

Sulfuric Acid Production Using Catalytic Oxidation

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Abstract— The Report aims at providing brief overview of the overall process and Methods involved with Production of Sulfuric Acid using Catalytic Oxidation. Starting with the Raw Materials/Feedstock, Industrial Processes involved, Reaction Sequence Mechanism, Catalyst Used, its Role and finally the annual production and Revenue. Langmuir-Hinshelwood Model and Rideal-Eley Model have been used to explain the mechanism of the processes involved, the basic differences between the two different approaches and a similarity between the results obtained by varying parameters involved in the models and analysis of a possible reason for the observed values are included in the report .

Index Terms— Sulfuric Acid, Production, Revenue. Langmuir-Hinshelwood Model, Rideal-Eley Model.

I. INTRODUCTION

Sulfuric acid is an important raw material for fertilizer production specially for Phosphate fertilizers and to a much lesser extent for nitrogen and potassium fertilizers. World production of sulfuric acid was about 121 million tons in 1977 and surpassed 230.7 million tonnes in 2012 more than half of this production is used in the fertilizer production.

II. INDUSTRIAL METHODS FOR PRODUCTION OF SULFURIC ACID

There are two main available processes for the production of Sulfuric Acid on large Scale, One being Lead Chamber Process and other Contact Process. Lead Chamber Process is the oldest Process Used to manufacture Sulfuric Acid. The main principle behind the process is that the moist Sulphur dioxide in presence of nitrogenous oxides present as Active form of Catalyst is oxidized to sulphur trioxide with the oxygen present in air which is then made to react with water to form sulfuric acid.

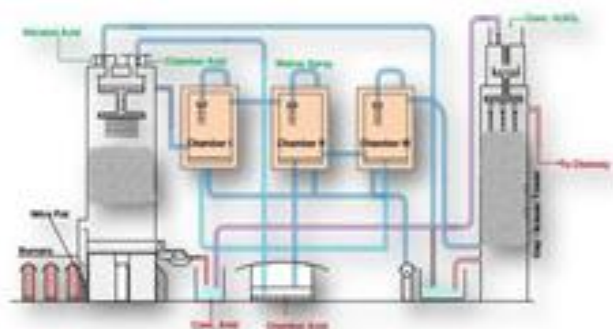


Figure 1: Flow Diagram for Lead Chamber Process

The Acid Produced by Chamber Process had Concentration of less than 0.8 and soon it was replaced by a more efficient

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Process, The Contact Process is so called because sulfur dioxide and oxygen must come in contact with the catalyst to complete the reaction. Today most of the Sulfuric Acid is produced using Contact Process which uses metal oxide catalyst for conversion of sulfur dioxide to sulfur trioxide which then is converted to sulfuric acid. Great Increase in purity levels of sulfuric acid obtained and considering the facts that the overall reaction in lead chamber process consisting of number of partial reactions taking place in liquid phase, the development of surfaces which are covered in this liquid is a cause of fundamental importance in promoting the production of sulfuric acid using contact process rather than lead chamber process. Flow diagram for Manufacturing Process of Sulfuric acid by contact shown below clearly illustrates the main steps involved in the process.

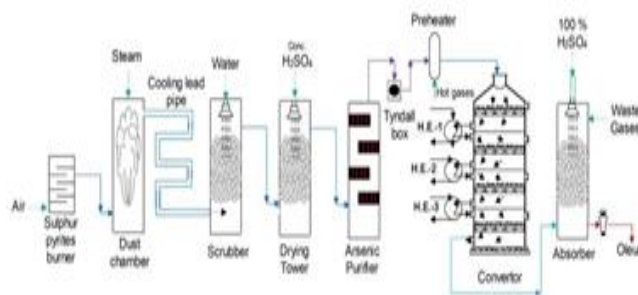


Figure 2: Flow diagram for Contact Process

III. USES OF SULFURIC ACID:

Sulfuric Acid has widely varied uses and plays some part in the production of nearly all manufactured goods. Some of them are industries from fertilizers, pharmaceuticals, Metal Processing (Finds application in pickling in which layers of basic oxides are removed before electroplating, enameling, galvanizing and soldering.), The Manufacture of Rayon, The Manufacture of Lead-Acid Type Batteries, Gasoline, Automobiles Batteries, Paper bleaching, Water treatment, Sugar bleaching, Sulfonation agents, Cellulose fibers, Steel manufacturing, Coloring agents Amino acid intermediates Regeneration of ion exchange resins. It plays a major role in manufacture of Fertilizers e.g., superphosphate of lime and ammonium sulfate. It is Used for drying almost all gases, except NH_3 and H_2S . Sulfuric acid is a strongly acidic, oily liquid which may be clear to cloudy in appearance. An example of use of sulfuric acid in addition to all stated above is Potato farmers employ specialist to spray their elds of potatoes just before harvesting so that the green tops die back and blacken within a day or two. This helps to dry out the stem and prevents potatoes from becoming tangled in the harvesting equipment. The usual method of spraying potato tops is with a solution of sulphuric acid. Concentrated sulfuric acid acts as both an oxidizing (Gives Oxygen on strong heating, hence concentrated sulfuric acid also acts as

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an oxidising agent) and dehydrating agent(Has a great affinity for water and the reaction is extremely exothermic). The below shown pie-chart represents the percentage usage of sulfuric acid in different industrial sectors.

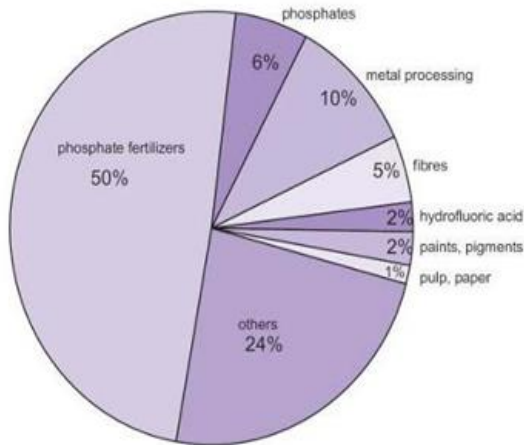


Figure 3: Sector wise Uses of sulfuric Acid

IV. RAW MATERIALS REQUIRED:

Sulfur/Sulfur dioxide, A small excess of Oxygen, A catalyst of vanadium(V) oxide supported on silica. Further, discussing the sources of Sulfur/Sulfur dioxide, Sulfur can be recovered from mines, Petroleum desulfurization of H₂S re-covered from Petroleum desulfurization. With reference to sulfur dioxide, gases containing upto 90 percent sulfur dioxide used in the production of can be organic compounds can be used after the extraction of organic compounds, it can also be isolated from pyrites, recovered from smelting of metalliferous ores, from purification of natural gas and from refining operations. Unreacted gases are recycled to the converter for another cycle of passing over the catalyst and hence significant amount of input gases are used in production of sulfuric acid.

V. CATALYST USED:

Initially Platinum was used as a catalyst for Contact process but in addition to the Major Cost problem with Platinum, platinum was more susceptible to poisoning in comparison to vanadium(V)oxide hence Vanadium(V)oxide has replaced it largely. Further in some plants Cs doped Vanadium(V)oxide is also used. It is supported on the surface of silica and temperature of catalyst beds varies from 400(deg)cel. to 550 (deg)cel. depending on the requirement of either higher Conversion or higher Rate. The Main points of Differences have been listed in the table below.

Aspect	Vanadium catalyst	Platinum catalyst
Conversion	Higher	Lower and decrease with use
Investment	Initially less, 5% replacement is required per year	High, Lower life and highly fragile
Catalyst poisoning	Relatively immune to poison	Poisoned, especially by arsenic
Handling of SO ₂	Less (7-8%)	High (8-10%)
Requirement per 1000kg (100% acid)/day	14kg catalyst mass containing 7-8% V ₂ O ₅	189gms

Figure 4: Differences between Vanadium and Platinum Catalyst

VI. REACTION MECHANISM AND USE OF CATALYST:

In Contact Process, there are three main steps involved:

1. Conversion of sulfur to sulfur dioxide
2. Reaction between sulfur dioxide with excess oxygen in presence of Vanadium(V)oxide to form sulfur trioxide.
3. Reaction between Sulfur-trioxide with Sulfuric acid(98percent) to form disulfuric acid or pyrosulfuric acid also known as oleum. Further the oleum formed reacts with water to form Sulfuric acid(98 percent).

Now, in the last step if we directly add water to sulfur-trioxide formed in second step, it yields sulfuric acid but the reaction is slow and tends to form a mist in which the particles refuse to coalesce. Hence treating it with Sulfuric acid to form oleum and later adding water yields the Sulfuric acid in desired form and purity.

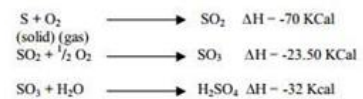


Figure 5: Reactions Involved with the information of Heat involved with each step

Now with reference to first step of reaction involving burning of sulfur, the data suggests that the reaction is highly exothermic and heat released can be utilized for some productive work. The heat released increases the temperature of the gas tremendously and the heated gas is led through a gas pipe with water passing through, the formed steam rises and the Gas is cooled.

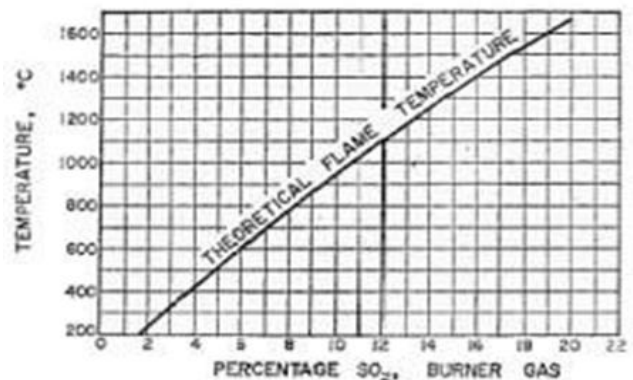


Figure 6: Temperature Vs Percentage SO₂

As the above graph demonstrates that the Increase in Temperature with Percentage Sulfur-dioxide is large and hence we can conclude that the steam risen by above stated method yields significant energy output.

The second step is also exothermic in nature hence decrease in temperature favors forward reaction but at very low temperature the rate of combination of sulfur-dioxide and oxygen is very slow, the reaction finds a balance at a temperature of about 450(deg) cel. where the rate of combination of sulfur-dioxide and oxygen is high and rate of dissociation of sulfur-trioxide is low. Hence, the forward reaction is favored. Further because of decrease in Volume of gases from input to output side, increase in pressure favors the forward reaction(using Le-Chatelier Principle) because

practically it has been observed that increase in pressure does not yield appreciable increase in Rate of formation of sulfur-trioxide and further, because of increase in pressure the rate of corrosion of iron used in the plants increases, hence the economics of the process are disturbed. The second step also involves presence of Vanadium(V)oxide as a catalyst. As stated in above sections the temperature range for Catalyst bed varies from 400 to 550(deg) cel. depending on the requirement in form of either higher conversion or higher rate. The suitable pressure ranges from 1.5 to 1.7 atm.

Because of vanadium being present in solid state in a reaction involving gases, so we observe a heterogeneous catalysis. Now using theory of heterogeneous Catalysis the steps involved in second reaction are:

1. Diffusion of reactant molecules from the bulk to the surface of Solid catalyst.
2. Adsorption of reactant molecules on the surface of catalyst.
3. Conversion of reactant into products on the surface of catalyst.
4. Desorption of products molecules.
5. Diffusion of Product molecules away from the surface of catalyst.

With reference to the Catalyst, Advantage is taken of the variable oxidation state of the Transition metals. Initially vanadium(V)oxide gets converted to vanadium(IV)oxide and converts sulfur-dioxide to sulfur-trioxide and in the second half of the reaction vanadium(IV)oxide is re-oxidized back to vanadium(V) oxide as shown by the equations below:



Figure 7: Reaction step 1 involving the Catalyst



Figure 8: Reaction step 2 involving the Catalyst

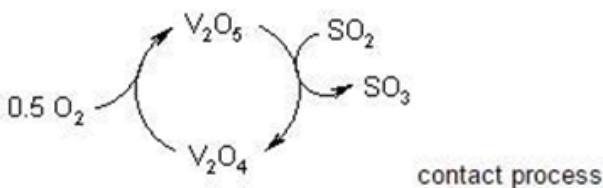


Figure 9: Diagram representing the above process

It has been observed that steps involving diffusion are slow and hence rate determining. Now, since these two steps does not involve any chemical transformation hence we can easily eliminate these diffusion involving steps from being rate determining steps by appropriate measures dependent on reactor geometry. For eg: Decreasing the size of particle in a batch reactor will decrease the pores and effective stirring of the catalyst and reactant can become the rate controlling step. Now, we have one of the step 2,3 and 4 left as rate determining step. All of these involve chemical change and have rates with temperature dependence and hence obey Arrhenius equation. Now, using Langmuir theory of

Chemisorption of reactant molecules, we have rate of adsorption and desorption involved in the reaction given by the equations:

$$r_a = k_a (1 - \theta)/P$$

Figure 10: Rate of Adsorption

$$r_d = k_d \theta$$

At equilibrium $\theta = \frac{bp}{1+bp}$

Figure 11: Rate of Desorption and Value of Fraction of Covered Sites

Now as we can see the Rate of adsorption depends on Fraction of unoccupied sites and Pressure of the gas above it. Further we can also visualize that greater the pressure, greater the rate. For the case of desorption, the rate depends only on the fraction of sites occupied and is independent of pressure of the gas. At the equilibrium the rate of adsorption and rate of desorption are equal and hence equating these rates, we obtain an expression for Fraction of Occupied sites (Theta) in terms of pressure of gas and some constant $b (=k_a/k_d)$. Now, Relating the rate of surface reaction ($=v$) to the variables introduced, we have the following equation:

$$v = k \frac{bp}{1+bp}$$

Figure 12: Rate of surface reaction

Now, since we have two reactant gases in step 2, we derive the surface reaction rate in terms of b and partial pressures of both sulfur dioxide and oxygen. Now, for this type of system we have two models, one being Langmuir-Hinshelwood and other being Rideal-Eley Model. The equation of rate of reaction using these models differ because of the assumption that Langmuir-Hinshelwood Model assumes Reaction between Gases reactants only whereas the Rideal-Eley Model assumes Reaction between reactant molecule adsorbed on catalyst surface and other molecule from gaseous phase or weakly adsorbed layer. The equations for both these models have been stated below:

$$v = k \frac{b_A p_A b_B p_B}{(1 + b_A p_A + b_B p_B)^2}$$

Figure 13: Rate using Langmuir-Hinshelwood Model

$$v = k \frac{b_A p_A p_B}{(1 + b_A p_A + b_B p_B)} \quad \text{or} \quad v = k \frac{b_B p_B p_A}{1 + b_A p_A + b_B p_B}$$

Figure 14: Rate using Rideal-Eley Model

In the above equations p_a denotes partial pressure of sulfur-dioxide and p_b denotes partial pressure of oxygen. Further we also know that since the reaction is exothermic and b denotes the equilibrium constant for absorption-desorption process, therefore as the temperature increases the value of b decreases. Now, from the equation we can observe that as the pressure of the reactants increases the rate of surface reaction increases as if we plot Rate vs Pressure graph, it will increase with increasing pressure, starting from origin and saturates at

1. Hence from this we conclude that increasing pressure and decreasing temperature favors forward reaction but as discussed in earlier section above that increasing pressure affects economics of process because of rusting of iron used in plants and also how decreasing temperature affects the reaction. So, the optimum temperature is about 450(deg) cel and pressure is in the range of 1.5 atm to 1.7 atm.

VII. PRODUCTION DETAILS AND REVENUE GENERATION:

Because of the vast uses discussed in earlier section, one can clearly observe that Sulfuric acid usage and production can act as an index to study the Financial Standing of a country. It plays a major role in determining GDP of a country. In terms of production, India has about 140 Sulfuric acid plants with Annual installed capacity of 12 Million Tonnes but current output is 5.5 Million Tonnes. About 25 percent of installed capacity is located in orissa. Below Table states the installed capacity and number of plants.

Installed Capacity (MT/Day)	Number of Plants	%
upto 50	18	12.9
51-100	45	32.1
101-200	40	28.6
201-300	17	12.1
301-500	5	3.6
501-1000	9	6.4
1001- 2000	4	2.9
above 2000	2	1.4
Total	140	100.0

Figure 15: Installed Capacity and Number of Plants

Now Considering average price of Sulfuric acid as 10INR/kilogram and average dollar conversion rate, India produces Sulphuric acid of approx. 765 USD annually. Now, Considering the approx. Annual global production as 230.7 million tonnes, but since the value of sulfuric acid vary widely from one part of the continent to the other, but to get an approximate idea of the value, assuming average price of sulfuric acid as 10INR/kilogram, the global annual production of nearly 30 Billion dollar (Only a rough idea and can vary widely according to the global prices of Sulfuric acid). So to conclude Sulphuric Acid is truly a king of chemicals as has been seen that it is involved in manufacture of almost all industries and has the potential to influence the Economy of a country.

REFERENCES:

- [1] <http://www.infoplease.com/encyclopedia/science/sulfuric-acid-uses-sulfuric-acid.html>
- [2] <http://www.essentialchemicalindustry.org/chemicals/sulfuric-acid.html>
- [3] <http://www.infoplease.com/encyclopedia/science/sulfuric-acid-uses-sulfuric-acid.html>
- [4] <http://www.organic-chemistry.org/chemicals/oxidations/vanadiumpentoxide.shtml>
- [5] <http://www.inclusive-science-engineering.com/manufacture-of-h2so4-by-chamber-process>
- [6] <http://www.inclusive-science-engineering.com/manufacture-of-h2so4-by-chamber-process/>
- [7] <http://minerals.usgs.gov/minerals/pubs/commodity/sulfur/myb1-2010-sulfu.pdf> [nptel.ac.in/courses/103106108/Lecture
- [8] http://www.sbioinformatics.com/design_thesis/Sulphuric_acid/Sulfuric-2520Acid_Methods-2520of-2520Production.pdf
- [9] <http://www.pearsonplaces.com.au/portals/0/teacherlounge/prchem2/ch21.pdf>



Smarthveer Sidana is pursuing his Bachelor's of Technology in Chemical Engineering from Indian Institute of Technology, Delhi. He is a Regional Mathematics Olympiad Scholar and got selected for Indian National Chemistry Olympiad (INCHO), Conducted by Homi Bhabha Research Centre. Having Keen interest in Research involving Mathematics and Chemistry, he has undertaken courses including Transport Phenomenon, Numerical Methods in Chemical Engineering, Energy and Mass Balances, Surface Catalysis, Differential and Integral Calculus, Applied Mechanics etc. He has also been an active member of different Non-Government Organisations (NGO) involved in Educating students from Financially weak background