

**EXPERIMENTAL STUDY OF PREPARING SULFURIC ACID FROM
SULFUR DIOXIDE USING CATALYTIC PHOTOSYNTHESIS METHOD**

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ABSTRACT

Sulfuric acid is an acid that is commonly used worldwide in various fields especially in chemical field. In fact, the demand for sulfuric acid increases nowadays due to its benefits. In the process of producing sulfuric acid (H_2SO_4), the most common processes that have been used worldwide are lead chamber process, contact process and wet sulfuric acid gas process. Sulfur dioxide usually known as a dangerous gas as it causes acid rain once it has been emitted to the air. But on the other hand, it can be a beneficial gas because sulfur dioxide (SO_2) normally used as a feed to produce sulfuric acid. Thus, catalytic photosynthesis method will be used in this research study where chemical reaction is induced by light. This study will be conducted using a simple method which using a stainless steel reactor with a high intensity photosynthesis lamp. The sulfur dioxide (SO_2) will be fed under different flow rate (20, 60 and 100 ml/h) and the reaction will be contacted for about 1 to 2 hours. In the end of the study, different flow rate of the sulfur dioxide (SO_2) will affect the pH reading of the product. The pH of the product which is sulfuric acid (H_2SO_4) will be analyzed using pH meter as well the composition will be analyzed by FTIR (Fourier Transform Infrared Spectroscopy).

ABSTRAK

Sulfur dioksida dikenali sebagai gas yang berbahaya kerana ia boleh menyebabkan hujan asid apabila terbebas di udara. Tetapi, ia boleh dijadikan sebagai gas yang berfaedah kerana sulfur dioksida digunakan untuk menghasilkan asid sulfurik. Oleh itu, process katalitik photosintesis telah digunakan di dalam penyelidikan ini di mana tindak balas kimia didorong oleh cahaya. Penyelidikan ini telah dijalankan dengan menggunakan cara yang mudah di mana gas sulfur dioksida telah disalurkan ke dalam bekas air yang diperbuat dari kaca dan bekas air tersebut mengandungi air dan ferum (III) oksida sebagai pemangkin. Sebuah lampu yang mempunyai keamatan cahaya yang tinggi telah dipasang berhampiran dengan bekas pemanas air di mana bekas air telah dimasukkan ke dalamnya. Gas sulfur dioksida (SO_2) telah disalurkan dengan kadar aliran gas yang berbeza (20, 60 dan 100 ml/h) dan tindak balas telah dibiarkan berjalan selama satu hingga dua jam. Di akhir penyelidikan ini, dapat disimpulkan bahawa kadar aliran gas sulfur dioksida (SO_2) telah mempengaruhi nilai pH produk yang telah dihasilkan. Nilai pH produk yang dihasilkan iaitu asid sulfurik (H_2SO_4) telah dianalisa dengan menggunakan meter pH. Selain itu, komposisi produk telah dianalisa dengan menggunakan FTIR (Fourier Transform Infrared Spectroscopy) untuk menguji kehadiran komposisi yang terdapat di dalam asid sulfurik.

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LIST OF SYMBOLS

mL	-	milliliter
h	-	hour

CHAPTER 1

INTRODUCTION

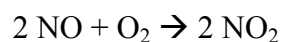
1.1 Background of Study

Sulfuric acid (H_2SO_4) is a strong mineral acid. It is soluble in water at all concentrations. Besides that, sulfuric acid has many applications and is one of the top products of the chemical industry. The major use for sulfuric acid is in the "wet method" for the production of phosphoric acid, used for manufacture of phosphate fertilizers as well as trisodium phosphate for detergents (T.M Orlando,2005). It is also used in large quantities by the iron and steel making industry to remove oxidation, rust and scale from rolled sheet and billets prior to sale to the automobile and white goods industry (Chenier, 1987).

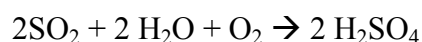
Another important uses for sulfuric acid are for the manufacture of aluminum sulfate, remove oxides from iron and steel before galvanizing or electroplating, and used in the production of nitroglycerine which is an inorganic ester and organic nitrate (Greenwood, 1997). Since sulfuric acid (H_2SO_4) is known as beneficial chemical compound, the demand of this chemical compound is high. Therefore, previous research connected with this topic in producing sulfuric acid are contact process, wet sulfuric acid process and lead chamber process (Greenwood, 1997).

1.1.1 Lead Chamber Process

Lead Chamber process is the oldest process in producing the sulfuric acid and it was invented much stronger, less expensive, and could be made much larger than the glass containers which had been used previously. This method was started by John Roebuck in 1746 and has been used in the industry to produce sulfuric acid in large quantities (Edward M.Jones,1950). Sulfur dioxide is generated by burning elemental sulfur or by roasting pyritic ore in a current of air. Nitrogen oxides are produced by decomposition of niter in the presence of sulfuric acid or hydrolysis of nitrosylsulfuric acid. In the reaction chambers, sulfur dioxide and nitrogen dioxide dissolve in the reaction liquor. Nitrogen dioxide is hydrated to produce nitrous acid which then oxidizes the sulfur dioxide to sulfuric acid and nitric oxide. The reactions are not well characterized but it is known that nitrosylsulfuric acid is an intermediate in at least one pathway. Nitric oxide escapes from the reaction liquor and is subsequently reoxidized by molecular oxygen to nitrogen dioxide. This is the overall rate determining step in the process (F. A. Gooch,1950) :



Nitrogen oxides are absorbed and regenerated in the process, and thus serve as a catalyst for the overall reaction:

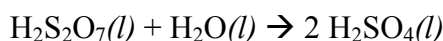


1.1.2 Contact Process

Contact process is the current method of producing sulfuric acid (H_2SO_4) in the high concentrations needed for industrial processes. The contact process was patented in 1831 by the British vinegar merchant Peregrine Phillips. There are three stages involved which are preparation and purification of sulfur dioxide, catalytic

oxidation (using vanadium pentoxide catalyst) of sulfur dioxide to sulfur trioxide and conversion of sulfur trioxide to sulfuric acid. Contact process plants are of two types. The simpler type is the sulfur-burning contact plants where molten sulfur is burned to form sulfur dioxide which is cooled and then oxidized to form sulfur trioxide at moderately high temperatures.

The other type of contact-process plant produces sulfur dioxide from low-grade, sulfur-bearing materials, such as pyrite. Cooling of the gas is necessary to remove impurities and to condense and remove part of the water vapor which would dilute the acid product. The sulfur dioxide gas is then dried with concentrated sulfuric acid. As a result of its purification, the gas in this process is cold instead of hot as in sulfur-burning plants and must be heated to the temperature at which the catalyst begins to function (*Encyclopedia Britannica*,2009). The average percentage yield of this reaction is around 30%.(Jim Clark,2002)



1.1.3 Wet Sulfuric Acid Process

Wet sulfuric acid process is the gas desulfurization processes on the market today used in producing sulfuric acid (H_2SO_4). It was first patented by the Danish catalyst company Haldor Topsoe in 1980's. Wet catalysis processes differ from other contact sulfuric acid processes in that the feed gas still contains moisture when it comes into contact with the catalyst (U.H.F Sander et al,1984.). The wet catalysis process is especially suitable for processing the wet gasses obtained by the combustion of hydrogen sulfide (H_2S) containing off-gasses . Through this process, it will yielded up to 97-98% liquid sulfuric acid (Gary, J.H. and Handwerk, 1984).

Figure 1.1 below shows the national sulfur dioxide emissions by source sector in 2005. The bar graph indicates that on electricity generation is the major contributor to emission of sulfur dioxide. The emissions of sulfur dioxide (SO_2) have decreased

by 31% between 1990 and 2002. In 2002, the most significant sources of SO₂ emissions were the road transport sector (72%), fossil fuel combustion (15%), industrial energy use (7%) and the non-road transport sector (2%).

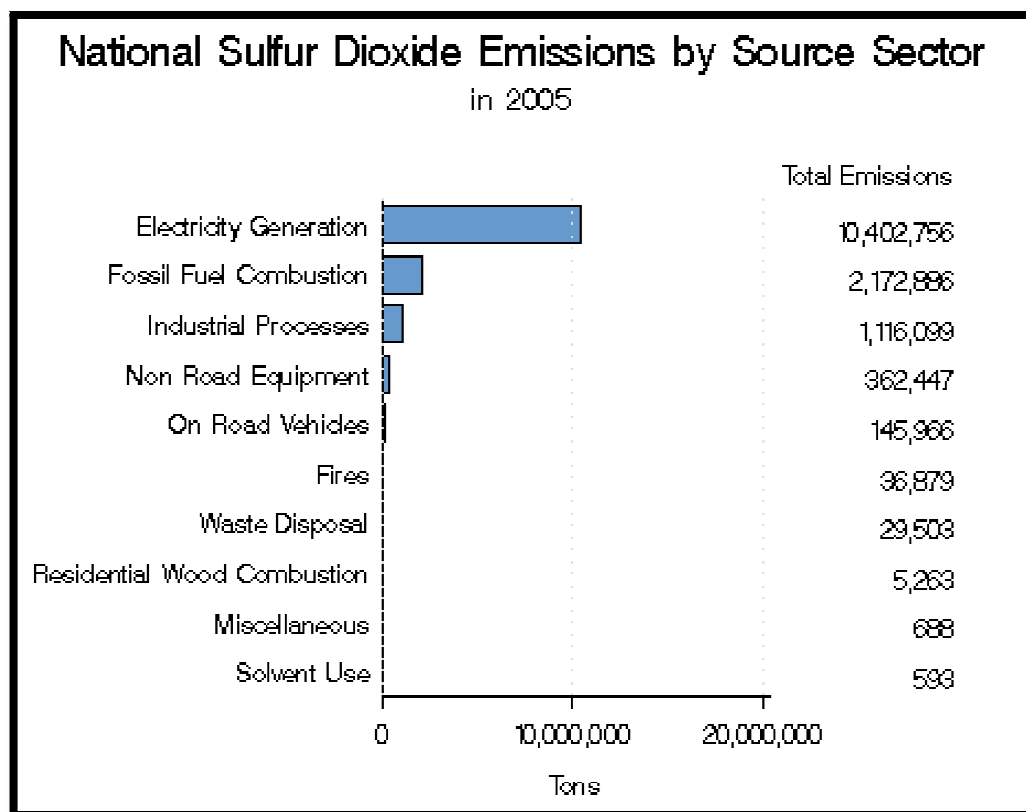


Figure 1.1: Sulfur dioxide Emission by Sector (Bayless, 2007)

1.2 Sulfuric Acid Global demand

According to SRI Consulting (SRIC) California, sulfuric acid is one of the world's largest-volume industrial chemicals. The production of phosphate fertilizer materials especially wet-process phosphoric acid is the major end-use market for sulfuric acid accounting for nearly 53% of total world consumption in 2008. The balance is consumed in a wide variety of industrial and technical applications. Apparent world sulfuric acid consumption increased by about 25% between 1990 and 2008. Socialist Asia is the major market accounting for about 28% of world

consumption in 2008, followed by the United States which consumed about 19% (Bala Suresh, 2009).

The global sulfuric acid market experienced an unprecedented rise and fall in pricing between fall 2007 and spring 2009. Consumption of sulfuric acid for fertilizers fell steeply in the second half of 2008 due to the collapse in the global economy (Bala Suresh, 2009). The second half of 2009 is expected to experience almost flat to slightly positive growth, anticipating the improvement in market conditions in 2010. Trade is expected to fall globally, except for Southeast Asia which would continue to depend on imports. As of early spring 2009, the market is continuing to deteriorate as the supply shortage situation has been replaced by product oversupply in almost all regions.

Previously negotiated contract prices do not reflect the actual market conditions as consumers look for excess storage capacity since consumption has declined as a result of lack of demand. Contract renegotiations are happening worldwide, even in cases where cargo is in transit to its destination. In places such as China, smelters have reported selling at negative prices, as the oversupply situation is forecast to persist in the near future. Prices have been falling as a result of reduced demand and also the increasing availability of surplus sulfur. However, in Central and South America, there are pockets where acid supply is still tight because there is relatively less product reaching the region and there are not that many local smelter capacities to satisfy demand (Bala Suresh, 2009).

Future growth for sulfuric acid is hard to predict and depends a lot on the fertilizer market. Fertilizer demand is seen to be influenced by the ongoing global economic crisis, credit availability, and dietary changes in the general population. It will also be influenced by the rate of increase in biofuels production, especially corn-based fuels. Within this context, global demand for sulfuric acid is projected to rise at an annual rate of about 1.4% in the next five years. Fertilizer demand for sulfuric acid is forecast to grow at about 1.2% during 2008–2013 (Bala Suresh, 2009). Several new phosphate fertilizer plants are scheduled to be constructed over the forecast period mostly in northern Africa, the Middle East and China.

Figure 1.2 shows the world consumption of sulfuric acid in year 2008. Socialist Asia (30%) is the major consumer for sulfuric acid, followed by United States(15%). Africa consumed 10% of sulfuric acid in their industrial activity. The other consumers of sulfuric acid including Former USSR, Central/South America and Western Europe are using the same amount of sulfuric acid in their region for industrial use. Besides that, other region whom has less demand of sulfuric acid are Southeast Asia, Southwest Asia, Middle East, Oceania, Japan, Mexico and Canada.

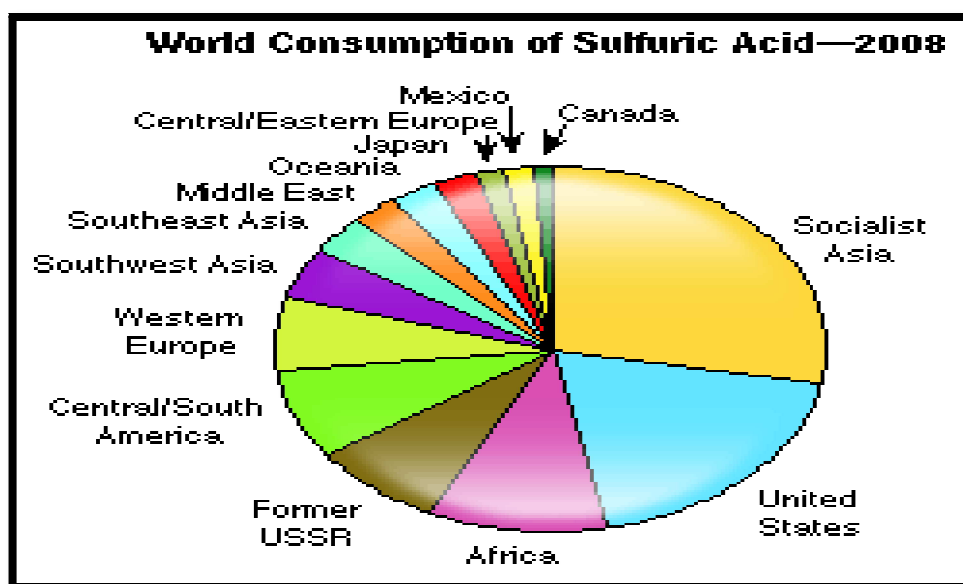


Figure 1.2: World consumption of sulfuric acid(2008)

1.3 Problem Statement

There were few processes that has been carried out to produce sulfuric acid (H_2SO_4) such as lead chamber process, contact process and wet sulfuric acid process. These processes has been ran and been studied on how well the performances are. Some processes may be good in terms of production but there were some weaknesses that has been detected (Edward M.Jones, 1950). For lead chamber, the weakness of this process is the mechanism of the process is still remain awkward as the chambers would go out of service only to be coaxed back into operation while the contact

process is it needs very pure sulfur to avoid catalyst poisoning (Jim Clark, 2002). Since sulfuric acid is used widely especially in chemical industry and in high demand, it requires a high cost to carry out using these methods. On the other hand, the sulfur dioxide can be dangerous as it is formed as acid rain once been released to the air.

Thus, to avoid certain circumstances, we had found solution for the problem with the recent research which is catalytic photosynthesis method. A high intensity lamp was installed near the water bath where the glass vessel was put inside it. The sulfur dioxide gas (SO_2) was fed under different flow rate (20, 60 and 100 ml/h) and the reaction was contacted for about 1 to 2 hours. In the end of the study, different flow rate of the sulfur dioxide (SO_2) has affected the pH reading of the product. The pH of the product, sulfuric acid (H_2SO_4) was analyzed using pH meter as well the composition was then analyzed by FTIR (Fourier Transform Infrared Spectroscopy).

1.4 Objectives

The purpose of this research study will focus on :

- i. To study the process of catalytic photosynthesis technique in the preparation of sulfuric acid.
- ii. To study the maximum concentration and flow rate of sulfur dioxide as a raw material to produce sulfuric acid.
- iii. To analyze the pH of sulfuric acid (H_2SO_4) concentration using pH meter and FTIR (Fourier Transform Infrared Spectroscopy).
- iv. To reduce pollution caused by sulfur dioxide.

1.5 Scope of Study

There are some important tasks to be carried out in order to achieve the objective of this study. The important elements have been identified for this research in achieving the objective:

- i. In this research, the method that we chose is photosynthesis and irradiation technique. We ran the experiment in a photo-reactor with 1000 watt Metal Halide Lamp, a lamp to enhance the photosynthesis.
- ii. Fourier Transform Infrared (FT-IR) was used to analyze the product at the of the experiment.
- iii. Study the effects of operating parameter such as temperature and flow rate.

1.6 Benefit and Significance of Study

The rationale of this research is that it could encounter environmental and health problems caused by the emission of SO_2 . Besides that, we can make use of SO_2 in profitable way instead of emitting the SO_2 to atmosphere.

Moreover, this method would create another solution for reproducing Sulfuric Acid with more economical way. The most vital part of this research is that it could improve and reduce pollution and change the environment towards 'green world'.

1.7 Thesis Layout

Thesis layout is emphasizing the chapter in this research. There are generally four main chapters.

Chapter 2 covers topic on properties and synthesis of sulfuric acid. Besides, it covers the lead chamber process and contact process on production of sulfuric acid in industry then followed by the formation of acid rain and its effect on the environment.

In chapter 3, methodology of this research was included with the material for sample preparation as well as the experiment set up and method. This chapter explains on the sample preparation method which was divided into three parts. Those parts are the effect of flow rate, temperature and amount of catalyst used.

Chapter 4 focused on the result and discussion where the result of the experiment was compared with the result from literature review. If the result is valid with the literature and the optimization process is succeed, that means our research is correct but if there are any different value or result, that means there are some mistakes that we did in this research. Thus, we must find a solution to correct it and find out what is the mistake that we had done.

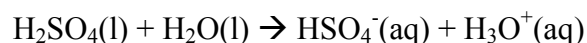
Chapter 5 includes conclusion and recommendation. In this chapter, it concludes all the various review and finding area in this work. Recommendation must stated in this research that can give more accurate result, using Gas Chromatography – Mass Spectrometer (GC-MS) will give the more detail component of the product, and others step that can make result of this research accurate.

CHAPTER 2

LITERATURE REVIEW

2.1 Properties of sulfuric acid

Sulfuric acid is a colorless and odorless viscous liquid that is heavier than water. It is diprotic acid which can donate two protons to a base. Sulfuric acid is a strong acid that readily dissolved in water to form hydrogen and sulfate ion which complete dissociation in water, K_a approaches infinity. The acid strength of a sulfuric acid solution is determined by the amount or percentage of sulfuric acid it contains which is the higher the amount of the chemical, the stronger the acid strength. 100% sulfuric acid has a melting point of $10.4^\circ\text{C} - 10.5^\circ\text{C}$ and boiling point of 290°C . Besides that, it also can take part in redox reaction. Furthermore, sulfuric acid ionizes in water in two stages (T.M Orlando, 2005) :

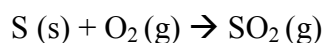


2.2 Manufacture of acid sulfuric

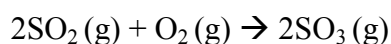
2.2.1 Contact process

Figure 2.1 below shows the process flow of Contact process. The Contact Process is a process involving the catalytic oxidation of sulfur dioxide, SO_2 , to sulfur trioxide, SO_3 .

- a) Solid sulfur, $\text{S}(\text{s})$, is burned in air to form sulfur dioxide gas, SO_2 in the combustion chamber.



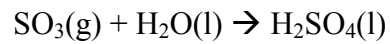
- b) The gases are then mixed with more air then cleaned by electrostatic precipitation to remove any particulate matter
- c) The mixture of sulfur dioxide and air in the converter is heated to 450°C and subjected to a pressure of 101.3 - 202.6 kPa (1 -2 atmospheres) in the presence of a vanadium catalyst (vanadium (V) oxide) to produce sulfur trioxide, $\text{SO}_3(\text{g})$, with a yield of 98%.



- d) Any unreacted gases from the above reaction are recycled back into the above reaction
- e) Sulfur trioxide, $\text{SO}_3(\text{g})$ is dissolved in 98% (18M) sulfuric acid, H_2SO_4 , to produce disulfuric acid or pyrosulfuric acid, also known as fuming sulfuric acid or oleum, $\text{H}_2\text{S}_2\text{O}_7$.



This is done because when water is added directly to sulfur trioxide to produce sulfuric acid



the reaction is slow and tends to form a mist in which the particles refuse to coalesce.

- f) Water is added to the disulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$, to produce sulfuric acid, H_2SO_4

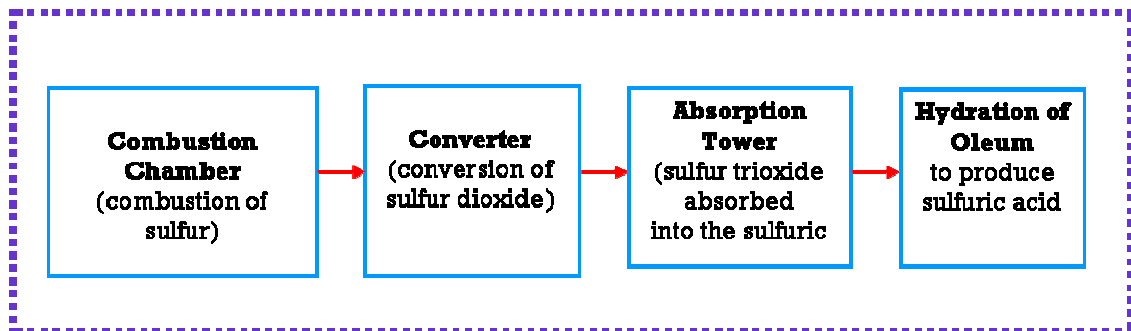
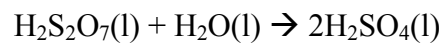


Figure 2.1: Contact process

2.2.2 Lead chamber process

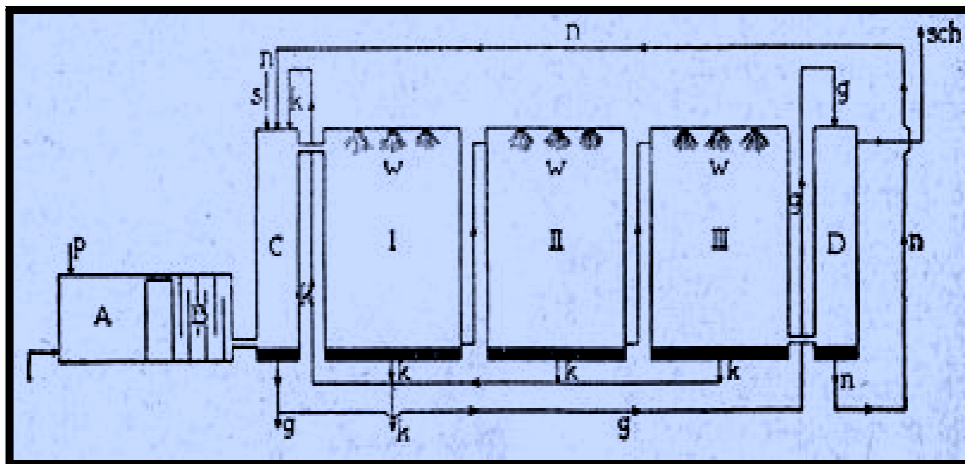


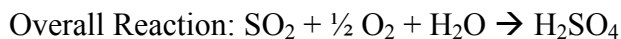
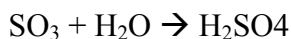
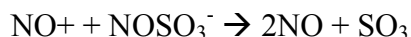
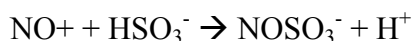
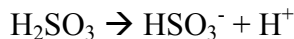
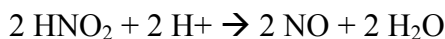
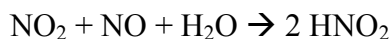
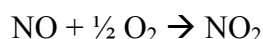
Figure 2.2: Lead chamber process

Figure 2.2 shows the pictorial figure of the lead chamber. The classic lead chamber process consists of 3 stages which are Glover tower, lead chambers and Guy-Lussac Tower. The process starts with hot sulfur dioxide gas entering the bottom of a reactor called a Glover tower where it is washed with nitrous vitriol (sulfuric acid with nitric oxide, NO, and nitrogen dioxide, NO₂, dissolved in it) and mixed with nitric oxide and nitrogen dioxide gases. The Glover tower serves two functions; concentration of the chamber acid and stripping of nitrogen oxides from the liquid to the gas or denitration.

Concentration of the chamber acid (62% to 68% H₂SO₄) is achieved by the hot gases entering the tower which evaporate water from the acid. Some of the sulfur dioxide is oxidized to sulfur trioxide and dissolved in the acid wash to form tower acid or Glover acid (about 78% H₂SO₄). The dissolved nitrogen oxides are stripped from the acid and carried with the gas out of the Glover tower into the lead chambers.

From the Glover tower a mixture of gases (including sulfur dioxide and trioxide, nitrogen oxides, nitrogen, oxygen, and steam) is transferred to a lead-lined

chamber where it is reacted with more water. The chamber may be a large, boxlike room or an enclosure in the form of a truncated cone. Sulfuric acid is formed by a complex series of reactions; it condenses on the walls and collects on the floor of the chamber. There may be from three to twelve chambers in a series; the gases pass through each in succession. The acid produced in the chambers, often called chamber acid or fertilizer acid, contains 62% to 68% H₂SO₄. The reactions occurring in the lead chamber are :



After the gases have passed through the chambers they are passed into a reactor called the Gay-Lussac tower where they are washed with cooled concentrated acid (from the Glover tower); the nitrogen oxides and unreacted sulfur dioxide