

Techno-Economic Assessment for The Production of 400 tpd of Sulphuric Acid Using Waste Sulphur Gases from Coal Combustion and Pyrolysis Gases

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Abstract

This study focused on the techno-economic assessment of sulphur gas removal from coal combustion, pyrolysis and gasification in the flue gas stream in order to reduce harmful emissions from the coal industry which causes adverse effects to the environment. A potential of valorisation of the SO₂ to valuable, sulphuric acid (H₂SO₄) is therefore analysed. The design of a 400 tpd H₂SO₄ production process utilizing sulphur from coal combustion and pyrolysis flue gases is proposed. Experiments conducted indicated a 2.12%.wt by mass of coal is the sulphur content in the flue gases. The modified Claus Process, Amine Process and the Contact Process were selected as the best processes for optimum H₂SO₄ production. Based on the mass balances, the calculated gas flow rate from the power station boilers which utilize an average of 6000 tpd of coal was 146.33 t/hr. Economic analysis showed that the production cost of a tonne of H₂SO₄ is USD 32.47 and the profit margin was USD 57.53, the return on investment (ROI) was 44%, with a payback period of 2.28 years and the breakeven point was 60 tpd indicating the viability of utilizing the recovered sulphur to produce H₂SO₄ both technically and economically.

Keywords: Coal, flue gases, H₂SO₄, techno-economic assessment

1. Introduction

In Zimbabwe majority of industries use coal as their major source of heat and in order to meet the Environmental Management Authority emission regulations many companies use scrubbers to remove sulphur from their fumes. Zimbabwe has an estimated total of 10.6 billion tons of coal in situ in 21 deposits. Proven reserves can last for 107 years and total reserves over 2000 years at the present production rate of 4.7 million tons per year. Thermal power generation is the prominent user of coal seconded by the manufacturing sector where coal is used for steam generation and smelting in furnaces. Coal is composed of carbon, hydrogen, oxygen, nitrogen and sulphur with small amounts of other trace elements (Yelebe et al., 2013). The sulphur present in coal is of two types: inorganic sulphur mainly present as pyrites and organic sulphur which forms the part of overall coal matrix (Karl et al., 2001). The oxides of sulphur (SO_x) and of nitrogen (NO_x) are the principal chemical pollutant products of coal combustion. When these gases are emitted by the power station stacks over half of the emissions fall to earth in dry form, relatively close to the source. In the presence of sunlight and other chemical oxidants present in the atmosphere, some of the remaining air-borne sulphur and nitrogen oxides are transformed into sulphites and nitrates and finally these sulphites and nitrates form H₂SO₄ and HNO₃ resulting in acidic rain (Kapungwe et al., 2001). The only sulphide source mined

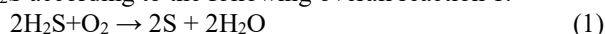
for the sole purpose of providing sulphur for H₂SO₄ production is the Iron Duke Pyrite mine, 45 km north of Harare, Zimbabwe. This underground mine produces pyrite ore containing 35.5%. General annual production rates of pyrite over the last 40 years have ranged between 50 000 and 70 000 tons. This work seeks to conduct a techno-economic assessment for the design of a H₂SO₄ making process from coal combustion and pyrolysis exit gases as a measure to utilise the waste sulphur.

2. Process Selection for Sulphur Recovery Methods

There are many sulphur gas recovery methods which are currently in use but mostly they recover sulphur from H₂S gas. The detailed processes are described below:

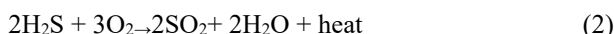
2.1 The Claus Process

The Claus Process was invented in 1883 by the English scientist; Carl Friedrich Claus. The conversion of H₂S to elemental sulphur in Claus plants is widely practiced. These sulphur recovery units make use of the so-called Claus reaction, i.e. the reaction of H₂S and SO₂ to yield sulphur and water. The SO₂ is supplied either by burning one third of the H₂S containing acid gas in a slip-stream and recombining the gases with a limited amount of air (The Linde Group., 2012). The process consists of multistage catalytic oxidation of H₂S according to the following overall reaction 1.



Each catalytic stage consists of a gas reheater, a catalyst chamber, and a condenser. There are four main variations of the Claus process which differ primarily on the way in which the heat balance is maintained. These are the straight through process, the split flow process, the split flow process with preheating of feed stream, and the sulphur recycle process. The straight through process is utilized when the H₂S concentration in the acid gas feed is greater than 50 mole%. The split flow process configuration is used when the H₂S concentration in the feed is between 20-50 mole%. If the feed stream contains less than 20 mole% H₂S and the flame is not self-sustaining at ambient temperature, the split flow scheme with preheat is employed. The sulphur recycle process is used when the feed contains less than 10 vol. % H₂S and a self-sustaining flame occur (The Linde Group., 2012)

The Claus process involves burning one third of H₂S with air in a reactor furnace to form SO₂ according to the following reaction 2



The remaining uncombusted two thirds of the H₂S undergoes Claus reaction (reacts with SO₂) to form elemental sulphur as follows in reaction 3:

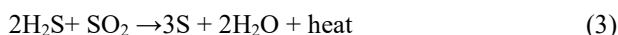


Table 1: Advantages and disadvantages of using Claus Process as a sulphur recovery method

Advantages	Disadvantages
Well proven process technology for recovering sulphur from acid gas streams	The process is not economical and/or might not be operable when the concentration of H ₂ S is below 10%.
	The process can only achieve a sulphur recovery of 96%, hence, a tail gas treatment unit is required if complete removal of sulphur is necessary.
	Presence of hydrocarbons heavier than C ₄ will lead to catalyst fouling and deactivation and a lower quality sulphur product.

2.2 Lo-Cat sulphur recovery

The process was first developed by Humphreys and Glasgow in 1965 as the chelated iron process. Ethylene Diamine Tetra Acetic Acid was used to hold the iron in solution. The Lo-Cat process is a patented, wet scrubbing, liquid redox system that uses a chelated iron solution to convert H₂S to innocuous, elemental sulphur. It does not use any toxic chemicals and does not produce any hazardous waste by-products. The Lo-Cat process has fundamentally two basic systems the aerobic and an anaerobic system (Buckens, 2005). The advantages and disadvantages of the Lo-Cat sulphur recovery process are shown in Table 2.

Table 2: Advantages and disadvantages of Lo-Cat process as a sulphur recovery method

Advantages	Disadvantages
Non-toxic chemicals are used in the catalyst reagent ARI-310	The catalyst reagent is corrosive so equipment cannot be fabricated from carbon steel
The catalyst is readily available and at low cost	The process can only remove H ₂ S, so a hydrogenation reactor is required to convert all other sulphur compounds to H ₂ S
The catalyst is stable at any pH hence low catalyst consumption	
High turn down capacity	

Produces elemental sulphur without flotation	
The catalyst reagent tolerates CO ₂ , NH ₃ and other gas contaminants	
The process is adaptable to aerobic or anaerobic gas streams	
Essentially complete removal of with low H ₂ S content	

2.3 Selectox sulphur recovery

The Selectox process, processes lean acid gas with a catalytic burner which oxidizes the H₂S to SO₂ at a temperature of 370 °C. There are three operating modes of the Selectox process depending on the H₂S content of the feed gas stream. The first is the Once-through Selectox process. It is useful for recovering sulphur from gas streams containing about 5% H₂S. Lean acid gas mixed with stoichiometric air is fed directly to the first stage. About 82% of the H₂S is converted to elemental sulphur over the Selectox catalyst. H₂S and SO₂, leaving the first stage in a 2:1 mole ratio, react to form an additional 14% sulphur over Claus catalyst present in the second and third stages (Paubel et al., 2007). The overall sulphur recovery is 96%. The tail gas leaving the third stage can be catalytically incinerated over a bed of Selectox catalyst using air. For acid gases containing 5-40 mole % of H₂S the Recycle Selectox process is used. Since the selective oxidation of H₂S to S reaction is highly exothermic, the H₂S concentration in the acid gas feed is reduced to about 5 mole % by mixing with the spent gas from the first-stage condenser. Hence the reactor temperature rise is controlled by use of recycle gas. The balance of the spent gas containing unconverted H₂S and SO₂ in a 2:1 mole ratio is sent to one or two stages of Claus catalyst for conversion to sulphur. About 82% of the product sulphur is recovered from gases leaving the first stage, 12% in the second stage, and an additional 2% in the third stage. The advantages and disadvantages of this technology are given in Table 3.

Table 3: Advantages and disadvantages of the Selectox sulphur recovery process

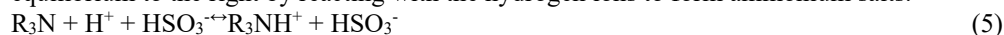
Advantages	Disadvantages
Process can feed gas containing a wide range of H ₂ S concentrations	Acid gas containing olefins and aromatics cannot be processed due to danger of catalyst fouling
The Selectox catalysts can also serve as a catalyst for catalytic incineration	Except for Selectox, only 96% of the total sulphur can be recovered without an additional tail gas treatment unit

2.4 Amine process

The Amine process has particular merit due to the fact that H₂S removal, in some fashion, is routinely required as a part of the basic oil and gas de-sulphurizing processes and that a convenient use for the recovered H₂S is found in the ubiquitous sulphur recovery unit. The aqueous amine solvent used in the amine system process is very stable and highly selective for SO₂. In water solution, dissolved SO₂ undergoes reversible hydration and ionization to produce bisulphite and sulphite according to the following reactions 4 and 5:



Adding a buffer, such as an amine, to the water increases the quantity of SO₂ dissolved. The buffer drives the above equilibrium to the right by reacting with the hydrogen ions to form ammonium salts.



Reaction 2, the overall reaction, indicates that as the concentration of SO₂ in the feed gas increases, the equilibrium moves to the right, i.e. the quantity of SO₂ dissolved in the rich solvent increases. Thus, the scrubbing of more concentrated gas streams requires a less than proportional increase in solvent circulation rate. Since the gas volume, and therefore the gas side equipment, remains constant, a relatively small total cost increase is caused by an increase in feed SO₂ concentration. Steam stripping of the SO₂ loaded solvent in a counter-current multi-stage column will force the equilibrium of reaction the left and consequently, reactions 4 and 5 are reversed, regenerating the absorbent. Table 4 shows the advantages and disadvantages of the Amine Process as a sulphur recovery method.

Table 4: Advantages and disadvantages of the Amine Process as a sulphur recovery method

Advantages	Disadvantages
Removes a higher % of SO ₂ which is up to 99.99%	Minor impurities in the feed gas often cause undesirable side reactions in the absorption column.
	Many units have not performed up to design specifications

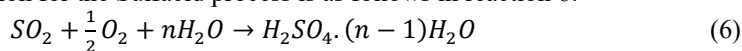
The modified Claus and Amine process will then be used for sulphur recovery from the flue and pyrolysis gases.

3. Process Selection for H₂SO₄ Manufacturing Methods

There are many alternative routes and processes that can be used in this manufacture of the H₂SO₄. It is therefore of importance to select the best route toward the production of the acid that is efficient and economically viable.

3.1 Sulfacid Process

SO₂, H₂O and O₂ react in an activated carbon catalyst to form H₂SO₄ in the Donau Carbon Sulfacid process. The H₂SO₄ produced from this process is weak and is less than 20% H₂SO₄. Multiple activated carbon beds arranged in parallel are often used. The acid making reaction for the Sulfacid process is as follows in reaction 6:



The advantages and disadvantages for the Amine Process as a sulphur recovery method are shown in Table 5.

Table 5: Advantages and disadvantages of Sulfacid process as a H₂SO₄ production process

Advantages	Disadvantages
Relatively low capital and operating cost	The strength of the acid it produces does not meet the desired specifications of 98 %
Efficient at removing SO ₂ from gases	

Due to the process' inability to meet design specifications of 98 % H₂SO₄ acid we cannot apply this technology to the proposed plant even though it presents favourable advantages.

3.2 Contact Process

Step 1 - Production of sulfur dioxide

This reaction is described by the reaction 7:



Elemental sulphur is purchased on the international market having been recovered as a by-product of the oil refining process. This sulphur is melted by steam coils at 140 °C in brick lined tanks. The molten sulphur is filtered to remove any impurities. Lime is added to reduce the acidity of the molten sulphur therefore reducing its corrosivity. The molten sulphur is pumped to the burner where it is burnt in an excess of dry air. The gas exiting the burner is maintained at 8 - 9% SO₂ at approximately 830 °C due to the heat produced by the exothermic reaction. The SO₂/air gas mixture is then passed through the hot gas filter, where any ash contamination is removed.

Step 2 Conversion to sulphur trioxide

The SO₂ is converted to sulphur trioxide by reacting with oxygen over a catalyst. This reaction is described by the reaction 8:



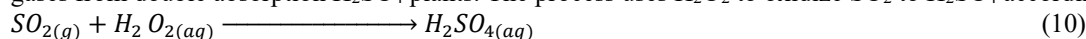
Step 3-Absorption of SO₃ to form H₂SO₄

The gas is passed to the absorption tower, a packed tower where SO₃ is absorbed into a counter-current flow of 98 - 99% H₂SO₄. The overall reaction can be described by the reaction 9, where sulphur trioxide reacts with the free water to produce H₂SO₄: SO_{3(g)} + H₂O_(l) → H₂SO_{4(l)} (9)

This is the best technology to apply as it produces the desired 98 % acid. Also since it is used by many recent plants it is easy to evaluate our performance as far as local and international competition is concerned.

3.3 Peracidox Process

This process was developed by Lurgi Metallurgie and Süd-Chemie. It aims to specifically to remove residual SO₂ from tail gases from double absorption H₂SO₄ plants. The process uses H₂O₂ to oxidize SO₂ to H₂SO₄ according to the reaction 10.



Scrubbing is achieved by direct contact in a counter-current spray tower. The peroxide reacts with SO₂ in the first chamber and overflows to the second chamber. The bleed acid concentration is approximately 50% H₂SO₄, which can be recycled to the acid plant as dilution water. The advantages and disadvantages of the Peracidox process are given in Table 6.

Table 6: Advantages and disadvantages of Peracidox Process as a H₂SO₄ production process

Advantages	Disadvantages
Simple	High operating cost due to peroxide
It has a high SO ₂ removal efficiency	Relatively low acid strength product (~50% H ₂ SO ₄) which does not meet the required specifications of 98 %
Low capital cost	

This process was discarded due to the fact that it does not produce the desired H₂SO₄ acid concentration of 98%

4. Reactors for Consideration in H₂SO₄ Production

There are many reactors which can be used in chemical industries but the choice of the reactor depends on many factors which include the homogeneity of reactants, rate of reaction and other factors.

4.1 Batch Reactors

A batch reactor is used for small-scale operation for testing new processes that have not been fully developed for the manufacture of expensive products and for processes that are difficult to convert to continuous operations. The reactor can be charged through the holes at the top. The batch reactor has the advantage of high conversions that can be obtained by leaving

the reactant in the reactor for long periods of time but it also has the disadvantages of high labour costs-per batch, the variability of products from batch to batch and the difficulty of large-scale production. Considering that our feed is a gas and the cost of operation of the batch reactor is high this is not suitable.

4.2 Continuous-Stirred Tank Reactor

A type of reactor used commonly in industrial processing is the stirred tank operated continuously and is referred to as the continuous-stirred tank reactor (CSTR). The CSTR is used primarily for liquid phase reactions. It is normally operated at steady state and it is assumed to be perfectly mixed. A CSTR is economically used for liquid reactants and considering the nature of our reactants it does not apply.

4.3 Packed-Bed Reactor

It consists of a cylindrical pipe with catalyst bedding and is normally operated at steady state, as in the CSTR. Tubular reactors are used most often for gas-phase reactions. This is the best reactor as it has high conversion rate for the gas reactants due to high surface area of contact with the catalyst and also this is the best reactor for gases.

4.4 Plug Flow Reactor

Plug flow reactors are more like packed bed reactors and they are both classified as tubular reactors. They are both usually used for gases and the only difference is that the catalyst in packed bed reactor is on the packings and in plug flow the catalyst is on the walls. This is the best reactor for gases but the conversion rate is lower than in packed bed reactor for the considered reactants. Analysing the processes which are available for treating coal combustion and pyrolysis exit gases, most of the processes deals with gases from coal gasification and pyrolysis which have a great percentage of H₂S than SO₂ but the gas we are dealing with has a greater percentage of SO₂ than H₂S. So from the analysed processes the amine process will be favourable for treating our gases but the amines easily form heat stable salts with the impurities in the gas steam which include COS, HCN, CS₂ etc. so there is need of treating this gas before it is introduced into the absorber. There is also a percentage of H₂S in the gas stream and the first part of the Claus process which have a combustion chamber can be adopted and combined with the amine process to help eliminate or combust all the H₂S to SO₂ to increase the removal of sulphur compound from the gas stream. From the stripper of the amine process the final product is 99.99% SO₂ and channelling this gas to the part of the contact process our desired product can be produced which is 98% H₂SO₄. Therefore the process being designed will be a combination of the Claus process, Amine process and the Contact process considering the plug flow reactors as the reactor types.

5. Materials and Methods

5.1 Materials

The materials required for the sulphur composition determination were: A IKA's C 6000 bomb calorimeter, coal sample, barium chloride, filter paper and filter funnel, crucible, distilled water and phenolphthalein indicator. An Orset gas analyser for determining the flue gas and pyrolysis gas composition.

5.2 Methods

The following methodology was adopted for the determination of sulphur content in the coal sample: A sample of coal was taken and crushed it into powder. A 10g sample was put in a crucible and placed in a bomb calorimeter. The coal was ignited and given enough time for complete combustion. After complete combustion the distilled water was filtered to remove ash. The sulphur content was determined by measuring 10ml of the water and adding phenolphthalein indicator and then titrating it with barium chloride.

6. Results and Analysis

6.1 Inlet gas composition

The composition of the exit gases from the coal power station are indicated in Table 7. SO₂ and CS₂ had the highest composition of 6% and 20% respectively.

Table 3: Typical exit gas composition from coal combustion and pyrolysis

Component	Mr	% Composition in coal combustion gas	% Composition in coke oven exit gas
NH ₃	17	1	0.81
SO ₂	32	6	Trace
H ₂ O	18	3	-
HCN	27	Traces	Traces
SO ₃	80	100ppm	Traces
CO ₂	44	62	2.07
HCl	33	Trace	-
H ₂ S	~	-	33.18

CO	28	3	60.0
COS	60	3000ppm	
CS ₂	76	3000ppm	3.34
Particulate matter	~	20	-
Organic compounds	~	4	-

The average physical properties of the Thermal Power station gas are shown in Table 8.

Table 4: Thermal Power Station exit gas physical properties

Parameter	Value
Flow rate (Kg/hr.)	143.75
Temperature (°C)	118-149
Density (kg/m ³)	1.31
Pressure (atmos)	1.0

From the above results it shows that there is a significant amount of SO₂ and H₂S in combustion exit gases and coke oven gases respectively.

6.2 Sulphur composition

The sulphur composition in the flue gas was 2.12% wt. The percentage composition of sulphur in coal combustion and coke oven gases is a significant amount which poses as a threat to the environment but it has an economic value when utilized. Using the results given above and the coal consumption data from the colliery company: 6 000 tonnes of coal is being combusted a day. Sulphur in coal used per day = average amount of coal used/day × % of sulphur in coal = 6000 × 0.0212 = 127.2 tonnes/day.

Assumptions

90% of the sulphur in coal is turned to gases

92% of these gases is SO₂ and the remaining is constituted by COS and CS₂

SO₂ in the Thermal Power station exit gas = (Mr of SO₂ ÷ Mr of S) × 0.92 × 125 × 0.9 = (64 ÷ 32) × 0.92 × 127.2 × 0.9 = 210.64 tonnes/day.

Flow-rate of SO₂ per hour = 210.64 tonnes/day ÷ 24 hours = 8.78 tonnes /hr.

Total gas flow-rate from Thermal Power Station = (100 ÷ % composition of SO₂ in gas) × flow rate of SO₂ = (100 ÷ 6) × 8.78 = 146.33 tonnes/hr.

Amount of S in coal used per day at the coke ovens = coal used at coke ovens per day × % of sulphur in coal × % of S = 1 400 × 0.021 = 29.68 tonnes/day

H₂S from coke oven gas = (Mr of H₂S ÷ Mr of S) × S in coal used × % S in gas = (34 ÷ 32) × 29.68 × 0.9 × 0.92 = 26.11 tonnes/day

Flow rate of H₂S per hour = 26.11/day ÷ 24 = 1.09 tonnes/hr.

Total flow rate of coke oven gas = (100 ÷ % composition of H₂S) × 1.14 tonnes/hr. = (100 ÷ 33.18) × 1.14 = 3.29 tonnes/hr.

Total flow rate of both combustion and coke oven gas = 146.33 tonnes/hr. + 3.29 tonnes/hr. = 149.62 tonnes/hr.

From calculations using the experimental results an average of 127 tonnes of sulphur are in coal used per day at Hwange thermal power station and if there is complete combustion this amount is emitted into the atmosphere which is a significant amount which can be used to improve the economy of the country if channelled to produce H₂SO₄ in the designed process.

7. Process Design for H₂SO₄ Production

The detailed process description is shown in Figure 1 and the list of equipment is given in Table 9. The process flow diagram is designed and the mass and energy balances are calculated. Mass balances are done over the chosen equipment in the process which is the hydrolysis reactor. Energy balances are also done over the hydrolysis reactor.

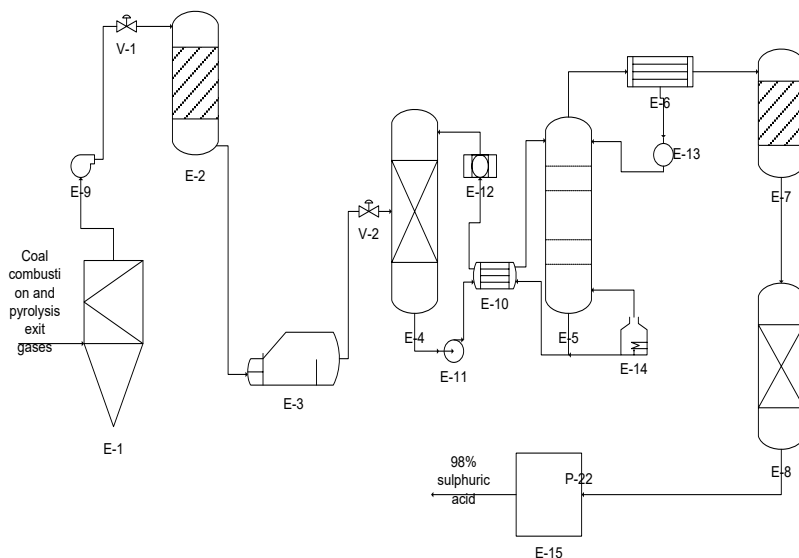


Figure 1: Designed process flowchart for H₂SO₄ production from sulphur recovered from flue gases
 The equipment shown in Figure 3 is described as in Table 10.

Table 9: Major H₂SO₄ production process equipment

Equipment number	Equipment name
E1	Electrostatic precipitator
E2	Hydrolysis packed bed reactor
E3	Combustion chamber
E4	Absorption column
E5	Stripping column
E12	Amine regenerator
E6	Condenser
E7	SO ₃ Converter
E8	Absorption tower
E15	Storage tank

7.1 Removal of dust particles

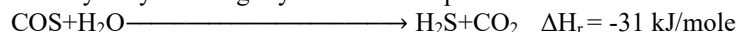
In the removal of fly ash the electrostatic precipitator is the major equipment. During coal combustion some of the ash contained in the coal is released as fly ash into the atmosphere together with the combustion gases. Fly ash can have fouling effects to the equipment in the process and electrostatic precipitators are employed to remove these particles. Precipitators typically collect 99.9% of the dust from the gas stream. An electrostatic precipitator uses electrical forces to capture fly ash particles in an incoming combustion gas. The fly ash particles are given an electrical charge by forcing them to pass through a corona, a region in which gaseous ions flow. The electrical field that forces the charged particles to the wall comes from the electrodes maintained at high voltage in the centre of the flow path. This arrangement causes: Formation of an avalanche of electrons in a corona around the negative rod electrodes ; movement of these electrons towards the positive dust collection plates; negative charging of gas molecules outside the corona by collision and combination of electrons with gas molecules; negative charging of dust by collision and attachment of gas ions to dust particles; electrical attraction of negatively charged dust to the positive collection plates and adhesion of the dust to the collection plates by electrical, mechanical and molecular forces. When enough dust has accumulated, the collectors are shaken to dislodge the dust, causing it to fall with the force of gravity to hoppers. The dust is then removed by a conveyor system for disposal or recycling.

7.2 Hydrolysis of COS and CS₂ in the gas stream

In the hydrolysis of COS and CS₂ the hydrolysis packed bed reactor is the major equipment. The hydrolysis unit converts the COS and CS₂ into H₂S, which can then be converted to SO₂ in the combustion chamber. COS and CS₂ can be partially

removed by some amines, especially primary and secondary ones. However, removal of such gas impurities subject the solution to degradation as those impurities react, either reversibly or irreversibly, with the amines to form degradation products. In irreversible reactions, such as those of MEA with COS and CS₂, formation of non-regenerable degradation products result in excessive solvent losses if the gas contains high concentrations of those sulphur compounds. After prolonged use, accumulation of the degradation products in the solution reduces its absorption efficiency. The conversion of COS and CS₂ to H₂S is an important step to increase the total sulphur recovery to 99.9% levels.

COS hydrolysis is slightly exothermic equimolar reaction:



COS hydrolysis is complete at 175-275 °C and proceeds on activated alumina, titania and zirconia catalysts. The main reason for catalyst deactivation is sulphate formation. The hydrolysis of CS₂ is more difficult than that of COS, requiring higher operating temperatures of >300 °C. The hydrolysis reactor is heated using super heated steam from the cooling of the combustion chamber exit gases.

7.3 Conversion of H₂S to SO₂

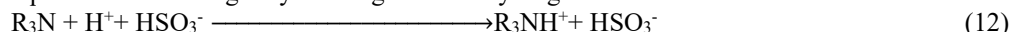
The major equipment in the conversion of H₂S to SO₂ is the combustion chamber. The gas stream is then passed through the combustion chamber where H₂S will burnt to form SO₂, CO is also oxidized to CO₂ which is more environmentally friendly and the unburnt hydrocarbons are also burnt. The furnace normally operates at temperatures ranging from 980-1000 °C with pressures not more than 5 atm. Hot gas from the furnace is quenched in a waste heat boiler that generates high to medium pressure steam. Much of the heat released from burning H₂S is recovered as useful energy. It is also used to super heat steam which will be used in heating up the hydrolysis reactor.

7.4 Absorption of SO₂ from gas stream

In the removal of SO₂ stage the absorption column is the major equipment. Counter current contact in a structured packed tower of the lean solvent with the process gas transfers the SO₂ to the liquid, producing the rich solvent and a cleaned gas. The gas stream is contacted with the aqueous absorbing medium at a temperature of from about 10° to about 60° C. To absorb SO₂ from the gas stream in amounts of at least about 100 g of SO₂ per kg of absorbing medium. Diamines which are used in the process are N-(2-hydroxyethyl) piperazine N, N'-di (2-hydroxyethyl) piperazine. The concentration of the Heat Stable Salt (HSS) is such that at least a portion of the weaker amine of the diamine is neutralized by the HSS. The aqueous amine solvent used in the system process is very stable and highly selective for SO₂. In water solution, dissolved SO₂ undergoes reversible hydration and ionization to produce bisulphite and sulphite according to the following reactions 11-12:



Adding a buffer, such as an amine, to the water increases the quantity of SO₂ dissolved. The buffer drives the above equilibrium to the right by reacting with the hydrogen ions to form ammonium salts.



The overall reaction indicates that as the concentration of SO₂ in the feed gas increases, the equilibrium moves to the right, i.e. the quantity of SO₂ dissolved in the rich solvent increases. The scrubbing of more concentrated gas streams requires a less than proportional increase in solvent circulation rate. The system process is based on a unique class of diamine absorbents that optimally balance the ability to absorb and regenerate SO₂. One absorbent molecule has two amine functionalities. One of the amine functionalities is strongly basic and non-heat-regenerable. Once it has reacted with SO₂ it remains in salt form in the scrubbing process. The second amine functionality is less basic than the first and is referred to as the sorbing nitrogen; it operates in the buffering range that gives the optimal balance for absorption and regeneration of SO₂. The system amine absorbents provide the following significant advantages: No losses to vapour since the absorbent is in salt form and therefore non-volatile, selectivity of SO₂ over CO₂ by factor of 50 000, high thermal and chemical stability, even in the presence of oxygen in the treated gas, high water solubility, giving a homogeneous liquid absorbent of relatively low toxicity and low foaming tendency.

7.5 Stripping of SO₂ from the amines

The major equipment in this stage is the stripping column. The SO₂ is stripped from the rich solvent in the regenerator with steam produced by the boiling aqueous solvent in the reboiler. Most of the water is removed from the regenerator overhead stream by condensation, leaving water saturated SO₂ as the by-product. The condensed water is returned to the tower as reflux. SO₂ is stripped from the spent absorbing medium at a temperature of 50-110 °C. The heat stable salt concentration is selected to reduce steam consumption in the steam stripping step to an amount in the range 4 kg steam/kg SO₂ recovered to 2 kg steam/kg SO₂ recovered.

7.6 Purification of the amine from the stripping column

The quality of the solvent is maintained by removing strong acids from a small slipstream of lean solvent in the absorbent purification unit. Streams containing SO₂ generally also contain H₂SO₄ mist that passes the pre-scrubbing stage and is captured by the amine solvent, producing heat stable salts, which if not removed would eventually neutralize the scrubbing

capacity of the solvent. An electro dialysis heat stable salt removal unit replaces the heat stable sulphate anions from a slipstream of lean amine with bisulphite, which is regenerable.

7.7 Removal of water from the stripped SO₂

From the stripping column the gas stream is composed of a high percentage of water vapour which is used for stripping. A condenser is employed to remove all the water in the stream and this water are used in the reflux to the stripping column.

7.8 Conversion of SO₂ to sulphur trioxide

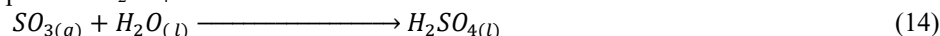
The SO₂ is converted to sulphur trioxide by reacting with oxygen over a catalyst. This reaction is described by the reaction 13:



This reaction occurs in the converter, a four-stage reaction vessel with each stage I-Chemicals-B-H₂SO₄ consisting of a solid catalyst bed through which the gas is passed. The catalyst used is vanadium pentoxide (V₂O₅) and potassium sulphate dispersed on a silica base which forms a porous support, giving a large surface area for reaction. It is believed that the V₂O₅ increases the rate of the overall chemical reaction by oxidising the SO₂ to SO₃ and being re-oxidised itself by the oxygen in the gas stream. This reaction is exothermic and its equilibrium constant decrease with increasing temperature in accordance to Le Chatellier's Principle. In practice, the gas temperature must be maintained between 400 – 500 °C to maintain a high reaction rate and high conversion equilibrium. As the reaction is exothermic, heat is generated across each of the catalyst beds. This heat must be removed between each stage to maintain the optimum reaction temperature into the following stage.

7.9 Absorption of SO₃ to Form H₂SO₄

The gas is passed to the absorption tower, a packed tower where SO₃ is absorbed into a counter-current flow to form 98 - 99% H₂SO₄. The overall reaction can be described by the following equation, where sulphur trioxide reacts with the free water to produce H₂SO₄ as in reaction 14:



The circulating H₂SO₄ must be maintained at about 98% concentration and 70 °C to maximise the absorption efficiency. The acid strength is important because the vapour pressure of sulphur trioxide above H₂SO₄ is at a minimum at an acid strength of 98%. At higher concentrations the increased vapour pressure is caused by SO₃ and at lower concentrations the water vapour pressure increases sharply and the resultant acid mist is not readily re-absorbed and escapes to the atmosphere. The H₂SO₄ is circulated at such a rate that there is only a very small increase in concentration through the absorber tower. Dilution water is added to the circulating acid tank and also as atmospheric water absorbed in the drying tower. A stream of H₂SO₄ is continuously bled off and cooled through a plate heat exchange before being passed into the storage tanks.

From the above designed process, the hydrolysis packed bed reactor is the chosen equipment which will be concentrated on.

7.10 Mass balances

Mass into the system = Mass out of the system + Accumulation.

In a steady state condition which is assumed in this case, the accumulation term = 0. The assumption that was made was the entire COS and CS₂ is converted to H₂S and CO₂ and the process is at steady state. The com position of the electrostatic precipitator exit gas stream is given in Table 10.

Table 10: Composition of electrostatic precipitator exit gas stream

Component	Mr of component	Mass fraction of component	Mass flow-rate of components tonnes/hr.	Molar flow rate of component ×10 ³ kmoles/hr.
SO ₂	64	0.0730	8.7856	0.1373

COS	60	0.0037	0.4453	0.007422
CS ₂	76	0.0037	0.4453	0.005859
CO ₂	44	0.7544	90.7920	2.0635
H ₂ O	18	0.0365	4.392775	0.2440
CO	28	0.0529	6.366515	0.2274
H ₂ S	34	0.0091	1.0952	0.03221
Organic compounds		0.04864	1.3359	

A summary of the material balance over the hydrolysis reactor is given in Table 11.

Table 11: Material balance over the hydrolysis reactor

Component	Total number of moles that reacted per hour	Total number of moles produced from reaction per hour	Component molar flow rate into the system	Molar flow rate of reactor exit stream	Mass flow rate of reactor exit stream	Mass fraction of exit gas stream
COS	0.007422	-	0.007422	-	-	-
CS ₂	0.005859	-	0.005859	-	-	-
H ₂ S	-	0.01914	0.03221	0.05135	1.7459	0.01451
CO ₂	-	0.01328	2.0635	2.0648	90.8512	0.7550
H ₂ O	0.01914	-	0.2440	0.22486	4.0475	0.03363
SO ₂	-	-	0.1373	0.1373	8.7872	0.0730

7.11 Energy Balances

Energy balance over the hydrolysis reactor with a basis of 1hr operation.

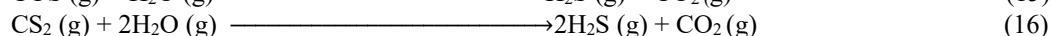
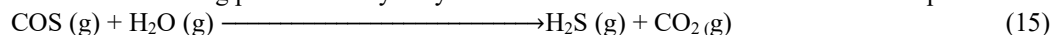
Energy out = Energy in + generation - consumption – accumulation

Enthalpy calculation

Because enthalpy cannot be known absolutely, it is convenient to assign H=0 to some reference state. If enthalpies of states 1 and 2 are known relative to the same reference condition H_{ref}, ΔH is calculated as follows:

$$\Delta H = (H_2 - H_{ref}) - (H_1 - H_{ref}) = (H_2 - H_1)$$

The reactions taking place in the hydrolysis reactor and combustion chamber are as represented in 15 and 16:



Hess' law states that

$$\Delta H_{\text{reaction}} = \Sigma \Delta H_{\text{formation}} (\text{products}) - \Sigma \Delta H_{\text{formation}} (\text{reactants})$$

$$\Sigma \Delta H_{\text{formation}} (\text{COS}) = -142.0 \text{ kJ/mole}$$

$$\Sigma \Delta H_{\text{formation}} (\text{SO}_2) = -296.80 \text{ kJ/mole}$$

$$\Sigma \Delta H_{\text{formation}} (\text{CS}_2) = + 116.8 \text{ kJ/mole}$$

$$\Sigma \Delta H \text{ formation (CO}_2\text{)} = -393.5 \text{ kJ/mole}$$

$$\Sigma \Delta H \text{ formation (H}_2\text{O)} = -241.8 \text{ kJ/mole}$$

$$\Sigma \Delta H \text{ formation (H}_2\text{S)} = -20.6 \text{ kJ/mole}$$

For reaction 15

$$\Delta H \text{ reaction} = [\Delta H \text{ formation (H}_2\text{S)} + \Delta H \text{ formation (CO}_2\text{)}] - [\Delta H \text{ formation (H}_2\text{O)} + \Delta H \text{ formation (COS)}]$$

$$= [(-20.6) + (-393.5)] - [(-142.0) + (-241.8)] = [-414.1] - [-383.8] = -30.3 \text{ kJ/mole}$$

For reaction 16

$$\Delta H \text{ reaction} = [[2 \times \Delta H \text{ formation (H}_2\text{S)}] + \Delta H \text{ formation (CO}_2\text{)}] - [[2 \times \Delta H \text{ formation (H}_2\text{O)} + \Delta H \text{ formation (COS)}] = [2(-20.6) + (-393.5)] - [(116.8) + 2(-241.8)] = [-434.7] - [-366.8] = -67.9 \text{ kJ/mole}$$

8. Economic Analysis

In this section the process plant cost is estimated using the factorial method and the cost of the equipment is overviewed. The breakeven point and the return on investment is also determined from calculations.

8.1 Capital Cost Calculation

In calculating capital cost the prices of equipment as indicated in Table 12.

Table 12: Cost of major equipment in the H₂SO₄ manufacturing process

Equipment	Quantity	Unit Price (USD)	Total Cost (USD)
Electrostatic precipitator	1	130 000	130 000
Hydrolysis packed bed reactor	1	200 000	200 000
Combustion chamber	1	150 000	150 000
Absorption column	1	750 000	750 000
Stripping column	1	750 000	750 000
Amine regenerator	1	188 900	188 900
Condenser	1	160 000	160 000
SO ₃ Converter	1	700 000	700 000
Absorption tower	1	750 000	750 000
Storage tank	4	25 000	100 000
Blowers	2	5 000	10 000
Pump	3	5 000	15 000
Heat exchanger	1	160 000	160 000
Total Cost			4 063 900

Fixed capital

This is the total cost of a plant ready for start-up and operation Sinnott (1993) states that these costs include the items indicated in Table 13:

Table 13: Fixed capital cost of the designed process

Component	Range	Selected %	Cost (USD)	
Purchased equipment			4 063 886.30	
Yard improvement	5-10	10	406 388.63	
Instrumentation and control	10-25	25	1 015 971.50	
Service facilities	5-10	10	406 388.63	
Land	10-25	25	1 015 971.50	
Piping	3-20	20	812 777.26	
Buildings	10-25	22	894 055	
Electrical	25-40	31	1 259 804	

Installation	25-40	40	1 625 554	
Total direct costs				11 500 778.3
Engineering and suspension	4-21	15	609 583	
Construction expenses	4-20	20	812 777.26	
				1 422 360.20
Total direct and indirect cost				12 923 158.40
Contractors	2-15	10	406 388.63	
Contingency	5-15	15	609 583	
				1 015 971.63
Fixed capital investment				13 939 13

Working capital

The working capital is the required additional investment to start up the plant and operate it to the point where income is earned, over and above the fixed capital. Included in these start-up costs are: initial catalyst charge, raw materials and intermediates, product inventory accumulation and funds to cover outstanding accounts from customers. Working capital for this economic evaluation has been approximated to be equal to 15% of the fixed capital. However, the sum of the working capital (C_w) and the fixed capital (C_f) is equal to the total capital cost (C_T) calculated before.

$$C_T = C_f + C_w$$

For most chemical plants,

$$C_w = 15\%C_f = 0.15 \times 13\,939\,130 = \text{USD } 2\,090\,890$$

Thus

$$C_T = C_f(1 + 0.15) = 13\,939\,130(1.15) = \text{USD } 16\,030\,000$$

Production costs estimation

To judge the validity of the project, an estimate of the operating costs, the costs of producing the product is required. There are two types of operating costs are fixed operating costs and variable operating costs.

Variable operating costs

For this stage we will take these as represented by only the raw material costs and the utilities and they are taken as on the basis of one operational year.

$$\text{Raw materials} = 15\% \text{ of total capital investment} = 0.15 \times \text{USD } 16\,030\,000 = \text{USD } 2\,404\,500$$

$$\text{Utilities} = 10\% \text{ of working capital} = 0.1 \times \text{USD } 2\,090\,890 = \text{USD } 209\,089$$

$$\text{Total variable cost} = \text{raw materials} + \text{utilities} = \text{USD } 2\,404\,500 + 209\,089 = \text{USD } 2\,613\,589$$

Fixed operating costs

These are costs that do not vary with production rates, in this case the bills that have to be paid whatever the quantity produced. A summary of the fixed costs is given in Table 14.

Table 14: Fixed operation cost

	Percentage of C_w	Amount (USD)
Capital charges	15	313 633.50
Operation Labour	6	125 453.40
Laboratory (20% of labour costs)	1.2	25 090.68
Maintenance	5	104 544.50
Insurance	1	20 908.90
Supervision (20% of labour costs)	1.2	25 090.68

Taxes	1	20 908.90
Plant overhead (50% of labour costs)	3	62 726.70
Total	33.4	698 357.26

8.2 Economic Review

$$\begin{aligned} \text{Direct production costs} &= \text{variable cost} + \text{fixed cost} = \text{USD } 2\,613\,589 + \text{USD } 698\,357.26 \\ &= \text{USD } 3\,311\,946.26 \end{aligned}$$

Company's general operating expenses will include: General overheads, Research and development costs, Sales expense and Reserves. In most cases these would add about 20 - 30% to direct production costs at the site.

$$\begin{aligned} \text{Additional expences} &= 20\% \text{ of direct production cost} \\ &= (0.2 \times \text{USD } 3\,311\,946.26) = \text{USD } 662\,389.25 \end{aligned}$$

$$\begin{aligned} \text{Annual production cost} &= \text{direct production cost} + \text{additional expences} \\ &= \text{USD } 3\,311\,946.26 + \text{USD } 662\,389.25 = \text{USD } 3\,974\,335.51 \end{aligned}$$

Assuming an overall plant efficiency of 85% for the first years of operation, the number of productive days in a year can be estimated as (0.85×360)

$$\begin{aligned} \text{Production cost per tonne} &= \frac{\text{Annual production cost}}{\text{Annual production rate}} = \left[\frac{\text{USD } 3\,974\,335.51/\text{yr}}{(400 \times 360 \times 0.85 \text{ tonnes/yr})} \right] \\ &= \text{USD } 32.47 \text{ per tonne of } H_2SO_4 \end{aligned}$$

The known selling price of the 98% grade H_2SO_4 was pegged at USD 90 per tonne.

$$\begin{aligned} \text{Annual sales revenue expected} &= \text{selling price/t} \times \text{annual production rate} \\ &= \text{USD } 90 \times (400 \times 360 \times 0.85) \text{ tonne/yr} = \text{USD } 11\,016\,000 \end{aligned}$$

$$\begin{aligned} \text{Expected profit margin} &= \text{selling price/tonne} - \text{production cost/tonne} \\ &= \text{USD } 90 - \text{USD } 32.47 = \text{USD } 57.53 \end{aligned}$$

$$\begin{aligned} \text{Net returns expected per annum} &= \text{sales revenue} - \text{production cost} \\ &= \text{USD } 11\,016\,000 - \text{USD } 3\,974\,335.51 = \text{USD } 7\,041\,664.49 \end{aligned}$$

$$\text{Payback period} = \frac{\text{Capital Cost}}{\text{Net returns}} = \frac{\text{USD } 16\,030\,000}{\text{USD } 7\,041\,664.49} = 2.28 \text{ yrs}$$

$$\text{ROI} = \frac{\text{Annual profit}}{\text{Capital invested}} \times 100\% = \frac{\text{USD } 7\,041\,664.49}{\text{USD } 16\,030\,000} \times 100\% = 44\%$$

$$\text{Break even point} = \frac{\text{Fixed capital cost}}{\text{Sales} - \text{Direct costs}}$$

The breakeven point is at 15% of the total production rate, Therefore: Breakeven = $0.15 \times 400 = 60$ tonnes/day

9. Conclusion

From the analysis carried out it can be concluded that it is possible to produce 400 tpd of H_2SO_4 from sulphur recovered from coal combustion gas and coke oven gas. The operational considerations such as the process design and economic assessment were taken into account. The production cost of the H_2SO_4 is USD 32.58/tonne with a payback period of 2.28 years. The selling price is USD 90/tonne which is the current price of H_2SO_4 . Therefore the H_2SO_4 production from coal combustion and coal pyrolysis process is technically and economically viable.

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