S_1} = k_{p1} a P_{H_2S} \qquad (2.14)$$

The reaction rate was measured by applying initial rate method following changes in the reaction conditions as the reaction proceeded. The method of initial rate analysis was applied because at the moment that the reaction between H_2S and H_2SO_4 starts, the conditions of the reaction system are well known, such as the liquid surface that is clear and its surface area that is also known. To measure the reaction rate, the influence of mass transfer and diffusion effects were eliminated. For example, the produced solid state sulfur might block the reaction surface. Therefore the reaction rate between hydrogen sulfide and sulfuric acid was determined by using the recorded pressure drop against time in a constant volume (Figure 2.4).

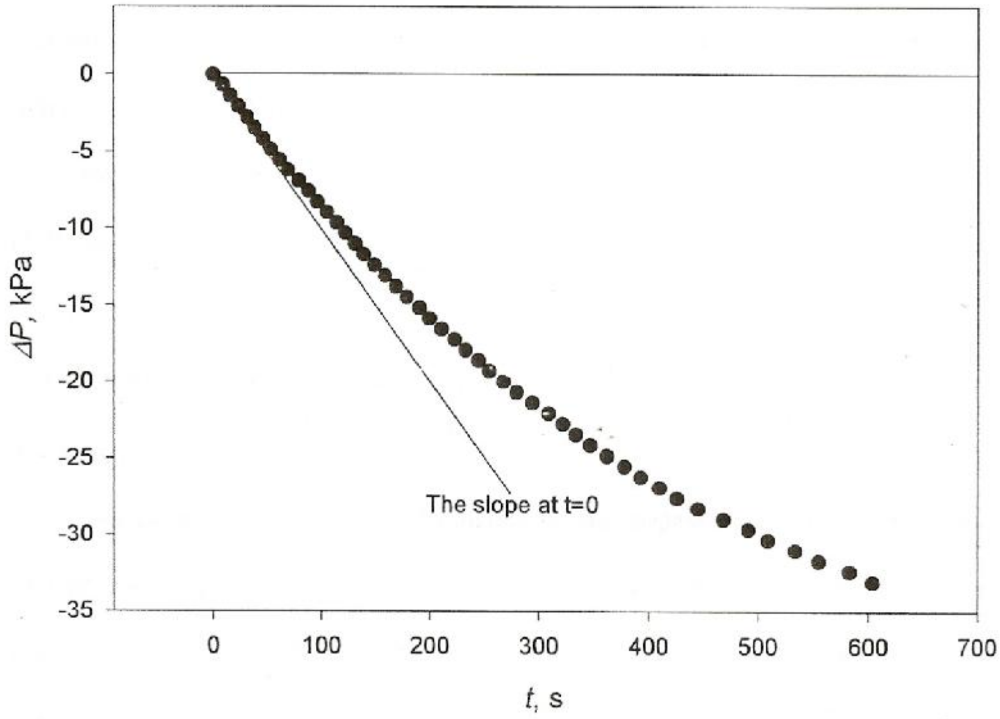


Figure 2.4 pressure drop against time for the reaction between H_2S and H_2SO_4. The slope in the graph at time zero gives the initial rate of the reaction (Wang *et al.*2003).

The order of the reaction and the reaction rate were obtained by correlating the initial rates of reaction, $-r_{H_2S}$, and initial partial pressure, P_{H_2S}. In the study Wang *et al*. (2002 a), sulfuric acid concentrations ranging from 88 to 100 wt% were reacted with hydrogen sulfide at different temperatures, between 20 and 60 ºC. The results showed that the mass transfer and diffusion in the liquid phase at time zero were insignificant. The interfacial area was also evaluated to see its influence on the reaction rate. The conclusion was that the reaction rate was proportional to the interfacial area; however, the interfacial area was independent of the volume of the acid. To determine the order of the reaction between hydrogen sulfide and sulfuric acid, the initial reaction rate was measured using different initial partial pressures of hydrogen sulfide at fixed temperatures and acid concentrations. Using concentrations between 88 and 100 wt % and temperatures from 20 to 60 ºC, the results indicated that the reaction was first order with respect to hydrogen sulfide pressure (Wang *et al*. 2002 a).

Following kinetics studies, the reaction between hydrogen sulfide and sulfur dioxide (2.13) in the sulfuric acid solution was studied. There was no reaction when dry hydrogen sulfide reacts with sulfur dioxide, the system required moisture in order to react with each other. In order to omit the significant interaction between H_2S and sulfuric acid, sulfuric acid concentration had to be diluted. According to Wang 2003, decreasing the acid concentration, the reaction between hydrogen sulfide and sulfuric acid slows down. Moreover, using acid concentrations below 65 wt%, the reaction between H_2S and H_2SO_4will not be effective. Therefore the acid concentrations used were between 30 and 60 wt. %, and the temperatures were between 20 and 50 ºC (Wang *et al*. 2002 b).

Using a similar method that was applied to measure the reaction rate for reaction (2.11), the reaction rate for the reaction between H_2S and SO_2 in sulfuric acid solution was measured by plotting pressure versus time at time zero. The reaction rate was measured at the equilibrium between the partial pressure in the gas phase, P_{H_2S}, and the concentration of SO_2 in the liquid phase $[SO_2]$, (Eq. 2.15). In this equation, *a* represents the surface area between gas and liquid and k'_{p2} is the rate constant.

$$r_{H_2S_2} = k'_{p2} a P_{H_2S}[SO_2] \tag{2.15}$$

The conclusion was that the reaction between hydrogen sulfide and sulfur dioxide in sulfuric acid solution is second order reaction: first order with respect to both H_2S and to SO_2. In addition, it could be concluded that the reaction occurred only at the surface of the acid solution. The activation energy and pre-exponential in reaction between hydrogen sulfide and sulfur dioxide were also analyzed and both parameters were found to be independent of the acid concentration, contrary to that of H_2S oxidation reaction (Wang *et al.*2002 b).

As mentioned, the effect of mass transfer was avoided in order to study the kinetics on the reaction between hydrogen sulfide and sulfuric acid. Until now, the thermodynamics and kinetics studies of the reaction between hydrogen sulfide and sulfuric acid helped to identify the parameters that have influence on the reaction. In order to estimate parameters that can help scale-up a reactor for the reaction, a study in mass transfer properties for gas-liquid reaction was also investigated.

The mass transfer for the gas-liquid reaction between H_2S and H_2SO_4 was studied using a packed column filled with ceramic Raschig rings (Wang *et al.*, 2004). The analysis was based on two-film theory which showed that when the hydrogen sulfide was transferred from the gas phase to the surface of concentrated sulfuric acid solution in the reaction, the overall H_2S mass transfer resistance consists of the gas phase mass transfer and surface reaction. A model was used to estimate parameters in terms of packing material and operating conditions. The effectiveness of the model was verified by estimating gas-liquid interfacial area of the packed column filled with ceramic Raschig rings (Wang *et al.,* 2004)

The comparison between reaction rate constant and mass-transfer coefficient was able to demonstrate the rate-controlling regimes in terms of acid concentration, temperature, and acid and gas flow rates. The knowledge from this study will be suitable for further reactor scale-up calculations and controlling variables for the H_2S splitting cycle technology. Even though, studies on the reaction kinetics, thermodynamics and mass-transfer have been well investigated in the reaction between hydrogen sulfide and sulfuric acid, there is still a lack of information about one of its products, elemental sulfur. When hydrogen sulfide reacts with sulfuric acid, sulfur is produced and stays with remaining sulfuric acid in the reactor. Therefore, separation process is important. Consequently, it is important that to understand the dynamics of the sulfur and sulfuric acid solution mixing to suggest a proper separation process. Moreover, the quality of the produced sulfur is to be investigated to establish its commercial value.

2.4 Elemental sulfur

2.4.1 General properties

Sulfur is a non metallic component and can be found from natural deposits such as volcanic sources and is a by-product of oil refining processes such as recovery of hydrogen sulfide (H_2S) (Holleman and Wiberg, 2001). The sulfur originated from natural deposits is usually extracted through the Frasch process which uses heated water (155°C) to melt the sulfur. Using compressed air, the melted sulfur is then brought to the surface and is either allowed to solidify into different shapes to sell in its liquid form (Chesworth, 2008). According to Holleman and Wiberg (2001), 40% of the world sulfur production comes from natural deposits and the rest most of it comes from H_2S recovery process (Kutney (2007); Holleman and Wiberg (2001)). The most common process for the recovery of hydrogen sulfide is the Claus process as mentioned section (2.2.2). Commercial uses of sulfur are in fertilizers, matches and insecticides.

Elemental sulfur has been studied for many years due to its many different allotropes. According to Steudel and Eckert (2003), the allotrope of an element is the different crystal structures that the molecule can be presented. There are more than 20 molecular forms of sulfur with cyclo-octasulfur (S_8) being the most stable form at ambient temperature and pressure. S_8 has crown- shaped form and yellow color (Figure 2.5) (Steudel and Eckert, 2003). Sulfur atoms have ability to combine each other to form chains of indefinite length and to form ring molecules. Some of these molecular forms have more than one crystalline phase, which are represented by Greek letters. The crystalline phases of sulfur which consists of ring molecules are usually indicated as α, orthorhombic, β and λ, monoclinic. Sulfur allotropes consisting of chains, polymeric forms, are indentified by the Greek letters ω and ψ (Steudel and Eckert 2003).

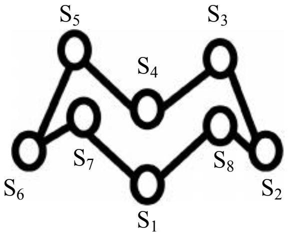


Figure 2.5 The molecular structure of S_8 (adapted from Schmit, 1978)

Orthorhombic sulfur or α-sulfur, is the most commercialized sulfur because of its stability at standard temperature and pressure. Upon heating, the color of sulfur becomes darker and when the temperature reaches about 96ºC, it is slowly converted to monoclinic sulfur, β-S_8. At 120ºC, β-sulfur melts to form liquid sulfur which is also called λ-sulfur. (Nickless 1968; Meyer 1976).

Liquid sulfur has different physical properties upon increasing temperature. For example, at melting point, 120ºC, sulfur has a honey-yellow color with low viscosity. The sulfur color appearance goes darker until its boiling point, 444.4ºC, and its viscosity increases to a maximum at about 187ºC (Steudel, 2003). The figure 2.6 shows the different forms of sulfur by increasing temperatures. A change occurs if the molten sulfur is kept above 120ºC for hours, rings containing from 5 to 30 sulfur atoms are formed in equilibrium with each other and S_8. This mixture is called π-sulfur. If the sulfur is slowly cooled, the sulfur forms changed by an increase in temperature will reappear in reverse order.

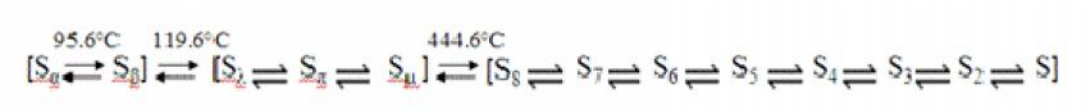


Figure 2.6 Forms of sulfur at different temperatures (Wiberg, *et al.,* 2001).

Vapor sulfur consists mainly of S_8, S_7 and S_6 molecules. S_5, S_4, S_3 and S_2 molecules are also present on small amounts. Increasing the temperature more of the smaller molecules are formed: the S_2 atoms start to decompose into to S atoms with temperature higher than 1800 °C (Wiberg, *et al*., 2001).

2.5 Knowledge gap and research objectives

Although, the H_2S splitting cycle has been studied for many years, there is still a lack of information regarding maximizing SO_2 production during the H_2S oxidation step. SO_2 is required for hydrogen production through the subsequent step in the H_2S splitting cycle: Bunsen reaction. Therefore, in order to increase hydrogen production, SO_2 production must be maximized.

Another important point in H_2S splitting cycle is the separation of the produced sulfur from the acid. There is no data on how well is the separation between the produced sulfur and remaining sulfuric acid after reaction. The product sulfur may block the reaction surface area and consequently may negatively affect the overall hydrogen production. Hence, understanding sulfur separation during the H_2S splitting cycle is crucial.

The main objective of this research is to maximize SO_2 production in the reaction of H_2S with H_2SO_4, by changing the acid concentration, stirring rate and temperature. Moreover, the phase separation between sulfuric acid and the produced elemental sulfur will receive a special attention in this study.

In this chapter, some background information and technologies for hydrogen production from natural gas and thermochemical splitting cycles were introduced. Studies on the reaction between hydrogen sulfide and sulfuric acid were reviewed as well the properties of elemental sulfur. The reason and the objectives for this research were also covered. The following chapter will describe the experimental procedure for studying the reaction between H_2S and H_2SO_4 and for the separation between sulfuric acid and elemental sulfur.

Chapter 3

EXPERIMENTAL METHODS

This chapter describes the experimental setup and procedure for the reaction between H_2S and H_2SO_4 and for the separation between sulfuric acid and elemental sulfur.

3.1 Experimental setup and procedure for the reaction between H_2S and H_2SO_4

In this report the experimental setup and procedure are detailed for the reaction between hydrogen sulfide and sulfuric acid for the analysis of sulfur dioxide production and kinetics modeling.

3.1.1 Experimental setup

The experiment used mini-reactor, 300 ml, made of 316 stainless steel (Model 5500, Parr Instrument Co, Moline, IL, USA) equipped with a magnetic stirrer drive and supplied with a glass liner. The glass liner, ID 6.35 cm, was used to protect the cylinder (reactor) from corrosive solutions such as sulfuric acid. The reactor was equipped with block heater which was connected to the reactor controller (Model 4848, Parr Instrument Co, Moline, Illinois, USA). The reactor pressure was measured using the pressure transducer (Scadasense 4102, Control Microsystems, Kanata, ON, Canada). The temperature of the reactor was monitored using the reactor controller. A two-stage vacuum pump (Model 15601, Robinair Co, Owatonna, MN, USA) was used to remove the air of the reactor and the feed system that was connected to the reactor. The schematic diagram of the experiment setup is shown in the Figure 3.1.

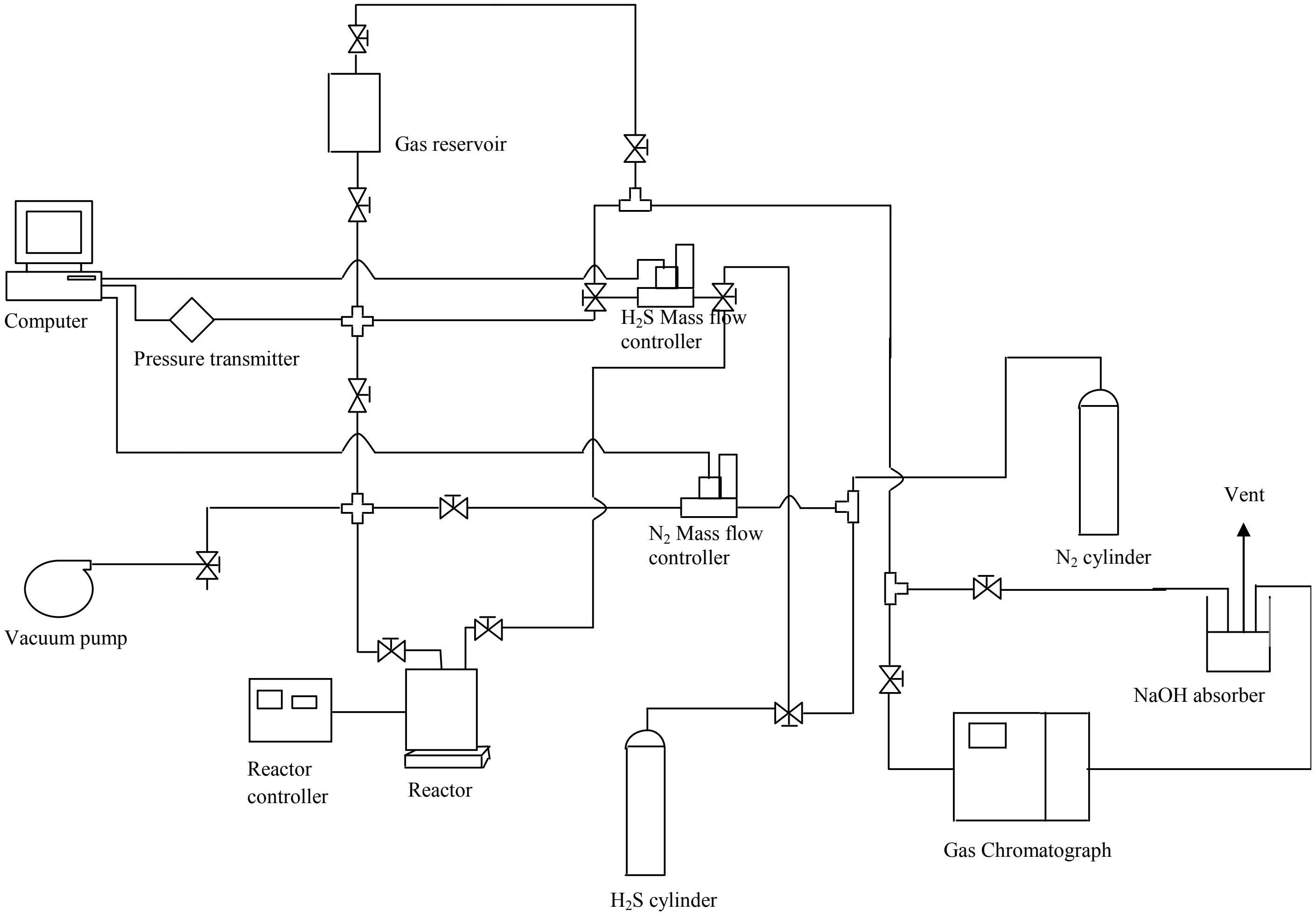


Figure 3.1 Experimental setup for the study of kinetic modeling from the reaction between H_2S and H_2SO_4.

3.1.2 Experimental procedure for H_2S and H_2SO_4 reaction

Three different concentrations of sulfuric acid solution were used to do the reaction runs between hydrogen sulfide and sulfuric acid: 90, 93 and 96 wt %. In addition, three different temperatures were used in the reaction: 120, 140 and 160°C. The H_2SO_4 concentrations of 90 and 93 wt % were prepared by diluting 96 wt% of acid solution. The concentration of each solution was determined by titration using 0.1N sodium hydroxide solution and 0.5 % methyl orange solution as indicator.

A known volume and concentration of sulfuric acid solution was charged into the reactor and after that, the reactor was connected to the system. Nitrogen gas was used in the system to check any leaks by using Swagelok liquid leak detector (Snoop solution). After checking that the system didn't have any leak, the vacuum pump was used to remove the air from the reactor and the system. The sulfuric acid solution was then heated to a temperature of 120°C. After the temperature reached equilibrium, the gas reservoir was filled with pure H_2S from the cylinder. The following step was to introduce H_2S from the gas reservoir into the reactor and the reaction run overnight. In the next day, the reactor was purged with nitrogen for about 2 hours to remove any SO_2 produced in the reaction between hydrogen sulfide and sulfuric acid. Some experimental runs were performed at temperature, 120°C, and did not use impeller. After performing this part, the reactor was setup with an impeller. The experimental runs using stirring had the same procedure as described without it. These runs were performed at three different temperatures (120, 140 and 160ºC) and also three different stirrer speed (100, 200 and 400 rpm).

The mixture of remaining acid solution after reaction and elemental sulfur produced was transferred from the glass liner to a beaker, which was placed in the oven at temperature of 140°C for 2 hours to remove elemental sulfur from sulfuric acid.

After 20 minutes of reaction, it was observed that the pressure remained constant. The constant pressure was considered the final pressure of the reaction. The final gas phase in the reactor was analyzed using Varian CP3800 gas chromatograph (GC) equipped with pulsed flame photometric detector (PFPD).

3.2 Materials and procedure for analysis of sulfur and H_2SO_4 content

The material preparation, experimental procedure, analysis method to determine the content of sulfuric acid in contact with elemental sulfur is described in the following sections.

3.2.1 Experimental materials

Powder elemental sulfur (99.5%, -325 mesh, Alfa Aesar, Ward Hill, MA, USA) and 96 wt% sulfuric acid (EMD Chemicals, Gibbstown, NJ, USA) were used in this experiment. Two different concentrations of sulfuric acid were prepared: 88 and 96 wt%. The solution of 88 wt% was prepared by diluting 96 wt% of sulfuric acid. The concentration of the solutions were determined by titration using standard 0.1M of sodium hydroxide (Sigma-Aldrich, Oakville, ON, Canada) with 0.1% methyl orange solution (Sigma-Aldrich, Oakville, ON, Canada) as an indicator. The contact of sulfuric acid and elemental sulfur was performed using a glass contact apparatus in an oven (Memmert UE 200, Memmert GmbH). Two different temperatures for the experiment were performed: 120 and 140°C.

3.2.2 Description of the extraction apparatus

The contact apparatus consists of three main chambers, 1, 2 and 3 (Figure 3.2). The glass stopper is composed of a long tube immersed in sulfur and a short tube which is immersed in sulfuric acid solution. The sulfur and sulfuric acid extraction tubes are connected to sampling chambers. The silicone tubing is connected to each sampling chamber.

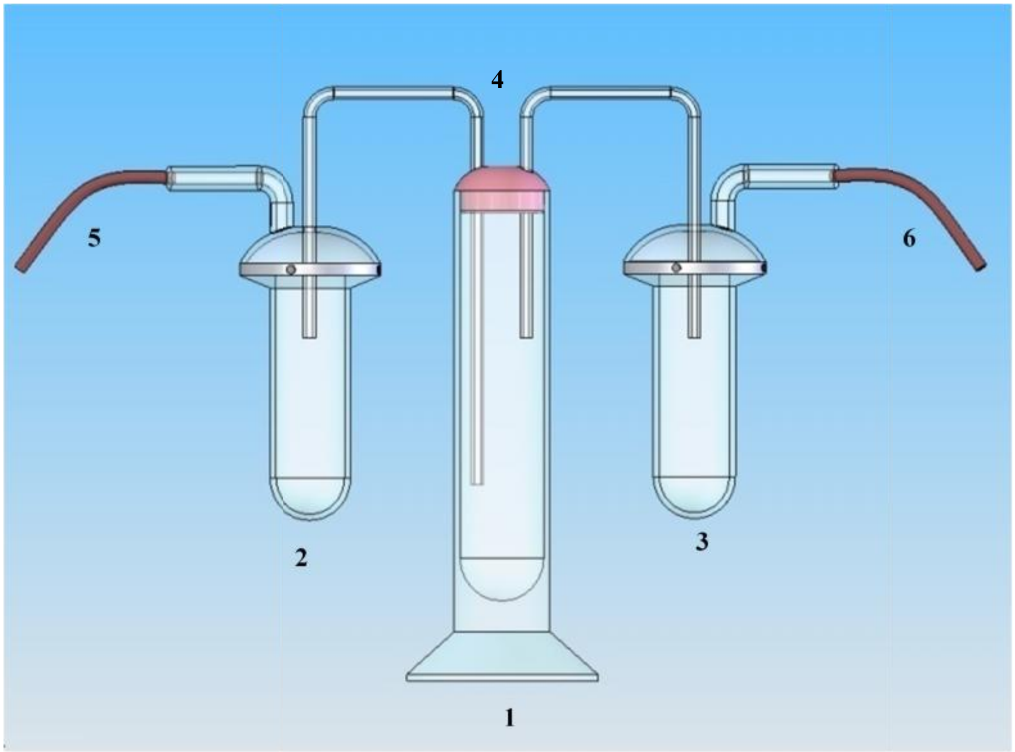


Figure 3.2 Drawing of glass contact apparatus: 1) Contact chamber; 2) Solid sampling chamber; 3) Liquid sampling chamber; 4) Glass stopper; 5) and 6) Silicone tubing.

3.2.3 Procedure of experiment for sulfuric acid separation

The experimental procedure is described below:

(1) A known amount of sulfur powder was placed in a 25 ml beaker.

The beaker was heated in the oven until the sulfur melted.

(2) The glass stopper was detached from the contact chamber and the inner long tube was immersed in the molten sulfur in the beaker upon removal from the oven. The molten sulfur was allowed to cool.

(3) The glass stopper was left standing in an appropriate place at room temperature until the sulfur inside the long tube solidified, blocking the orifice of the tube. This procedure prevents the sulfuric acid from entering the inner long tube when closing the contact chamber.

(4) 12.614 ± 0.002 g of sulfur powder was weighed and placed in the contact chamber. The sulfur was then melted in the oven at 120 °C for 2.5 hours.

(5) The contact chamber was taken out of the oven and 7 ml of sulfuric acid was introduced to the chamber. Because the sulfur turned solid on contact with the sulfuric acid, the contact chamber had to be placed again in the oven for 1.5 hour to re-melt the sulfur.

(6) As soon as sulfuric acid with molten sulfur was removed from the oven, the glass stopper was placed with the contact chamber.

(7) The apparatus was returned to the oven for 2 hours.

(8) Using a syringe connected in each silicone tube to draw the air out, approximately 3 ml sample of molten sulfur and 3 ml of sulfuric acid were taken to the sampling chamber. The collected samples were then analyzed.

3.2.4 Solid sulfur sample analysis

The collected sulfur in the sampling chamber turned solid after cooling (rapidly after removed from oven). For this reason the sulfur sample had to be melted again to be removed from the sampling chamber.

Each sulfur sample was melted for 1.5 hour. As soon as the sulfur sampling chamber was out of the oven, the liquid sulfur was poured into 2 weighing papers. These samples were then weighed and labeled as sulfur #1 and sulfur #2. After, each sample was transferred to a filter paper, placed in a Buchner funnel using an Erlenmeyer side arm flask hooked to a vacuum filter unit. Different amount of water was used to wash each sample. For sulfur #1, 150 ml of water was added and for sulfur #2, 200 ml. The water then was collected from these samples and analyzed.

The two samples of sulfur were left aside to air dry for one hour. Each sulfur sample, #1 and #2, was placed into 25 ml beaker to be melted in the oven for 1 hour at temperature of 120°C. The samples were removed from the oven and broken up using a stainless steel spatula to produce fine particles. The procedure of washing the ground sulfur samples and analyzing were the same as described for solid sulfur sample.

3.2.5 Sulfuric acid sample analysis

During the heating of sulfuric acid and elemental sulfur in the contact chamber, either using temperature of 120°C or 140°C, the sulfuric acid solution presented color changed from clear a transparent to black. According to Steudel, R. and Eckert, B. (2003), sulfuric acid can turn black due to oxidization of an organic compound that is incorporated in the elemental sulfur. The concentration of sulfuric acid solutions were determined by titration.

In this chapter a detailed description about the experimental setup and procedure for the reaction between H_2S and H_2SO_4 was presented. Moreover, the procedure for the separation between sulfuric acid and elemental sulfur, and the analysis method to determine the content of sulfuric acid in contact with sulfur were described. Chapter 4 focuses on discussing the results on the effects of temperature, stirring rate and acid concentrations on the production of sulfur dioxide from the reaction between H_2S and H_2SO_4. The results on the separation between the sulfur produced from this reaction and the remaining sulfuric acid are also discussed.

Chapter 4

Results and Discussion

This chapter discusses the effects of different operating conditions on the production of SO_2 from the reaction between H_2S and H_2SO_4 and also discusses the results on the separation between sulfuric acid and sulfur. This chapter is divided into 4 sections. Section 4.1 shows the reproducibility of the data with the experiments. Section 4.2 discusses the results of different operating conditions (temperature, stirring rate and sulfuric acid concentration) applied on SO_2 production. The results on the comparison between simulation and experimental data at specific condition are shown on Section 4.3. The results about the separation between the sulfur produced and the remaining sulfuric acid are presented in Section 4.4 as well the structure of the produced sulfur.

4.1 Reproducibility of data

Reproducibility of the data is important to test the reliability of the experiment measurements. For this reason, for each specific experimental condition (temperature, stirring rate and acid concentration) applied in the reaction between hydrogen sulfide and sulfuric acid to analyze the SO_2 production, the experiment was repeated; the total number of experiments was 20. Figure 4.1 shows the pressure drop from two experimental runs performed under identical conditions: using 96 wt% of sulfuric acid solution, a temperature of 120°C and stirring speed of 400 rpm.

For the analysis on the separation between sulfuric acid and elemental sulfur, two acid concentrations, 87.54 ± 0.30 wt% and 96.22 ± 1.312wt%, were used for the experiment. Titration analysis was performed three times for each concentration of sulfuric acid solution used in separation. The uncertainties were analyzed using the Student t test which calculated the confidence interval at the 95% (Eq. 4.1).

$$\bar{x} = \underline{\sum} (x_i - \bar{x})^2 \pm (t_{0.95} * \ s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}} \ ) \qquad (4.1)$$

Where x_i represents each measurement, $\bar{x}$ is the mean value and N-1 is the degree of freedom.

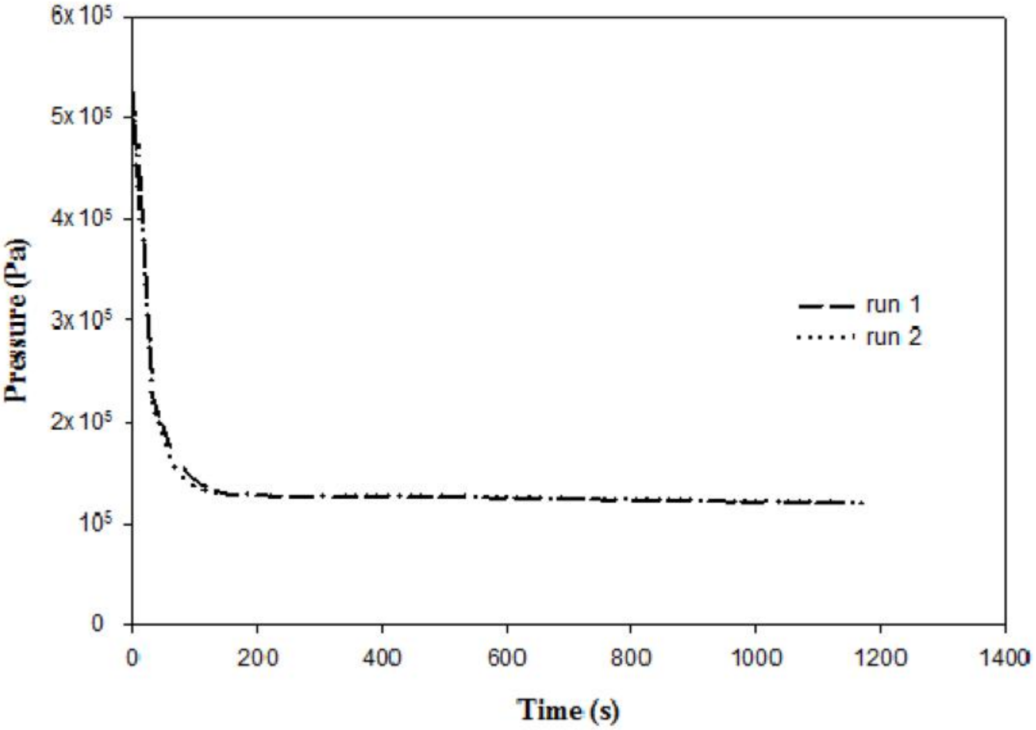


Figure 4.1 Duplicate experiments at acid concentration = 96 wt%, stirring rate = 400 rpm and temperature = 120°C.

4.2 SO_2 production

After 20 minutes of the reaction between H_2S and H_2SO_4, it was observed that the pressure remained constant. The constant pressure was considered the final pressure of reaction. Therefore, the final gas phase in the reactor was analyzed using gas chromatography (GC) with pulsed flame photometric detector (PFPD) to see if only SO_2 was in the gas phase. Nitrogen gas was added to a certain pressure for two reasons: to dilute the gas in the reactor before sending to GC analysis and to have a sufficient pressure to maintain a gas flow for GC sampling time. Because the PFPD method was used, the N_2 could not be detected; consequently, the gas chromatography results showed that only SO_2 is in the gas phase with no trace of remaining H_2S (Figure 4.2). It was assumed that the vapor pressure of sulfuric acid solution in different concentrations was insignificant for the different temperatures applied (120, 140 and 160ºC). According to Perry (1997), the vapor pressure of H_2SO_4 solutions, at temperature of 120°C, using 90, 93 and 96 wt% are 0.571 x 10^{-2} bar (8.282 x 10^{-2} Psi), 0.186 x 10^{-2} bar (2.70 x 10^{-2} Psi) and 0.851 x 10^{-3} bar (1.234 x 10^{-2}Psi) respectively.

According to Zhang *et al.* (2000), the amount of SO_2 produced from the reaction between hydrogen sulfide and sulfuric acid has high dependency on the acid concentration. Increasing sulfuric acid concentration increases the efficiency of H_2S oxidation (Figure 4.3); therefore enhances the production of SO_2. Zhang *et al.* (1998) developed a model to correlate the solubility of SO_2 in different concentrations of sulfuric acid at different temperatures. Henry's constant and its dependency on temperature could be determined from this correlation. Based on the data shown in Table 4.1, Henry's law was used to determine the amount of SO_2 in the liquid phase at different temperatures for a fixed H_2SO_4 concentration (96 wt%) (Table 4.2), and amount of SO_2 in liquid phase at different H_2SO_4 concentrations for a fixed temperature (120°C) (Table 4.3). The equation of state for an ideal gas was used to calculate the amount of SO_2 in the gas phase for different temperature and acid concentrations (Table 4.2 and 4.3).

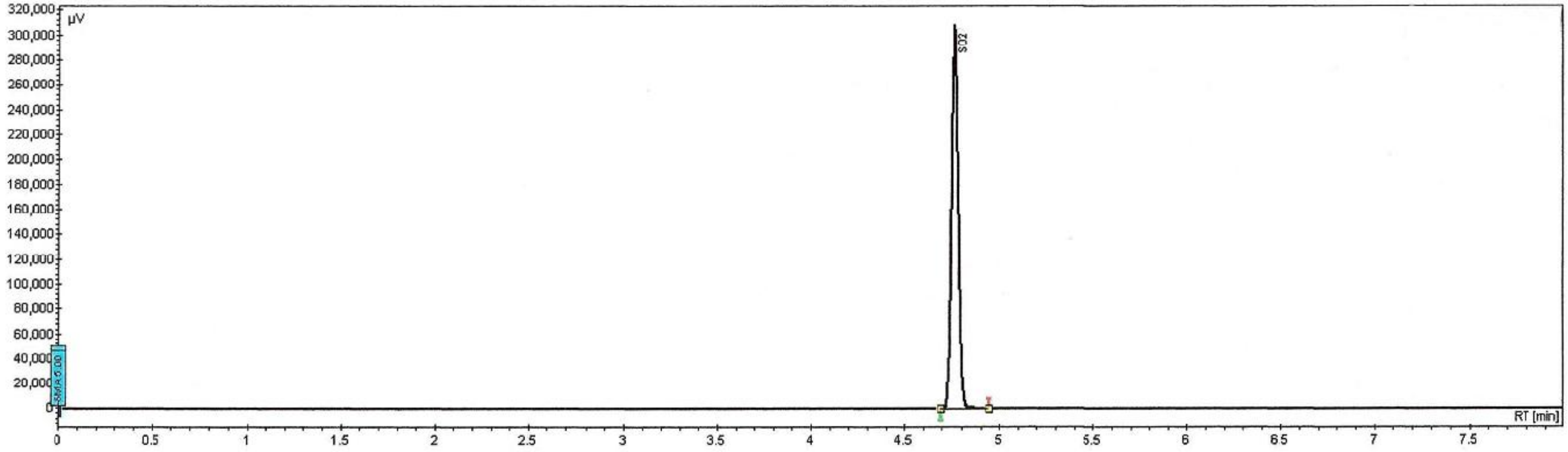


Figure 4.2 GC chromatogram of SO2 after the reaction between H_2S and H_2SO_4.

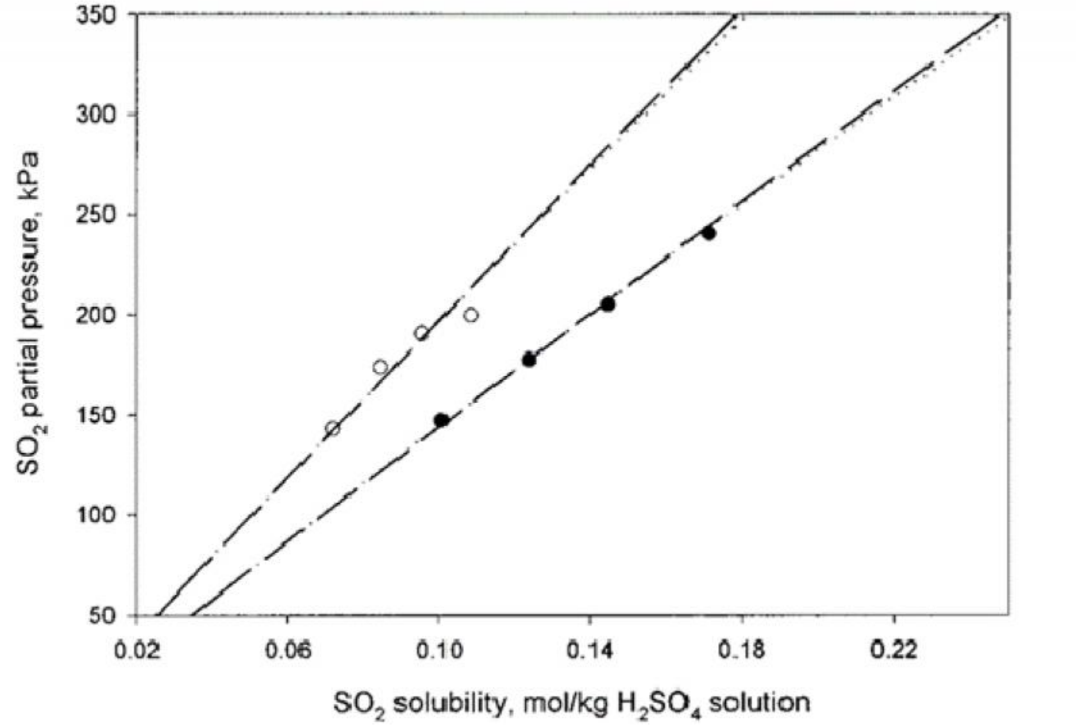


Figure 4.3 Solubility of SO_2 at different concentrations of sulfuric acid.

(○) 79 wt% H2SO4 and (●) 95.91 wt% H2SO4 (Zhang *et al*., 2000).

Table 4.1 Values of estimated Henry's Law constant at different H_2SO_4 concentrations and different temperatures (modified from Zhang *et al.*, 1998).

Temperature (K)	H_2SO_4 concentration (wt%)	H mPa (kg H_2SO_4 solution)/mol
298	79.01	0.29 ± 0.02
298	95.91	0.23 ± 0.01
298	97.00	0.20 ± 0.01
383	79.01	1.99 ± 0.08
383	95.91	1.46 ±0.02
393	65.71	1.46 ± 0.08
393	75.19	1.80 ± 0.02
393	79.01	2.29 ± 0.09
393	84.37	2.09 ± 0.07
393	87.72	1.61 ± 0.06
393	95.91	1.84 ± 0.09

Table 4.2 Final SO_2 amounts in the gas and liquid phases at different temperatures

Temperature (°C)	Amount of SO_2 in liquid phase (mol/H_2S mol)	Amount of SO_2 yield in gas phase (mol/H_2S mol)	Total of SO_2 produced (mol/H_2S mol)
120	0.439	0.259	0.698
140	0.453	0.293	0.746
160	0.484	0.361	0.845

Table 4.3 Final SO_2 amounts in the gas and liquid phases with different concentrations of H_2SO_4.

H_2SO_4 acid concentration (wt%)	Amount of SO_2 in liquid phase (mol/H_2S mol)	Amount of SO_2 in gas phase (mol/H_2S mol)	Total of SO_2 produced (mol/H_2S mol)
90	0.469	0.253	0.722
93	0.510	0.285	0.795
96	0.526	0.298	0.824

4.2.1 Effect of the temperature on SO_2 production

An investigation into the effect of temperature on the production of SO_2 in the reaction between hydrogen sulfide and sulfuric acid was conducted. Three different temperatures were used for the analysis: 120, 140 and 160 ºC. Using temperatures higher than 160°C would oxidize the elemental sulfur. The experiments were carried out using sulfuric acid with the concentration of 96 wt%, and stirring rate was 400 rpm. In Figure 4.4, it can be observed that increasing temperature resulted in an increase in the SO_2 production.

In section 2.2.2 shows that in the H_2S-H_2SO_4 reaction system there are two reactions: the reaction between hydrogen sulfide and sulfuric acid (2.11) and the reaction between hydrogen sulfide and sulfur dioxide (2.13). The two reactions are parallel with respect to H_2S, but consecutive with respect to SO_2. They compete for H_2S consumption. However, a relatively faster second reaction will convert more SO_2 produced by the first reaction into elemental sulfur. Wang *et al*. (2003), has shown that the Gibbs free energy change of reaction (2.13), increased with increasing temperature, while for reaction (2.11), it was not significantly affected by the temperature changes. This means that the spontaneity of reaction (2.13) decreases with increasing temperature, while for reaction (2.11) it is unchanged.

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (2.11)$$

$$H_2S + H_2SO_4 \rightarrow S + SO_2 + 2H_2O \qquad (2.13)$$

Using the experiment results and Matlab software program, the reaction constants, k_{p1} and k_{p2}, were determined (detailed approach is further discussed in section 4.3). The natural log of k as a function of the inverse temperature represents the Arrhenius plot (Figure 4.5). The Arrhenius equation gives the relationship the temperature and the reaction rate constant (Eq 4.2).

$$k = A_0 \exp\left(-\frac{E_a}{RT}\right) \tag{4.2}$$

Where A_0 is preexponential factor, E_a is activation energy, R is the gas constant and T is the absolute temperature.

Figure 4.5 highlights two important findings: the rate constant of reaction (2.11) is larger than that of reaction (2.13), and the increase of the rate constant of reaction (2.11) with the increasing temperature is greater than that on reaction (2.13). The activation energies and pre-exponential factors of reaction (2.11) and reaction (2.13) are 40.1 kJ/mol and 3.6 x 10^{-2} mol $s^{-1}m^{-2}Pa^{-1}$ and 10.8 kJ/mol and $6.7x10^{-11}$ mol $s^{-1}m^{-2}Pa^{-1}$, respectively. The increase in temperature accelerates more the reaction between H_2S and H_2SO_4 (2.11) than the reaction between H_2S and SO_2 (2.13), resulting in more net SO_2 production.

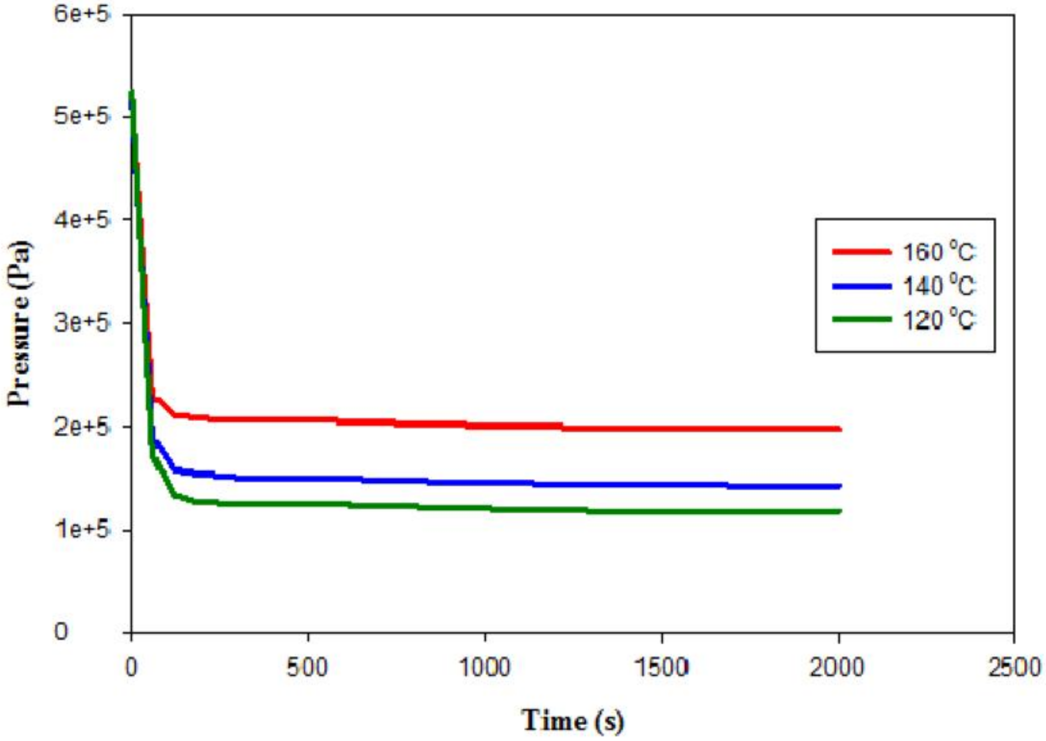


Figure 4.4 Effect of the temperature on the final SO_2 production. Acid concentration = 96 wt % and stirring rate = 400 rpm. Data recorded every second. The graph shows that increasing temperature, the final SO_2 partial pressure also increases. Therefore, the optimum temperature is 160ºC.

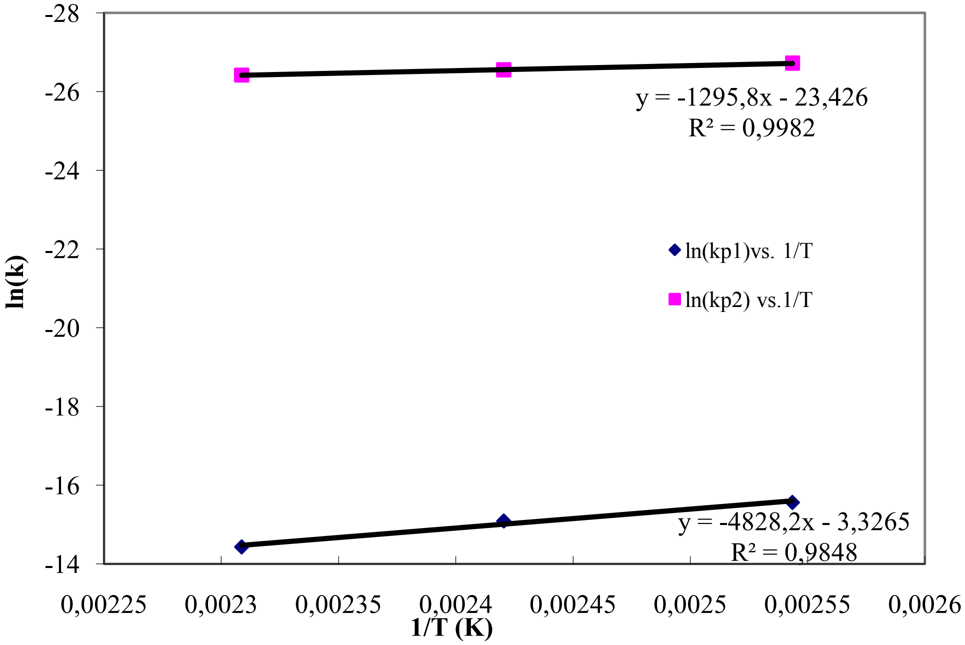


Fig 4.5 Arrherius plot of the reaction between H_2S and H_2SO_4. The figure shows that the increase on temperature affects more the rate constant of the reaction between H_2S and H_2SO_4 than the reaction between H_2S and SO_2.

4.2.2 Effect of stirring rate on SO_2 production

To study the effect of stirring rate on the SO_2 production in the reaction between hydrogen sulfide and sulfuric acid, experiments were performed using constant temperature and acid concentration of 120ºC and 96 wt. %, respectively. Four stirring rates were considered: 0, 100, 200, and 400 rpm. The maximum of stirring rate that could be used in the reactor was 500 rpm that was not used in the reaction because some of sulfuric acid solution would splash out of the reactor. As shown in Figure 4.6, increasing stirring rate led to lower SO_2 production. As the stirring rate was increased from 0 to 100 rpm the final SO_2 partial pressure decreased from 2.61×10^5 Pa to 2.14×10^5 Pa. Further increases in stirring rate did not result in significant decreases in the final SO_2 partial pressure.

The effect of stirring rate can be attributed to variation on the reaction surface area. The surface area was calculated based on the initial rate data. The surface area when there was no stirring was calculated to be 2.55×10^{-3} m^2, and for the stirring rate of 100, 200, 400 rpm, it was determined to be ~ 4.56×10^{-3} m^2; the applied stirring caused a ~1.8 fold increase in the surface area.

Reaction (2.13) takes place between H_2S and dissolved SO_2 (Wang *et al*., 2002b). SO_2 has higher dissolution, in H_2SO_4 (Zhang *et al*., 1998); hence, due to the low dissolution rate of H_2S the reaction is bound to take place primarily at the gas-liquid interface. As shown above, increasing stirring rate results in an enlargement of this interface, and consequently, higher rate of reaction (2.13) and ultimately lower SO_2 production.

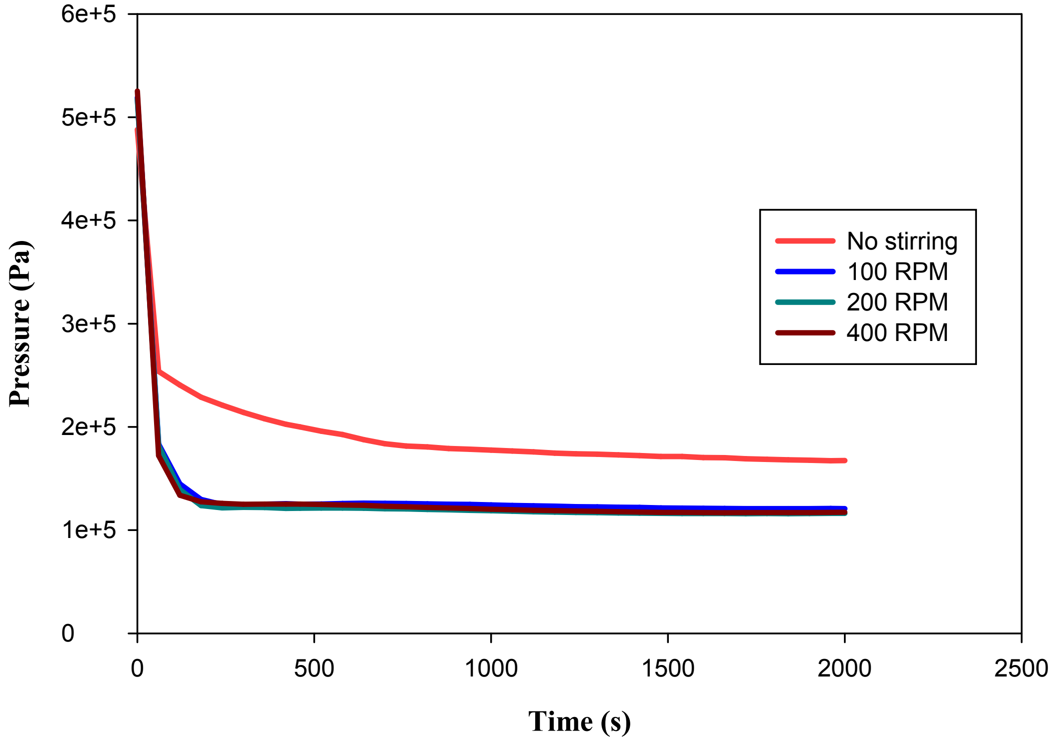


Figure 4.6 Effect of the stirrer rate on SO_2 production. Acid concentration = 96 wt%. Temperature = 120°C. Data recorded every second. By no applying stirring rate, the final SO_2 partial pressure increased. The final SO_2 partial pressure decreased when the stirring rate was from 100 to 400 rpm due to the increase of the surface area.

4.2.3 Effect of changing sulfuric acid concentration on SO_2 production

The effect of acid concentration on SO_2 production was studied. Three different concentrations of sulfuric acid solution were used to do the reaction runs between hydrogen sulfide and sulfuric acid: 90, 93 and 96 wt %. These acid concentrations were chosen because, based on previous studies, higher concentration of sulfuric acid will decrease the solubility of SO_2 in the liquid. The experiments were performed at temperature of 120 ºC; no stirring was applied.

Figure 4.7 shows that increasing acid concentration resulted in an increase SO_2 production. Wang *et al*. (2002a) has shown that, at the acid concentration range of 90 to 96 wt. %, the rate of reaction 2.11 (between H_2S and H_2SO_4) increases with increasing acid concentration, while that of reaction 2.13 (between H_2S and SO_2) is not significantly affected. Accordingly, it can be seen in the first segment of Figure 4.7 (<500 second) that higher pressure drop, reflecting higher reaction rate, is observed as the acid concentration is increased.

Since, reaction (2.11) is enhanced as the acid concentration is increased; more H_2S is consumed via this reaction pathway, consequently, the amount of H_2S consumed by reaction (2.13) pathway decreases. Therefore, the overall effect of increasing sulfuric acid concentration is an increase in SO_2 production.

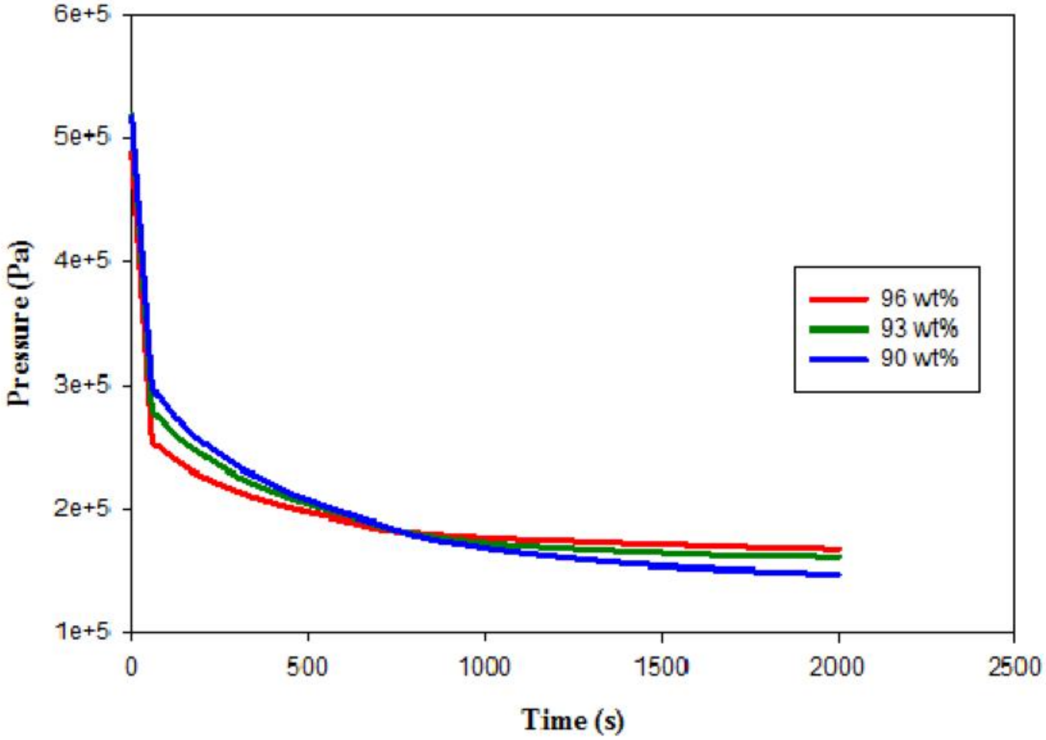


Figure 4.7 Effect of different sulfuric acid concentrations on SO_2 production. Temperature = 120°C. No stirring rate applied. Data recorded every second. Higher the sulfuric acid concentration, higher is the pressure drop and reaction rate which will increase the final partial pressure.

4.3 Simulation and kinetic studies on SO_2 production

The studies on kinetics of the two reactions (reaction (2.11) and reaction (2.13)) that are involved in the H_2S-H_2SO_4 system established the rate equation (Eq. 2.14 and Eq. 2.15) for each of the reactions (Wang *et al.,* 2002a and Wang *et al.,* 2002b).

$$H_2S + H_2SO_4 \rightarrow S + SO_2 + 2H_2O \qquad (2.11)$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (2.13)$$

As mentioned through the kinetics, the dependency on sulfuric acid concentrations was determined on both reactions. In the reaction between hydrogen sulfide and sulfuric acid, the reaction behaves as first order with respect to H_2S. In addition, the acid concentration affects the reaction rate on this reaction and in the reaction between H_2S and SO_2.

$$r_{H_2S_1} = k_{p1} a P_{H_2S} \tag{2.14}$$

$$r_{H_2S2} = k_{p2} a P_{H_2S}[SO_2] \tag{2.15}$$

Based on the rate equations (Eq.2.14 and Eq. 2.15), Wang (2003) developed a mathematical model to predict the partial pressure of SO_2 change in closed reactor system. The model was used in the experiment to investigate if can be used in a different reactor. The simulated result was compared with the experimental results used on the section for effect of temperature on SO_2 production (section 4.2.1), which different temperatures were applied (120, 140 and 160°C), and the stirring rate and the acid concentration were maintained at 400 rpm and 96 wt%, respectively.

Ignoring sulfuric acid evaporation, it was assumed that the gas phase comprises of H_2S and SO_2. Hydrogen sulfide is consumed by both reactions, while SO_2 is produced by reaction (2.11) and consumed by reaction (2.13). In addition other assumptions were made such as the effect of the heat of the reaction is ignored and the temperature during the measurement is constant; the amount of water produced in the reaction is ignored and the change of sulfuric acid concentration is insignificant; the produced sulfur does not block the surface under strong stirring and the interfacial area is not changed during the measurement and the mass transfer effect is negligible. Therefore, the changes of H_2S and SO_2 partial pressures with time can be described by equations (4.3) and (4.4) (Wang, 2003).

$$\frac{dx_1}{dt} = -K\,(k_{p1}x_1 + k_{p2}x_1x_2) \tag{4.3}$$

$$\frac{dx_2}{dt} = K\,(k_{p1}x_1 - \frac{1}{2}k_{p2}x_1x_2) \tag{4.4}$$

Where:

$$K = \frac{RT_G a}{V_G} \tag{4.5}$$

$P_{H_2S} = x_1$

$P_{SO_2} = x_2$

The boundary conditions are,

At $t = 0$, $x_1 =$ initialP_{H_2S}; $x_2 =$ initial $P_{SO_2} = 0$

The parameters K, k_{p1} and k_{p2} (Eq. (4.3), (4.4), (4.5)), respectively, are constants that are independent of time. The temperature and volume of the gas phase in the experiment, T_G and V_G, were constant.

The value of K, 7200 Pa m^2 mol^{-1}, was calculated through the equation 4.5. The rate constant of reaction between H_2S and H_2SO_4 (reaction (2.11)) and the reaction between H_2S and SO_2 (reaction (2.13)) are k_{p_1} and k_{p_2}, respectively. The initial guess values for k_{p_1} and k_{p_2} in the simulation were obtained from Wang (2003). Using Matlab, the values of k_{p_1} and k_{p_2} were adjusted such that the simulated values fit the experimental results (Table 4.4).

The comparison between the simulated and the experimental data is presented in Figure 4.8, indicating a good fitness of the model.

Figure 4.9 shows the partial pressure for H_2S and SO_2 during the reaction with sulfuric acid, 96 wt%. Through the simulation results, a graph could be built to show the partial pressure of H_2S and SO_2 and the total pressure. The partial pressure of H_2S decreases with time until becomes zero, while the partial pressure of SO_2 increases with time until it reaches steady state. The total pressure is the sum of the changes of H_2S and SO_2 partial pressures. This indicates that the final gas is purely made of SO_2 and this fact is confirmed by the GC results.

Table 4.4 Values of k_{p_1} and k_{p_2}. The k_{p_1} and k_{p_2} were determined by using Matlab ^{Tm} program ($R^2 = 0.9992$)

Temperature 0(°C)	k_{p1} mol $s^{-1} m^{-2} Pa^{-1}$	k_{p2} mols $s^{-1} m^{-2} Pa^{-1}$
120	1.73×10^{-7}	2.473×10^{-12}
140	2.784×10^{-7}	2.933×10^{-12}
160	5.406×10^{-7}	3.352×10^{-12}

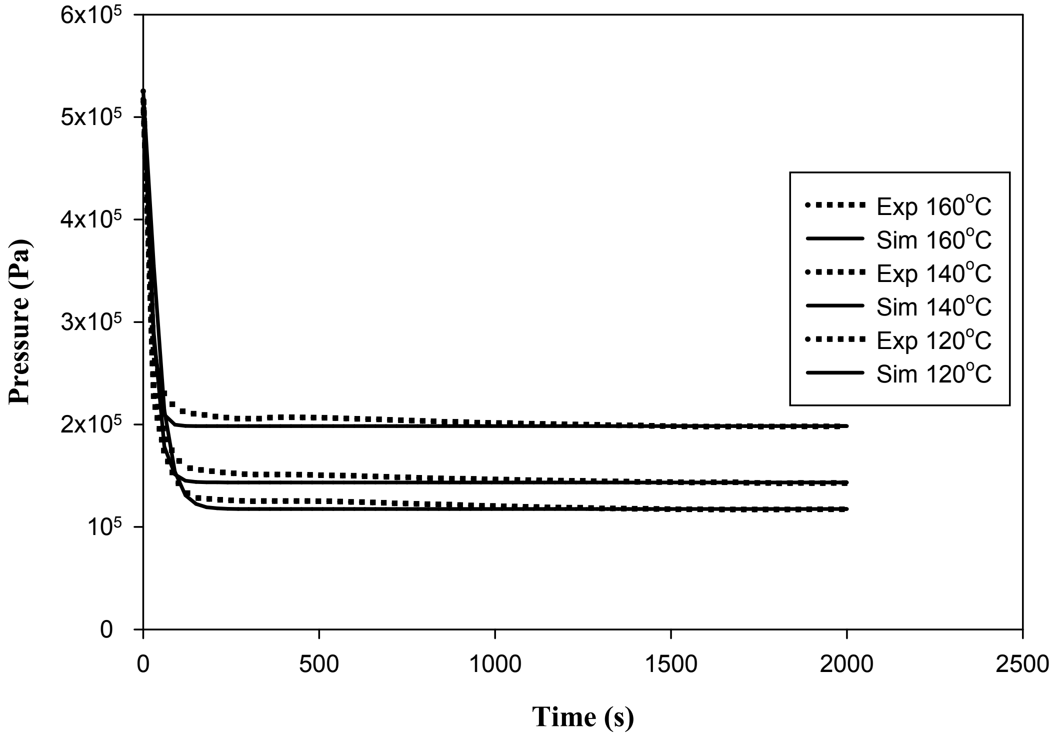


Figure 4.8 Comparison between simulation and the experimental data. The experimental data was taken from the experiment which applied different temperatures (120, 140 and 160ºC) in the reaction between H_2S and H_2SO_4 to analyzed final SO_2 partial pressure. This figure shows that the model fits the data well.

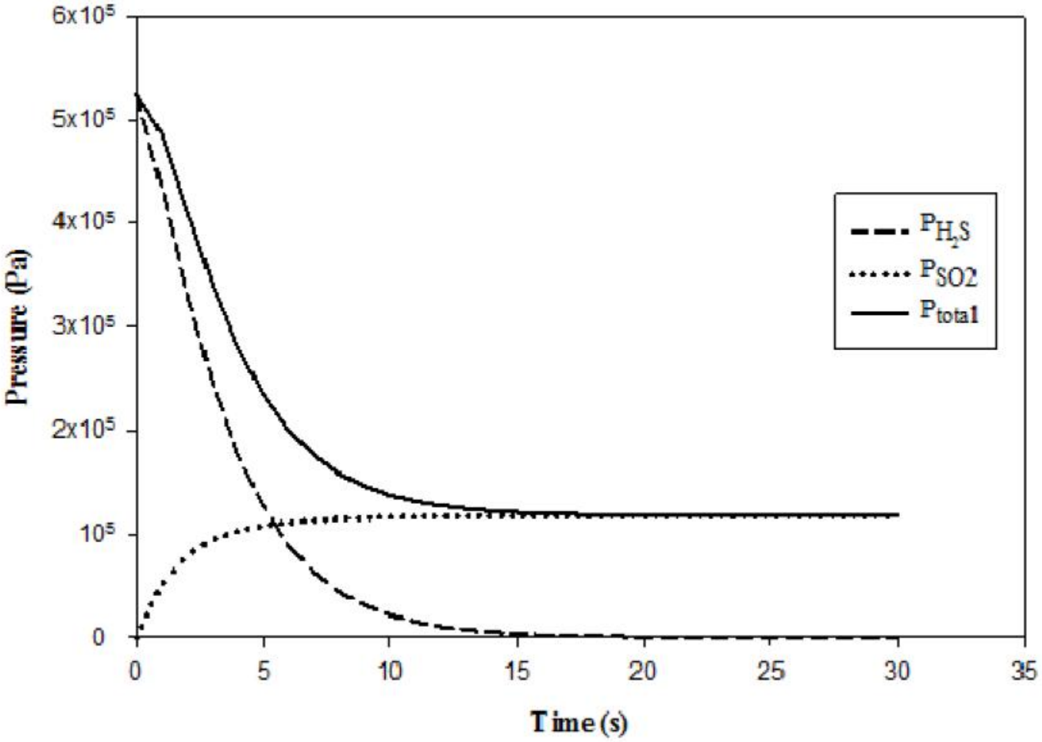


Figure 4.9 Changes in partial pressure of H_2S, SO_2 and in total pressure during the reaction between H_2S and H_2SO_4. Through the simulation results this graph was built for the total pressure and for the partial pressure of H_2S and SO_2.

4.4 Sulfur production

4.4.1 Separation between H_2SO_4 and sulfur

The sulfur produced after the reaction between hydrogen sulfide and sulfuric acid, stays with the remaining sulfuric acid. To investigate the separation between H_2SO_4 solution and sulfur, the solution of sulfuric acid was heated with commercial elemental sulfur in the contact chamber, using a temperature of 120ºC. After collecting the sulfur from the sampling chamber, it was washed and the water used for washing was analyzed by titration. The collected molten sulfur samples did not show trace of acid solution. Titration results of the water samples collected from washing the molten sulfur samples indicated neutral solutions; hence, absence of acid content.

The change of the acid concentration using 88 and 96 wt% were analyzed after the contacting experiments and the results of each concentration were 97.13 ±0.34 wt% and 88.38 ± 0.07 wt%, respectively. The comparison between the acid concentration before and after the experiment showed that the sulfuric acid concentrations did not change significantly from their initial values. Therefore, it can be concluded that there are not change of sulfuric acid concentration after being in contact with elemental sulfur in the oven for two hours.

An analysis using the produced elemental sulfur with downgraded sulfuric acid from the reaction between hydrogen sulfide and sulfuric acid was conducted. During the reaction, droplets of sulfur were formed and stayed in the bottom of the reactor in the solution of sulfuric acid (Figure 4.10) due to the sulfur being hydrophobic. After the reaction, this two-phase mixture was transferred to a beaker and was taken to the oven for two hours at 140°C. Through this analysis, the sulfuric acid solution became clearer than before going to the oven. In addition, the droplets of elemental sulfur agglomerate forming one large droplet (Figure 4.11). Therefore, through the heating process there is good separation between elemental sulfur and sulfuric acid solution.

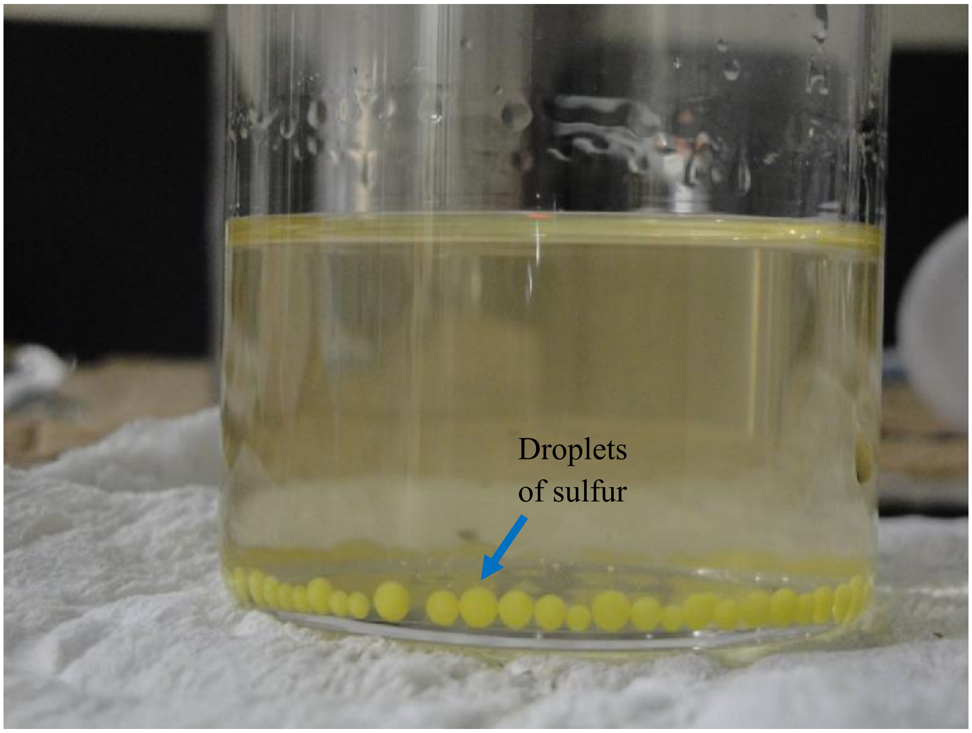


Figure 4.10 Droplets of sulfur with the solution of sulfuric acid after reaction.

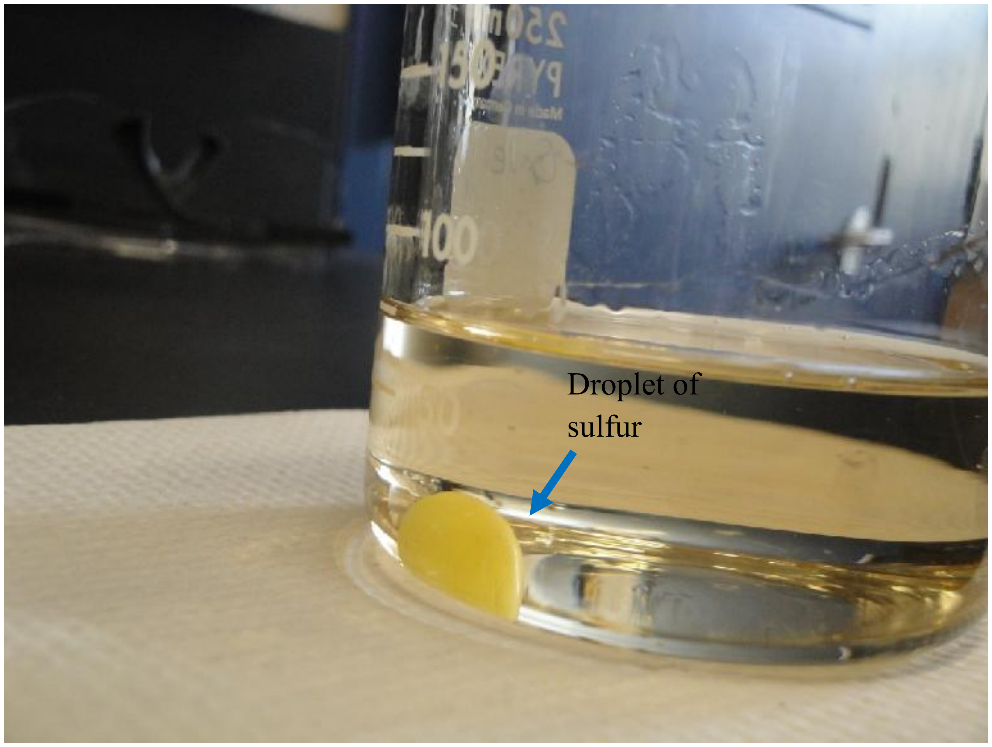


Figure 4.11 Droplet of elemental sulfur after staying 2 hours in the oven at 140 °C.

4.4.2 Sulfur crystal structure

According to Steudel and Eckert (2003), elemental sulfur has many allotropes, Sα, orthorhombic sulfur, is the one that is commercially available. After analyzing the separation between remaining sulfuric acid solution and sulfur, the structure of produced elemental sulfur was investigated. The objective was to compare the crystal structure between commercial sulfur and the sulfur produced from the reaction between sulfuric acid and hydrogen sulfide. The sulfur samples were taken to be evaluated in crystallography. The samples could not be analyzed through the crystallography because single crystals of sulfur could not be found; for this reason the samples were analyzed using X-ray powder diffraction (XRD) which is used for very small crystallites. The results indicated that the crystal structure of commercial and produced elemental sulfur presented the same structure, α-sulfur (Figure 4.12).

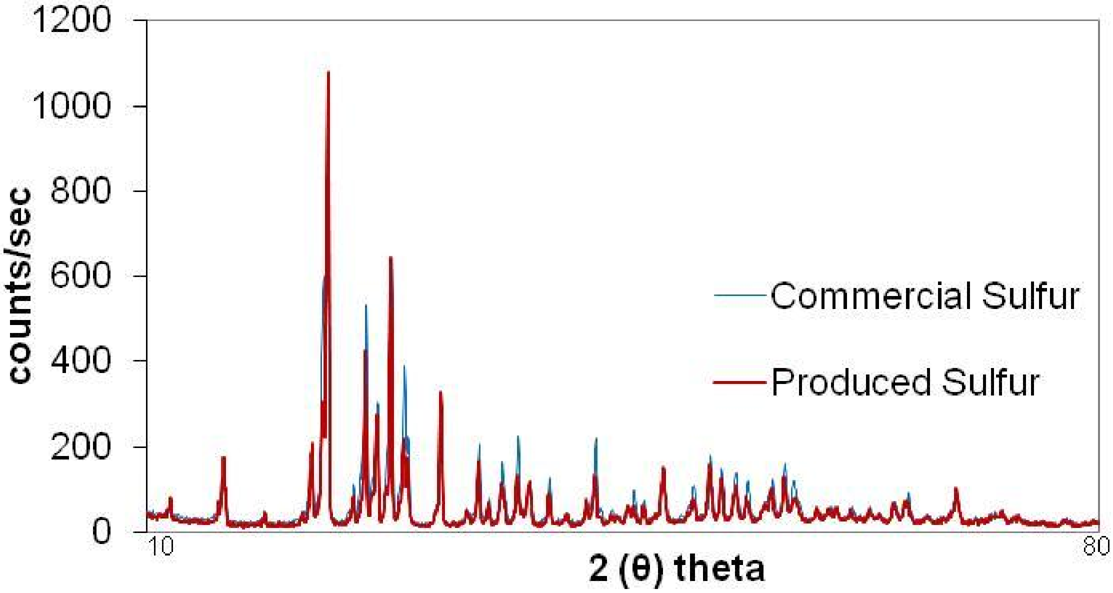


Figure 4.12 X-ray powder diffraction analysis of commercial and produced elemental sulfur from the reaction between H_2S and H_2SO_4. The graph shows that the produced elemental sulfur has the same structure of the commercial sulfur, therefore orthorhombic sulfur.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The main objective of this thesis was to investigate different operating conditions such as temperature, stirring rate and acid concentration to maximize SO_2 production in the reaction between hydrogen sulfide and sulfuric acid. In addition, the phase separation between remaining sulfuric acid after reaction and produced elemental sulfur were analyzed. According to the experimental results, the following conclusions are made:

1. Increasing the temperature in the reaction between H_2S and H_2SO_4 increased the SO_2 production.
2. There is no need for applying stirring in the reaction between H_2S and H_2SO_4 in a close reactor system. The experimental results showed that more SO_2 was produced when no stirring was applied.
3. Higher initial H_2SO_4 acid concentration for the reaction between H_2S and H_2SO_4 resulted in more SO_2 production.
4. There is a good fit when the experimental was compared with simulated data using the two equation models (4.3 and 4.4). These equations can simulate the partial pressure change of hydrogen sulfide and sulfur dioxide

$$\frac{dx_1}{dt} = -K\,(k_{p1}x_1 + k_{p2}x_1x_2) \tag{4.3}$$

$$\frac{dx_2}{dt} = K\,(k_{p1}x_1 - \frac{1}{2}\,k_{p2}x_1x_2) \tag{4.4}$$

5. There is no sulfuric acid content in elemental sulfur after the reaction between H_2S and H_2SO_4 reaction. There is a good separation between sulfuric acid and elemental sulfur after being heated.
6. According to X-ray diffraction analysis, elemental sulfur produced in H_2S-H_2SO_4 reaction has the same structure as the commercial elemental sulfur, α-sulfur.

5.2 Recommendations

The parameters to maximize the production of SO_2 on the reaction between hydrogen sulfide and sulfuric acid were investigated. Further investigation needs to be conducted to see to integrate the sulfur dioxide produced into the following reaction, Bunsen reaction. In addition,

The study on the separation between remaining sulfuric acid and produced elemental sulfur showed that the two components separate well after being heated. Further research on the type of separator equipment and its material needs to be investigated; moreover because sulfuric acid is also produced in the Bunsen reaction, a study on how integrate both of acid solutions to be reused in the H_2S splitting cycle and how many times can be used on the reaction between hydrogen sulfide and sulfuric acid.

The analysis on structure of produced elemental sulfur from the reaction between H_2S and H_2SO_4 showed that it can be commercialized. The literature indicates that Canada is one of the countries that has high production on sulfur.

Research on use of the produced elemental sulfur from this reaction to be converted into SO_2 is suggested and also how the elemental sulfur will be stored.

References

Baade, W. F., Parekh, U. N. and Raman, V. S. “Hydrogen.” Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons, New York, (2001).

Balat, M. “Potential importance of hydrogen as a future solution to environmental and transportation problems.” *International Journal of hydrogen Energy*, 33(15), 4013-4029 (2008).

Cheswoth. W. “Encyclopedia of soil science.” Springer, Netherlands, (2008).

Clark, P. D. “ Sulfur and hydrogen sulfide recovery.” Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons, New York, (2006).

Fanchi, J. R. “Energy in the 21st century.” World Scietific, Hackensack, (2005).

Gary, J. H. and Handwerk,G. E. “Petroleum refining: technology and economics.” M.Dekker, New York, (2001).

Gary, J. H. and Handwerk, G. E. “Petroleum refining: technology and economics.” M.Dekker, New York, (2007).

Granovskii, M., Dincer, I. and Rosen, M. A. “Environmental and economic aspects of hydrogen production and utilization in fuel cell vehicles.” *Journal of Power Sources*, 157(1), 411-421, (2006).

Holleman, A. F. and Wilberg, E. “ Inorganic chemistry.” Academic Press, Berlin, (2001).

Huang, C. and A.T-Raissi. “Analysis of sulfur-iodine thermochemical cycle for solar hydrogen production. Part I: decomposition of sulfuric acid.” *Solar Energy*, 78(5), 632-646, (2005).

Kabe, T., Qian, W. and Ishihara, A. “Hydrodesulfurization and hydrodenitrogenation: chemistry and engineering.” Wiley-VCH, New York, (1999).

Kane, C. and Revankar, S. T. “Sulfur-iodine thermochemical cycle: HI decomposition flow sheet analysis.” *International Journal of Hydrogen Energy,* 33(21), 5996-6005, (2008).

Kohl, A. L. and Nielsen, R. “Gas purification.” Gulf Publications, Houston, (2007).

Kothari, R., Buddhi, D. and Sawhey,R. L. “Comparison of environmental and economic aspects of various hydrogen production methods.” *Renewable and Sustainable Energy Reviews*, 12(2), 553-563, (2008).

Kutney, G. “Sulfur: history, technology, applications and industry.” ChemTec Publishing, Toronto, (2007).

Lee, S., Speight, J. G. and Loyalka, S. K. “Handbook of alternative fuel technologies.” CRC Press, USA, (2007).

Levi, M. A. “The Canadian oil sands: energy security vs. climate change.” Council on Foreign Relations, USA, (2009).

Naterer, G., Suppiah, S., Lewis, M. and Gabriel, K., Dincer, I., Rosen, M. A., Fowler, M., Rizvi, G., Easton, E.B. and Ikeda, B. M. “Recent Canadian adances in nuclear-based hydrogen production and the thermochemical Cu-Cl cycle.” *International Journal of Hydrogen Energy*, 34(7), 2901-2917, (2009).

Nickless, G. “Inorganic sulphur chemistry.” Elsevier Publication Company, New York-Amsterdam, (1968).

Perry, R.H. “Perry’s chemical engineers’ handbook”. McGraw-Hill, New York, (1997).

Salary, R., Nasr, J., Reza, M., Amidpour, M. and Kamalinejad, M. "Design of oil refineries hydrogen network using process integration principles." *Iran Journal of Chemistry and Chemical Engineering,* 27(4), 1-16, (2008).

Schindler, D. K. J. and Zittel, W. "Crude oil- the supply outlook." Energy Watch Group, 1-101, (2007)

Schmidt, M. "The scientific basis for pratical application of elemental sulfur". *Advances in Chemistry*, 165, (1978).

Soderbergh, B., Robelius, F. and Aleklett, K. " A crash programme scenario for the Canadian oil sands industry." *Energy Policy*, 35(3), 1931-1947, (2007).

Soderbergh, B. "Canada's oil sands resources and its future impact on global oil supply." MSc. Thesis, Uppsala University, Australia, (2005).

Speight, J. G. "Fuel science and technology handbook." M.Dekker, New York, (1990).

Steudel, R. "Liquid sulfur." *Topics in Current Chemistry*, 230, 81-116, (2003).

Steudel, R. and Eckert, B. "Solid sulfur allotropes." *Topics in Current Chemistry*, 230, 1-80, (2003).

Vitart, X., Le Duigou, A. and Carles, P. "Hydrogen production using the sulfur-iodine cycle coupled to a VHTR: an overview." *Energy Conversion and Management*, 47(17), 2740-2747, (2006).

Wang, H., Dalla Lana, I. G. and Chuang, K. T. "Kinetics and mechanism of oxidation of hydrogen sulfide by concentrated sulfuric acid." *Industrial and Engineering Chemistry Research*, 41(26), 6656-6662, (2002a).

Wang, H., Dalla Lana, I. G. and Chuang, K. T. "Kinetics of reaction between hydrogen sulfide and sulfur dioxide in sulfuric acid solutions." *Industrial and Engineering Chemistry Research*, 41(19), 4707-4713, (2002b).

Wang, H., "A study of the gas-liquid reaction system of hydrogen sulfide and sulfuric acid." Ph.D. Thesis, University of Alberta, Canada, (2003).

Wang, H. "Hydrogen production from a chemical cycle of H_2S splitting." *International Journal of Hydrogen Energy*, 32(16), 3907-3914, (2007).

Yildiz, B. and Kazimi, M. S. "Efficieny of hydrogen production system using alternative nuclear energy technologies." *International Journal of hydrogen Energy*, 31(1), 77-92, (2006).

Zhang, Q., Wang, H., Dalla Lana, I. G. and Chuang, K. T. "Solubility of sulfur dioxide in Sulfuric acid of high concentration." *Industrial and Engineering Chemistry Research*, 37(3), 1167-1172, (1998).

Zhang, Q., Dalla Lana, I. G., Chuang, K. T. and Wang, H., "Reactions between hydrogen sulfide and sulfuric acid: a novel process for sulfur removal and recovery." *Industrial and Engineering Chemistry Research*, 39(7), 2505-2509, (2000).

Web sites:

Alberta Chamber of Resources, (2004). "Oil sands technology roadmap."Acessed: October, 2010, http://www.acr-alberta.com/OSTR_report.pdf .

CAPP (Canadian Association of Petroleum Producers), (2009). "Canadian oil and natural gas overview and outlook." Acessed: October, 2010. http://www.capp.ca/library/presentations/Pages/default.asp#JoyqKKul459F

NEB (The Canadian National Energy Board), (2008). "Canadian energy overview." Acessed: October, 2010. http://www.neb-one.gc.ca/clf-nsi/rnrgynfmtn/nrgyrprt/nrgyvrvw/cndnnrgyvrvw2008/cndnnrgyvrvw2008-eng.pdf

APPENDICES

Appendix A: Calibration curves for mass flow controllers

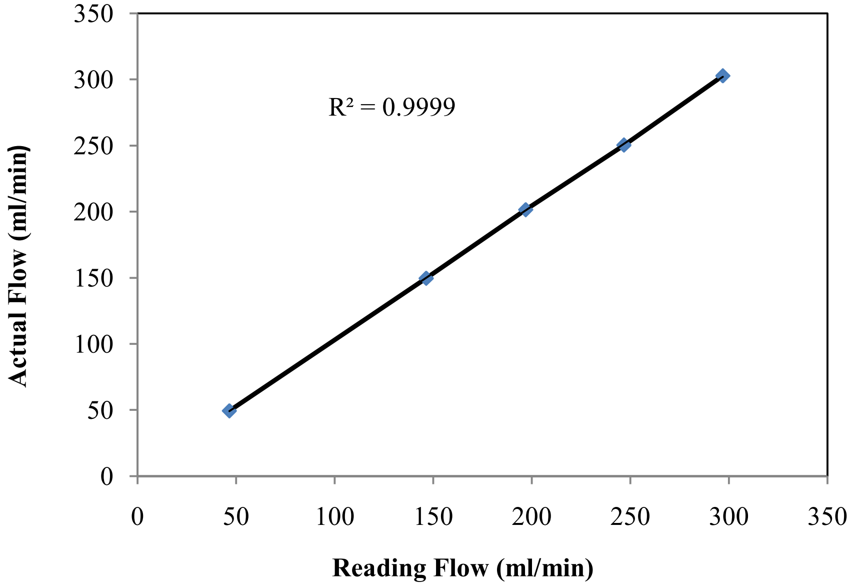


Figure A.1: Calibration curve for mass flow controller 5850S (maximum flow: 1000mL/min).

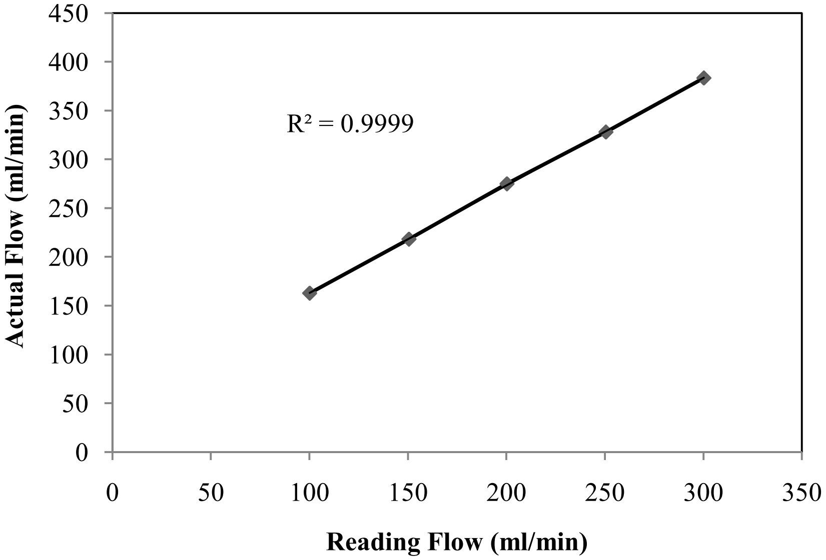


Figure A.1: Calibration curve for mass flow controller 5850S (maximum flow: 10000mL/min).

Appendix B: Experimental raw data

The reading for the pressure for each experimental condition (temperature, stirring rate and acid concentration) was through the transducer in which the unit of the pressure was in Psi. Because the transducer read the pressure for every second, the tables with experimental raw data presented in this appendix only shows the first 60 seconds after the reaction between H_2S and H_2SO4 started to save space.

Table B1: Experimental data for the effect of temperature on SO_2 production

	Temperatures (ºC)		
	120	140	160
Time (s)	Pressure (Psi)	Pressure (Psi)	Pressure (Psi)
0	60.702	60.677	60.769
1	45.623	57.029	39.336
2	36.197	36.785	36.720
3	35.817	36.217	36.500
4	35.960	36.022	36.390
5	35.658	36.106	36.491
6	35.165	36.181	36.630
7	34.784	36.083	36.832
8	34.432	36.422	37.123
9	33.842	36.731	37.347
10	33.732	36.777	37.741
11	33.166	36.987	37.923
12	32.886	37.170	38.053
13	32.689	37.118	38.457

Table B1: Experimental data for the effect of temperature on SO_2 production (cont).

14	32.380	37.104	38.576
15	32.140	37.119	39.102
16	31.996	37.419	39.440
17	31.770	37.543	39.712
18	31.626	37.784	39.975
19	31.479	38.091	40.191
20	31.330	38.090	40.407
21	31.200	38.084	40.532
22	31.107	38.083	40.994
23	30.935	38.173	41.361
24	30.657	38.462	41.623
25	30.530	38.699	41.881
26	30.396	38.641	42.139
27	30.311	38.952	42.399
28	30.311	38.952	42.510
29	30.135	38.953	42.862
30	30.109	39.211	43.223
31	29.934	39.117	43.282
32	29.785	39.419	43.735
33	29.670	39.856	43.918
34	29.712	39.949	43.818
35	29.604	40.061	43.964
36	29.407	40.169	43.838
37	29.301	39.831	43.958
38	29.370	40.149	43.908
39	29.144	40.443	43.739

Table B1: Experimental data for the effect of temperature on SO_2 production (cont).

40	29.047	41.012	43.629
41	29.087	41.295	43.546
42	28.995	41.793	43.434
43	28.805	42.261	43.367
44	28.693	42.974	43.015
45	28.661	43.441	43.219
46	28.555	43.906	43.111
47	28.502	44.273	42.792
48	28.406	41.951	42.975
49	28.446	41.623	42.901
50	28.257	41.664	42.854
51	28.171	41.516	42.547
52	28.243	41.722	42.740
53	28.041	41.670	42.662
54	28.017	41.615	42.640
55	27.934	41.773	42.314
56	27.904	41.775	42.499
57	27.826	41.775	42.455
58	27.780	42.029	42.392
59	27.740	42.189	42.336
60	27.694	42.103	42.032

Table B2: Experimental data for the effect of stirring rate on SO_2 production.

	Stirring speed			
	No stirring	100 RPM	200 RPM	400 RPM
Time (s)	Pressure (Psi)	Pressure (Psi)	Pressure (Psi)	Pressure (Psi)
0	56.089	60.571	60.421	61.498
1	49.583	36.015	35.172	42.890
2	31.614	35.626	35.192	35.683
3	30.742	35.381	35.080	35.585
4	29.902	35.291	33.866	34.446
5	29.233	33.777	33.120	33.552
6	28.682	32.773	32.417	32.177
7	28.164	32.143	31.754	31.254
8	27.940	31.142	30.559	30.462
9	27.486	31.065	29.669	29.736
10	27.101	30.363	28.940	28.807
11	26.902	30.015	28.243	27.778
12	26.715	28.970	27.711	27.619
13	26.462	28.105	26.960	26.541
14	26.149	27.424	26.601	25.755
15	26.099	26.898	25.678	25.144
16	25.779	26.278	25.490	24.595
17	25.691	25.549	24.627	24.242
18	25.524	25.201	23.898	23.472
19	25.357	24.437	23.512	23.024
20	25.216	23.797	23.040	22.294

Table B2: Experimental data for the effect of stirring rate on SO_2 production (cont).

21	25.065	23.266	22.708	21.638
22	24.965	22.679	22.182	21.285
23	24.819	22.205	21.926	20.627
24	24.776	21.875	21.267	20.363
25	24.742	21.610	20.877	19.919
26	24.567	20.934	20.620	19.594
27	24.379	20.563	20.110	19.052
28	24.301	20.012	19.841	18.614
29	24.216	19.754	19.475	18.373
30	24.125	19.264	19.026	17.821
31	23.908	18.973	18.742	17.552
32	23.930	18.700	18.162	17.223
33	23.774	18.046	17.972	16.966
34	23.659	17.856	17.613	16.529
35	23.718	17.609	17.436	16.176
36	23.609	17.318	17.030	15.878
37	23.406	16.904	16.861	15.584
38	23.457	16.626	16.426	15.349
39	23.250	16.481	16.161	14.953
40	23.316	16.041	15.899	14.795
41	23.234	15.944	15.597	14.488
42	23.196	15.509	15.401	14.279
43	23.098	15.318	15.067	13.924
44	22.898	15.132	14.972	13.671
45	22.970	14.832	14.595	13.440
46	22.770	14.682	14.397	13.125

Table B2: Experimental data for the effect of stirring rate on SO_2 production (cont).

47	22.848	14.380	14.229	13.032
48	22.659	14.255	13.971	12.703
49	22.725	13.970	13.805	12.589
50	22.543	13.796	13.459	12.294
51	22.622	13.602	13.289	12.094
52	22.398	13.250	13.070	11.837
53	22.475	13.131	12.907	11.565
54	22.307	12.989	12.725	11.487
55	22.362	12.848	12.547	11.221
56	22.191	12.675	12.406	11.111
57	22.139	12.419	12.169	10.758
58	22.233	12.288	12.006	10.643
59	22.032	12.105	11.771	10.473
60	22.122	11.884	11.641	10.278

Table B3: Experimental data for the effect of sulfuric acid concentration on SO_2 production.

	Sulfuric acid concentration		
	90 wt%	93 wt%	96 wt%
Time (s)	Pressure (Psi)	Pressure (Psi)	Pressure (Psi)
0	60.305	60.467	56.089
1	47.965	45.392	49.583
2	35.060	34.853	31.614
3	35.093	34.895	30.742
4	35.187	34.749	29.902
5	35.387	34.495	29.233
6	35.481	33.786	28.682
7	35.295	33.459	28.164
8	35.282	32.550	27.940
9	35.177	32.067	27.486
10	35.081	31.839	27.101
11	34.755	31.402	26.902
12	34.579	31.242	26.715
13	34.485	30.935	26.462
14	34.068	30.792	26.149
15	33.859	30.487	26.099
16	33.626	30.365	25.779
17	33.692	30.098	25.691
18	33.224	29.796	25.524
19	33.154	29.749	25.357
20	32.880	29.420	25.216

Table B3: Experimental data for the effect of sulfuric acid concentration on SO_2 production (cont).

21	32.713	29.291	25.065
22	32.561	29.213	24.965
23	32.404	29.115	24.819
24	32.263	28.807	24.776
25	32.109	28.664	24.742
26	32.033	28.550	24.567
27	31.780	28.402	24.379
28	31.652	28.309	24.301
29	31.546	28.143	24.216
30	31.485	28.098	24.125
31	31.262	27.966	23.908
32	31.153	27.816	23.930
33	31.070	27.864	23.774
34	30.885	27.652	23.659
35	30.828	27.549	23.718
36	30.653	27.467	23.609
37	30.554	27.396	23.406
38	30.432	27.268	23.457
39	30.307	27.156	23.250
40	30.216	27.093	23.316
41	30.069	26.994	23.234
42	30.069	26.915	23.196
43	29.875	26.806	23.098
44	29.770	26.775	22.898
45	29.718	26.669	22.970
46	29.597	26.588	22.770

Table B3: Experimental data for the effect of sulfuric acid concentration on SO_2 production (cont).

47	29.562	26.522	22.848
48	29.443	26.441	22.659
49	29.266	26.372	22.725
50	29.260	26.310	22.543
51	29.179	26.139	22.622
52	29.104	26.172	22.398
53	28.997	26.122	22.475
54	28.965	26.039	22.307
55	28.863	25.976	22.362
56	28.814	25.923	22.191
57	28.699	25.845	22.139
58	28.503	25.825	22.233
59	28.553	25.747	22.032
60	28.459	25.714	22.122

Table B4: Experimental and simulation data for kinetics analysis SO_2 production.

	Temperatures (ºC)					
	120		140		160	
	Experimental data	Simulation data	Experimental data	Simulation data	Experimental data	Simulation data
Time (s)	Pressure (Psi)	Pressure (Psi)	Pressure (Psi)	Pressure (Psi)	Pressure (Psi)	Pressure (Psi)
0	61.498	61.498	60.006	60.006	60.352	60.352
1	42.890	61.433	34.843	59.887	51.329	60.190
2	35.683	61.244	34.959	59.550	42.065	59.733
3	35.585	60.944	34.753	59.021	37.730	59.026
4	34.446	60.541	34.718	58.324	36.904	58.111
5	33.552	60.046	34.269	57.485	36.368	57.026
6	32.177	59.467	32.766	56.523	35.965	55.803
7	31.254	58.815	31.732	55.460	35.643	54.475
8	30.462	58.100	31.096	54.311	35.316	53.065
9	29.736	57.325	30.029	53.095	34.602	51.598
10	28.807	56.500	29.443	51.826	33.387	50.098

Table B4: Experimental and simulation data for kinetics analysis SO_2 production (cont).

11	27.778	55.631	28.524	50.518	33.126	48.578
12	27.619	54.724	28.149	49.180	32.032	47.055
13	26.541	53.787	27.295	47.827	31.320	45.539
14	25.755	52.824	27.057	46.466	30.680	44.039
15	25.144	51.839	26.157	45.103	30.060	42.570
16	24.595	50.838	25.635	43.746	29.474	41.134
17	24.242	49.826	25.137	42.400	28.747	39.736
18	23.472	48.804	24.687	41.070	28.541	38.379
19	23.024	47.778	24.325	39.757	27.869	37.071
20	22.294	46.751	23.630	38.468	27.594	35.811
21	21.638	45.725	23.468	37.206	27.044	34.599
22	21.285	44.701	22.879	35.974	26.510	33.440
23	20.627	43.686	22.400	34.771	26.133	32.335
24	20.363	42.676	22.088	33.600	25.767	31.281
25	19.919	41.675	21.553	32.461	25.417	30.275

Table B4: Experimental and simulation data for kinetics analysis SO_2 production (cont).

26	19.594	40.683	21.449	31.359	24.953	29.321
27	19.052	39.704	20.872	30.290	24.830	28.413
28	18.614	38.732	20.588	29.257	24.406	27.554
29	18.373	37.772	20.052	28.259	24.065	26.739
30	17.821	36.825	19.663	27.296	23.845	25.967
31	17.552	35.892	19.467	26.369	23.478	25.239
32	17.223	34.977	19.035	25.476	23.253	24.553
33	16.966	34.077	18.789	24.615	23.039	23.903
34	16.529	33.195	18.453	23.789	22.896	23.292
35	16.176	32.331	18.288	22.994	22.625	22.718
36	15.878	31.482	17.909	22.231	22.290	22.176
37	15.584	30.654	17.512	21.497	22.121	21.666
38	15.349	29.842	17.369	20.796	21.921	21.188
39	14.953	29.048	17.006	20.122	21.725	20.735
40	14.795	28.272	16.911	19.476	21.462	20.313

Table B4: Experimental and simulation data for kinetics analysis SO_2 production (cont).

41	14.488	27.514	16.577	18.857	21.355	19.914
42	14.279	26.775	16.432	18.266	21.081	19.540
43	13.924	26.054	16.032	17.701	20.954	19.190
44	13.671	25.349	15.858	17.158	20.796	18.863
45	13.440	24.665	15.590	16.642	20.607	18.554
46	13.125	23.996	15.364	16.147	20.471	18.265
47	13.032	23.346	15.202	15.674	20.310	17.997
48	12.703	22.712	15.050	15.223	20.133	17.743
49	12.589	22.094	14.910	14.792	20.054	17.506
50	12.294	21.495	14.586	14.380	19.765	17.283
51	12.094	20.911	14.432	13.987	19.667	17.075
52	11.837	20.344	14.292	13.612	19.516	16.880
53	11.565	19.791	14.029	13.255	19.419	16.697
54	11.487	19.253	13.927	12.914	19.369	16.526

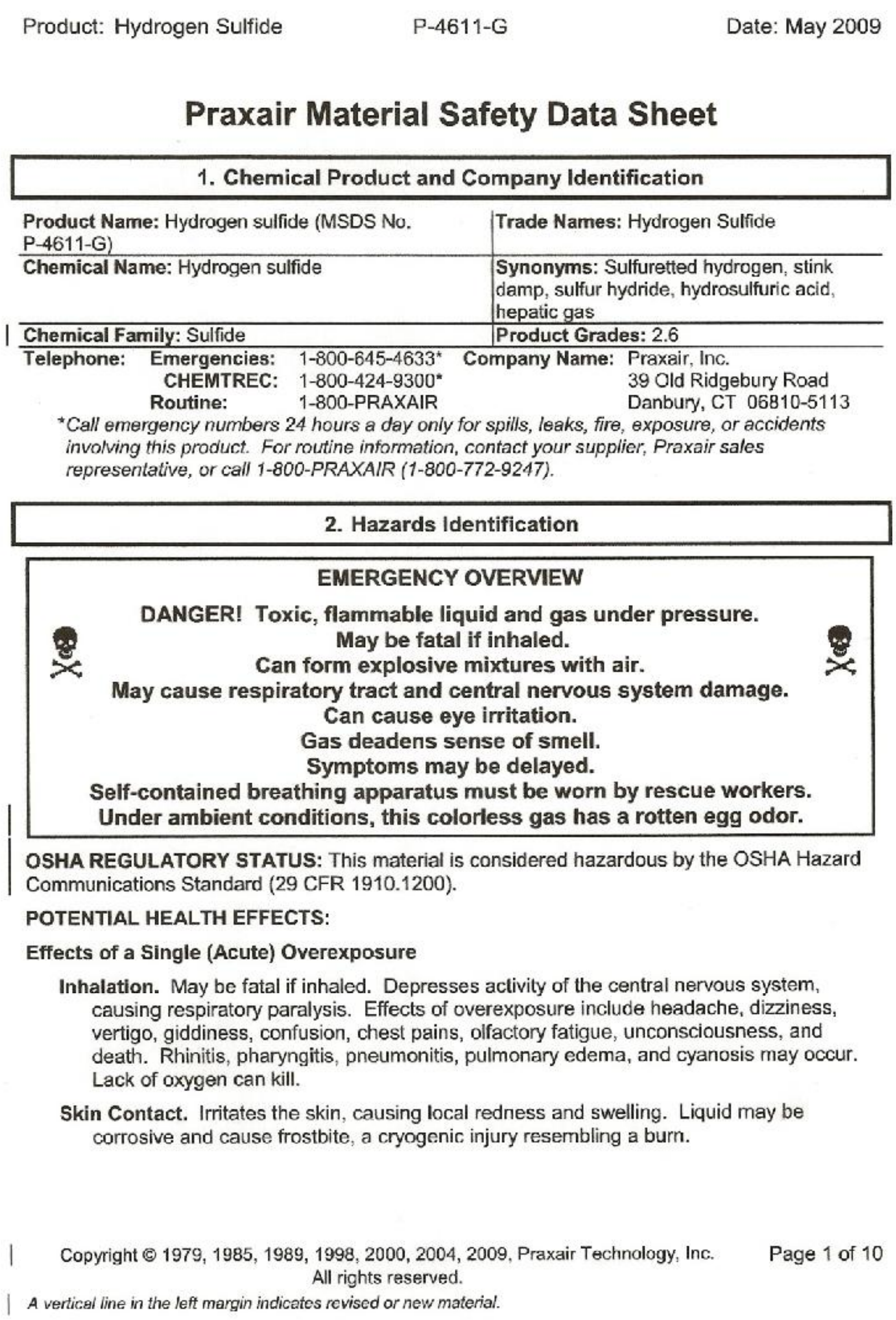
Table B4: Experimental and simulation data for kinetics analysis SO_2 production (cont).

55	11.221	18.732	13.695	12.587	19.325	16.365
56	11.111	18.224	13.632	12.276	19.055	16.217
57	10.758	17.731	13.424	11.980	18.933	16.077
58	10.643	17.252	13.243	11.697	18.978	15.947
59	10.473	16.788	13.125	11.430	18.833	15.825
60	10.278	16.336	12.892	11.173	18.633	15.709

Appendix C:

Praxair Material Safety data Sheet (MSDS) for hydrogen sulfide and

EMD Material Safety Data Sheet (MSDS) for Sulfuric acid solution



Praxair Material Safety Data Sheet

1. Chemical Product and Company Identification

Product Name: Hydrogen sulfide (MSDS No. P-4611-G)	**Trade Names:** Hydrogen Sulfide
Chemical Name: Hydrogen sulfide	**Synonyms:** Sulfuretted hydrogen, stink damp, sulfur hydride, hydrosulfuric acid, hepatic gas
Chemical Family: Sulfide	**Product Grades:** 2.6

Telephone: **Emergencies:** 1-800-645-4633*
CHEMTREC: 1-800-424-9300*
Routine: 1-800-PRAXAIR

Company Name: Praxair, Inc.
39 Old Ridgebury Road
Danbury, CT 06810-5113

**Call emergency numbers 24 hours a day only for spills, leaks, fire, exposure, or accidents involving this product. For routine information, contact your supplier, Praxair sales representative, or call 1-800-PRAXAIR (1-800-772-9247).*

2. Hazards Identification

EMERGENCY OVERVIEW

DANGER! Toxic, flammable liquid and gas under pressure.
May be fatal if inhaled.
Can form explosive mixtures with air.
May cause respiratory tract and central nervous system damage.
Can cause eye irritation.
Gas deadens sense of smell.
Symptoms may be delayed.
Self-contained breathing apparatus must be worn by rescue workers.
Under ambient conditions, this colorless gas has a rotten egg odor.

OSHA REGULATORY STATUS: This material is considered hazardous by the OSHA Hazard Communications Standard (29 CFR 1910.1200).

POTENTIAL HEALTH EFFECTS:

Effects of a Single (Acute) Overexposure

Inhalation. May be fatal if inhaled. Depresses activity of the central nervous system, causing respiratory paralysis. Effects of overexposure include headache, dizziness, vertigo, giddiness, confusion, chest pains, olfactory fatigue, unconsciousness, and death. Rhinitis, pharyngitis, pneumonitis, pulmonary edema, and cyanosis may occur. Lack of oxygen can kill.

Skin Contact. Irritates the skin, causing local redness and swelling. Liquid may be corrosive and cause frostbite, a cryogenic injury resembling a burn.

A vertical line in the left margin indicates revised or new material.

Swallowing. A highly unlikely route of exposure; this product is a gas at normal temperature and pressure, but frostbite of the lips and mouth may result from contact with the liquid.

Eye Contact. Irritates the eyes, causing excess redness of the conjunctiva. Prolonged exposure to vapor at low concentrations may cause painful conjunctivitis and corneal injury with vesiculation of the corneal epithelium.

Effects of Repeated (Chronic) Overexposure. Repeated exposure may cause nausea, vomiting, weight loss, persistent low blood pressure, and loss of the sense of smell.

Other Effects of Overexposure. Survivors sometimes exhibit neurologic sequelae such as amnesia, intention tremor, neurasthenia, disturbance of equilibrium, or more-serious brain stem and cortical damage.

Medical Conditions Aggravated by Overexposure. Breathing of vapor or mist may aggravate asthma and inflammatory or fibrotic pulmonary disease.

CARCINOGENICITY: Hydrogen sulfide is not listed by NTP, OSHA, or IARC.

POTENTIAL ENVIRONMENTAL EFFECTS: None known. For further information, see section 12, Ecological Information.

3. Composition/Information on Ingredients

See section 16 for important information about mixtures.

COMPONENT	CAS NUMBER	CONCENTRATION
Hydrogen Sulfide	7783-06-4	>99%*

**The symbol > means "greater than."*

4. First Aid Measures

INHALATION: Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, qualified personnel may give oxygen. Call a physician.

SKIN CONTACT: Remove contaminated clothing and flush skin with plenty of water. For exposure to liquid, immediately warm frostbite area with warm water, not to exceed 105°F (41° C). In case of massive exposure, remove clothing while showering with warm water. Call a physician. Wash clothing before reuse.

SWALLOWING: An unlikely route of exposure. This product is a gas at normal temperature and pressure.

EYE CONTACT: For contact with the liquid, immediately flush eyes thoroughly with water for at least 15 minutes. Hold the eyelids open and away from the eyeballs to ensure that all surfaces are flushed thoroughly. See a physician, preferably an ophthalmologist, immediately.

NOTES TO PHYSICIAN: *Keep victim under observation for delayed onset of pulmonary edema. There is no specific antidote. Treatment of overexposure should be directed at the control of symptoms and the clinical condition of the patient.*

Contact the Poison Control Center in your area for additional information on patient management and follow-up.

5. Fire Fighting Measures

FLAMMABLE PROPERTIES: Toxic, flammable, corrosive gas.

SUITABLE EXTINGUISHING MEDIA: CO_2, dry chemicals, water spray, or fog.

PRODUCTS OF COMBUSTION: Sulfur dioxide. Sulfur and hydrogen are products of thermal decomposition. (See section 10.)

PROTECTION OF FIREFIGHTERS: DANGER! Toxic, flammable liquid and gas under pressure. Evacuate all personnel from danger area. Do not approach area without self-contained breathing apparatus and protective clothing. Immediately cool cylinders with water spray from maximum distance, taking care not to extinguish flames. Remove ignition sources if without risk. If flames are accidentally extinguished, explosive reignition may occur. Totally evacuate area and reapproach with extreme caution. Reduce corrosive vapors with water spray or fog. Reverse flow into cylinder may cause rupture. Stop flow of gas if without risk while continuing water spray. Remove all cylinders from area of fire if without risk. Allow fire to burn out. On-site fire brigades must comply with OSHA 29 CFR 1910.156.

Specific Physical and Chemical Hazards. Forms explosive mixtures with air and oxidizing agents. Heat of fire can build pressure in cylinder and cause it to rupture. Hydrogen sulfide cylinders are equipped with a pressure-relief device. (Exceptions may exist where authorized by DOT.) No part of a cylinder should be subjected to a temperature higher than 125°F (52°C). If venting or leaking hydrogen sulfide catches fire, do not extinguish flames. Flammable vapors may spread from leak, creating an explosive re-ignition hazard. Vapors can be ignited by pilot lights, other flames, smoking, sparks, heaters, electrical equipment, static discharge, or other ignition sources at locations distant from product handling point. Explosive atmospheres may linger. Before entering area, especially confined areas, check atmosphere with an appropriate device. Vapors are irritating. Contact may cause skin and eye burns. Hydrogen sulfide deadens the sense of smell; some means of detecting its presence other than smell should be readily available.

Protective Equipment and Precautions for Firefighters. Firefighters should wear self-contained breathing apparatus and full fire-fighting turnout gear.

6. Accidental Release Measures

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED:

DANGER! Toxic, flammable liquid and gas under pressure.

Personal Precautions. Forms explosive mixtures with air. Immediately evacuate all personnel from danger area. Use self-contained breathing apparatus where needed. Remove all sources of ignition if without risk. Reduce vapors with fog or fine water spray. Reverse flow into cylinder may cause it to rupture. Shut off flow if without risk. Ventilate area or move leaking cylinder to well-ventilated area. Flammable, corrosive, toxic vapors may spread from spill. Hydrogen sulfide deadens the sense of smell. Before entering area, especially confined areas, check atmosphere with an appropriate device.

Environmental Precautions. Prevent waste from contaminating the surrounding environment. Keep personnel away. Discard any product, residue, disposable container, or liner in an environmentally acceptable manner, in full compliance with federal, state, and local regulations. If necessary, call your local supplier for assistance.

7. Handling and Storage

PRECAUTIONS TO BE TAKEN IN HANDLING: May be fatal if inhaled. Do not breathe gas. Do not get vapors or liquid in eyes, on skin, or on clothing. ***May form explosive mixtures with air.*** Keep away from heat, sparks, or open flame. Ground all equipment. Use only spark-proof tools and explosion-proof equipment. Keep away from oxidizing agents and from other flammables. Have safety showers and eyewash fountains immediately available. Protect cylinders from damage. Use a suitable hand truck to move cylinders; do not drag, roll, slide, or drop. All piped systems and associated equipment must be grounded. Electrical equipment must be non-sparking or explosion-proof. Leak check with soapy water; never use a flame. Never attempt to lift a cylinder by its cap; the cap is intended solely to protect the valve. Never insert an object (e.g., wrench, screwdriver, pry bar) into cap openings; doing so may damage the valve and cause a leak. Use an adjustable strap wrench to remove over-tight or rusted caps. Open valve slowly. If valve is hard to open, discontinue use and contact your supplier. For other precautions in using hydrogen sulfide, see section 16.

PRECAUTIONS TO BE TAKEN IN STORAGE: Store and use with adequate ventilation. Separate cylinders from oxygen and other oxidizers by at least 20 ft (6.1 m) or use a barricade of noncombustible material. This barricade should be at least 5 ft (1.53 m) high and have a fire resistance rating of at least ½ hr. Firmly secure cylinders upright to keep them from falling or being knocked over. Hydrogen sulfide cylinders designed to accept a valve protection cap must be provided with a cap. Screw cap firmly in place by hand. Post "No Smoking or Open Flames" signs in storage and use areas. There must be no sources of ignition. All electrical equipment in storage areas must be explosion-proof. Storage areas must meet national electric codes for Class 1 hazardous areas. Store only where temperature will not exceed 125°F (52°C). Store full and empty cylinders separately. Use a first-in, first-out inventory system to prevent storing full cylinders for long periods.

RECOMMENDED PUBLICATIONS: For further information on storage, handling, and use, see Praxair publication P-14-153, *Guidelines for Handling Gas Cylinders and Containers*. Obtain from your local supplier.

8. Exposure Controls/Personal Protection

COMPONENT	OSHA PEL	ACGIH TLV-TWA (2008)
Hydrogen Sulfide	20 ppm (c)*; 50 ppm, 10 min, once only, if no other measurable exposure occurs.	10 ppm; 15 ppm, 15-min STEL

*(c) – ceiling. Ceiling values are not Time-Weighted-Average (TWA).

TLV-TWAs should be used as a guide in the control of health hazards and not as fine lines between safe and dangerous concentrations.

IDLH = 100 ppm

ENGINEERING CONTROLS:

Local Exhaust. Use an explosion-proof, corrosion-resistant local exhaust system.

Mechanical (General). Inadequate. See SPECIAL.

Special. Use only in a closed system. An explosion-proof, corrosion resistant, forced-draft fume hood is preferred.

Other. None

PERSONAL PROTECTIVE EQUIPMENT:

Skin Protection. Wear work gloves when handling cylinders; neoprene, butyl rubber, or PVC gloves where contact with product may occur. Metatarsal shoes for cylinder handling; protective clothing where needed. Select in accordance with OSHA 29 CFR 1910.132 and 1910.133. Regardless of protective equipment, never touch live electrical parts.

Eye/Face Protection. Select in accordance with OSHA 29 CFR 1910.133.

Respiratory Protection. A respiratory protection program that meet OSHA 29 CFR 1910.134, ANSI Z88.2, or MSHA 30 CFR 72.710 (where applicable) requirements must be followed whenever workplace conditions warrant respirator use. Use an air-supplied or air-purifying cartridge if the action level is exceeded. Ensure the respirator has the appropriate protection factor for the exposure level. If cartridge type respirators are used, the cartridge must be appropriate for the chemical exposure (e.g., an organic vapor cartridge). For emergencies or instances with unknown exposure levels, use a self-contained breathing apparatus.

9. Physical and Chemical Properties

APPEARANCE:	Colorless gas
ODOR:	Rotten eggs. Hydrogen sulfide deadens the sense of smell.
ODOR THRESHOLD:	Not available.
PHYSICAL STATE:	Gas at normal temperature and pressure
pH:	Not applicable.
MELTING POINT at 1 atm:	-121.85°F (-85.47°C)
BOILING POINT at 1 atm:	-76.63°F (-60.35°C)
FLASH POINT (test method):	Not available.
EVAPORATION RATE (Butyl Acetate = 1):	Not available.
FLAMMABILITY:	Flammable
FLAMMABLE LIMITS IN AIR, % by volume:	**LOWER:** 4.3% **UPPER:** 46.0%
VAPOR PRESSURE at 68°F (20°C):	258.4 psia (1781 kPa abs)
VAPOR DENSITY at 70°F (21.1°C) and 1 atm:	0.0881 lb/ft^3 (1.411 kg/m^3)
SPECIFIC GRAVITY (H_2O = 1) at 60°F (15.6°C):	0.79
SPECIFIC GRAVITY (Air = 1) at 59°F (15°C) and 1 atm:	1.18
SOLUBILITY IN WATER at 68°F (20°C) and 1 atm:	0.317 lb/gal (38 kg/m^3)
PARTITION COEFFICIENT: n-octanol/water:	Not available.
AUTOIGNITION TEMPERATURE:	500°F (260°C)
DECOMPOSITION TEMPERATURE:	Not available.
PERCENT VOLATILES BY VOLUME:	100
MOLECULAR WEIGHT:	34.08
MOLECULAR FORMULA:	H_2S

10. Stability and Reactivity

CHEMICAL STABILITY: ☐ Unstable ☒ Stable

CONDITIONS TO AVOID: None known.

INCOMPATIBLE MATERIALS: Ammonia, bases, bromine pentafluoride, chlorine trifluoride, chromium trioxide and heat, copper (powdered copper and air), fluorine, lead, lead oxide, mercury, nitric acid, nitrogen trifluoride, nitrogen sulfide, organic compounds, oxidizing agents, oxygen difluoride, rubber, sodium and moisture, water

HAZARDOUS DECOMPOSITION PRODUCTS: Thermal decomposition may produce sulfur and hydrogen.

POSSIBILITY OF HAZARDOUS REACTIONS: ☒ May Occur ☐ Will Not Occur

Thermal decomposition may produce sulfur and hydrogen.

11. Toxicological Information

ACUTE DOSE EFFECTS: LC_{50}, 1 hr, rat = 712 ppmv

STUDY RESULTS: Although not demonstrated with hydrogen sulfide, repeated or prolonged maternal hypoxia induced by overexposure to other chemical asphyxiants has produced embryofetal toxicity in laboratory animals.

12. Ecological Information

ECOTOXICITY: No known effects.

OTHER ADVERSE EFFECTS: Hydrogen sulfide does not contain any Class I or Class II ozone-depleting chemicals.

13. Disposal Considerations

WASTE DISPOSAL METHOD: Do not attempt to dispose of residual or unused quantities. Return cylinder to supplier.

14. Transport Information

DOT/IMO SHIPPING NAME: Hydrogen sulfide

HAZARD CLASS:	2.3	**PACKING GROUP/Zone:**	NA/B	**IDENTIFICATION NUMBER:**	UN1053	**PRODUCT RQ:**	100 lb (45.4 kg)

SHIPPING LABEL(s): POISON GAS, FLAMMABLE GAS **

PLACARD (when required): POISON GAS, FLAMMABLE GAS **

**NA=Not applicable.*

***The words in the POISON GAS diamond are INHALATION HAZARD.*

SPECIAL SHIPPING INFORMATION: Cylinders should be transported in a secure position, in a well-ventilated vehicle. Cylinders transported in an enclosed, nonventilated compartment of a vehicle can present serious safety hazards.

Additional Marking Requirement: INHALATION HAZARD

Shipment of compressed gas cylinders that have been filled without the owner's consent is a violation of federal law [49 CFR 173.301(b)].

MARINE POLLUTANTS: Hydrogen sulfide is not listed as a marine pollutant by DOT.

15. Regulatory Information

The following selected regulatory requirements may apply to this product. Not all such requirements are identified. Users of this product are solely responsible for compliance with all applicable federal, state, and local regulations.

U.S. FEDERAL REGULATIONS:

EPA (ENVIRONMENTAL PROTECTION AGENCY)

CERCLA: COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION, AND LIABILITY ACT OF 1980 (40 CFR Parts 117 and 302):

Reportable Quantity (RQ): 100 lb (45.4 kg)

SARA: SUPERFUND AMENDMENT AND REAUTHORIZATION ACT:

SECTIONS 302/304: Require emergency planning based on Threshold Planning Quantity (TPQ) and release reporting based on Reportable Quantities (RQ) of Extremely Hazardous Substances (EHS) (40 CFR Part 355):

TPQ: 500 lb (277 kg)
EHS RQ (40 CFR 355): 100 lb (45.4 kg)

SECTIONS 311/312: Require submission of MSDSs and reporting of chemical inventories with identification of EPA hazard categories. The hazard categories for this product are as follows:

IMMEDIATE: Yes
DELAYED: Yes
PRESSURE: Yes
REACTIVITY: No
FIRE: Yes

SECTION 313: Requires submission of annual reports of release of toxic chemicals that appear in 40 CFR Part 372.

Hydrogen sulfide is subject to the reporting requirements of Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA) and 40CFR Part 372.

40 CFR 68: RISK MANAGEMENT PROGRAM FOR CHEMICAL ACCIDENTAL RELEASE PREVENTION: Requires development and implementation of risk management programs at facilities that manufacture, use, store, or otherwise handle regulated substances in quantities that exceed specified thresholds.

Hydrogen sulfide is listed as a regulated substance in quantities of 10,000 lb (4536 kg) or greater.

TSCA: TOXIC SUBSTANCES CONTROL ACT: Hydrogen sulfide is listed on the TSCA inventory.

OSHA: OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION:

29 CFR 1910.119: PROCESS SAFETY MANAGEMENT OF HIGHLY HAZARDOUS CHEMICALS: Requires facilities to develop a process safety management program based on Threshold Quantities (TQ) of highly hazardous chemicals.

Hydrogen sulfide is listed in Appendix A as a highly hazardous chemical in quantities of 1,500 lb (681 kg) or more.

STATE REGULATIONS:

CALIFORNIA: Hydrogen sulfide is not listed by California under the SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986 (Proposition 65).

PENNSYLVANIA: Hydrogen sulfide is subject to the PENNSYLVANIA WORKER AND COMMUNITY RIGHT-TO-KNOW ACT (35 P.S. Sections 7301-7320).

16. Other Information

Be sure to read and understand all labels and instructions supplied with all containers of this product.

OTHER HAZARDOUS CONDITIONS OF HANDLING, STORAGE, AND USE: ***Toxic, flammable liquid and gas under pressure.*** Use piping and equipment adequately designed to withstand pressures to be encountered. Store and use with adequate ventilation at all times. Use only in a closed system constructed only of corrosion-resistant materials. Close valve after each use; keep closed even when empty. ***Prevent reverse flow.*** Reverse flow into cylinder may cause rupture. Use a check valve or other protective device in any line or piping from the cylinder. ***Never work on a pressurized system.*** If there is a leak, close the cylinder valve. Blow the system down in an environmentally safe manner in compliance with all federal, state, and local laws; then repair the leak. ***Follow safe practices when returning cylinder to supplier.*** Be sure valve is closed; then install valve outlet plug tightly. ***Never place a compressed gas cylinder where it may become part of an electrical circuit.***

NOTE: *Prior to using any plastics, confirm their compatibility with hydrogen sulfide.*

Mixtures. When you mix two or more gases or liquefied gases, you can create additional, unexpected hazards. Obtain and evaluate the safety information for each component before you produce the mixture. Consult an industrial hygienist or other trained person when you evaluate the end product. Remember, gases and liquids have properties that can cause serious injury or death.

RECOMMENDED EQUIPMENT: In semiconductor process gas and other suitable applications, Praxair recommends the use of engineering controls such as gas cabinet enclosures, automatic gas panels (used to purge systems on cylinder changeout), excess-flow valves throughout the gas distribution system, double containment for the distribution system, and continuous gas monitors.

HAZARD RATING SYSTEMS:

NFPA RATINGS:
HEALTH = 4
FLAMMABILITY = 4
INSTABILITY = 0
SPECIAL = None

HMIS RATINGS:
HEALTH = 2
FLAMMABILITY = 4
PHYSICAL HAZARD = 2

STANDARD VALVE CONNECTIONS FOR U.S. AND CANADA:

THREADED:	CGA-330
PIN-INDEXED YOKE:	Not applicable.
ULTRA-HIGH-INTEGRITY CONNECTION:	CGA-722

Use the proper CGA connections. **DO NOT USE ADAPTERS.** Additional limited-standard connections may apply. See CGA pamphlet V-1 listed below.

Ask your supplier about free Praxair safety literature as referred to in this MSDS and on the label for this product. Further information can be found in the following materials published by the Compressed Gas Association, Inc. (CGA), 4221 Walney Road, 5th Floor, Chantilly, VA 20151-2923, Telephone (703) 788-2700, http://www.cganet.com/Publication.asp.

AV-1	*Safe Handling and Storage of Compressed Gases*
P-1	*Safe Handling of Compressed Gases in Containers*
SB-2	*Oxygen-Deficient Atmospheres*
V-1	*Compressed Gas Cylinder Valve Inlet and Outlet Connections*
—	*Handbook of Compressed Gases, Fourth Edition*

Praxair asks users of this product to study this MSDS and become aware of product hazards and safety information. To promote safe use of this product, a user should (1) notify employees, agents, and contractors of the information in this MSDS and of any other known product hazards and safety information, (2) furnish this information to each purchaser of the product, and (3) ask each purchaser to notify its employees and customers of the product hazards and safety information.

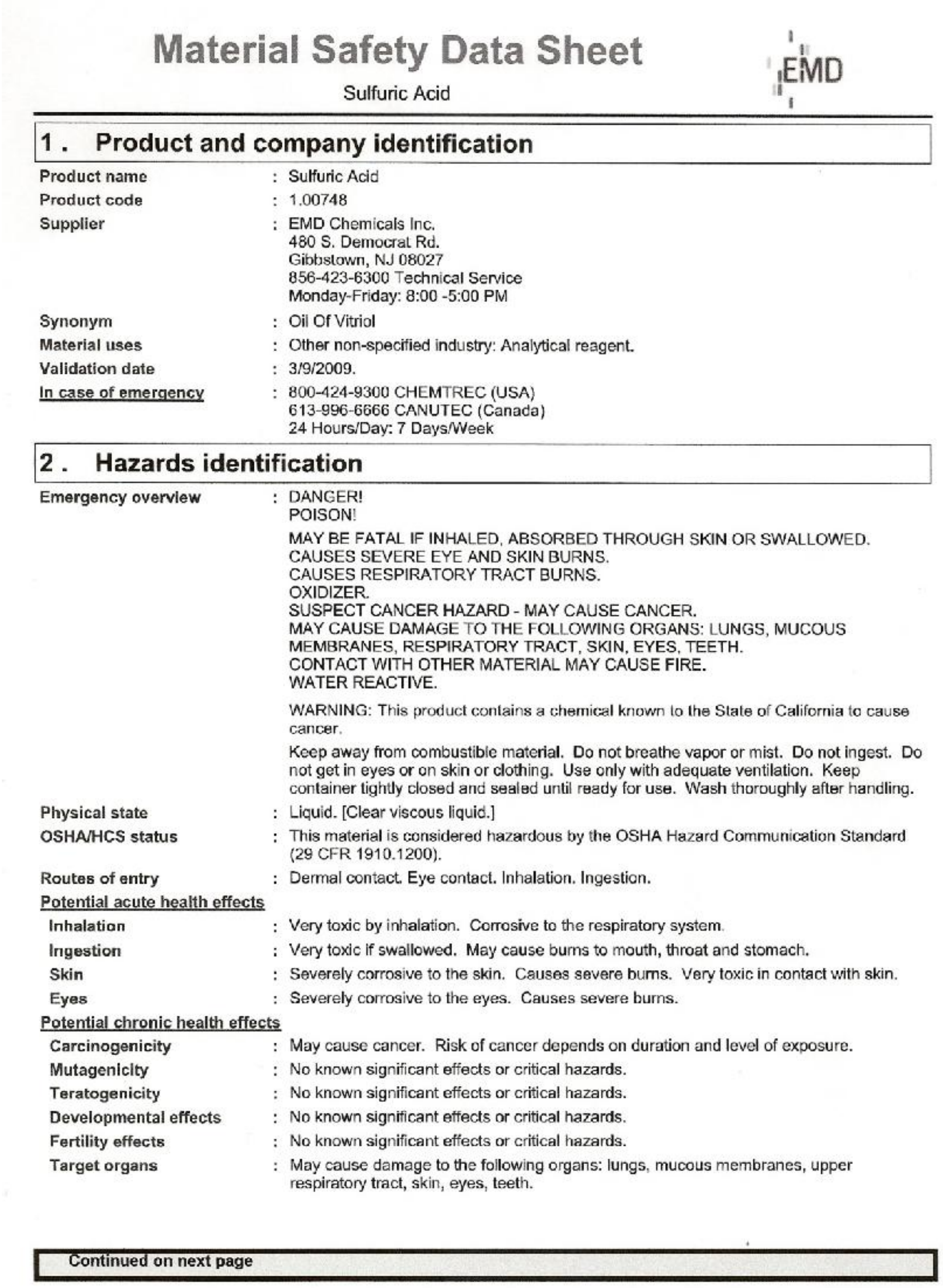
The opinions expressed herein are those of qualified experts within Praxair, Inc. We believe that the information contained herein is current as of the date of this Material Safety Data Sheet. Since the use of this information and the conditions of use of the product are not within the control of Praxair, Inc., it is the user's obligation to determine the conditions of safe use of the product.

Praxair MSDSs are furnished on sale or delivery by Praxair or the independent distributors and suppliers who package and sell our products. To obtain current MSDSs for these products, contact your Praxair sales representative or local distributor or supplier, or download from www.praxair.com. If you have questions regarding Praxair MSDSs, would like the form number and date of the latest MSDS, or would like the names of the Praxair suppliers in your area, phone or write the Praxair Call Center (**Phone:** 1-800-PRAXAIR; **Address:** Praxair Call Center, Praxair, Inc., PO Box 44, Tonawanda, NY 14151-0044).

PRAXAIR

Praxair, Inc.
39 Old Ridgebury Road
Danbury, CT 06810-5113

Printed in USA



Material Safety Data Sheet

Sulfuric Acid

1 . Product and company identification

Product name	: Sulfuric Acid
Product code	: 1.00748
Supplier	: EMD Chemicals Inc. 480 S. Democrat Rd. Gibbstown, NJ 08027 856-423-6300 Technical Service Monday-Friday: 8:00 -5:00 PM
Synonym	: Oil Of Vitriol
Material uses	: Other non-specified industry: Analytical reagent.
Validation date	: 3/9/2009.
In case of emergency	: 800-424-9300 CHEMTREC (USA) 613-996-6666 CANUTEC (Canada) 24 Hours/Day: 7 Days/Week

2 . Hazards identification

Emergency overview	: DANGER! POISON! MAY BE FATAL IF INHALED, ABSORBED THROUGH SKIN OR SWALLOWED. CAUSES SEVERE EYE AND SKIN BURNS. CAUSES RESPIRATORY TRACT BURNS. OXIDIZER. SUSPECT CANCER HAZARD - MAY CAUSE CANCER. MAY CAUSE DAMAGE TO THE FOLLOWING ORGANS: LUNGS, MUCOUS MEMBRANES, RESPIRATORY TRACT, SKIN, EYES, TEETH. CONTACT WITH OTHER MATERIAL MAY CAUSE FIRE. WATER REACTIVE. WARNING: This product contains a chemical known to the State of California to cause cancer. Keep away from combustible material. Do not breathe vapor or mist. Do not ingest. Do not get in eyes or on skin or clothing. Use only with adequate ventilation. Keep container tightly closed and sealed until ready for use. Wash thoroughly after handling.
Physical state	: Liquid. [Clear viscous liquid.]
OSHA/HCS status	: This material is considered hazardous by the OSHA Hazard Communication Standard (29 CFR 1910.1200).
Routes of entry	: Dermal contact. Eye contact. Inhalation. Ingestion.
<u>Potential acute health effects</u>	
Inhalation	: Very toxic by inhalation. Corrosive to the respiratory system.
Ingestion	: Very toxic if swallowed. May cause burns to mouth, throat and stomach.
Skin	: Severely corrosive to the skin. Causes severe burns. Very toxic in contact with skin.
Eyes	: Severely corrosive to the eyes. Causes severe burns.
<u>Potential chronic health effects</u>	
Carcinogenicity	: May cause cancer. Risk of cancer depends on duration and level of exposure.
Mutagenicity	: No known significant effects or critical hazards.
Teratogenicity	: No known significant effects or critical hazards.
Developmental effects	: No known significant effects or critical hazards.
Fertility effects	: No known significant effects or critical hazards.
Target organs	: May cause damage to the following organs: lungs, mucous membranes, upper respiratory tract, skin, eyes, teeth.

Continued on next page

2 . Hazards identification

Medical conditions aggravated by over-exposure : Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.

See toxicological information (section 11)

3 . Composition/information on ingredients

Name	CAS number	% by weight
Sulfuric Acid	7664-93-9	100

4 . First aid measures

Eye contact : Call medical doctor or poison control center immediately. Check for and remove any contact lenses. Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical attention immediately.

Skin contact : Call medical doctor or poison control center immediately. In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Clean shoes thoroughly before reuse. Get medical attention immediately.

Inhalation : Call medical doctor or poison control center immediately. Move exposed person to fresh air. If not breathing, if breathing is irregular or if respiratory arrest occurs, provide artificial respiration or oxygen by trained personnel. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

Ingestion : Call medical doctor or poison control center immediately. Wash out mouth with water. Do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Get medical attention immediately.

5 . Fire-fighting measures

Flammability of the product : Contact with combustible material may cause fire. This material increases the risk of fire and may aid combustion. In a fire or if heated, a pressure increase will occur and the container may burst.

Extinguishing media : Use an extinguishing agent suitable for the surrounding fire.

Not suitable : None known.

Special exposure hazards : Promptly isolate the scene by removing all persons from the vicinity of the incident if there is a fire. No action shall be taken involving any personal risk or without suitable training. Move containers from fire area if this can be done without risk. Use water spray to keep fire-exposed containers cool.

Hazardous thermal decomposition products : Decomposition products may include the following materials:
sulfur oxides

Special protective equipment for fire-fighters : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

Special remarks on fire hazards : Flammable hydrogen gas may be produced on prolonged contact with metals such as aluminum, tin, lead and zinc.

6 . Accidental release measures

Personal precautions : No action shall be taken involving any personal risk or without suitable training. Evacuate surrounding areas. Keep unnecessary and unprotected personnel from entering. Do not touch or walk through spilled material. Shut off all ignition sources. No flares, smoking or flames in hazard area. Do not breathe vapor or mist. Provide adequate ventilation. Wear appropriate respirator when ventilation is inadequate. Put on appropriate personal protective equipment (see section 8).

Environmental precautions : Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains and sewers. Inform the relevant authorities if the product has caused environmental pollution (sewers, waterways, soil or air).

Methods for cleaning up

Continued on next page

6 . Accidental release measures

Spill : Stop leak if without risk. Move containers from spill area. Approach release from upwind. Prevent entry into sewers, water courses, basements or confined areas. Contain and collect spillage with non-combustible, absorbent material e.g. sand, earth, vermiculite or diatomaceous earth and place in container for disposal according to local regulations (see section 13). Do not absorb in sawdust or other combustible material. It may lead to a fire risk when it dries out. Use spark-proof tools and explosion-proof equipment. Dispose of via a licensed waste disposal contractor. Contaminated absorbent material may pose the same hazard as the spilled product. Note: see section 1 for emergency contact information and section 13 for waste disposal. Dilute with water and mop up if water-soluble or absorb with an inert dry material and place in an appropriate waste disposal container.

7 . Handling and storage

Handling : Do not get in eyes or on skin or clothing. Do not breathe vapor or mist. Do not ingest. Use only with adequate ventilation. Wear appropriate respirator when ventilation is inadequate. Keep in the original container or an approved alternative made from a compatible material, kept tightly closed when not in use. Keep away from combustible material. Empty containers retain product residue and can be hazardous. Do not reuse container.

Storage : Store in accordance with local regulations. Store in original container, protected from direct sunlight. Separate from reducing agents and combustible materials. Keep container tightly closed and sealed until ready for use. Containers that have been opened must be carefully resealed and kept upright to prevent leakage.

8 . Exposure controls/personal protection

Ingredient	Exposure limits
Sulfuric Acid	**ACGIH TLV (United States, 1/2008).** TWA: 0.2 mg/m³ 8 hour(s). **OSHA PEL 1989 (United States, 3/1989).** TWA: 1 mg/m³ 8 hour(s). **NIOSH REL (United States, 6/2008).** TWA: 1 mg/m³ 10 hour(s). **OSHA PEL (United States, 11/2006).** TWA: 1 mg/m³ 8 hour(s).

Consult local authorities for acceptable exposure limits.

Engineering measures : Use only with adequate ventilation. Use process enclosures, local exhaust ventilation or other engineering controls to keep worker exposure to airborne contaminants below any recommended or statutory limits.

Hygiene measures : Wash hands, forearms and face thoroughly after handling chemical products, before eating, smoking and using the lavatory and at the end of the working period. Appropriate techniques should be used to remove potentially contaminated clothing. Wash contaminated clothing before reusing. Ensure that eyewash stations and safety showers are close to the workstation location.

Personal protection

Respiratory : Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.

Hands : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary. Recommended: neoprene

Eyes : Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists or dusts. Recommended: splash goggles , face shield

Continued on next page

8 . Exposure controls/personal protection

Skin : Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.
Recommended: chemical-resistant protective suit

Environmental exposure controls : Emissions from ventilation or work process equipment should be checked to ensure they comply with the requirements of environmental protection legislation. In some cases, fume scrubbers, filters or engineering modifications to the process equipment will be necessary to reduce emissions to acceptable levels.

9 . Physical and chemical properties

Physical state : Liquid. [Clear viscous liquid.]
Color : Colorless.
Odor : Odorless.
Molecular weight : 98.08 g/mole
Molecular formula : H2-O4-S
pH : Not available.
Boiling/condensation point : 290°C (554°F)
Melting/freezing point : 10.6°C (51.1°F)
Relative density : 1.84
Vapor pressure : 0.13 kPa (1 mm Hg)
Vapor density : Not available.
Odor threshold : >1 ppm
Evaporation rate : <1 (Butyl acetate. = 1)
Solubility : Soluble in the following materials: water (Generates much heat.)

10 . Stability and reactivity

Chemical stability : The product is stable.

Possibility of hazardous reactions : Hazardous reactions or instability may occur under certain conditions of storage or use.
Conditions may include the following:
contact with combustible materials
Reactions may include the following:
risk of causing or intensifying fire

Hazardous polymerization : Under normal conditions of storage and use, hazardous polymerization will not occur.

Conditions to avoid : Drying on clothing or other combustible materials may cause fire. Avoid exposure - obtain special instructions before use.

Materials to avoid : Highly reactive or incompatible with the following materials: oxidizing materials, reducing materials, combustible materials, metals, acids, alkalis and moisture.
An acidic oxidizer which can ignite or explode on contact with many materials, i.e., acetic acid, acetonitrile, acetone cyanhydrin. Concentrated acid oxidizes, dehydrates, or sulfonates most organic compounds.

Hazardous decomposition products : Under normal conditions of storage and use, hazardous decomposition products should not be produced.

Conditions of reactivity : Flammable in the presence of combustible materials

11 . Toxicological information

Acute toxicity

Product/ingredient name	Test Route	Species	Result

Continued on next page

11 . Toxicological information

Sulfuric Acid	LD50 Oral	Rat	2140 mg/kg
	LD50 Oral	Rat	2140 mg/kg
	LD50 Oral	Rat	2140 mg/kg
	LD50 Oral	Rat	350 mg/kg
	LC50 Inhalation Vapor	Rat	510 mg/m3
	LC50 Inhalation Vapor	Mouse	320 mg/m³

Carcinogenicity

Classification

Product/ingredient name	ACGIH	IARC	EPA	NIOSH	NTP	OSHA
Sulfuric Acid	A2	1	-	-	Proven.	-

May cause cancer. Risk of cancer depends on duration and level of exposure.

Mutagenicity

No known significant effects or critical hazards.

Teratogenicity

No known significant effects or critical hazards.

12 . Ecological information

Aquatic ecotoxicity

Product/ingredient name	Result	Species	Exposure
Sulfuric Acid	Acute LC50 70000 to 80000 ug/L Marine water	Crustaceans - Common shrimp, sand shrimp - Crangon crangon - Adult	48 hours
	Acute LC50 42500 ug/L Marine water	Crustaceans - Aesop shrimp - Pandalus montagui - Adult	48 hours
	Acute LC50 42000 ug/L Fresh water	Fish - Western mosquitofish - Gambusia affinis - Adult	96 hours

Environmental effects : No known significant effects or critical hazards.

Other adverse effects : No known significant effects or critical hazards.

13 . Disposal considerations

The information presented only applies to the material as supplied. The identification based on characteristic(s) or listing may not apply if the material has been used or otherwise contaminated. It is the responsibility of the waste generator to determine the toxicity and physical properties of the material generated to determine the proper waste identification and disposal methods in compliance with applicable regulations. Disposal should be in accordance with applicable regional, national and local laws and regulations.

14 . Transport information

Regulatory information	UN number	Proper shipping name	Classes	PG*	Label	Additional information
DOT Classification	UN1830	SULFURIC ACID	8	II		**Reportable quantity** 1000 lbs. (454 kg)

PG* : Packing group

Continued on next page

15 . Regulatory information

United States

HCS Classification : Oxidizing material
Highly toxic material
Corrosive material
Carcinogen
Target organ effects

U.S. Federal regulations : **United States inventory (TSCA 8b):** This material is listed or exempted.

TSCA (Toxic Substance Control Act): This product is listed on the TSCA Inventory.

SARA 302/304/311/312 extremely hazardous substances: Sulfuric Acid
SARA 302/304 emergency planning and notification: Sulfuric Acid
SARA 302/304/311/312 hazardous chemicals: Sulfuric Acid
SARA 311/312 MSDS distribution - chemical inventory - hazard identification:
Sulfuric Acid: reactive, Immediate (acute) health hazard, Delayed (chronic) health hazard

Clean Water Act (CWA) 307: No products were found.

Clean Water Act (CWA) 311: Sulfuric Acid

Clean Air Act (CAA) 112 accidental release prevention: No products were found.

Clean Air Act (CAA) 112 regulated flammable substances: No products were found.

Clean Air Act (CAA) 112 regulated toxic substances: No products were found.

DEA List I Chemicals (Precursor Chemicals) : Not listed

DEA List II Chemicals (Essential Chemicals) : Listed

SARA 313

	Product name	CAS number	Concentration
Form R - Reporting requirements :	Sulfuric Acid	7664-93-9	100
Supplier notification :	Sulfuric Acid	7664-93-9	100

SARA 313 notifications must not be detached from the MSDS and any copying and redistribution of the MSDS shall include copying and redistribution of the notice attached to copies of the MSDS subsequently redistributed.

Massachusetts Substances : This material is listed.

New Jersey Hazardous Substances : This material is listed.

New York Acutely Hazardous Substances : This material is listed.

Pennsylvania RTK Hazardous Substances : This material is listed.

California Prop. 65

WARNING: This product contains a chemical known to the State of California to cause cancer.

Ingredient name	Cancer	Reproductive	No significant risk level	Maximum acceptable dosage level
Sulfuric Acid	Yes.	No.	No.	No.

Canada

WHMIS (Canada) : Class C: Oxidizing material.
Class D-1A: Material causing immediate and serious toxic effects (Very toxic).
Class E: Corrosive material

Continued on next page

15 . Regulatory information

Canadian lists : **CEPA Toxic substances:** This material is not listed.
Canadian ARET: This material is not listed.
Canadian NPRI: This material is listed.
Alberta Designated Substances: This material is not listed.
Ontario Designated Substances: This material is not listed.
Quebec Designated Substances: This material is not listed.

CEPA DSL / CEPA NDSL : This material is listed or exempted.

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations and the MSDS contains all the information required by the Controlled Products Regulations.

EU regulations

Hazard symbol or symbols :

Risk phrases : R22- Harmful if swallowed.

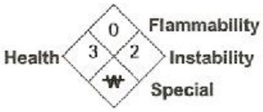
Safety phrases : S2- Keep out of the reach of children.
S46- If swallowed, seek medical advice immediately and show this container or label.

International regulations

International lists : **Australia inventory (AICS):** This material is listed or exempted.
China inventory (IECSC): This material is listed or exempted.
Japan inventory (ENCS): This material is listed or exempted.
Japan inventory (ISHL): Not determined.
Korea inventory (KECI): This material is listed or exempted.
New Zealand Inventory of Chemicals (NZIoC): This material is listed or exempted.
Philippines inventory (PICCS): This material is listed or exempted.

16 . Other information

National Fire Protection Association (U.S.A.) :



Notice to reader

The statements contained herein are based upon technical data that EMD Chemicals Inc. believes to be reliable, are offered for information purposes only and as a guide to the appropriate precautionary and emergency handling of the material by a properly trained person having the necessary technical skills. Users should consider these data only as a supplement to other information gathered by them and must make independent determinations of suitability and completeness of information from all sources to assure proper use, storage and disposal of these materials and the safety and health of employees and customers and the protection of the environment. EMD CHEMICALS INC. MAKES NO REPRESENTATION OR WARRANTY OF ANY KIND, EXPRESS OR IMPLIED, INCLUDING MERCHANTABILITY OR FITNESS FOR A PARTICULAR USE, WITH RESPECT TO THE INFORMATION HEREIN OR THE PRODUCT TO WHICH THE INFORMATION REFERS.