

ROLAND ESQUIVEL

COAL TO METHANOL DESIGN REPORT

ACID GAS REMOVAL

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1. Executive Summary

Acid Gas removal process was developed for the coal to methanol production plant. A syn gas containing 35 tones/day of hydrogen sulfide was processed through the Claus process with 16 tones/ day of oxygen needed for combustion. A combined 23 tones/day of sulfur were recovered. Comparing the many commercial technologies in use and a promising sulfur removal process in pilot scale the methanol based Rectisol[®] is recommended in the design to meet the 0.1ppmv sulfur purity in the syngas. The cleaned syngas was the sent to a water gas shift reactor where the 0.6 H₂:CO ratio was converted to 2:1 mole to mole ratio. The water gas shift extent of reaction to meet the requirement was calculated to be 0.46 and a equilibrium temperature of 677K. Excess water of 1,351 tones/day is required for conversion. The lean syngas in 2:1 ratio is 478K and 1 bar. Aspen simulations using the RGibbs model to determine the products was completed. Preliminary utility cost were estimated at \$23 million annual cost for water and oxygen. Safety considerations are discussed for the acid gas removal section.

2. Introduction to Syn Gas Acid Gas Removal

Gasification of coal into syngas yields an abundant feed stock for a variety of energy production technologies. In particular, global methanol production plants produced 30 million tones of methanol from a variety of feed stocks⁹. Syngas (CO, H₂ & CO₂) accounts for 10% of this feed stock and has a variety of sources from coal to petroleum to coke. Common by products of Syngas production are toxic and corrosive gases such COS, H₂S and CO₂. These toxic gases also known as Acid Gases need to be removed from Syngas for downstream fuel synthesis and for environmental considerations. Refineries world-wide are being subjected to increasing pressures both legislative and economic. The effects of the Clean Air Act (CAA) in the United States of America are well documented⁶. Acid-gas removal technologies that are currently available or under development include: low-temperature or refrigerated solvent-based scrubbing systems using amines, such as MDEA, or physical solvents, such as Rectisol[®], Selexol, Sulfinol, or high temperature sorbents (not yet demonstrated at commercial scale)¹⁰.

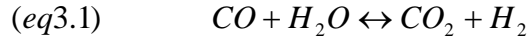
To further evaluate the Coal to Methanol design report (Initial project proposal and gasification process in appendices) acid gas removal systems were investigated. Sulfur removal technologies were evaluated and alternatives were considered based on the design specifications and material balances of the 5000MT methanol synthesis capacity. A process flow diagram of material balances to remove the sulfur is presented, along with an Aspen simulation description of the RGibbs model to simulate production elemental sulfur from 35 tones/day of H₂S gas. Elemental sulfur is an environmentally safe means to transport sulfur. The sulfur can later be sold and the cost of the methanol plant offset by the side production.

Once sulfur is removed from the syngas, the 3,910 tones/day of lean syngas is processed through a water gas shift reactor to convert to a stoichiometric mole ratio of 2:1 H₂ to CO. Reaction shift calculations were completed and a Aspen flow diagram using the RGibbs model was conducted to meet the 2:1 ratio. To complete the shift reactor 1,351 tonnes/day of pure oxygen is needed for the water gas shift reactor.

Based on the Aspen flow diagram and material balances annual utilities cost to run acid gas removal section was estimated.

3.1 Water Gas Shift

The water gas shift reaction is a widely used for the manufacture of hydrogen and to prepare syngas for synthetic fuel synthesis. Industrial shift reactions are carried at pressures ranging from 1bar to 50 bar². The composition of the water gas may range from 80% CO to less than 3% CO. The chemical equation



is an equal molar reaction with well understood kinematics. Given a syngas input ratio it is possible to shift the mole ratios of the syngas. The slightly exothermic reaction undergoes molar shifts at lower temperatures around 500 – 600 K.

Based on the 3000 tones/day of sub bituminous coal and after H₂S removal the lean syngas mole ratio of H₂:CO was 3:5 or 0.6. Methanol synthesis requires a stoichiometric ratio of 2:1. The extent of reaction the composition required to change was calculated to be 0.46. Assuming a first order reaction equation the equilibrium constant was calculated to be 12.07. The equilibrium constant for the water gas shift reaction can be approximated by the following relationship.

$$(eq3.2) \quad \ln K_p = \ln \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = \ln \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = -4.33 + \frac{4577.8}{T(K)}$$

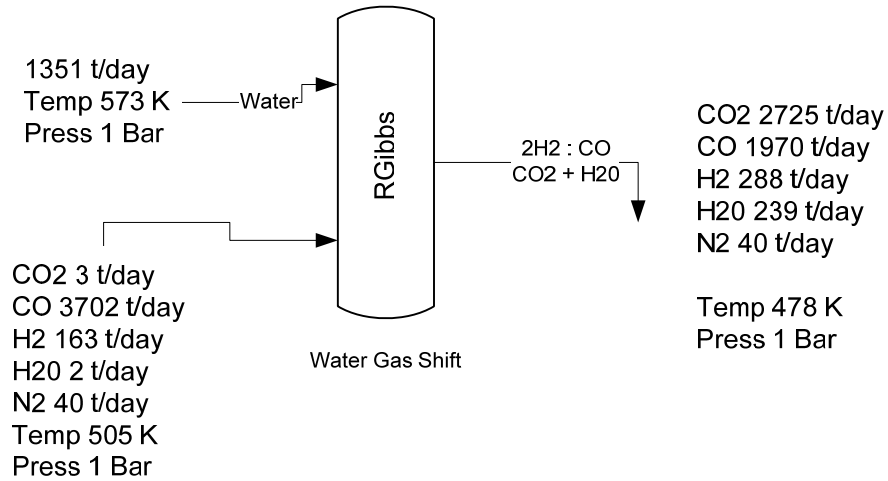
Using this relationship the equilibrium temperature was estimated at 671K. The water composition was the limiting reactant; therefore excess water will need to be added to the equilibrium reactor. To achieve this shift 1,351 tones/day of water at 573K and 1 bar will need to be feed to the syngas stream. The syngas flow rate after the water gas shift reactor was 288 tones/day of H₂ and 1,970 tones/day of CO which achieves the 2:1 molar ratio at 478K and 1 bar. Other inert by products include 40 tones/day of N₂, 239 tones/day H₂O, and 2,725 tones/day CO₂.

CO₂ removal would best be handled by the Rectisol[®] process using methanol as a solvent. Two reasons for choosing the methanol solvent is the high selectivity of removing H₂S to meet the specification of 0.1ppmv, so the proven process is already in house and eliminates the need for additional technology. And the second reason is methanol solvent is produced on site already.

3.2 Water Gas Shift Process Flow Diagram

The material flow through the reactors and the required water required to feed the reactor are illustrated by figure 3.2. A complete process flow diagram can be found in appendices.

Figure 3.2 Water Gas Shift reactor



3.3 Water Gas Shift Aspen

RGibbs model was used in Aspen to simulate the reaction by minimizing the Gibbs free energy for each possible product based on the components feed. The setting *restrict chemical equilibrium – specify temperature approach or reactions* was selected and eq 3.1 inserted to eliminate possible by products. All other compounds were set as inert. Temperature and Pressure of the reactor was specified to 477K and 1bar with 1,351 tones/day of water at 573K and 1 bar. Aspen simulation input file and simulation can be found in appendices.

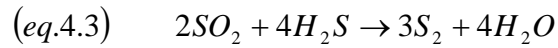
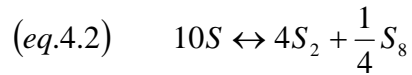
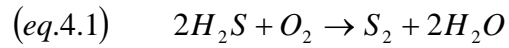
4 Sulfur Removal

It is unacceptable to emit H₂S, a highly toxic, foul-smelling gas, to the atmosphere, so it is necessary to fix it in one form or other. There are essentially two alternative products in which one can fix the sulfur, either as liquid or solid elemental sulfur, or as sulfuric acid¹. The existence of sulfur compounds in raw synthesis gas represents a poison for the catalysts of most chemical applications, including ammonia, methanol, Fischer-Tropsch, low temperature shift, and others. Based on the coal to methanol plant (appendix) feed stock of 3000 tones/day of coal 35 tones/day of H₂S needs to be removed and processed in an environmentally friendly and efficient manner. There are several technologies to choose from, based on the specification of sulfur removal to 0.1ppmv to minimize the risk of poisoning the zinc oxide / copper oxide catalyst in the methanol synthesis step, the Claus process was modeled using Aspen simulation for flow sheeting purposes.

Several commercial technologies and one developing technology by the University of California for sulfur removal process was investigated and compared.

4.1 Claus

The Claus process is the principle method by which sulfur is recovered from separated hydrogen sulfide. Its purpose is to recover sulfur from gas stream which itself is a product of a previous gas purification process⁴. The Claus process is usually carried out in two stages – a thermal stage where part of the hydrogen sulfide is burned to elemental sulfur and sulfur dioxide, and a catalytic stage where the remaining hydrogen sulfide is reacted with sulfur dioxide in the presence of a catalyst to form additional sulfur. The textbook version of the Claus Process is eq 4.1:

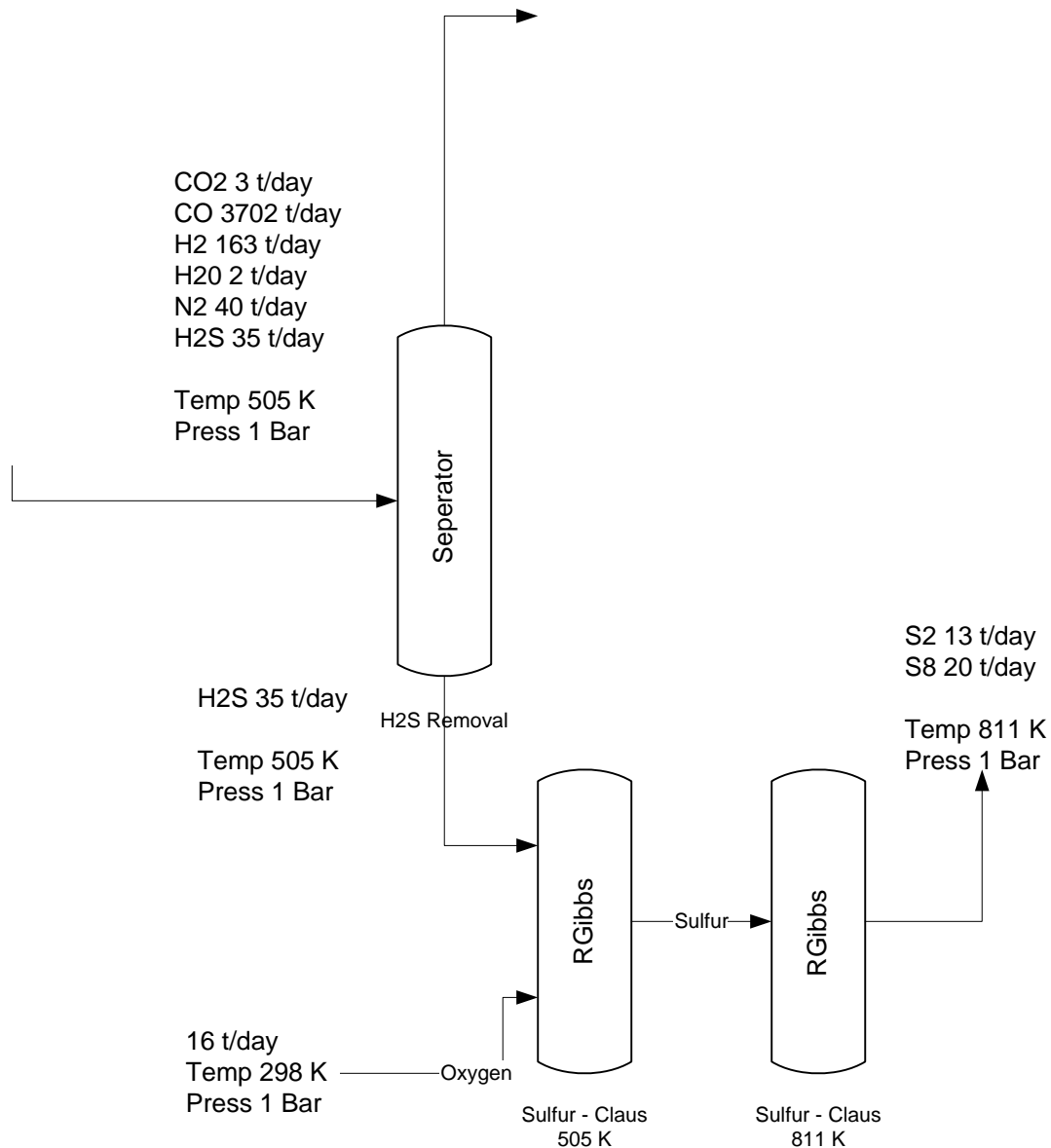


The hydrogen sulfide is burned near atmospheric pressure at temperatures of 1300K to 1500K. The second stage uses a catalytic reaction of aluminum oxide and is slightly exothermic.

Gas streams with over 25% H₂S are sufficient for direct feed to a Claus process. There are several technologies on the market that remove H₂S from syngas. Rectisol[®], Purisol[®] and amine scrubbers are just a few. Each has unique capabilities and selectivity and gas purities depending on the down stream processes.

4.2 Sulfur Process Flow Diagram

The gas feed rate and sulfur content can be seen in Figure 4.2. This process flow diagram illustrates the stream flow, temperature, and pressure data based on the 3000 tonnes/day of sub bituminous coal feedstock. 35 tonnes/day of H₂S gas requires removal at a level of 0.1ppmv. For flow diagram purposes a simple separator by split fraction was used. 35 tonnes/day of H₂S by eq 4.1 requires an additional 16 tonnes/day of pure oxygen in the first reactor to convert to elemental sulfur. The reactor is set at 505K and 1 bar to convert hydrogen sulfide to Sulfur. A second reactor is used in a clause process to convert the remaining hydrogen sulfide to sulfur solid. Final yield of sulfur is 13 tonnes/day of S₂ and 20 tonnes/day of S₈.



4.3 Sulfur Clause Model with Aspen Simulation

Aspen simulation was used to model the sulfur recovery unit. RGIBBS model does not require any reactions be entered and it will figure out the distribution of different forms of sulfur in the product stream by minimizing the Gibbs. Therefore, RGIBBS is recommended. In modeling the Claus process, user should not follow reaction (eq 4.1) to use S to represent all the elemental sulfur products. Using S would result in an incorrectly low sulfur yield. According to a paper by J. Chao (J. Chao, "Properties of Elemental Sulfur", Hydrocarbon Processing, November 1980, p217-223), the most abundant sulfur vapor species present at high temperatures is mainly S₂ (diatomic sulfur)⁷. At

low temperatures (room temperature), S8 is the more stable form. If one enters reaction (eq 4.1) very little sulfur would be generated. Using S instead of S2 is most likely the source of error in modeling sulfur processes. At lower temperatures, S8 should be added to the component list. The model contains two RGIBBS blocks operating at two different temperatures (505 K and 811 K). At 505 K, the model shows S8 is the most significant product. At 811 K, the overall conversion was reduced, but the S2 in the product stream increased⁷.

5. Technology & Alternatives Considered

Rectisol

The most proven technology in acid gas removal is owned by LURGI and uses sub cooled methanol as the solvent. Unmatched purities are possible. Sulfur removal up to 0.1ppmv. However, price for refrigeration is high requiring temperatures from -30 to -60°C. Requires a zinc oxide / copper oxide catalyst. CO₂ is processed down stream for Urea or other uses. Accounts for 27% of methanol production⁹.

Selexol

Originally developed by Allied Chemical Corporation. It is dimethyl ethers of polyethylene glycol. Benefits are that it can be operated at 0-40°C reducing operating costs. Leaves 1 ppmv H₂S and COS each which is still more than the synthesis catalysts can tolerate and requires high pressures to operate up to a 130 bar.

Purisol

Used in LURGI's Purisol process. 15-40°C operating range makes it attractive for most syn gas acid remover plants. However, is not capable of removing enough sulfur to not destroy the methanol synthesis catalyst.

Amines

Are traditionally proven methods and use MEA, DEA, MDEA. CO₂ is more slowly absorbed than H₂S however, this is a chemical reaction and not a physical scrubber therefore would require extra processing and cost.

UCSRP

University of California Sulfur Recovery Process that directly converts H₂S into elemental sulfur at 285°F to 300°F and at any sour gas concentration and pressure. Still in infancy, but may potentially yield substantial benefits upon maturation⁹.

Figure 5.1 comparison of product purities

Product Gas Purity		
Process	Purified Gas Quality	Impurities
Rectisol [®]	0.1 – 1 ppm 10 – 50 ppm 5 ppm	Total Sulfur (H ₂ S + COS) CO ₂ H ₂ S in CO ₂ by - product
Purisol [®]	5 – 50 ppm	H ₂ S, no COS removal
MDEA	3 – 50 ppm	H ₂ S, no COS removal
aMDEA [®]	1 – 50 ppm 5 – 50 ppm	H ₂ S CO ₂

5 Utility Cost Acid Gas Removal System

To operate the acid gas removal section water and oxygen are required to feed the two reactors. For the water gas shift reactor where excess water is required to shift the H₂ CO ratio, and the second for the oxygen requirement to process hydrogen sulfide into elemental sulfur in the Claus process. Figure 5.1 shows annual cost of these utilities based on the stream tables from 3000 tones/day of coal gasification.

Figure 5.1 Utility cost for acid gas removal

Utility	Units	Annual Cost
Water Heat Exchanger	Mgal	\$2,268,034
Oxygen	Mton	\$21,230,093
Total		\$23,498,127

7. Health, Safety, Toxicity and Environmental Impact

Pure oxygen tanks will need to be store appropriately to prevent oxygen explosions. Hydrogen sulfide gas is highly toxic and proper maintenance for corrosion of transfer piping and equipment are required to operate safely. In addition, to chemical safety precautions there will be a need to maintain the reactors in proper structural strengths due to the high pressures and temperatures.

8. Recommendation

There are various technologies that can be used to remove unwanted components, including particulates, sulfur, and ammonia, from the producer gas stream after gasification. Based on the specification of sulfur levels to 0.1ppmv Rectisol[®] is the only current commercial technology in use to meet this requirement. Furthermore, cost may be reduced by using methanol solvent produced onsite. Lurgi is the only process for which the technology has been sufficiently developed and demonstrated to be considered available for large scale production in the U.S.³

Reference:

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- 9) H.S. Meyers, *Development of an Integrated, Multi-Contaminant Removal Process for Syn Gas Clean Up*. Final Technical Report. June 30, 2007.