QATAR UNIVERSITY

COLLEGE OF ENGINEERING

SIMULATION OF SULFUR RECOVERY PROCESS AND OPTIMIZATION OF THE MAIN OPERATIONAL PARAMETERS

BY

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COMMITTEE PAGE

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ABSTRACT

Strict environmental regulations has pushed sulfur emissions from natural gas and crude oil refining plants to very low levels. The current and most widely used method for reducing those emissions is the Claus sulfur recovery process, which is not sufficient to satisfy stringent air pollution requirement as the typical standards limit sulfur emission from sulfur recovery plants to 250 ppm.

Hydrogen sulfide, which is a byproduct of natural gas and crude oil processing plants, is very poisonous gas and its presence requires great deal of attention in order to meet environmental regulations and pipeline specifications. The most widely used method to treat the acid gas is by absorbing it by amine solvent in an amine sweetening unit followed by sulfur recovery unit. This is essentially recover up to 98 percent sulfur from the acid gas feed. However, with more strict regulations additional processes are required to treat the tail gas by the addition of tail gas treatment unit. The overall sulfur recovery from the integrated Claus sulfur recovery and tail gas treatment units is in the excess of 99.9 percent.

ProMax process simulation software was used to model the integrated sulfur recovery process and tail gas treatment unit. The model was then compared and validated against industrial data and a close match was found. Several operating parameters and conditions was then investigated and optimized in order to determine their sensitivity on the performance of the system. Those parameters include but not limited to factors such as the ratio of H_2S/SO_2 in the tail gas, CO_2 slippage, steam stripping ratio, and Claus converters temperature.

The addition of SCOT process raised the sulfur recovery efficiency to 99.93% with some modification to operational parameters that have the most influence on the process. The output of the project is to provide a platform for effectively managing the operations of the sulfur recovery process in terms of improving sulfur recovery while minimizing energy and operating cost in order to meet sulfur emission regulations.

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LIST OF ABBREVIATIONS

AG	Acid gas
CO_2	Carbon dioxide
COS	Carbonyl sulfide
CS_2	Carbon disulfide
EPA	Environmental protection agency
gpm	Gallon per minutes
H_2S	Hydrogen sulfide
MDEA	Methyl diethanolamine
ppm	Parts per million
RF	Reaction furnace
SCOT	Shell Claus offgas treating
SRU	Sulfur recover unit
TGTU	Tail gas treatment unit
TRS	Total Reduced Sulfur
WHB	Waste heat boiler

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We have taken all efforts and responsibilities to make this project a success story since day one. Nevertheless, it would not have been without each member's dedication and determination.

Chapter 1 Introduction

Long time ago, the production of sulfur was thought of as producing a low value byproduct. However today, emitting sulfur dioxide in the atmosphere is not questionable and must be controlled. Pollution reduction is now equally important as making profit.

Natural gas and crude oil reserves contain sulfur components, which must be treated and removed before further processing. Strict regulations and requirements for sulfur recovery are now in the excess of 99.9% in many countries and industries [1]. The traditional method for treating hydrogen sulfide is by amine sweetening unit, which absorbs H_2S from the gas stream and sends it to the Claus plant. In the Claus sulfur recovery plant, H_2S is converted to elemental sulfur and the residual unreacted H_2S is burned and incinerated. H_2S is unstable in the presence of SO_2 or O_2 and easily converted to elemental sulfur [2]. Recovery of 85% could be achieved in one stage Claus reactor, up to 95% could be achieved in two stages Claus plants, and up to 98% is achievable in three stages Claus plants [1].

With more emphasis on achieving higher recovery in the sulfur plants, the addition of tail gas treatment unit is often needed. Most countries now demand sulfur recovery efficiency in the range of 99% to 99.9% [2]. The tail gas is the outlet stream of the conventional Claus plant, which must be further treated to reduce sulfur content before being incinerated. This involves passing the tail gas to a catalytic process to convert sulfur components back to H_2S. Then, passes this stream to a low pressure amine sweetening unit, which selectively absorbs H_2S and recycles it back to the front of the Claus plant.

The overall recovery from this process could possibly reached +99.9% if the integrated units are fully optimized [1].

Sulfur recovery units is not meant to generate profit for plants operators, however, it's a crucial processing step as releasing of sulfur compounds is strictly prohibited. Consequently, the main concern for oil and gas operators is to maximize the recovery and production of sulfur at minimum cost. This means debottleneck the process and find the most suitable operating conditions that improve the performance [3].

1.1 Hydrogen Sulfide

Hydrogen sulfide is a chemical compound that is found naturally in natural gas and crude oil and has a chemical formula of H_2S. It is a colorless gas with rotten egg odor, extremely poisonous, flammable, explosive and very corrosive. When H_2S is present in a gas stream, the gas is called acid or sour gas. Of course, other species such as CO_2 and mercaptans may also be present and contribute to its acidity. However, here acid gas stream refers to a gas stream with H_2S content.

There are many reasons that dictate the removal and treatment of H_2S from process stream. This is due to it being very poisonous and flammable. It is heavier than air and will settle down in the proximity of the leaking area. Though it has a pungent smell, nevertheless, it quickly damages the nasal functions and the victim will be left unconscious and eventually die [4]. Moreover, due to its corrosiveness, its presence in the process pipelines leads to many problems such as corrosion of equipment and pipelines as well as catalysts deactivation [1]. The product of burning H_2S is sulfur dioxide (SO_2), which is also regulated by environmental standards due to its contribution to the acid rain and potential risk to people's health [5].

1.2 Sulfur

Though Sulfur as a product does not have a profitable value, producing it is mandatory for controlling air pollution and complying with environment. It has a low marketable price. However, great deal of attention in research is progressing in order to develop useful applications to benefit from its wide availability in the market and enhance its value. Sulfur usefulness comes from its wide range of applications and end-uses. Its prevalent application is for fertilizers manufacturing. Rubber industries also uses sulfur in the rubber vulcanization processes. Other users of sulfur include pharmaceuticals, cosmetics, and cement as well as chemical preparations such as sulfuric acid and explosives [6].

1.3 Process Improvement

Engineers around the world are constantly looking for ways to enhance existing processes and systems, performing regular analysis to test the operational efficiency and process requirement, as well as recommending the proper modification plans and design changes that improve the process performance.

The main goal of process simulation is process optimization. The simulation models facilitate in finding process bottlenecks and underperforming equipment as well as defining the steps needed to optimize process performance. Process simulation models help in understanding the capabilities and limitations of the new design as well as the optimum operating conditions. They also help in predicting process behavior and response for given changes in process conditions [3].

The primary focus of the project will be to optimize the sulfur recovery process and find the optimum operational parameters that enhance the performance while minimizing the cost and processing difficulties.

ProMax [7] software will be used for process modelling and simulation along with sensitivity analysis tools, excel spreadsheets and literature. ProMax is a powerful process simulation software and is being used by engineers around the globe for the past 30 years. The software offers very helpful tools to design and optimize gas, refining, and chemical processes [8].

Chapter 2 Literature Review and Methodology

Sulfur recovery process is a well-known and well-established process with a history of many decades. A literature review was conducted to obtain a general overview of the process and the current situation in the industry. The process flowsheets and components are readily available in literature (i.e., refer to [2] [9] [1]).

The key motivation for this project was to study the sulfur recovery process and to optimize the operational parameters and variables in order to maximize the sulfur recovery efficiency. Having this in mind and with the aid of the ProMax process simulator, several scenarios and cases can be conducted and evaluated.

Research methodology consists of reviewing the Claus sulfur recovery process with tail gas treatment and studying the various effects that affect the performance. In order to study the performance of the process, a typical industrial Claus unit is studied. The process flowsheet and data for the sulfur recovery process is taken from [2] and will be considered as the base case or benchmark for the project. Simulation of the base case flowsheet will be carried out by the commercial ProMax process simulation software. The software will be used to get a preliminary model by matching the data for the sulfur recovery unit and the results will then be compared. The model will then be modified to include the tail gas clean up unit and to investigate how improvement could be made. ProMax software was selected due to its exceptional capabilities in modelling sulfur recovery and gas sweetening processes.

Sensitivity analysis provides the most effective method to examine the performance of chemical processing plants with respect to changes in process conditions. Scenario tools and parametric studies will be implemented in ProMax software and excel spreadsheets and then, the results will be discussed and evaluated. The ultimate goal of process simulation is process optimization. The output of this study is an optimized integrated process for sulfur recovery.

Chapter 3 Available Technologies

Numerous alternatives are available when attempting to design and select the primary sulfur recovery unit configuration for processing rich acid gas that contains H_2S and CO_2. The selection is based on many factors such as the acid gas content in the feed gas and the degree of sulfur removal required.

H_2S concentration in the feed gas varies and depends on the upstream process used to sweeten the acid gas, where the most used method is absorption by amine solvents. For small quantities of H_2S in the sour gas, scavengers and direct oxidization are usually used [10]. For large concentration of H_2S and relatively high quantity, Claus process is the most widely selected method for sulfur recovery and it is the most well-established [2].

3.1 Claus Technology

The Claus process is the best-known sulfur production process in industry, which is the modification for the first process used in 1883. It is applicable for acid gas containing from about 20-100% H_2S [2].

Carl Friedrich Claus, an English scientist, who first invented the Claus process in 1883 [9]. He mixed oxygen with the hydrogen sulfide and passed the products into a catalyst bed. The resulting products were water and elemental sulfur. The reaction in the gas phase is exothermic and releases a considerable amount of heat and due to this nature, only small quantity of H_2S was processed without overheating the reactor. Improvement was made in 1938 by a German company, by adding free flame oxidization step before the reactor to prevent the catalyst bed from overheating and to increase sulfur conversion. This improvement has greatly enhanced the efficiency of the sulfur recovery and formed the basis for the majority of sulfur recovery units found today in the industry.

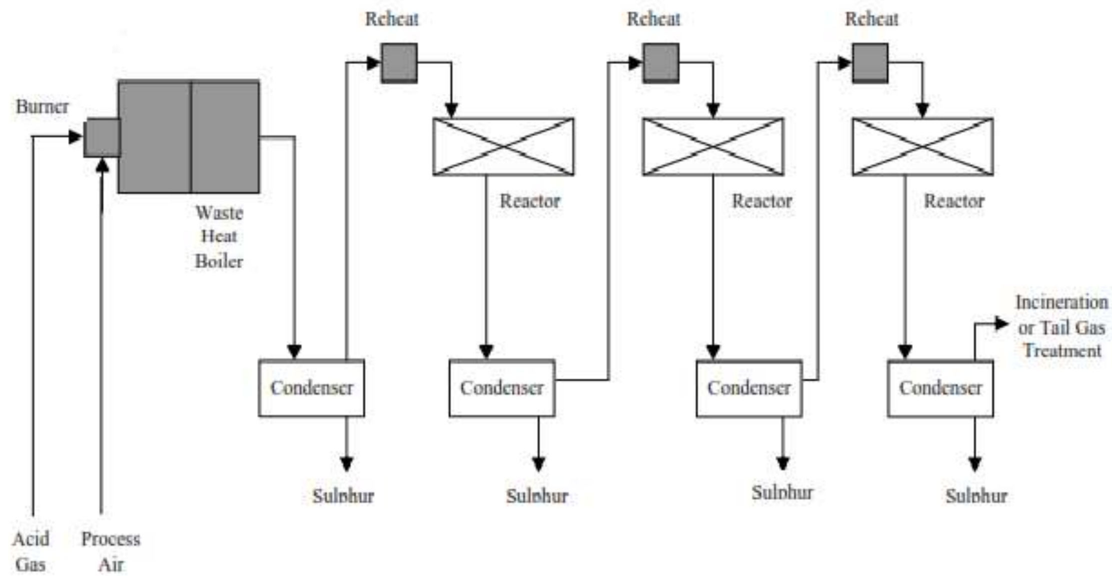

Figure 3.1 Three Claus beds sulfur recovery configuration

Figure 3.1 (above) shows a typical configuration for the straight-through three bed Claus unit [11].It consists of a thermal stage where part of the H_2S is converted to SO_2 in the reaction furnace according to the following reaction:

$$H_2S + 1\frac{1}{2} O_2 \leftrightarrow SO_2 + H_2O \qquad (1)$$

The above reaction is exothermic and occurs in the gas phase during which one third of H_2S is burnt with the stoichiometric quantity of air. The remaining H_2S in the feed gas is reacted with the SO_2 produced in the furnace to form elemental sulfur in the subsequent catalytic reactors stage according to the following reaction:

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

This reaction above is thermodynamically limited and, therefore, two or more catalytic converters are usually needed for high conversion [10]. It is important to note that part of this reaction also happens in the reaction furnace. The above two reactions are the main reactions that happen in the SRU or Claus unit, as the acid gas feed usually contain other components such as hydrocarbons, carbon dioxide, ammonia, and mercaptans, so that the actual reactions set is usually very complex [11]. Combining equation (1) and (2), the overall Claus reaction can be written as:

$$2H_2S + O_2 \leftrightarrow 2S + 2H_2O \qquad (3)$$

The combustion products from the reaction furnace, usually at 1000 ^oC to over 1400 ^oC depending on the acid gas composition [12], pass in the waste heat boiler to cool the gaseous products and produce medium to high pressure steam. The gas mixture then goes to the first sulfur condenser, where it is further cooled and the sulfur will be condensed and separated, which is then flows by gravity to the sulfur collection pit.

The outlet stream from the sulfur condenser enters a heat exchanger where the temperature is raised to prevent sulfur from condensing in the subsequent catalyst beds.

In the catalytic reactor, H_2S and SO_2 will again react and produce sulfur vapor, which will then flows to the second sulfur condenser and separates from the tail gas as liquid sulfur.

Subsequent two heating, catalytic reactions, and cooling steps will be followed so that most of the H_2S is converted to elemental sulfur. The outlet tail gas from this Claus unit is sent to the tail gas treatment unit to convert most of the unreacted sulfur components to H_2S and recycle it back to the front of the SRU.

3.2 Tail Gas Conditioning

A standalone Claus sulfur recovery unit cannot attain the minimum requirement of the global environmental protection rules for sulfur emission. Hence, further cleaning process for the tail gas outlet stream from the SRU is often required [9]. Current environmental regulations limit total sulfur emission to 250 ppm from all new and existing sulfur recovery process [13].

The primary function of tail gas treatment unit is to increase sulfur conversion and consequently minimize the amount of sulfur-based constituents discharged to the atmosphere. Many variations and alternatives are available for this purpose such as the Cold Bed Adsorption (CBA) process and the Shell Claus Offgas Treating (SCOT) process [2].

3.2.1 Cold Bed Adsorption Process

Because Claus reaction is thermodynamically limited, adding one or more Claus reactors will not increase the efficiency of sulfur recovery unit beyond the maximum achievable recovery [9]. CBA process can achieve higher recoveries by operating the Claus reactors in the sulfur sub-dew point region. This greatly enhances the conversion of H_2S to sulfur as the reaction favors the low temperature operation and this will shift the equilibrium to the right towards more sulfur products.

In this facility, at least two CBA reactors are used. One is used for low temperature Claus reaction with sulfur adsorption on the catalyst, while the other is to be regenerated and cooled [2]. Accordingly, sulfur product is adsorbed on the catalyst, and this reduces its partial pressure in the vapor and allow additional H_2S and SO_2 to react and produce sulfur. The condensed sulfur in the reactor would eventually occupy all the active sites of the catalyst, and the catalyst would have to be regenerated.

3.2.2 Shell Claus Offgas Treating Process

The Shell Claus Offgas Treating (SCOT) process was developed by Shell Dutch Company. It is the most widely used tail gas treatment process in the industry with over 100 plants currently in operation [2]. The process is reliable as long as the upstream SRU is operated with the proper conditions. However, it is sensitive to changes in Claus tail gas composition.

The SCOT process includes four sections [10]:

1) Tail gas reduction section, where the tail gas is mixed with reducing gases (hydrogen and carbon monoxide) over a catalyst bed to convert and reduce all sulfur component to H_2S.
2) Conditioning section, where the outlet hot gas from the reduction unit is cooled in a waste heat boiler and followed by a direct quench by cooling water.
3) Amine sweetening section, which consists of a typical contactor and regenerator towers with selective amine solvent such as MDEA. The MDEA is more selective towards H_2S, which absorbs it and recycle it back to SRU.
4) Incineration section, where the waste gas from the top of the contactor is burned and incinerated to the atmosphere.

The SCOT process gives superior design features and stability, which can nearly recover almost all the unrecovered sulfur compounds produced in the Claus SRU.

Chapter 4 Process Modelling and Simulation

In order to set up a base case process for the project, a typical sulfur recovery process is simulated and modelled by ProMax simulation software. Specifications of the feed acid gas to be treated is given in Table 4.1 (below) along with Claus unit operating conditions:

Table 4.1 Acid gas feed specifications and Claus unit operating conditions

Property	Value
Temperature (^oC)	43
Pressure (bar)	1.56
Flow Capacity (MSCFD)	9108
Composition (mole%)	
H_2S	66.83
CO_2	27.13
COS	0.07
CH_4	0.34
C_2H_6	0.02
H_2O	5.61
Number of Claus Beds	3
Tail Gas Ratio (H_2S /SO_2)	1.8
Burner Temperature (^oC)	1109
Sulfur Recovery (%)	98.1

The unit has a designed acid gas feed capacity of 9108 (MSCFD). Sour gas from the acid gas removal unit at 43 ^oC and 1.56 bar is sent to the sulfur plant. The sulfur plant employs three Claus catalytic reactors with thermal reaction furnace ahead of them. The achieved sulfur efficiency is 98.1% and the outlet tail gas stream is sent directly to the incinerator to be burned and flared.

4.1 Comparison and Validation of the Model

To match the simulation with the base case data, the air flow rates fed to the reaction furnace is manipulated to ensure that H_2S to SO_2 ratio in the tail gas is 1.8. Additionally, the reported burner temperature was also manipulated to obtain a very close result. Iteration was performed until reasonable and very close results were achieved in the waste heat boiler effluent composition. A controller was set to ensure that the outlet temperature of the first bed is set at 310 ^oC.

In order to compare the actual data with the simulated results, the following comparison is presented in Table 4.2 (below):

Table 4.2 Comparison of actual data with the model prediction

Parameter	Data	ProMax	Error (%)
Burner Temperature (^oC)	1109	1088	1.89
Sulfur Recovery (%)	98.10	98.04	0.06
Tail Gas Ratio (H_2S/SO_2)	1.80	1.82	1.11

The results shows 0.06% error in calculating sulfur efficiency, which is very small and negligible. The calculated burner temperature is 1088 ^oC is lower than the actual reaction furnace temperature by 21 ^{o}C, which can be neglected as it resulted in small error of 1.89%. All compositions and flow rates showed good agreement with the original data. Now that the model have successfully converged and matched the base case data, alternatives now for improving the performance of the process are explored.

4.2 Addition of SCOT Process

As noted in the discussion above that the current sulfur recovery is around 98%, which is not compatible with the current environmental regulations and allows for huge sulfur dioxide emission to the atmosphere. Table 4.3 (below) shows the outlet waste gas compositions after the last sulfur condenser and before being incinerated:

Table 4.3 Outlet waste gas compositions from Claus plant

Component	Composition (mol%)
H_2	1.67
Ar	0.64
N_2	53.18
CO	0.61
CO_2	11.81
H_2S	0.30
COS	0.02
CS_2	0.01
SO_2	0.17
H_2O	31.58
S	0.01

In the current plant operation, this stream is burned in the sulfur incinerator and this corresponds to sulfur emission level of 4900 ppm. This is why a tail gas cleanup unit has to be installed to treat this waste gas stream and reduce the total sulfur emission to below 250 ppm.

The current strict environmental regulations dictate higher amount of sulfur recovery beyond the capability of the standalone sulfur recovery unit. This is because complete conversion of hydrogen sulfide to elemental sulfur is constrained by the equilibrium relationship of the Claus process chemical reaction [9]. Another limitation of the conversion is the formation of carbonyl sulfide and sulfur dioxide in the thermal stage of the Claus process due to the presence of carbon dioxide and light hydrocarbons in the acid gas feed [9]. Those compound are stable and pass the Claus reactors unchanged, thereby reducing the overall conversion and the basic Claus would not be able to satisfy air pollution rules.

Thus to meet those requirement, the base case flowsheet is to be modified by the addition of tail gas treatment unit after the fourth sulfur condenser in place of incinerator. The modifications include the use of SCOT type [2] process for tail gas treatment. It involves the use of a hydrogenation reactor to convert all sulfur based compound back to hydrogen sulfide, followed by amine sweetening process to recycle back H_2S to the Claus plant.

It is important to note all this modification is really expensive to install. However, as said in the beginning, that complying with environment is a number one priority. SRU and TGTU are not typically considered economical, in the sense that they do not directly increase the net profit of plants. They are built for the purpose of controlling air pollution. Thus, the aim of this project is to increase the recovery to reach the 99.9% target by adding TGTU and to perform the full simulation of the integrated process. Therefore, the model has to modified to represent the integrated sulfur recovery unit plus a tail gas treatment unit. Then, the only concern would be to optimize the process and choose the operating parameters that minimize operating cost and enhance the efficiency.

4.3 Base Case Operating Conditions

The developed model in the previous section has been validated only for the Claus process. However, the addition of SCOT process has to be included in the base case model. For this purpose, the model was modified and a comparison is given in Table 4.4 (below):

Table 4.4 Comparison of plant data with model prediction for SCOT rector outlet

Hydrogenation Reactor Effluent	Actual Data	Model Data
Temperature (^oC)	369.8	370
Pressure (kPa)	144.5	144.6
Composition (mol%)		
N_2	40.237	40.322
H_2S	0.846	0.832
H_2	1.473	1.501
CO	0.141	0.142
CO_2	35.400	35.041
H_2O	21.901	22.091
COS Conversion (%)	40.0	41.4

The predicted model data shows good agreement with the actual plant data and now that the model has been modified and the base case is created. A summery of the base case operating conditions is presented in Table 4.5 (below):

Table 4.5 Base case operating conditions

Parameter	Data
Type of Amine	MDEA
Concentration (wt%)	30
Amine Circulation (gpm)	305
Rich Loading (mol/mol)	0.21
Absorber Ideal Stages	7
Regenerator Ideal Stages	10
Steam Stripping Ratio (lb/gal)	1

The following chapter describes the improvements made for the integrated sulfur recovery plus tail gas treatment unit.

Chapter 5 Process Optimization

Several problems encountered in the sulfur plants can be avoided by the use of process simulation and sensitivity analysis. Developing an envelope of operating regions for important process parameter is of great value for controlling the process and increasing the production efficiency [3]. The process simulator (ProMax) will be used to investigate the effects of various operating parameters on the performance of the sulfur recovery process. A series of simulations will be performed to set the operating parameters in the points that yield the highest recovery. In the following sections, a series of cases will be conducted to set the operational parameters that enhance the sulfur recovery process.

5.1 Sulfur Recovery Unit Optimization

Significant amount of energy in the form of steam can be recovered from the sulfur recovery unit, as well as the possibility of minimizing fuel consumption in the subsequent tail gas cleanup unit if proper optimization methods have been implemented for the integrated sulfur recovery and tail gas treatment process.

5.1.1 Reaction Furnace

The main function of the reaction furnace and waste heat boiler is to thermally oxidize one third of hydrogen sulfide to form sulfur dioxide. The flowsheet of the reaction furnace and the waste heat boiler is given in Figure 5.1 (below):

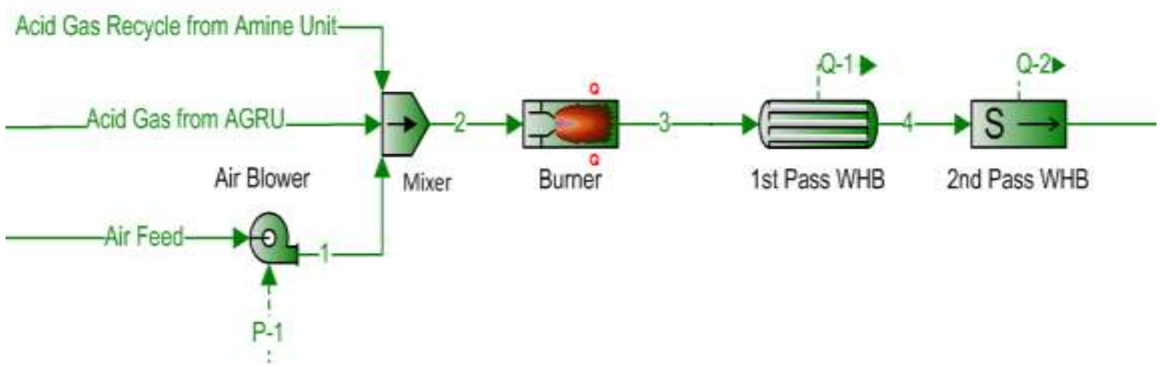

Figure 5.1 SRU reaction furnace flowsheet

Feed to the thermal furnace and SRU is coming from the acid gas removal unit with the following conditions.

Table 5.1 SRU acid gas feed specifications

Property	Value
Temperature (^oC)	43
Pressure (bar)	1.56
Molar Flow (kmol/h)	454
Composition (mole%)	
H_2S	66.83
CO_2	27.13
COS	0.07
CH_4	0.34
C_2H_6	0.02
H_2O	5.61

The second feed is the recycle stream from the tail gas treatment unit, where they are mixed together along with the combustion air stream before entering the furnace. The gas leaving the reaction furnace at around 1070 ^oC is cooled in the waste heat boiler by generating steam. The gas passes through the tube side of the waste heat boiler and the boiling water is maintained in the shell side of the boiler. Medium pressure steam (10 to 40 bar) is generated and the hot gas now is cooled to about 316 ^oC before sending it to sulfur condenser to eliminate sulfur condensation in the boiler.

The primary control of this process is the inlet air flowrate. Air flow rate has to be controlled in such a way to oxidize only one third of inlet hydrogen sulfide. According to the Claus reaction as given in equation (2) in section (3.1), the ratio of H_2S/SO_2 is 2.

The importance of maintaining tail gas ratio at around 2 can be seen in Figure 5.2 (below):

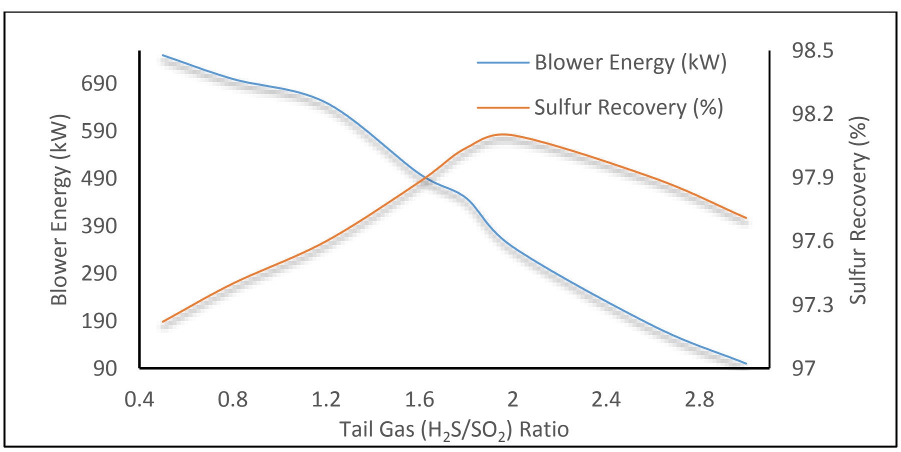

Figure 5.2 Effect of tail gas ratio on sulfur recovery

At around 2 for the H_2S/SO_2 molar ratio in the tail gas, the maximum sulfur recovery could be obtained. This is because there is always a guarantee that all Claus reactors inlets enough reactants (H_2S and SO_2) for the reaction to proceed and produce sulfur. Moreover, at this ratio, the air flow rate is optimized and consequently the energy needed in air blowers are less compared to the base case ratio of 1.82 as shown in Figure 5.2 (above). Therefore, for better operating conditions, the flowrate of air has to be calculated to ensure that the ratio of tail gas H_2S/SO_2 is maintained at around 2 for the whole process.

ProMax solver was used to perform this iterative simulation and the air flowrate was determined to be 680 kmol/h and the power for driving the air blower was found to be 346 kW. This represents a 22.9% reduction in energy requirement from the base case. The resulted sulfur conversion has increased by 0.96%. Though may not seem significant, but it has huge impact when considering the overall emission reduction obtained due to this tiny increase in sulfur recovery.

5.1.2 Claus Converters Optimization

Waste heat boiler outlet product at 316 ^{o}C, stream 5 in Figure 5.3 (below), enters the first sulfur condenser to remove liquid sulfur formed in the reaction furnace. The outlet gas stream 6 flows to the first reheat exchanger in order to heat the gas to the required conversion temperature needed in the first Claus converter. Low pressure steam is generated in sulfur condensers. This process is repeated in a number of cooling, heating, and reaction stages until the tail gas exits last condenser number 4. The tail gas stream is now routed to the tail gas treatment unit, which will be discussed in the subsequent sections.

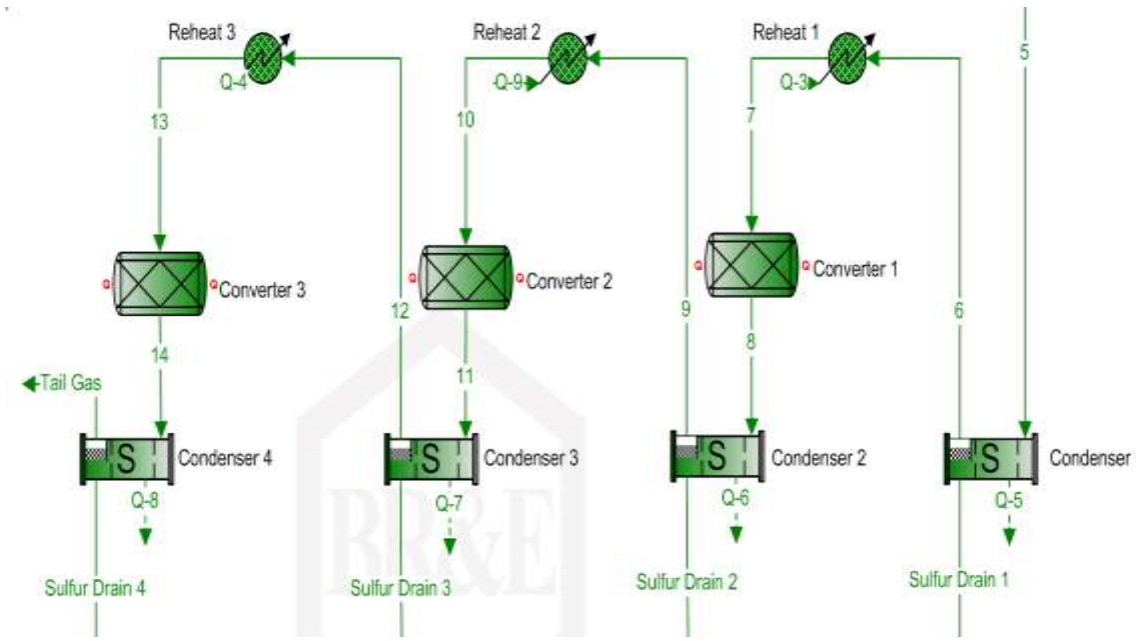

Figure 5.3 Claus reaction stage flowsheet

First Claus converter temperature:

The formation of carbon disulfide (CS_2) and carbonyl sulfide (COS) in the reaction furnace and waste heat boilers is always present and difficult to control. These compounds adversely disturb the subsequent Claus converters catalyst due to sulfate formation and must be destroyed by hydrolyzing them to H_2S in the first converter. The first Claus bed or converter employs a special type of catalysts to hydrolyze and destroy those compounds according to the following two hydrolysis reactions:

$$COS + H_2O \leftrightarrow CO_2 + H_2S \tag{4}$$

$$CS_2 + 2H_2O \leftrightarrow CO_2 + 2H_2S \tag{5}$$

The hydrogen sulfide formed from those hydrolysis reactions is then converted to elemental sulfur. The top section of the reactor bed employs aluminum-based catalyst, where H_2S is oxidized and elemental sulfur is produced. The lower part of the bed is operated with titanium based catalyst, which is used to hydrolyze COS and CS_2 molecules [12].

The following case study was implemented to study the effect of the first converter temperature on the conversion of H_2S, COS, CS_2.

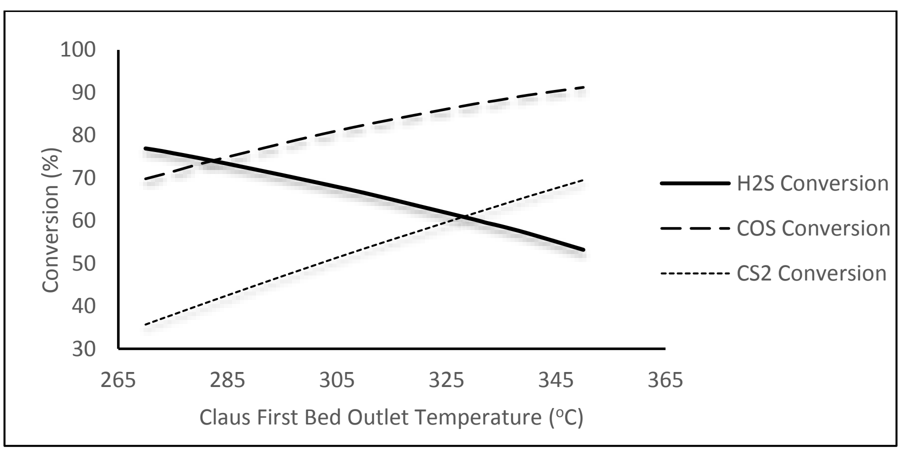

Figure 5.4 Effect of Claus bed outlet temperature on conversion

As can be seen from Figure 5.4 (above), that increasing the reactor temperature leads to increase in COS and CS_2 conversion at the expense of H_2S conversion, which decreases due to its thermodynamic reaction behavior. The current plant operating temperature is set at 310 ^{o}C and produces COS and CS_2 conversion of 82.4% and 53.5%, respectively. Increasing the temperature to 350 ^{o}C, for example, gives better conversion for these compounds at around 91.2% and 69.5%, respectively. However, this increase would be accompanied by an increase in the amount of reheat needed before the reactor in the excess of 17%, which is not feasible. Thus, the current operating temperature set seems to be optimal and we can compensate for the loss of efficiency due to the presence of these compounds in the TGTU.

Second and third Claus converters temperature:

After hydrolyzing great amount of COS and CS_2 compounds in the first Claus reactor, the primary objective for the second and third reactors is to produce elemental sulfur according to reaction (2). The reaction is favored at low temperature, however, not very low so that the reaction won't be able to proceed due to the reaction kinetic limitation and reduced reaction rate. Other important constraint is the expected reactor temperature should be higher than sulfur dew point to prevent liquid sulfur from forming inside the reactor and damaging the catalyst. Thus, a safety margin of (5-15) ^{o}C above the dew point temperature is usually used in industry.

It is important to accurately calculate the dew point, because an increase in the operating temperature above the safety margin or an error in dew point calculations will result in

SRU energy loss and reduction of the overall energy efficiency. Higher operating temperature requires higher energy input in the reheat exchanger ahead of the reactors.

For this purpose, the variation of the catalytic converters with temperature is investigated.

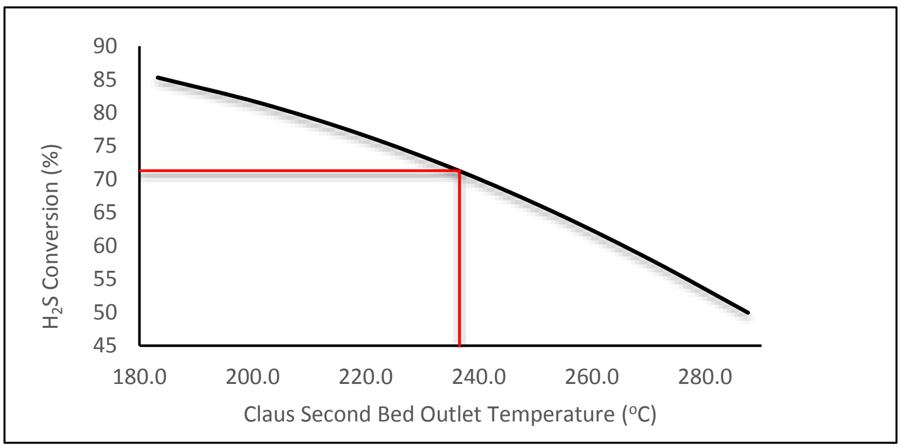

Figure 5.5 H_2S conversion as a function of second Claus bed temperature

High H_2S conversion can be obtained as can be seen in Figure 5.5 (above) by operating the second Claus bed at lower temperature due to the reaction being exothermic. Lowering the temperature shifts the equilibrium reaction to the right towards production of elemental sulfur. Figure 5.6 (below) shows the increase of liquid sulfur formed by decreasing reactor temperature.

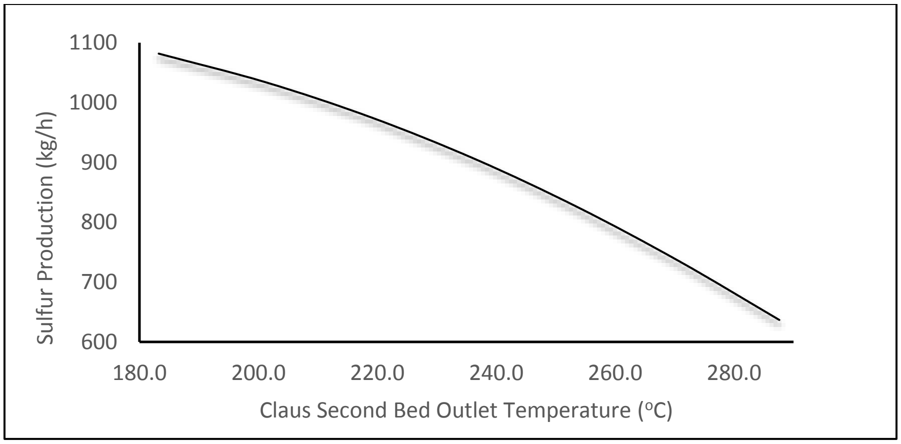

Figure 5.6 Sulfur production as a function of second Claus bed temperature

While low temperature is good from an economic point of view, in terms of less amount of heating requirement in the heat exchanger and more liquid sulfur production. However, we cannot go too low for two reasons:

1) The reaction won't proceed at very low temperature due to kinetic limitations.
2) Sulfur will condense in the reactor and poison the catalyst if we operate at lower than the dew point temperature.

Therefore, the optimum operating condition for the second Claus bed temperature is as shown in Figure 5.7 (below). This corresponds to 236 ^{o}C in the reactor outlet and 210 ^{o}C in the reheat exchanger before the reactor. The sulfur dew point at this condition is 226 ^{o}C. Hence, 10 ^{o}C is added above the dew point to ensure no liquid sulfur will form inside the catalytic reactor. Operating in this region corresponds to 7.8% reduction of energy from the base case.

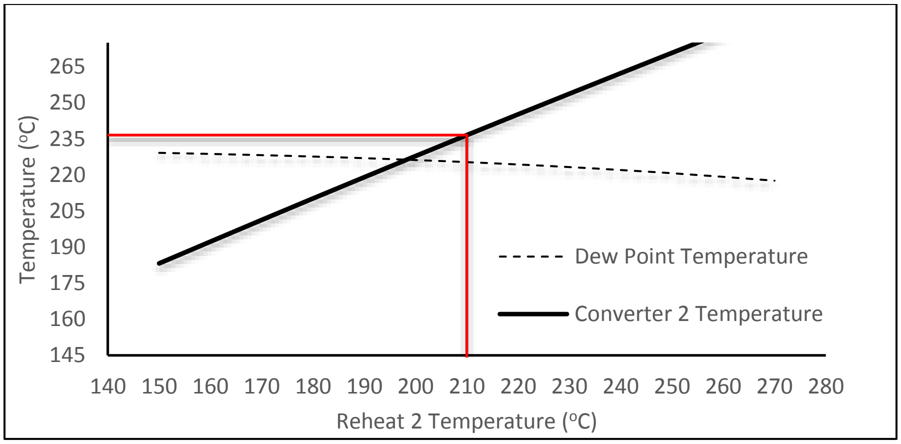

Figure 5.7 Variation of second Claus bed temperature with reheat temperature

A very similar analysis was carried out in order to determine the reheat temperature of the third Claus bed. The results showed that liquid sulfur starts to form at the dew point temperatures of 196 ^{o}C. Thus, using the safety margin criterion, operating the third reactor at 206 ^{o}C is the optimum for the effluent temperature by heating the tail gas in the reheat exchanger to about 193 ^{o}C, which is also represent an improvement of 10.2% in heating requirement from the base case.

5.1.3 Claus Condensers Optimization

The controlling parameter for sulfur condenser is the cooling temperature needed to condense and remove the liquid sulfur, which is determined by the balance between the amount of required liquid sulfur removal and the energy supply in the subsequent reheat exchangers. Hence, the cooling temperature would be as such that all sulfur vapor from the reactors has to condense and flow out of the condensers to the sulfur collection pit. In this cooling process, low pressure steam (3 to 10 bar) is produced.

5.1.4 Energy Recovery for the Claus Process

Claus sulfur recovery units in general produce energy in the form of steam more than what they consume by employing waste heat boilers to recover the huge amount of heat generated in the reaction furnace as well as recovering low pressure steam in sulfur condensers. The produced steam has many uses in the plant such as driving steam turbines and generate electricity that drive air blowers and pumps as well as for the heating purposes. Moreover, steam is also used in heat tracing for the sulfur pipeline to prevent sulfur from solidifying.

Energy inputs for SRU include:

- The energy associated with the inlet acid gas.
- The energy needed for the reheaters as fuel or steam.
- Combustion air blowers energy as electricity or steam.

Energy outputs for SRU include:

- Generation of different pressure steam.
- The energy associated with the produced sulfur and offgas sent to the incinerator.
- Reaction furnace, WHB, and other equipment heat losses.

Energy optimization involves attempts to reduce energy input and heat losses, while maximizing recovery of energy. Optimizing sulfur recovery by increasing the amount of produced sulfur will generally results in less flow of residual sulfur compounds to the incinerator. This will result in less amount of fuel needed to burn these compounds and will save the energy. To put it in other words, any optimization efforts to increase sulfur recovery will also optimize the efficiency of energy.

5.2 Hydrogenation Unit Optimization

The purpose of the hydrogenation unit is to reduce all residual sulfur compounds such as COS, CS_2, SO_2, and sulfur vapor back to H_2S, which is then recycled back to the Claus plant. The reducing gas burner generates the reducing gas (H_2) that is needed to hydrolyze sulfur components by burning fuel gas. The tail gas enters the unit and mixes with the burner exhaust gases and its temperature would rise before entering the hydrolyzing bed. Some of the reactions that occur in hydrolyzing reactor are given by equations (4) and (5), as well equation (6) and (7) below:

$$3H_2 + SO_2 \leftrightarrow H_2S + 2H_2O \tag{6}$$

$$H_2 + S \leftrightarrow H_2S \tag{7}$$

As can be seen from the reactions above, hydrogen is required to hydrogenate and convert the unreacted sulfur components so that later on H_2S is recycled back to the Claus plant. Therefore, a burner is installed in this unit to generate the hydrogen. The flowsheet of the unit is as given in Figure 5.8 (below):

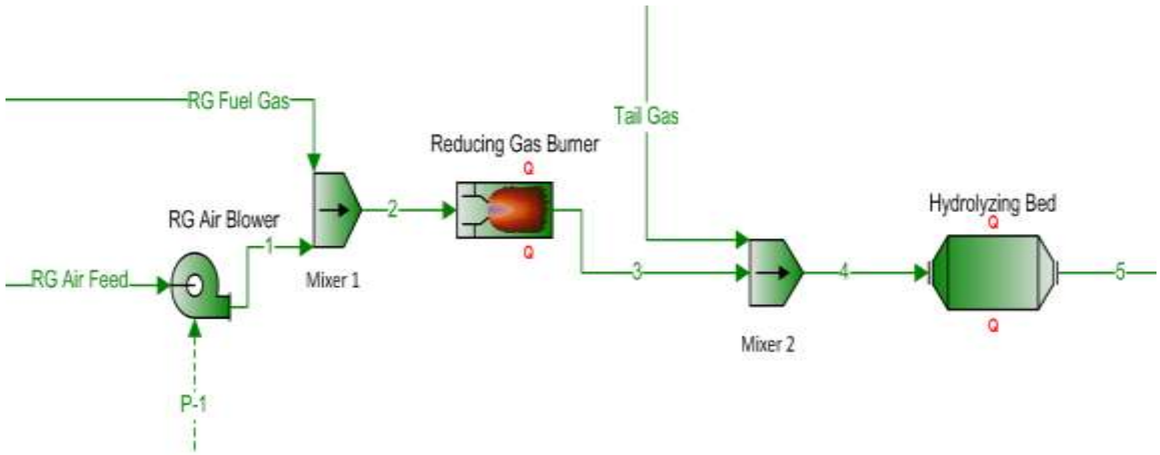

Figure 5.8 Hydrogenation unit flowsheet

Analysis of the current plant operation indicates that only 41.4% conversion is achieved for carbonyl sulfide compound. Increasing this value will yield high sulfur recovery and lower emission in the incinerator, because the residual sulfur components will pass unchanged to the amine unit and then to the incinerator if not practically hydrolyzed in this unit. In order to solve this problem, the fuel and air flowrates was manipulated by operating the reducing gas burner with sub-stoichiometric air to maintain an excess of the hydrogen throughout the process. In other word, maintaining an excess of H_2 ensures that nearly all sulfur compounds are converted to H_2S. Running this simulation resulted in 1% mole composition for H_2 in the effluent gas and consequently the conversion has increased to 96%. The fuel consumption in the incinerator was reduced due to this improvement.

5.3 Quench Unit Optimization

Quench tower is used to condense and remove excess water from the tail gas to prevent the accumulation of water in the amine absorber. The condensate is then sent to sour water stripper for further treatment. The flowsheet of the simulated unit is as given in Figure 5.9:

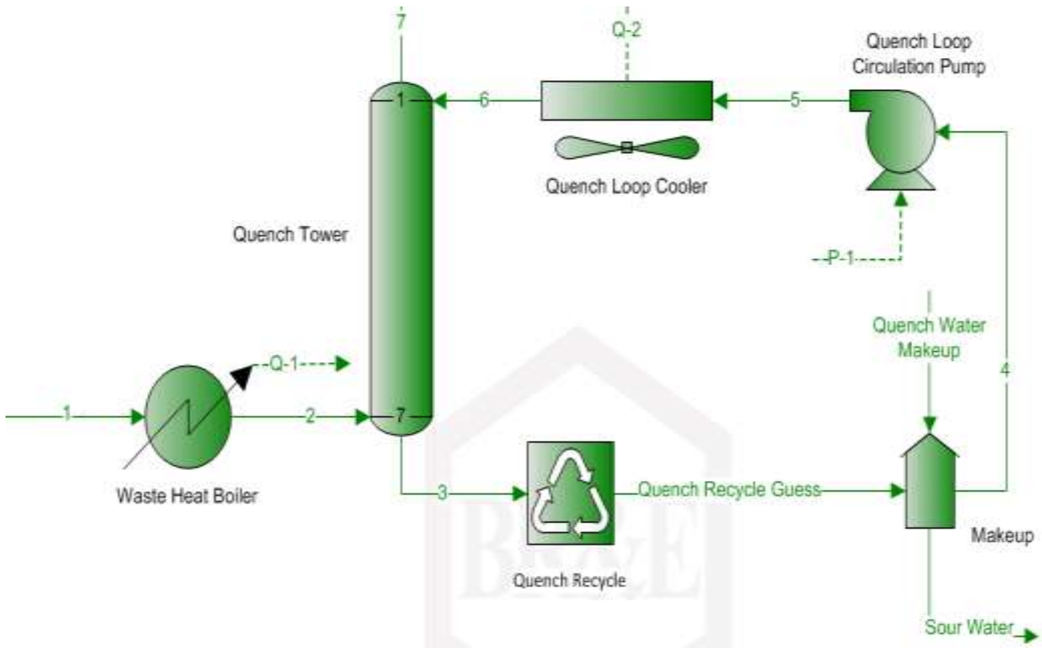

Figure 5.9 Quench unit flowsheet

Other benefit of the quench column is to cool the acid gas up to the temperature required for the absorber operation. Moreover, the quench column acts as barrier that prevents SO_2 to breakthrough to the amine absorber, as SO_2 degrades the amine solvent. The important parameter to control in this unit is the quench tower overhead temperature.

Quench unit was modified to operate with top overhead product temperature set at 40 ^{o}C instead of the current 50.2 ^{o}C as it decreased the amount of water produced in RF, which is passed to the amine unit, by absorbing it in the stream that flows to sour water treatment unit. In addition, this was very helpful in the amine sweetening unit operation as it enhanced the absorption efficiency. Air cooling requirement has increased from 1.12 MW to 1.38 MW by 23.2%. However, this increase will be appreciated by the huge benefit in the amine sweetening operation as will be seen in following sections.

5.4 Amine Sweetening Unit Optimization

Optimizing the amine sweetening unit involves the interactions of different variables and parameters that are most likely to be connected and depend on each other. Any change in upstream process conditions will have its impact on the performance of the unit. Hence, the unit should be able operate within optimum operating conditions for various cases and scenarios.

The main objective of the amine sweetening unit is to selectively absorbs hydrogen sulfide from the tail gas and recycle it back to the Claus SRU. Thereby, increasing the overall conversion to sulfur product. H_2S content of the treated sweet gas has to be below 250 ppm before sending it to the incinerator in order to comply with environmental regulations. Input tail gas to the amine sweetening unit specification is given in Table 5.2 (below):

Table 5.2 Input tail gas condition to amine sweetening unit

Property	Value
Temperature (^oC)	40
Pressure (bar)	1.18
Mass Flow (kg/h)	24878
Composition (mass%)	
H_2S	1
CO_2	24.95
N2	66.6
Ar	1.09
H2	0.02
H_2O	6.34

The current operating data for the amine process is given in Table 5.3 (below):

Table 5.3 Current base case operating data and conditions

Property	Value
Solvent Circulation (gpm)	305
MDEA Strength (wt%)	30
Rich AG Loading (mole AG/mole amine)	0.21
Lean Amine Temperature (^oC)	57
H_2S in the Waste Gas (ppm)	250
Reboiler Duty (MW)	3.88
Total Pumping Power (kW)	736
Air Cooling Duty (MW)	1.12

The flowsheet of the simulated amine unit is given in Figure 5.10 (below):

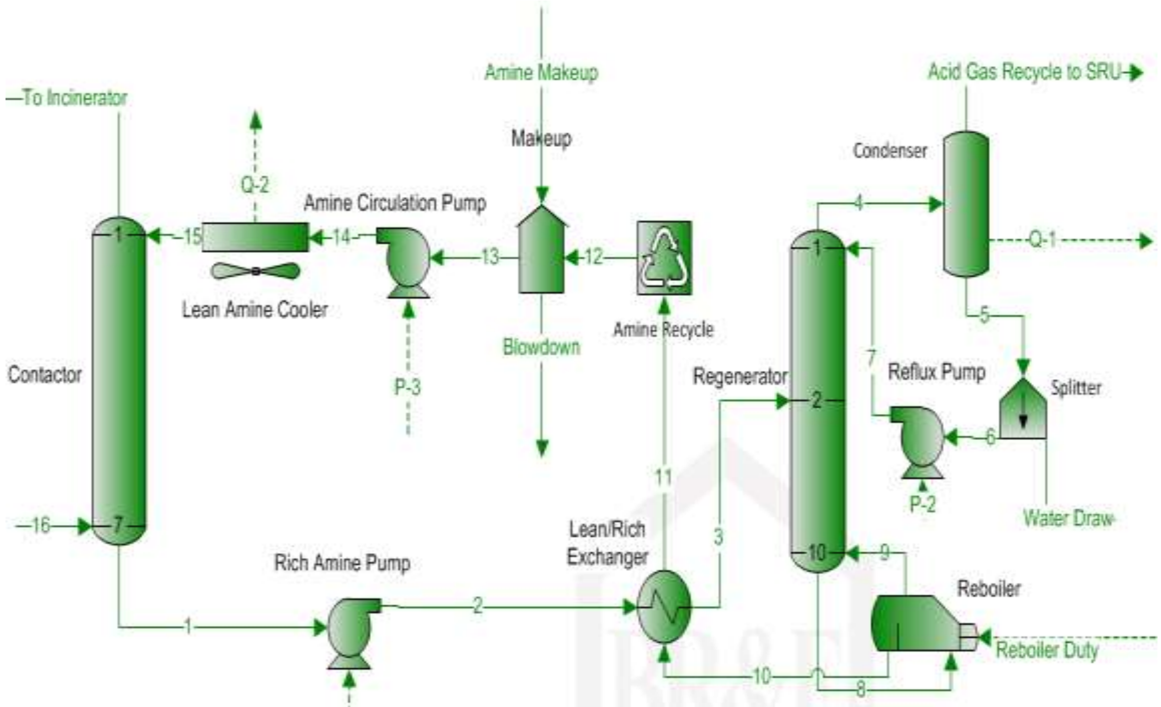

Figure 5.10 Amine sweetening unit flowsheet

The cooled gas from the quench tower overhead, stream 16 in Figure 5.10, enters the bottom of the contactor tower and flows upwards. The lean amine MDEA solvent enters the tower from top and counter-currently flows downwards. H_2S is selectively get absorbed by the circulating amine and exit the tower from the bottom, where this rich stream now flows to the regenerator tower to strip H_2S out of the solution and recycle it back to SRU. The treated waste gas from the top of the contactor is sent to the incineration unit.

5.4.1 CO_2 Slippage

An important factor to consider is the ability of amine solvent to reject most of the CO_2 and to absorb most of the H_2S. This is important because recycling CO_2 to the Claus plant will have great impact on the size of equipment and will reduce the overall efficiency to some degree because CO_2 is a diluent in the unit. Furthermore, carbon dioxide promotes the formation of COS and CS_2 in the Claus RF. The main solution to this problem is to operate the absorber with high selective amine solvent such as MDEA as well as to select the operating conditions that slip most of the inlet CO_2 in the tail gas with the overhead waste gas sent to the incinerator.

Amine concentration and circulation rate have the greatest effect on the CO_2 slippage. As can be seen in Figure 5.11 (below), the circulation rate has been kept constant at 170 gpm, and the effect of amine concentration was monitored. Lower amine concentration is good for high CO_2 slippage, which is in this case the 20 (wt%) MDEA amine solution.

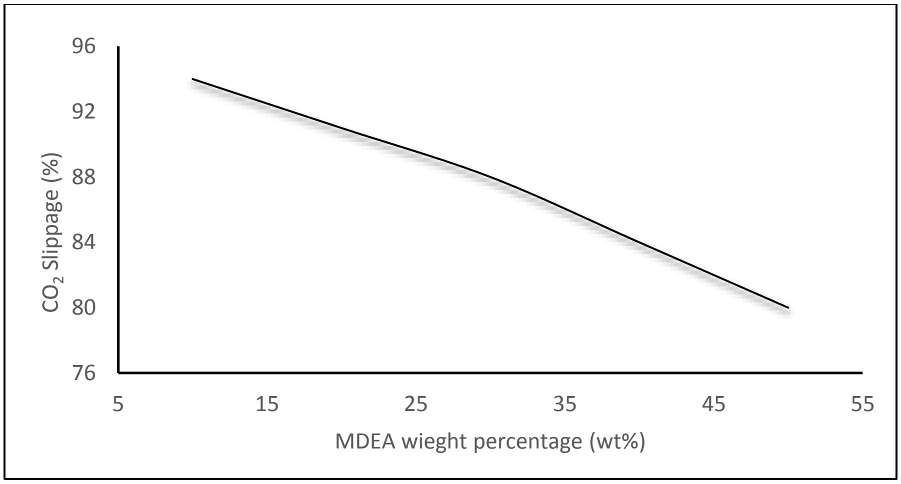

Figure 5.11 CO_2 slippage as a function of amine (wt%) at 170 (gpm)

Figure 5.12 (below) depicts the variation of CO_2 slippage with circulation rate for the 20 (wt%) MDEA. Higher amine flow rate increases the absorption of CO_2 into the MDEA, which will then be recycled back to the Claus plant. This will cause dramatic impact on the sulfur recovery as it decreases the reaction furnace temperature and leads to poor conversion.

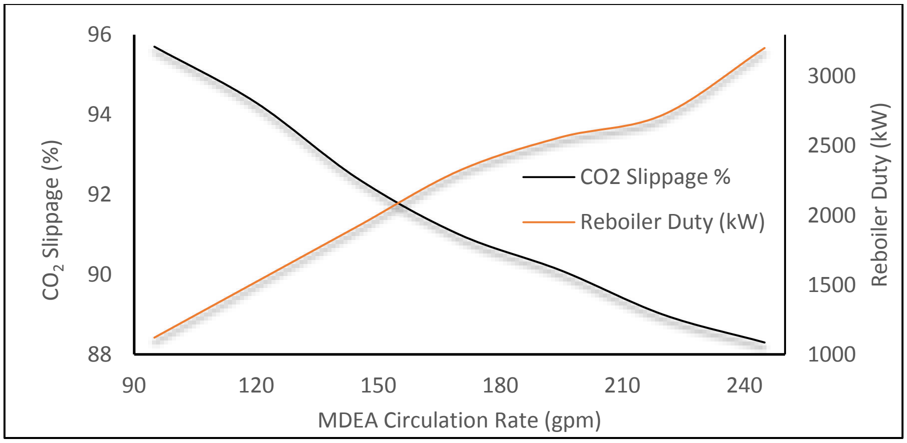

Figure 5.12 CO_2 slippage as a function of amine circulation rate at 20 (wt%)

Therefore, for high selectivity applications as in this case, MDEA concentration and circulation has to be maintained at low levels, in order to avoid the risk of sending CO_2 to the Claus plant, which promotes the formation of COS and CS_2 as well as overloading the unit.

5.4.2 Amine Circulation Rate

Acid gas absorber or contactor is the main equipment that is found in gas sweetening units. It facilitates the interactions between the acid gas and the solvent to occur, where the acid gas (H_2S and CO_2) will react and get absorbed by the amine solution. High pressure and low temperature are usually preferred operating conditions for absorbers operation.

One of the factor to consider is the concentration of absorbed acid gas (H_2S and CO_2) in the amine solvent circulated in the unit, which is known as rich loading. High acid loading increases the efficiency of the unit. However, not very high which causes corrosion and foaming.

High amine circulation flowrate dictates the use of high pumping energy needed to pump the amine solvent and high steam rate in the reboiler due to more heat that is necessary to regenerate the amine as in shown in Figure 5.13 (below):

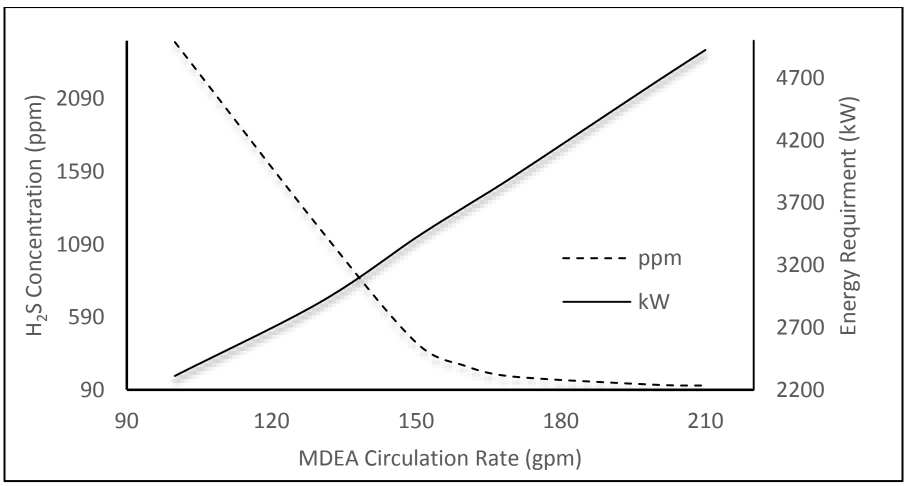

Figure 5.13 H_2S concentration and energy requirement variations with the amine rate

The foaming tendency will also be high because of the increased liquid velocity in the tower. Over circulation, also leads to increased degree of tear and wear on pipes and equipment, which cause corrosion. Thus, it is necessary to operate the unit with the optimum circulation rate to maintain stable operating condition, which will result in significant amount of cost saving without sacrificing on performance.

5.4.3 Lean Amine Temperature

Determining the optimum lean amine temperature is not always straightforward. Most plant operators and gas processing textbooks suggests that lean amine temperature to be 5 ^{o}C above feed temperature in order to prevent hydrocarbons condensation in the tower and related foaming issues [10]. It was obviously important to investigate the sensitivity of varying the lean amine temperature on operating parameters such as treated gas H_2S amount, pumping duty, water vapor content in waste gas, and dew point temperature.

The current plant operation indicates:

- Lean amine temperature of 57 ^{o}C.
- Tail gas feed temperature inlet to the absorber of 40 ^{o}C.
- Amine circulation rate of 305 gpm.

Therefore, a case study was conducted by varying the lean amine temperature and monitoring the effects on the system performance.

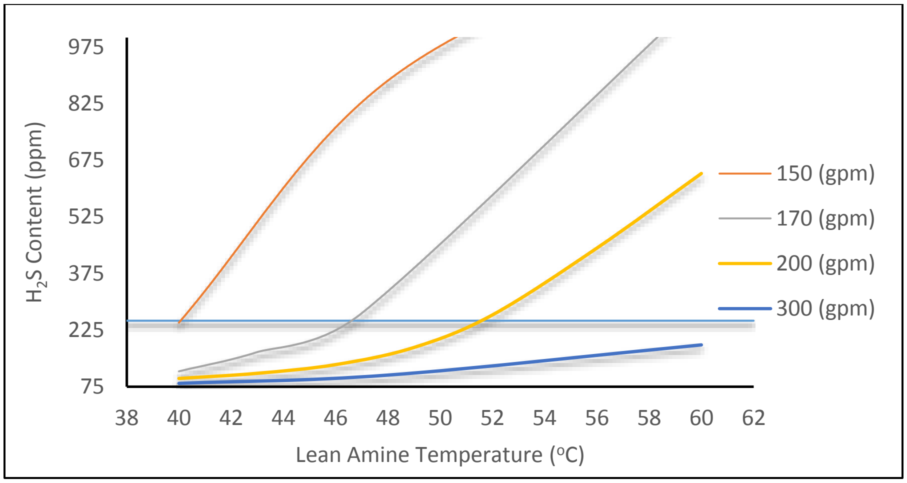

Figure 5.14 Treated gas H_2S content versus lean amine temperature

Reducing lean amine temperature leads to less H_2S content in the waste gas as shown in Figure 5.14 (above), which is as expected. This explains the preference of low temperature absorption operation, because the chemical of acid gas with MDEA is exothermic in nature, meaning that heat is released in the process, and by lowering temperature more H_2S will be absorbed by the solvent. For all circulation rates of 300 gpm and above, decreasing the temperature does not improve the process since all temperatures produce gas within specification (i.e., below 250 ppm).

On the other hand, operating the unit with 150 gpm and lower amine flowrates produce off-spec waste gas. Therefore, the optimum amine flowrate should be kept at 170 gpm for all lean amine temperatures below 47 ºC. For summer plant operation, where it is difficult to maintain this temperature by air cooler, we can increase the circulation rate to 200 gpm and still produce a treated gas within specification. Provided that temperature of lean amine does not exceed 52 ^{o}C. Performing this modification has resulted in pumping duties to decrease from the current 736 kW to 521 kW by 29%.

5.4.4 Regeneration Parameters

Table 5.4 (below) shows the energy consumption in the amine sweetening process. Significant amount of energy is consumed in the reboiler as compared to other energy required in the pumps and aerial coolers.

Table 5.4 Energy consumption comparison in amine sweetening unit

Property	Value
Reboiler Duty (MW)	3.88
Air Cooler Power (MW)	1.38

Therefore, the regeneration process offers a potential area of optimization in the amine sweetening unit. The rich amine flows from the absorber to the regenerator tower, where steam is used to heat the amine to its boiling point to strip H_2S out from the solution. Once regenerated, the amine is routed back to the absorber via lean amine pump. The regeneration process requires maintaining the amine at its boiling point in order to strip H_2S. The required energy in the form of steam can be optimized by supplying enough steam to the regenerator.

Steam ratio, which is defined as steam mass flow rate per amine circulation volumetric flow rate, as recommended by [14] and many other sources varies from (0.9 – 1.2) lb steam/gallon amine. The current plant operation uses steam stripping ratio of 1 lb steam/gallon amine and the corresponding reboiler duty is 3.88 MW. Conducting a sensitivity analysis to test the effect of changing the steam ratio on system performance, and particularly on reboiler duty is essentially required. The steam ratio was varied from (0.6 to 1.5) lb steam/gallon amine and the amine circulation was kept at the minimum required to achieve H_2S specification in the waste gas. The case study is presented in Figure 5.15 (below):

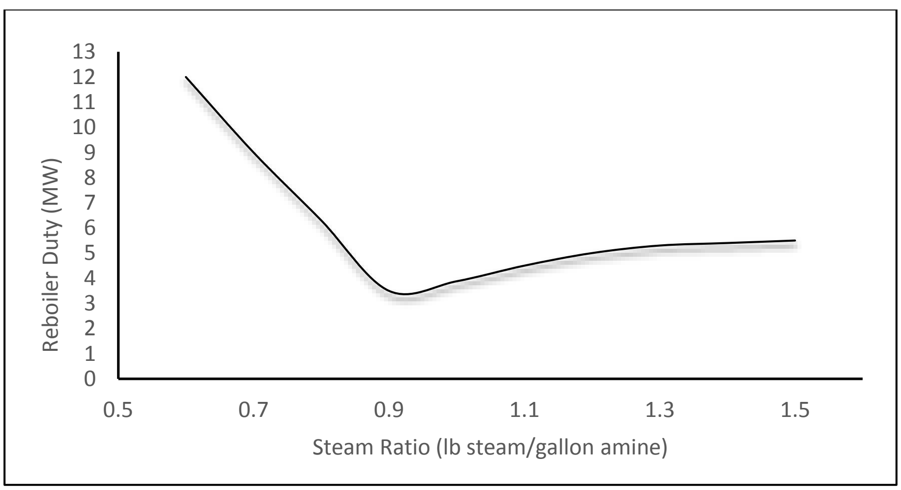

Figure 5.15 Steam stripping ratio effect on reboiler duty

From the conduced case study, it is obvious that the recommended steam ratio rule is valid as the reboiler duty is in the minimum possible range for (0.9 – 1.2) lb steam/gallon amine. However, improvement still can be made by lowering the steam ratio from the current 1 lb steam/gallon to 0.87 lb steam/gallon. As the reboiler duty will decrease from 3.88 MW to 3.47 MW, which amounts for 10.6% reduction in reboiler duty while still produce a treated gas within specification.

5.5 Incineration Unit Optimization

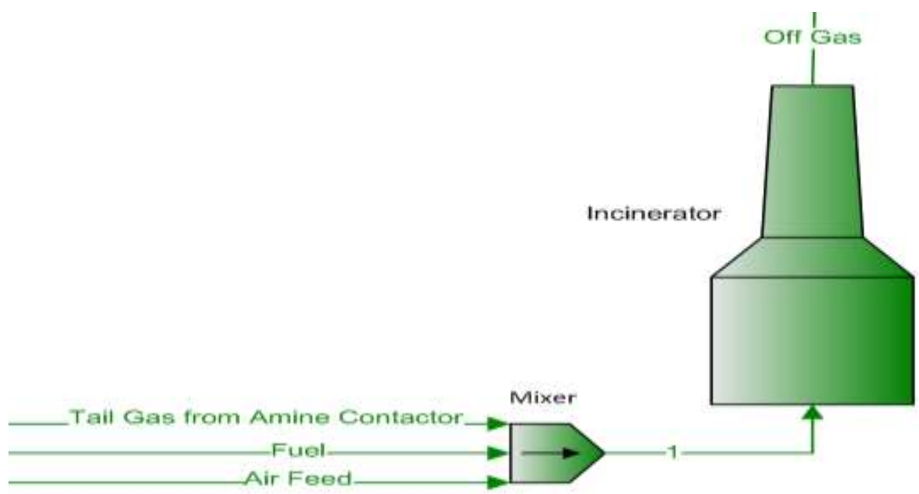

Figure 5.16 Incineration unit flowsheet

All residual sulfur components not recovered in the process will be sent to SRU incinerator. Those compounds include H_2S, COS, CS_2, and sulfur vapor (all together are known as Total Reduced Sulfur, TRS). The incinerator works by burning and oxidizing the tail gas that includes TRS to SO_2 prior to release them to atmosphere. Proper air to fuel ratio has to be controlled to ensure all TRS are oxidized and to eliminate pluming from the stack of the incinerator.

5.6 Optimized Operating Conditions

The preceding analysis in previous sections revealed variety of operational changes that resulted in improving the sulfur recovery process. The addition of SCOT process to treat the outlet tail gas from the SRU has resulted in improving the overall sulfur recovery from 98% to 99.93%. This has resulted in reducing the total sulfur emission from 4900 ppm down to 250 ppm in order to comply with air regulation.

Some of the modifications for operating parameters of the SRU are found in Table 5.5 (below):

Table 5.5 Optimal operating condition for SRU and energy recovery

Equipment	Controlling Factor	Base Case	Optimized	Potential Advantage
Reaction Furnace	Tail Gas Ratio (H_2S/SO_2)	1.82	2	0.96% Increase in Sulfur Recovery and 22.9% Decrease in Air Blower Power
Converter 1	Reheat Temperature (^oC)	232	232	–
Converter 2	Reheat Temperature (^oC)	216	210	7.8% Reduction in Reheat Duty
Converter 3	Reheat Temperature (^oC)	204	193	10.2% Reduction in Reheat Duty

The production of steam in the WHB and has also increased and overall, SRU can be considered as a net exporter of energy in the form of steam and usually the required fuel consumption is reasonable and not very high.

Studying the hydrogenation unit current operating conditions revealed that there is a deficiency of the reducing gas (H_2). Consequently, the inline burner was modified to operate in an air deficient mode to raise the H_2 content in the effluent gas. This resulted in increasing the conversion of carbonyl sulfide from 41.4% to 96%. Considerable amount of fuel reduction, around 7%, was noticed in the tail gas incinerator due to lower TRS compounds being sent there.

Other studies included the quench unit operation by lowering the overhead temperature to 40 ^oC. Air cooling requirement has increased from 1.12 MW to 1.38 MW by 23.2%, as expected. However, considerable gains were noticed in the amine sweetening unit operation such as the ability to increase the rich loading from 0.21 to 0.34 mol AG/mol amine and the ability to reduce the amine circulation rate and reboiler duty by applying little modification to key operational parameters.

Chapter 6 Conclusion

Sulfur recovery process is an essential and integral part of any crude and natural gas plants processing sour streams. Its importance originates from the need to meet environmental air regulation regarding sulfur emissions. The plant for the study was modified by adding a tail gas treatment unit to raise the sulfur recovery from 98% to 99.93%. This was done because the current plant sulfur emission was around 4900 ppm and in order to lower this value, some sort of cleanup process for the waste gas had to be implemented. As a result, sulfur emission has decreased below the 250 ppm standard value in the incinerator stack and the emission is now fulfill air pollution regulation.

The project presented the study of key sulfur recovery parameters and their impact on the efficiency of the system. The aim was to achieve the optimum operating points for each parameters. Key factors that affect the performance of the sulfur recovery process had been investigated by the aid of ProMax process simulator. First by developing the steady state model for the whole process. Then, the model was tested and evaluated to determine the sensitivity of the operational parameters that might affect performance of the process.

In this project, the performance of the sulfur recovery process was simulated and evaluated. Followed by optimization in order to improve the efficiency. Especially, those related to operational parameters because they are easy to implement in existing processes without additional capital investment and results in huge savings in terms of energy and operating cost. Operating at optimum conditions is a key factor for process improvement.

Amine circulation rate has the biggest effect on energy consumption among other parameters. Over circulation often leads to high energy consumption in the reboiler without significant improvement in the treated tail gas composition. Therefore, it's essential to maintain the circulation rate at optimum minimum value without compromising on product specifications. The amine circulation rate was lowered by 34.4%, which offered great improvement of throughput of the system. The 10.6% reduction in reboiler duty can be considered as a reduction of operating cost and improvement in system performance. The hydrogenation unit inline burner was modified to operate in an air deficient mode to raise the H_2 content in the effluent gas. This resulted in increasing the conversion of carbonyl sulfide from 41.4% to 96%. Considerable amount of fuel reduction, around 7%, was noticed in the tail gas incinerator due to lower TRS compounds being sent there.

These are very reasonable modifications and variations but they provide great enhancement and improvement of plant operation under study. Lastly, every plant and case is different and necessitates different analysis and rigorous investigations in order to optimize the performance and process.

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