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Process Analysis and Improvement of a Claus Unit of an Existing Gas plant

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ABSTRACT

This research is a part of Master degree research programme at Cranfield University to study Claus process and perform process analysis on an existing Sulphur recovery unit in a gas plant.

The Mellitah Plant, in Western Libya, is a gas plant designed to treat raw gas and condensate from offshore gas fields in several processing units where the sour gas (H$_2$S, CO$_2$, COS, SC$_2$) is removed to meet the international emission standard, in order to control the emission and pollution from the flue gas. The acid gases are treated in Claus unit where H$_2$S is converted to sulphur in multi-reaction steps. These reactions start in a combustion reaction zone, thermal reactor, to produce a suitable mixture of H$_2$S to SO$_2$. The mixture reacts in Claus catalytic reactors to produce sulphur vapour. The sulphur vapour is condensed in multi-condensing steps after each catalytic reactor.

The ultimate aim of this research is to carry out the process analysis for Claus unit in order to recover the waste energy to increase the plant productivity, minimise the use of the plant utilities, and decrease the environmental pollution. A process model of the plant was developed and validated in Aspen HYSYS. The process was then analysed, the analysis has resulted in a significant increase in Claus unit overall conversion ratio which has increased from 61% to 97.63% H$_2$S base. Consequently, Claus unit productivity has increased by approximately 1.72 times. In addition, a higher amount of energy is recovered in a form of heat by heating the boiler feed water to produce both high pressure steam in the waste heat boiler and low pressure steam in 1st and 2nd sulphur condensers. Both high pressure and low pressure steam total production are increased by 1.5 times. All this has been achieved at high conversion ratio number of 2 in tail gas which represents optimum O$_2$/H$_2$S ratio in the thermal reactor feed and the high conversion number can be kept in between 1.5 to 3 during plant normal operation.

Keywords: Acid gas composition, O$_2$ concentration, ratio O$_2$/H$_2$S, Claus Unit, H$_2$S/SO$_2$ ratio in tail gas, thermal reactor, catalytic reactor.
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Special thanks to Mr Keith Hurley who helped me a lot during my thesis writing up, his help is greatly appreciated.
DEDICATION

In the name of Allah, the Most Gracious, the Most Merciful. I dedicate my work to my Parents who taught me how to achieve the best, my loved wife who encouraged me to accomplish my project, my children and brothers.
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<tr>
<td>H.P.S</td>
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<tr>
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<td>High Conversion Ratio Number (Dimension less number)</td>
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<td>Thermal Reactor</td>
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1 Introduction

1.1 Background

Approximately 25% of produced natural gas from new resources must have a degree of treatment to be sold as clean fuel, and one of the undesirable impurities is hydrogen sulphide (H$_2$S). Furthermore, recovering the sulphur element from sour gas that contains a high concentration of H$_2$S has two main reasons (Mokhatab, Saeid & Poe, 2012). One of them is an economic reason to purify the sales gas to sell it at a higher price. The second is an environmental reason to meet the standard limits of emission being sent to the atmosphere (Pandey and Malhotra, 1999).

Sulphur Recovery involves the process of converting H$_2$S to element sulphur. The Claus process or one of its modification are the most common. Usually, such process is implemented on medium or small scale units, especially when the hydrogen sulphide concentration in the raw stream of the acid gas is relatively low (Mokhatab, Saeid & Poe, 2012).

The modern Clause process is a modification of a unit that was used for the first time in 1883 (Polasek and Bullin, 1993). The primary concept is the reaction between H$_2$S and Oxygen (O$_2$) over a catalytic bed to result in sulphur and water. Usually, this H$_2$S is an impurity that has been removed during natural gas and crude oil processing. Roughly 90 to 95 % of the element sulphur is produced by Claus (Taheri et al., 2012) and 95 to 97 percent Of the H$_2$S is recovered using Claus technology from the overall quantity in feed streams (Polasek and Bullin, 1993) . A Claus unit consists of burner or furnace where the H$_2$S is reacted with O$_2$, calls a thermal reactor and multi-stage catalytic reactors (two or three beds normally). Each stage also consist of a process gas re-heater to ensure the temperature maintained at a value greater than the sulphur dew point, to avoid poison the catalytic bed, and a condenser to liquefy sulphur vapour produced in that stage.
1.2 Mellitah plant

The Mellitah Plant, in Western Libya, is a gas plant designed to treat raw gas and condensate from offshore gas fields in several processing units, where the sour gas \((\text{H}_2\text{S}, \text{CO}_2, \text{COS}, \text{SC}_2)\) is removed to meet the international emission standard, in order to control the emission and pollution from the flue gas. Mellitah plant is the only Libyan natural gas exporting gate to the international marketing via 32" pipeline called Green Stream. The gas is compressed at Mellitah Gas Compression Station and sent to Italy where the gas is distributed to the consumers. The total sales of the natural gas is approximately 34 Sm\(^3\)/Day (Mellitah Oil & Gas, 2006).

Mellitah sulphur recovery plant consists of three sulphur recovery trains each train contain five units: \(\text{H}_2\text{S}\) enrichment, Claus unit, tail gas clean-up, incineration unit and sulphur degassing unit with two independent sour water stripping units. The plant is designed to convert all upstream \(\text{H}_2\text{S}\) to sulphur, and it was put in operation in January 2006 (Mellitah Oil & Gas, 2006).

Three operation modes can be used to operate Mellitah Claus unit. Each depends on the concentration of \(\text{H}_2\text{S}\) in the feed stream, flame stability and thermal reactor temperature. They can be listed as follow:

1. Straight through feed of \(\text{H}_2\text{S}\) (all Acid gas is burned with \(\text{O}_2\) in the thermal reactor burner when \(\text{H}_2\text{S}\) concentration is greater than 30% in the feed).
2. Split flow (Acid gas is split between thermal reactor burner and the thermal reactor second zone) when \(\text{H}_2\text{S}\) concentration is 25-30% in the feed.
3. Fuel gas support is used when \(\text{H}_2\text{S}\) concentration is less than 25% in the feed (Mellitah Oil & Gas, 2006).
1.3 General Claus process description

In general, Claus has a main reaction furnace called Thermal Reactor where the H$_2$S is burned with Oxygen O$_2$ to form SO$_2$ and water vapour. Temperature in the thermal reactor must be over 900°C and the first reaction is as below:

$$H_2S + 1.5 O_2 \leftrightarrow SO_2 + H_2O$$  \hspace{1cm} 1-1

The feed to the thermal reactor is preheated roughly to 250°C to increase the adiabatic flame temperature and Feed pressure is approximately 0.6 brag. One 1/3 of the hydrogen sulphide converts to sulphur dioxide where the remain 2/3 reacts with the formed SO$_2$ to produce sulphur and water vapour the conversion to sulphur in the thermal reactor is less than one 1/6 of the feed as the reaction here is equilibrium so it does not make the complete conversion. Hot gases leave the Combustion Zone to a waste heat boiler where the heat is recovered by means of heating of Demineralized water (BFW) to produce H.P.S and liquefy the sulphur formed at this section. Process gases which normally contain H$_2$S, SO$_2$, and COS, CS$_2$, H$_2$O and S vapour pass through another waste heat recovery call 1$^{st}$ sulphur condenser to remove the remaining sulphur vapour then to a process repeater to increase the process gas temperature 30°C over sulphur vapour dew point then it enters a catalytic reactor called 1$^{st}$ catalytic converter where the remaining of H$_2$S and SO$_2$ in the process gas reacts to form S and H$_2$O according to the next chemical reaction:

$$2 H_2S + SO_2 \leftrightarrow 3/x S_x + 2 H_2O$$  \hspace{1cm} 1-2

Then is cooled down again to remove sulphur formed in the 1$^{st}$ catalytic converter by mean of heating up low pressure BFW to produce low pressure steam in the 2$^{nd}$ sulphur condenser. The previous step is repeated for another preheating and catalytic converter if the unit consists of two catalytic beds or twice if the unit consists of three beds. The last step is to remove the formed sulphur in the final sulphur condenser before sending the flue gas either to a thermal incinerator or tail gas treatment if exist.
1.4 Research Justification

Sulphur recovery is a process of converting sulphur component in oil and gas industry to sulphur element for two main reasons. The first one is to purify the oil and gas to increase sales price and the other one is to protect the environment from the emission resulted from direct burn of sulphur component in atmosphere such as SO$_2$, SO$_3$, CS$_2$, and COS. All these gases can react with water vapour in the air and produce acidic rain that can cause harm to both human and environment. Mellitah Oil and Gas Company must follow the international regulation and respect the maximum range of sulphur component in the plant emission such as H$_2$S, SO$_2$, and SO$_3$.

The main target in oil and gas industry is profit maximisation and it does not mean producing as much oil and gas as possible, but it means reducing the operational cost that can save as much income as possible in some cases as much as one third of the plant production cost. Libya has significant oil and gas resources that can make Libya one of the biggest oil and gas producer, as well as a major sulphur producer. Many industries rely on sulphur, yet the majority of the sulphur produced in the world is used to make sulphuric acid. Sulphuric acid has multiple uses in the production of chemicals, petroleum products and a wide range of other industrial applications. Sulphur’s main use is in making chemicals for agriculture, mostly for fertilisers. Other uses of sulphur include metal mining and the production of organic and inorganic chemicals. A multitude of products (such as the production of rubber for automobile tires) requires sulphur in one form or another during some stage of their manufacture.

1.4.1 Research objective

Sulphur recovery section of the Mellitah plant can produce around 500 tonnes of pure solid sulphur per day. After about decade of operation, in order to improve the plant efficiency and continue to meet emission limits, an investigation study needs to be carried out on Claus unit. The research aims to increase the plant overall net profit by accomplishing a process analysis by improving the plant efficiency and to reduce the operational cost by saving more energy by increasing HPS and LPS production in the waste heat boilers.
The process analysis and improvement are carried out using a process simulation in HYSYS 8.6 where the model prediction is analysed to evaluate the Claus unit performance. The Process analysis shall keep the Claus unit production rate at the maximum of about 500 tons of solid sulphur and utility consumption at the minimum level by increasing energy recovery. The analysis is expected to provide the operation staff with the correct information to lead the operation team to the proper procedure of the process operation to Claus unit at the maximum conversion ratio of almost 97% and HPS, LPS production.

1.5 Research approach
The Core of this research is to simulate the key units in Claus process using Aspen HYSYS 8.6 process software. To model the process appropriately, consideration is given to the chemical reactions in the process, with respect to energy recovery. To improve Claus unit means to enhance the overall reaction in the plant and shift it to the right-hand side where the production of sulphur increases and the heat result from exothermic reaction could be recovered and used in the system.

\[
3H_2S + 1.5O_2 \leftrightarrow 3/nS_n + 3H_2O + \text{Heat} \quad 1-3
\]

The above reaction is an overall Claus reaction. In order to increase the conversion of H\textsubscript{2}S to sulphur an optimum quantity of oxygen must be fed to the thermal reactor which enough to convert the one-third of H\textsubscript{2}S to Sulphur. When the required feed ratio between O\textsubscript{2} and H\textsubscript{2}S is achieved then the conversion shall reach its maximum rate.

In order to get the required ratio in the Claus unit feed to the thermal reactor (O\textsubscript{2}/H\textsubscript{2}S), a case study is generated to explore different scenarios of plant load from 40% to 100%. To accomplish the process analysis several steps must be followed:

- Build a model of the Claus unit in HYSYS process software.
- Validate the model of the process with plant data.
- Perform process analysis by:
  1- Using different feed composition (combustion air/ acid gas).
2- Investigate the effect on the ratio of H₂S/SO₂ downstream Claus unit.
3- Evaluate the effect of O₂ feed stream flow on overall Clause Unit efficiency.
• Perform an investigation on energy recovery and Increasing HP Steam and LP steam production.

Claus unit process analysis and improvement

The process simulation is the first step of the research and is achieved using HYSYS 8.6 process software. The process is simulated by building a model of the existing Claus unit using HYSYS 8.6 process software then run the built model with the plant current feedstock of combustion air and AAG. When the model is validated, a case study is generated to using the plant different loads starting from 40% to 100% load in five different scenarios. Then a process analysis is carried out to evaluate the model predictions. Certain steps are used to verify whether the plant is being operated in respect of the unit operating procedure when the H₂S/SO₂ ratio is within the range of 2-5 and the feed ratio of O₂/H₂S equal to 2. The process analysis consists of the following three steps:

1. Different feed O₂/H₂S ratio
2. H₂S/SO₂ Investigation in tail gas
3. O₂ flow effect on the process
Figure 1-1 shows the research methodology in a simple chart starting from the basic of process simulation to the conclusion and required action.
2 Literature Review
2.1 General overview

The removal of the sulphur component from the natural gas is one of the main processes in oil and gas industry. Claus process has been used as a standard for sulphur recovery for more than 100 years (Manenti, Papasidero and Ranzi, 2013). The Claus process has undergone many modifications, based on feed compilation (i.e. H₂S, CO₂ and ammonia presence), to achieve the required performance that meets environmental standards by reducing toxic gases emission to the atmosphere. In general, Claus unit can be operated in three different operating modes, straight through, AAG split into two zones and fuel gas support, in respect of plant feed composition and overall conversion ratio (Pandey and Malhotra, 1999). Claus unit has been modified to increase H₂S overall conversion to sulphur and the increase in the process conversion result in more energy which, is recovered as HPS and LPS, there are different modification of Claus units starting from the old original direct oxidation Claus unit to SUPERCLAUS which is the one used by Mellitah Oil & Gas (Koscielnuk et al., 2014).

Figure 2-1 Theoretical equilibrium Conversion percent of H₂S & acid gas burner temperature from different H₂S sources (GPSA, 2012)
The Figure 2-1 shows different H₂S feed sources, each source’s H₂S conversion percent to sulphur and the resulted thermal reactor temperature. Curves 1 and 2 contain 3.5 mol% and 7 mol% respectively when curve 3 is pure H₂S (GPSA, 2012).

2.1.1 Claus process general concept

To fully understand the general concept of desulphurization unit using Claus technology an experimental Claus unit rig used in the laboratory is shown below. The principle of the chemical conversion of H₂S to element sulphur is to burn one-third of the hydrogen sulphide feed in presence of air to form sulphur dioxide SO₂ and water vapour in two exothermic reactions (Royan and Wichert, 1997) as follow:

![Figure 2-2 Example Package-Type Sulphur Plant](image-url)
Reaction 1 takes place in the combustion zone of the thermal reactor (reactor furnace). After the reaction above take place a second reaction occurs afterwards between the remaining two-thirds of the hydrogen sulphide and the formed sulphur dioxide as shown in reaction 2:

\[ 2H_2S + SO_2 \leftrightarrow \frac{3}{n} S_n + 2H_2O \]  

The second reaction does not go 100% conversion as it is equilibrium reaction so the overall reaction in the thermal reactor is reaction 3.

\[ 3H_2S + 1.5O_2 \leftrightarrow \frac{3}{n} S_n + 3H_2O \]  

The remaining quantity of the mixture of H\(_2\)S and SO\(_2\) that does not react in the thermal reactor (reaction furnace) reacts in the catalytic reactors in two or three reactors followed by a sulphur condenser to liquefy the sulphur vapour formed in each catalytic reactor (Pandey and Malhotra, 1999).

### 2.1.2 General Chemical Reaction Overview

The principle of the process is to burn one-third of H\(_2\)S in the thermal reactor (burner) in the presence of air O\(_2\) to form SO\(_2\) according to the next chemical reaction:

\[ H_2S + \frac{3}{2} O_2 \leftrightarrow SO_2 + H_2O \quad \Delta H = -560 kJ/mol \]  

The range of the operating combustion zone temperature is between 900°C and 1540°C (Polasek and Bullin, 1993) and operating pressure is about 0.7 Brag (Polasek and Bullin, 1993). The process gas leaving the thermal reactor is cooled down in a waste heat boiler in order to condense the sulphur formed in this step and produce saturated high pressure steam by means of heating of boiler feed water. The produced steam in this section is used as a heating medium to heat up the feed streams and process gas into the system. Approximately 80% of the heat released in Claus unit is recovered as useful energy, and 65 to 70% of the sulphur is recovered. The rest of the process gas exiting the waste heat boiler is feed to catalytic bed stage. Where the remaining two-thirds of the H\(_2\)S reacts with
SO₂ (Claus reaction) and the output of this reaction is element sulphur and water is shown below (2):

\[ 2H_2S + SO_2 \leftrightarrow \frac{3}{2} S_2 + 2H_2O \quad \Delta H = +47 \text{ kJ/mol} \quad 2-5 \]

H₂S and SO₂ mixture react at lower temperature (from 197 to 347°C) (Walas and Ph, 1999) over catalytic bed made of an activated alumina or titanium dioxide to recover more S₂ as follow:

\[ 2H_2S + SO_2 \leftrightarrow \frac{3}{8} S_2 + 2H_2O \quad \Delta H = -108 \text{ kJ/mol} \quad 2-6 \]

In reaction (3) 70% of the mixture reacts producing element sulphur in a form of S₈ and this reaction exothermic, whereas in the thermal reactor S₂ is the major product and the reaction is endothermic (Mokhatab, Saeid & Poe, 2012). The overall reaction for the entire process is written as follow:

\[ 3H_2S + \frac{3}{2} O_2 \leftrightarrow \frac{3}{n} S_n + 3H_2O \quad \Delta H = -626 \text{ kJ/mol} \quad 2-7 \]

This type of reaction is equilibrium chemical reaction, so it is impossible to recover all sulphur components in the feed stream of Claus unit to sulphur. Multi-stage catalytic is used to increase the overall efficiency that can reach 95 to 97% depending on the level of conversion, the number of the catalytic stages, and type of re-heaters used (Polasek and Bullin, 1993)
2.2 Claus operation option
Claus unit has different operation option and each operation mode has a certain feed composition requirement. Feed composition, particularly H$_2$S concentration and the presence of ammonia, is the main operation factor that shall determine the operation mode.

2.2.1 Rich Acid Gas Feed (H2S concentration over 50% in feed)
Controlling the unit with feed rich in H$_2$S (over 50%vol) is not difficult. It is possible to use two or three catalytic beds with or without direct oxidation or cold (sub dew point) bed (McIntyre and Lyddon, 1997).

![Figure 2-3 Schematic flow diagram of a straight-through, three catalytic reactors, in Claus sulphur recovery unit](Abedini, Koolivand Salooki and Ghasemian, 2010)

In 1960, two bed Claus plant was operated with 93% H$_2$S in the feed. The overall recovery was 96.1% and the process was simulated using TSWEET software (McIntyre and Lyddon, 1997). Overall recovery decreased to 91.8% (McIntyre and Lyddon, 1997) when outlet temperature was from 450°C to 370°C (Polasek and Bullin, 1993). An additional sulphur condenser was added to condense the vapour downstream the thermal reactor.
Removing liquid sulphur, step by step, and controlling the inlet temperature of process gas in the re-heaters to ensure that it remains above vapour sulphur dew point, prevents liquid sulphur condensation on catalytic beds and the outlet temperature of the first bed must be maintained at 340°C which is 46°C less than the original temperature has resulted a decrease in Claus unit overall conversion ratio of the plant as above from 96.1% to 91.8% (Mattsson-boze and Lyddon, 2006). It is fairly difficult to distract COS and CS$_2$ (carbonyl sulphide, carbonyl disulphide) that can be produced from the direct burning of H$_2$S in the combustion chamber when the second condenser had outlet temperature close to Sulphur vapour dew point. The 2$^{nd}$ condenser outlet temperature must be 30°C over sulphur vapour dew point because the equilibrium is very close the sulphur dew point and it improves the process and increases the overall conversion. The H$_2$S/ SO$_2$ ratio was 1.2/1 in the real plant but which is not ideal, 2/1 is the optimum value for this variable. All three catalytic reactors Claus unit and two catalytic reactors Claus unit with a cold bed can be used to treat the rich acid gas feed with H$_2$S concentration ranged (50% to 60%) with high efficiency almost 99% of the feed (Mattsson-boze and Lyddon, 2006).

### 2.2.2 Lean acid gas feed (H2S concentration less than 50%)

The operation of the burner in a Claus thermal reactor with a feed that contains a relatively low H$_2$S concentration (less than 50%) may result in an unstable flame. Furthermore, the hydrocarbon present in the feed cannot be completely burned causing a deterioration of the catalytic beds due to soot or carbon deposition (McIntyre and Lyddon, 1997). There are many modifications to aid flame stabilisation at the same adiabatic flame temperature as the straight through operation mode such as acid gas preheater with fuel gas burner, all-catalytic selectox process, acid gas bypass around the furnace (split flow), and oxygen enrichment feed to clause furnace (Boiko, 2007) (McIntyre and Lyddon, 1997).

### 2.2.3 Acid gas containing ammonia

Ammonia is one of the impurities that can be present in the acid gas feed to Claus unit because of MDEA solvent decomposition. To destroy the ammonia in
one of the following two methods is to be implemented: - first, a special burner can be used to burn the ammonia at a very high temperature around 1500°C or the feed is burnt with excessive of O₂.

2.3 Past studies on the Claus Unit

Many studies and research have conducted on Claus unit. Ultimately, all the modifications proposed do not change the principles of the process. They only have improved the original process.

2.3.1 Thermal and Catalytic Sections Temperature Control

Preheating the feed streams to the thermal reactor is one of the modifications that increases the thermal reactor temperature and provides flame stability. The high temperature in the combustion zone helps to shift the reaction between H₂S and O₂ to the right-hand side of the reaction 2-4. In a study by Mahdipoor et al., (2012), the feed mixture temperature is around 94°C, with the conversion ratio of H₂S to S is 96.5%, resulting from a combustion zone temperature of 820°C which is insufficient for burner flame stabilisation. Moreover, at such temperature the hydrocarbon that can be present in this process are not consumed. The feed temperature must be increased to 260°C to achieve a combustion zone temperature higher than 900°C as shown in Figure 2-4 but the temperature of this zone must not exceed 1400°C to protect the thermal reactor body from melting. Fuel gas support is used to achieve the same purpose, with the added combustion introducing extra reactions. All this makes it difficult to control the reactions of the system. Figure 2-5 shows the relation between thermal reactor (furnace) and the fuel gas flow rate to the main burner (Mahdipoor et al., 2012). Catalytic converters temperature is as important, therefore, the process gas is as reheated. The temperature of the process gas leaving each condenser must be higher than sulphur vapour dew point to avoid sulphur condensation on catalytic beds (catalyst poisoning). An external medium such as steam or electrical coil can be used to heat the process gas. An acid gas bypass around the furnace is also used but this can reduce the overall conversion rate. The 1st converter temperature has to be over 250°C (Mahdipoor et al., 2012).
The graphs below show the effect of both feed temperature and fuel gas flow on the thermal reactor temperature (furnace).

Figure 2-4 Thermal reactor temperature Vs Feed temperature

(Mahdipoor et al., 2012)

Figure 2-5 Thermal reactor temperature Vs Fuel gas flow to the thermal reactor (Mahdipoor et al., 2012)
2.3.2 Process and Reactions

According to Manenti et al., (2014), The problem considers about 2000 reactions, with 142 species and a network of 4 ideal reactors for the thermal section of the SRU, while the catalytic section of the process has 2 reactors with 2 reactions. For each reactor, one global mass balance, 141 species mass balances and one thermal balance are solved. The problem also has 3 optimization variables (Furnace Pressure, AG/Air ratio, WHB water temperature). These variables have upper and lower boundaries not to be exceeded.

2.4 Claus Unit Mathematic Modelling

2.4.1 Claus Process Reaction Furnace via a Radical kinetic Scheme

50 years of research were dedicated to improve the reaction furnace kinetic scheme by enlarging the kinetic schemes to expose the presence of species previously not thought to be significant. Many studies have come to the conclusion that equilibrium controls are inappropriate for expecting product distributions from the thermal reactor, because not all the species exiting in the reaction furnace are at equilibrium, particularly, CO, H₂, COS and CS₂ (Otadi et al., 2011) (Pierucci, Ranzi and Molinari, 2004). Empirical models were developed to explore the problem of the limitation with the equilibrium calculation in the kinetic scheme (Pierucci, Ranzi and Molinari, 2004). The result showed the flame temperature is a function of the combustion of the most reactive species such as H₂S (Pierucci, Ranzi and Molinari, 2004). Therefore, O₂ to H₂S ratio is a critical factor in thermal reactor operation where the ratio should equal 1/2 in the feed to the burner. This ratio of the feed assures a flame temperature over 900°C (GPSA, 2012).

The study preliminary results is aimed to modelling the thermal reactor with a detailed kinetic scheme based on a radical approach. The study has demonstrated that the flame temperature is mainly due to the combustion of the most reactive species such as H₂S. The modelling of the whole chamber with a PFR model is an acceptable approximation proved by the satisfactory agreement with experimental data (Pierucci, Ranzi and Molinari, 2004).
2.4.2 Dynamical Model of the Claus Process and its Identification

A model of the Claus process has been made of a combination of a generic first order plus dead time dynamics and a nonlinearity achieved via the material balance equations of the chemical reaction is suggested. The nonlinearity is characterised via one unidentified parameter, which is thought to be identified through the test on the process. It is substantiated via analysis that the relay feedback test is appropriate for the proposed model identification for two reasons. The first one is the serial connection of the Claus nonlinearity and the relay nonlinearity of the test loop. This arrangement results in the process nonlinearity "cancellation" and the possibility of the conventional approach involving the use of describing function of the relay nonlinearity. The second factor is the possibility of identification of three unknown parameters from a single test. The provided simulations demonstrate the proposed methodology. The proposed methodology was used at the sulphur recovery plant application and allowed for a very precise tuning of the Claus process (Boiko, 2007).

2.4.3 Effect of Sulphur Recovery Requirements on Optimization of Integrated Sweetening, Sulphur Recovery, and Tail gas Clean-up Units

Integrated gas sweetening, sulphur recovery, and tail gas clean-up units (TGCU) has been examined using a process simulation program to determine the influence of sulphur recovery requirements on the performance of the system. A base case with an \( \text{H}_2\text{S}/\text{CO}_2 \) ratio of 1/2 in the feed gas was selected to represent a "worst-case" scenario. For the variety of cases considered, the results indicated that the importance of many operating parameters was very dependent on the level of sulphur recovery required. For facilities with less than 10 Tonnes/day of sulphur and recovery requirements below 97%, all of the fine adjustments in the sulphur plants including the catalyst, type of reheat, and better controls should be pursued fully to eliminate the requirement for a TGCU. However, once the TGCU is added in the larger plants, the fine adjustments in the sulphur plant become less important. The major factors become the \( \text{CO}_2 \) slippage in the main amine unit (i.e. quality of Claus plant feed) and in the TGCU absorber. For cases where the \( \text{H}_2\text{S}/\text{CO}_2 \) ratio in the feed gas to the main sweetening unit is less than about
1.0, the CO₂ must be eliminated from the system by slippage in the main absorber or the TGCU absorber. For poor quality feeds to the sulphur recovery unit, recoveries of about 99.8% are close to the maximum achievable with TGCU technology. If the recovery requirements rise above the range 99.8% to 99.9%, other technologies for treating the tail gas such as Stretford or direct oxidation processes will be necessary, especially for the poorer quality feeds to the sulphur recovery units (Polasek and Bullin, 1993).
2.5 The Mellitah Plant General Description

2.5.1 General Description

Mellitah plant consists of three gas plant trains, all are connected with three sulphur recovery units (SRU) via a common acid gas header. The main function of the SRUs is to treat sour gas from the gas plant, which contains CO₂, H₂S, and H₂O and in some cases hydrocarbons (HC) (Mellitah Oil & Gas, 2006). The sour gas is fed to the H₂S enrichment unit to increase the H₂S concentration, and then the Amine Acid Gas (AAG) is fed to Claus unit where the H₂S is converted to sulphur.

2.5.2 Sulphur Recovery Unit Description

The SRU in Mellitah plant, shown in Figure 2-6, is categorised as a SUPERCLAUS process. Slight modifications are expected to optimise the process but they do not affect overall process description and principles. The Claus unit in Mellitah plant can be divided into four sections: - Thermal reactor, waste heat boiler, sulphur condensers and catalytic converters and final condenser.

1. Thermal Reactor Section

Thermal reactor section consists of a combustion chamber with a built-in Fuel gas and AAG burner. The AAG, at a pressure of 0.8 barg and Temperature of 45 ºC, is fed to a dedicated burner where the combustion takes place (Mellitah Oil & Gas, 2006). Remote dedicated instrumentation controls the pressure of the feed stream at 0.6 barg in order to maintain both Claus unit pressure and AAG header pressure. Online hydrocarbon and H₂S analysers are installed to measure changes in H₂S concentration and/or any presence of hydrocarbon in the AAG stream before the feed reaches the combustion chamber. Ambient air is required for AAG combustion is compressed in a combustion air blower. Both AAG and combustion air are preheated using a saturated HPS, in order to increase the adiabatic flame temperature as much as possible in the thermal reactor.
Figure 2-6 Claus Process Floe Diagram as Built in Western Libya Gas Project (Mellitah Oil & Gas, 2006)
The thermal reactor and the burner are the most important items in Claus Unit and correct operation in that section is essential to assure smooth run. The combustion of AAG is accomplished under a highly controlled condition to assure a proper air feeding and stoichiometry, delivering the required O₂/H₂S ratio. A trim combustion air stream is provided to control the slight change in H₂S concentration in the feed stream. The thermal reactor has been designed as two-zone reaction furnace and it has three operation modes: straight through run operation, split flow of AAG between 1st and 2nd zone of the thermal reactor and fuel gas support run. For the straight through operation run, the most common case, the entire quantity of the combustion air and AAG is fed to the dedicated burner and the reactor furnace is operated as a single zone equipment. For the split mode, the entire combustion air and a fraction of the AAG are burned in the burner, and the remaining AAG is fed into the 2nd zone. In the third operation mode, the fuel gas is burned in the entire combustion air in the 1st zone and the entire AAG is fed to the 2nd zone of the thermal reactor. In all cases the principles of Claus is maintained, the only difference is the operating temperature of the thermal reactor, which varies with operation mode due to the requirement of a stable flame and good heat distribution across the thermal reactor. The main purpose of the combustion chamber is the combustion of AAG to control H₂S/SO₂ ratio for subsequence Claus reactions in catalytic converters. Moreover, it provides the required residence time at high temperature to allow equilibrium condition between the different chemical species present in the thermal reactor. Table 2-1 below shows factors to consider when selecting the operation mode.

Table 2-1 Thermal reactor operation modes in Mhelliah sulphur recovery plant (Mellitah Oil & Gas, 2006)

<table>
<thead>
<tr>
<th>H₂S in AAG %</th>
<th>FG support</th>
<th>AAG fraction to 2nd zone</th>
<th>Adiabatic Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 30% mol</td>
<td>NO</td>
<td>100%</td>
<td>&gt;1100</td>
</tr>
<tr>
<td>25- 30 % mol</td>
<td>NO</td>
<td>50-100%</td>
<td>&gt;900</td>
</tr>
<tr>
<td>&lt; 25 % mol</td>
<td>YES</td>
<td>0%</td>
<td>&gt;900</td>
</tr>
</tbody>
</table>
All the combustion air is fed to the combustion chamber and the flame temperature is referring to the 2nd zone temperature and AAG is free of hydrocarbon. The H\textsubscript{2}S/SO\textsubscript{2} ratio leaving the thermal reactor is controlled to accomplish the highest conversion in downstream catalytic reactors. In principles, optimum ratio is 2:1 measured in the tail gas leaving Claus unit (Mellitah Oil & Gas, 2006). A 1% deviation in combustion air flow rate can generate a significant offset in H\textsubscript{2}S/SO\textsubscript{2} ratio and overall conversion (Mellitah Oil & Gas, 2006).

2. Waste Heat Boiler (WHB)

The process gas leaving the combustion chamber in the thermal reactor is cooled down to approximately 360°C in the waste heat boiler, single pass fire tube boiler, designed to produce saturated HP steam at 46 barg. The WHB is equipped with a separate steam drum. The heat is recovered by means of heating boiler feed water to produce HPS, controlled by flow and pressure controllers. The produced HPS is mainly used to preheat the thermal reactor feed. Liquid sulphur is foreseen in this step and discharged to liquid sulphur storage.

3. Sulphur Condensers and Catalytic Converters

The process gas leaving the WHB at 360°C is further cooled down to 190°C in the 1st sulphur condenser producing saturated LP steam. The 1st sulphur condenser is a single pass fire tube boiler generating LPS in the shell side and deliver it to the LPS header at 4.7 barg (Mellitah Oil & Gas, 2006). In parallel, the process gas temperature is reduced to condense the vapour sulphur produced in the previous section and discharge it to the liquid sulphur compartment. The process gas is then preheated to 230°C before being fed to the 1st catalytic converter, using shell and tube heat exchanger. At the 1st catalytic converter, the Claus reaction takes place to convert H\textsubscript{2}S and SO\textsubscript{2} to sulphur until equilibrium is reached at a temperature of approximately 305°C. The reaction is exothermic therefore a significant amount of heat is generated in this step. The process gas leaving the 1st catalytic converter at 305°C is cooled down in the 2nd sulphur condenser, a single pass shell and tube exchanger, to recover produced sulphur in this section and also generate LPS by mean of heating up low pressure boiler feed water. The process gas shall leave 2nd sulphur condenser at 168°C is again
heated to 205°C in process gas reheater and then enters the 2nd catalytic converter where the Claus reaction between H₂S and SO₂ continue until equilibrium is reached. The equilibrium temperature is approximately 239°C at the design condition.

4. Final Condenser and Final Separator
The process gas leaving the 2nd catalytic converter enters the final sulphur condenser at 239°C. The process gas is cooled down to 146°C to condense sulphur from the process gas with the added value of preheating low pressure boiler feed water that is fed to the WHB.

2.6 SRU Operation Challenges
To conclude, Claus unit in the Mellitah plant has shown a significant decrease in plant overall conversion ratio from 97% to 61% after approximately a decade of operation. A number of factors have led to a drop in the plant overall sulphur production and the utility consumption has increased, HPS and LPS consumption, to heat up the system. The incorrect Claus unit operation, caused by the poor control of the chemical reactions in the thermal reactor section, led to a decrease in plant profit and an increase in the emission of the toxic gases. Therefore, an analysis must be carried out to identify ways to improve the plant productivity and meet the stated emission levels.
3 Model development

Model development stage can be divided into two sections, the first section is the process modelling and the second section is the model validation. However, a process model was built up of HYSYS 8.6 using the plant current condition and feedstock in different unit loads, the H2S concentration in AAG feed to the thermal reactor is kept constant. The model is a combination of thermodynamic and Unit operation applications that have been chosen carefully to represent Claus unit main equipment where each feed stream is configured with the plant feed composition. An explanation of thermodynamic, unit operation and an overview of HYSYS process software shall be put forward to fully understand the model.

3.1 Introduction to HYSYS Process Software

Many useful softwares have improved petroleum industry in terms of the process modelling and simulation, these softwares can be used to simulate the oil and gas processing to improvement and enhance the process operation and increase the productivity. Pro II and Aspen HYSYS are the most common used software. Although Pro2 has been used to do the process modelling for Claus unit, it is not as accurate as HYSYS that is why HYSYS 8.6 has been used to simulate Claus unit in this research. HYSYS is a powerful engineering simulation software, designed with respect to the program architecture, interface, engineering capability and interactive operation, therefore, Aspen HYSYS process software is known as one of the best process simulation software (Hamid, 2007). Aspen HYSYS applies the conception of fluid package that contains all the required data and information to perform chemical and physical properties calculation, therefore, HYSYS property and/or Aspen property is the driver of the process and it must be chosen carefully by allowing the definition of all the information such as property package, components, hypothetical components, interaction parameters, reactions, etc. In addition, selecting the suitable fluid packages shall be done in concern of the feed composition and process type. Many fluid packages are used in such process for example Peng-Robinson, ASME steam, SRK, and SRK sour and each calculation method is suitable for a certain process simulation (Aspentech, 2013) (Hamid, 2007).
There are four advantages of Aspen HYSYS:

- All the information and data are defined in a single location therefore it is easy to be created and modified.
- The fluid package can be stored as completely defined entities for use in any simulation.
- The component lists can be stored separately from the fluid packages in different defined entities for use in any simulation.
- Multi-fluid packages can be used in one simulation if they defined in the common basis manger (Hamid, 2007).

3.1.1 Thermodynamic

The challenge of fluid package selection, the thermodynamic model, is usually difficult. The property packages available in HYSYS software allows to predicting the physical properties of mixtures from well-defined light hydrocarbons to non-ideal chemical and complex oil mixtures systems. This fluid package is called equation of state, Aspen HYSYS offers enhanced equation of state such as (PR and PRSV) each equation of state has its own inherent limitation (Hamid, 2007) (Hanyak, n.d.). Table 3-1 lists some typical systems and recommended correlations.

<table>
<thead>
<tr>
<th>Type of System</th>
<th>Recommended Fluid package</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEG Dehydration</td>
<td>PR</td>
</tr>
<tr>
<td>Sour Water</td>
<td>PR, Sour PR</td>
</tr>
<tr>
<td>Cryogenic Gas processing</td>
<td>PR, PRSV</td>
</tr>
<tr>
<td>Air Separation</td>
<td>PR, PRSV</td>
</tr>
<tr>
<td>Ethylene Tower</td>
<td>Lee Kesler Plocker</td>
</tr>
<tr>
<td>Reservoir System</td>
<td>Steam Package, CS or GS</td>
</tr>
<tr>
<td>Chemical System</td>
<td>PR, SRK or Sour SRK</td>
</tr>
</tbody>
</table>

Table 3-1 Recommended Fluid package Method Selection  (Hamid, 2007)

PR= Peng-Robinson; PRSV= Peng-Robinson Stryjek-Vera; GS=Grayson-Street; CS= Chao-Seader; NRTL= Non-Random-Two-Liquid.
Elliott and Lira et al, 1999 suggested a decision tree which helps to choose the proper fluid package as shown in Figure 3-1.

Figure 3-1 Fluid Package Decision Tree (Elliott and Lira, 1999)
3.1.2 Unit operation

The selection of the unit operation used in modelling such as (pumps, Reactors, blower) is the second step to build up the model. However the Key unit that must be simulated in different categories, it is essential to be chosen carefully to suit the process operation. The main section in Claus unit is the thermal reactor where the oxidation of the H₂S must be controlled to convert one 1/3 to SO₂. In order to oxidise partly the H₂S, a conversion rate must be set for the reaction and the consumption of O₂ shall be under control. The equipment that shall achieve the task is the converting reactor because the reaction type does not require any thermodynamic knowledge where the stoichiometry and the conversion of the reactant must be configured, the reaction will proceed until the specific conversion is reached or the limiting reagent has been consumed. Therefore the conversion reactor has been chosen to simulate the thermal section with a burner. The condensation and separation process (1st and 2nd condensers) is simulated using shell and tube heat exchanger plus a vertical separate to condense and separate liquid sulphur produced in the thermal reactor and/or each catalytic converter where it was possible to configure temperature and apply another fluid package for the steam generation and condensation. Finally, Gibbs reactor is a vessel that models equilibrium reactions, the reactor outlet stream is in the state of physical and chemical equilibrium. The set of reaction attached to the equilibrium can react to an unlimited number of equilibrium reactions which are consecutively or successively solved. It is not essential for the component and the mixing process to be ideal since HYSYS shall compute the chemical behaviour of each component in the mixture based on mixture and pure component fugacity. Therefore, the catalytic converters are simulated using Gibbs reactor (equilibrium reactor) the reactions in the catalytic reactors are stoichiometric and they take place and continue until the reactions reach the equilibrium.
3.2 Model Validation

To ensure the built model is predicting a data similar to the Claus unit real result a comparison between the Claus unit data and the model prediction is considered. For this reason, a validation has been performed to fully trust the model and use it for the analysis. A parametric study is generated with the real plant data such as feed flow, temperature, and pressure and stream composition for a different unit load. As shown in Figure 3-2.

![Figure 3-2 Claus Unit Feed Scenarios](image)

The Figure 3-2 shows five feed scenarios of Claus unit which have been used to operate the unit. The same feed was used as basic data to validate the model. To accomplish the validation a comparison between the real Claus unit productions such as $S_2$, HPS and LPS using the HYSYS model with five different Claus unit load.
3.2.1 Claus unit Conversion Ratio

The overall conversion ratio of Claus unit (the conversion of the $\text{H}_2\text{S}$ to $\text{S}_2$) has almost the same value, the overall conversion ratio was 61% in real Claus unit and approximately 60.58% in the model prediction. The difference between the real Claus conversion and the model conversion is roughly 0.7% which is negligible as shown in Figure 3-3.

![Claus Unit Capacity & Conversion Ratio](image)

*Figure 3-3 Claus Unit Capacity & Claus Unit Conversion Ratio*
3.2.2 Liquid Sulphur Production

Claus unit sulphur total production has approximately the same value in real Claus unit and model prediction and the difference between the model and real Claus is between 0.67% and 0.75 % which is less than 1%. The small difference shall confirm that the model is reliable and can be used to carry out the process analysis. As the process variables cannot be kept constant for a long period of time, the $S_2$ total production has had a small variation.

![Figure 3-4 Claus unit Capacity & $S_2$ Total Production](image)

**Figure 3-4 Claus unit Capacity & $S_2$ Total Production**

The above Figure shows the difference between real Claus unit sulphur production and the model prediction are very tiny which is a confirmation of the model validity as the difference is less than 0.75%.
3.2.3 HPS Production

HPS is one form of the energy recovery in Claus unit as it is produced in the WHB where the energy is recovered in a form of HPS with 350°C and 46Barg, this steam is used to heat up the system during normal operation.

![Claus unit Capacity & HPS total production graph](image)

**Figure 3-5 Claus unit Capacity & HPS Production**

Figure 3-5 show the HPS production in real Claus unit and model prediction in five different scenarios. HPS production is 0.75% higher than the HPS predicted by the model in the first scenario, the other 4 scenarios have a difference in HPS production ranged from 0.66% to 0.7%.
3.2.4 LPS Production

LPS is used in Claus unit to heat up liquid sulphur transporting pipes with a temperature of 175°C and 5 barg. LPS is generated in 1st and 2nd sulphur condensers by recovering the latent heat during the condensation of the sulphur vapour that produced in the thermal reactor and the 1st catalytic converter.

![Claus Unit Capacity & LPS production](image)

**Figure 3-6 Claus Unit Capacity & LPS Production**

Figure 3-6 show the difference compare between Real Claus unit LPS production and the model prediction. Claus unit production was close to the model prediction in LPS production where the difference between them ranged from 0.7% to 0.76 which is insignificant.
3.3 Conclusion

Overall, the model has predicted almost the same value for Claus unit production of $S_2$, HPS, LPS and the conversion ratio, the difference is very small, less than 0.76% in the worst scenarios. Therefore, the model is valid to be used in the process analysis.
4 Process Analysis and Energy Recovery

4.1 Process Analysis
Process analysis is performed to investigate the plant operating condition and the consequence of the variation in plant load from 40% to 100% with different combustion air flow. A number of variables have to be verified to determine if the Claus unit is poorly operated or not, many variables can be responsible for the low overall plant conversion HCRN, Combustion air, Plant load, $S_2$ total production, LPS and HPS total production (side product energy).

1. HCRN (Process Objective Function)
It is the ratio of the amount of $H_2S$ to $SO_2$ in the tail gas, the calculation of this dimensionless number is as follows:

$$HCRN = \frac{H2S}{SO2} \quad 4-1$$

HCRN  Dimensionless
$H_2S$  The Concentration of $H_2S$ in tail gas in ppm mass
$SO_2$  The Concentration of $SO_2$ in tail gas in ppm mass

The HCRN is optimised to control the process operation in order to keep the unit running at maximum productivity in respect of energy consumption.

2. Combustion air flow
The ambient air flow (Oxygen) to the thermal reactor either in mass or volume flow rate. It is the oxidation element to partly oxidise the $H_2S$ to $SO_2$ which means there must be enough air flow to achieve the molar ratio of $O_2/H_2S=1/2$. It is categorised as the decision variable in Claus process operation. The air flow shall be adjusted to optimise the process objective function and keep it within the allowable operation range.

3. Plant Load
Plant load is the measured AAG flow to the thermal reactor in mass flow rate at a constant $H_2S$ concentration of around 31.3%.
4. Sulphur total production and Claus Unit conversion Ratio
The main purpose of Claus unit is to recover sulphur element from AAG which is the main product. Keeping Claus unit at the maximum allowable conversion rate is the main aim with an acceptable utility consumption. The conversion of H₂S to sulphur should be around 96% as mentioned in the Claus unit operating manual (Mellitah Oil & Gas, 2006).

5. LPS and HPS total production
The fifth factor is the steam production as the reactions in Claus unit are exothermic, a significant amount of energy is released in a form of heat. The released heat is recovered in LPS and HPS. In order to increase the steam production which is produced by recovering the heat resulted from Claus overall reaction, more conversion is required.

6. Claus unit Overall Conversion Ratio
Unit overall conversion ratio is defined as the conversion rate of H₂S in AAG feed to S₂ across Claus unit, this ratio represents the Claus unit productivity.

The table 4-1 shows the real Clause unit feed and products

<table>
<thead>
<tr>
<th>Plant feed scenario</th>
<th>Acid gas feed</th>
<th>Combustion Air feed</th>
<th>Total S₂ Production</th>
<th>Conversion ratio %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m³/hr</td>
<td>kg/hr</td>
<td>kmol/hr</td>
<td>m³/hr</td>
</tr>
<tr>
<td>1</td>
<td>7000</td>
<td>19110</td>
<td>482.573</td>
<td>4738</td>
</tr>
<tr>
<td>2</td>
<td>9000</td>
<td>24570</td>
<td>620.452</td>
<td>6092</td>
</tr>
<tr>
<td>3</td>
<td>11000</td>
<td>30030</td>
<td>758.330</td>
<td>7446</td>
</tr>
<tr>
<td>4</td>
<td>15000</td>
<td>40950</td>
<td>1034.086</td>
<td>10154</td>
</tr>
<tr>
<td>5</td>
<td>17000</td>
<td>46410</td>
<td>1171.965</td>
<td>11507</td>
</tr>
</tbody>
</table>

Table 4-1 Claus unit feed combination of AAG and combustion air in the real Claus unit
Parametric study
After the step of model validation, a parametric study has been generated using Claus unit data and it consists of five different scenarios. In addition, the case study is analysing a constant AAG flow rate with ten different combustion air flow rate to determine the suitable combination of the feedstock that represents the best plant productivity and reduces the utility. A range of ten different combustion air feed has been applied in each scenario for two reasons, the first reason, Aspen HYSYS 8.6 had a bug that caused the software to crash excessively, and as a result, I was unable to save my results. Therefore, the model was used to perform simulations to ramp up the combustion air flow rate to help identify a range within which the optimum value that would result in a high conversion ratio in Claus unit and use that range to analyse the process by manually transferring results to MS Excel. Secondly, as HCRN is the guidance for the process improvement, the concentration was on the HCRN range form 1 to 6. The HCRN range 1 to 6 represents the highest Claus unit conversion ratio as shown in the process analysis.

4.1.1 Scenario 1 Claus unit minimum load about 40%
In this step AAG flow rate was 19110 kg/hr and combustion air flow rate was 5805 kg/hr. The output of this combination of feedstock was not optimum because the conversion ratio of the plant was only 61% and the total sulphur production was 2690 kg/hr as shown in table 4-1. The HPS total product and LPS total production were 10990 kg/hr and 4877 kg/hr respectively. The table below shows the plant different feed of combustion air and the outputs such as S$_2$ total production, HPS total production, LPS total production and the plant conversion ratio. Since the HCRN is the optimisation tool, the analysing must be carried out in relation HCRN. For a further explanation, the Case has been divided into five sections.
<table>
<thead>
<tr>
<th>Air Flow at AAG Flow of 19110 Kg/hr in kg/hr</th>
<th>Total Sulphur Product in kg/hr</th>
<th>HPS Total production</th>
<th>LP.S Total production</th>
<th>H₂S mole fraction in tail gas</th>
<th>SO₂ mole fraction in tail gas</th>
<th>HCRN H₂S/SO₂</th>
<th>Conversion ratio</th>
</tr>
</thead>
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<td>0.0012</td>
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<td>0.0043</td>
<td>0.0015</td>
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<td>10550</td>
<td>4641.9</td>
<td>12210</td>
<td>678</td>
<td>7098</td>
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<td>0.0017</td>
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<td>0.0031</td>
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<td>681.5</td>
<td>7155</td>
<td>397.1</td>
<td>0.0030</td>
<td>0.0029</td>
</tr>
</tbody>
</table>

Table 4-2 Scenario 1 40% Claus unit load
1. Combustion air & HCRN

To find out the optimum ratio of combustion air and AAG as a combined feed to the Claus unit. A range of ten different feeds of Combustion air is used with a constant AAG flow of 19110Kg/hr. The result shows that the highest conversion ratio was between the air flow rates of 10550 to 10660 kg/hr and it is ranged from 97.60% to 97.63%. The maximum $S_2$ production is at air flow rate of 10580 kg/hr which is the optimum value of HCRN = 2. At this flow, the total $S_2$ production was 4642.8 kg/hr. Figure 4-1 shows the effect of combustion air in thermal reactor feed on HCRN in tail gas.

![Combustion air flow rate & HCRN](image)

**Figure 4-1 Shows HCRN & combustion air flow rate at 40% unit load**

HCRN ratio shows a dramatic decline from almost 7 to 1 in parallel with a dramatic increase in the combustion air flow rate to the thermal reactor from 10350Kg/hr to 10730kg/hr at a constant flow rate of AAG19110 kg/hr. The high conversion ratio number (HCRN) should be 2 to 5 in tail gas in order to maintain the optimum combustion air flow. The combustion air flow shall be 10580 kg/hr to achieve the conversion ratio of 97.63% and the reaction is moved to the right-hand side with the maximum stoichiometric rate.
2. HCRN & Total Sulphur production

To carry out the analysis, the effect of HCRN change on total liquid sulphur production must analysed.

![HCRN & S2 total production](image)

Figure 4-2 Shows HCRN & S2 total production at 40% unit load

Section 2 discusses the effect of the HCRN changes on total liquid sulphur production. Figure 4-2 shows the total liquid Sulphur production increases sharply from almost 4636 kg/hr at HCRN=1.034 and reach a peak of 4643 kg/hr of liquid sulphur at HCRN=2 and get the maximum production then it turns down dramatically to reach the lowest liquid sulphur production with approximately 4621.5 kg/hr of total liquid sulphur at HCRN=7.25 because the conversion of H₂S starts to decrease due to the shortage of combustion air. Finally, the highest total liquid sulphur is ranged from 4640 kg/hr to 4643 kg/hr where the HCRN is ranged from 1.5 to 3.
3. HCRN & LPS Production

Figure 4-3 shows the effect of HCRN in tail gas which represents the combustion air flow rate in the process of producing LPS in both first condenser and second condenser. According to this figure, the LPS total production decreases sharply from 7155 kg/hr to 7082 kg/hr the decline is caused by an increase of HCRN from almost 1 to 3. Then the decline angle of L.P.S total production is turned to decrease steadily for the rest of the figure to reach 7031 kg/hr of LPS in HCRN of about 7.

![Figure 4-3 HCRN & LPS Total Production at 40% unit load](image)

To conclude, the LPS total production increases as the HCRN decreases and consequently combustion air increases but the reduction rate of the product before the point (3, 7080) is much higher than the reduction rate of the product at the rest of the figure. On the other hand, LPS total production has increased 1.5 times in comparison with real Claus unit production at the same AAG feed rate and composition.
4. HCRN & HPS Total Production

**Figure 4-4 HCRN & HPS Total Production at 40% unit load**

Figure 4-4 shows the effect of HCRN on HPS total production in the WHB of the thermal reactor in kg/hr. The figure can be divided into two parts. The first part shows the total HPS production has decreased sharply from 12280 kg/hr to 12200 kg/hr and this decrease is gathered with an increase of HCRN from almost 1 to almost 3. The second part represents the dramatic drop of the HPS total production in WHB from 12200 kg/hr to 12140 kg/hr when the HCRN increased from almost 3 to almost 7. In conclusion, the drop of HPS total production has decreased in the second part by 50%. It was 80 kg/hr in the first part of the figure and became 40 kg/hr.
5. HCRN & Unit Conversion Ratio

This section covers the effect of the HCRN on the unit overall conversion ratio. The term conversion means the process of converting hydrogen sulphide to element sulphur.

The improvement of the plant conversion ratio is related to the chemical reactions in the thermal reactor where the preparation to the main Claus reaction is performed, so the HCRN = 2 means the reactions is at the maximum rate. Figure 4-5 represents the effect of HCRN on Claus overall efficiency by means of how much of hydrogen sulphide is converted to element sulphur Claus unit overall conversion ratio shows a sharp increase from 97.53% to 97.62% when the HCRN increased from 1 to 1.4. Then it remained steady at 97.62% with HCRN rang of 1.4 to 1.6 after that it reached a pick of 97.63% at HCRN = 2. On contrast, the unit efficiency decreased dramatically from 97.63% to 97.32% at HCRN = 7.25. In conclusion, the conversion ratio between HCRN = 1 to 3 is over 97.5% which a very good value and the maximum value of the conversion is 97.63% which a result of HCRN= 2.

**Figure 4-5 HCRN & H₂S Conversion ratio to S₂ at 40% unit load**

The improvement of the plant conversion ratio is related to the chemical reactions in the thermal reactor where the preparation to the main Claus reaction is performed, so the HCRN = 2 means the reactions is at the maximum rate. Figure 4-5 represents the effect of HCRN on Claus overall efficiency by means of how much of hydrogen sulphide is converted to element sulphur Claus unit overall conversion ratio shows a sharp increase from 97.53% to 97.62% when the HCRN increased from 1 to 1.4. Then it remained steady at 97.62% with HCRN rang of 1.4 to 1.6 after that it reached a pick of 97.63% at HCRN =2. On contrast, the unit efficiency decreased dramatically from 97.63% to 97.32% at HCRN = 7.25. In conclusion, the conversion ratio between HCRN = 1 to 3 is over 97.5% which a very good value and the maximum value of the conversion is 97.63% which a result of HCRN= 2.
4.1.2 Scenario 2 53% Claus unit load

In this step Claus unit load has been increased to 53% with same H$_2$S concentration in order to analysis the unit variables at different loads. AAG flow rate was 24570 kg/hr and the combustion air flow rate was 7462.7 kg/hr. Table 4-3 shows Claus model prediction at this step.

<table>
<thead>
<tr>
<th>Air Flow at AAG Flow of 24570 Kg/hr in kg/hr</th>
<th>Total Sulphur Product in kg/hr</th>
<th>H.P.S production kmol/hr</th>
<th>Total L.P.S production kmol/hr</th>
<th>H$_2$S mole fraction in tail gas</th>
<th>SO$_2$ mole fraction in tail gas</th>
<th>HCRN H$_2$S/SO$_2$</th>
<th>Conversion ratio</th>
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</thead>
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<tr>
<td>13300</td>
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<td>510.8</td>
<td>0.0030</td>
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</tr>
</tbody>
</table>

Table 4-3 Scenario 2 53% Claus Unit load
The total sulphur production was 3458 kg/hr, HPS total production was 17450 kg/hr and LPS total production was 6270 kg/hr. However, the Claus unit production has increased, the output was not as should be at this load. The reason for this is the unsuitable ratio between $\text{H}_2\text{S}/\text{O}_2$ which lead to high HCRN and low conversion ratio of about 61%. Same flow of AAG is analysed with ten different flow rate of combustion air as shown in table 3. This stage will have steps similar to the first scenario as follow:

1. **Combustion air & HCRN**

![Air Flow Rate & HCRN](image)

**Figure 4-6 combustion Air & HCRN at 53% Claus Unit load**

The above figure shows the effect of the combustion air flow rate change on the HCRN. It shows a dramatic decrease of HCRN from 7 to 1 as the combustion air flow rate increased from 13300 kg/hr to 13800 kg/hr. It means there is an inverse relation between combustion air flow and HCRN.
2. HCRN & total Sulphur production

Figure 4-7 HCRN & Total Sulphur production at 53% Claus unit load

Figure 4-7 represents the relation between HCRN and Total sulphur production and it has been divided into three parts. The first part show a sharp increase in total sulphur production from 5960 kg/hr to 5969 kg/hr when the HCRN increased from 1 to 1.7. part 2 shows a stable total sulphur production at 5969 kg/hr with HCRN range from 1.71 to 2.16 then the third part has shown a dramatic decline in total sulphur production for the rest of the figure and reached the lowest value of 5941 kg/hr of total sulphur production at HCRN= almost 7. The result the highest sulphur production was between HCRN= 1.5 to 2.5 when total S₂ production was almost 5969kg/hr.
3. HCRN & H.P.S total production

In general in Claus unit HPS production increases as the combustion air increases because the heat transfer rate should increase and it will decline as the HCRN increase Equation 1 represents this relation between gases mass flow and overall heat transfer at the WHB:

![Figure 4-8 HCR & HPS Total production at 53% Claus unit load](image)

In spite of the decrease of HPS total production shown in Figure 4-8, HPS total production has increased comparing with the HPS total production at same AAG flow rate and concentration in the unit feed in the real plant output. Furthermore, the graph is divided into two sections. The first section shows a sharp decline of HPS total production from 15790 kg/hr to 15680 kg/hr with an increase of HCRN from 1 to 2.8. The second section represents a gradual reduction of total HPS production in the rest of the figure to reach 15610 kg/hr at HCRN=7. In conclusion, however the total HPS production is decreasing, it is higher than the HPS total production in real Claus unit.
4. HCRN & L.P.S total production

LPS total production shows an inverse proportionality with HCRN, so the total production decreases as the HCRN increases as shown in Figure 4-8.

![Graph showing HCRN & LPS total production](image)

**Figure 4-9 HCR & LPS Total production at 53% Claus unit load**

Figure 4-9 shows a dramatic decrease of LPS total production from 9200 to 9053 kg/hr at the same time the HCRN has increased from 1 to 7.25.
5. HCRN & Unit Conversion Ratio

Figure 4-10 shows the effect of HCRN on Claus unit overall conversion ratio which was almost 61% before the optimisation. However, the overall conversion ratio has shown a significant increase in the graph 9-4, it went down as the HCRN got over 3.

![HCRN & Unit Conversion Ratio](image)

**Figure 4-10 HCRN & Claus unit overall conversion ratio at 53% Claus unit load**

The above Figure can be divided into three section, the first section represents an increase in Claus unit overall conversion ratio from 97.53% to 97.62% in parallel with HCRN rise from 1 to 1.28. In the second section Claus unit overall conversion ratio went up to 97.63% and remind steady at this value until the HCRN reached 2.8. the third section shows the sharp decline in Claus unit overall conversion ratio from 97.63% to 97.25% for the rest of the figure.
### 4.1.3 Scenario 3 65% Claus unit load

Scenario 3 is run at Claus unit load of 65% at constant H₂S concentration. The real plant products at the same load: total sulphur production 4227 kg/hr, HPS production 21440 kg/hr, and LPS 7665 kg/hr. A case is generated by HYSYS 8.6 with constant AAG flow of 30030 kg/hr and ten different Combustion air flow. The model result is shown on the table 4-4.

| Air Flow at AAG Flow of 30030 Kg/hr in kg/hr | Total Sulphur Product in kg/hr | HPS Total production | LPS Total production | H₂S mole fraction in tail gas | SO₂ mole fraction in tail gas | H₂S/SO₂ | Conversion ratio
<table>
<thead>
<tr>
<th></th>
<th></th>
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<td>0.0031</td>
</tr>
</tbody>
</table>

Table 4-4 Scenario 3 65% Claus unit load
To analyse the results of this Scenario five steps must be Explained and verified as follow:

1. **Combustion air flow & HCRN**

The effect of the change of combustion air flow on the HCRN is an important HCRN is the reference that shows if the reaction in the thermal reactor is in stoichiometric or not. In order to choose the optimum combustion air flow rate that matches the AAG feed, the HCRN must be defined. The figure below shows the relation between combustion air flow rate and HCRN.

![Figure 4-11 Combustion air & HCRN 65% unit load](image)

The HCRN has gradual decline against the Combustion air flow to Claus unit. HCRN has decreased gradually from almost 7 at a combustion air flow rate of 16280 kg/hr to almost 1 at a combustion air flow rate of 16900 kg/hr.
2. HCRN & total sulphur production

HCRN has a positive effect on total sulphur production which has enhanced the process and increased production in a certain limit. Figure 4-12 shows the effect of the HCRN on total sulphur production.

![HCRN & Total sulphur production 65% unit load](image)

A significant increase of sulphur total production is shown in Figure 4-12. It rose from 7281 kg/hr of total sulphur production when the HCRN=1 to reach a peak of 7295.3 kg/hr of sulphur production at HCRN=2 then total sulphur production has sharply fallen to 7266.2 kg/hr of total sulphur production at HCRN=7.

3. HCRN & HPS total production

HPS total production is one of Clause unit products and must be considered in Claus unit process analysis. Normally, combustion air flow rate has a positive effect on HPS production as it aids to an increase in the heat transfer rate in Claus WHB by means of heating BFW to generate steam. However, HCRN has a revers effect on HPS total production when the feed
stock is optimum, HPS total production has shown an increase in comparison with same AAG feed at the same unit load.

![NHCR & HPS production](image)

**Figure 4-13** HCRN & HPS Total production at 65% Claus unit load

Although HPS total production is decreasing when the HCRN increases, it is higher than the real unit production. HPS total production has shown a decline in total production from 19310 kg/hr at HCRN=1 to 19090 kg/hr when HCRN=7. This means the total HPS production has decreased by 220 kg/hr during an increase of HCRN from 1 to 7.

1. **HCRN & L.P.S total production**

LPS total production is one of Claus unit waste heat recovery products, as well as HPS and the variation in the Claus unit operation, has an effect on the energy recovery. Moreover, LPS total product has increased in parallel with combustion air flow rate. Therefore, the heat transfer at 1st and 2nd sulphur condenser, where LPS is produced, is enhanced by two factors, the first one is the quantity of the heat carrier which is the gases leaving each catalytic
converter and the second is the heat supply which has increased when the Claus overall reaction is in stoichiometric across the unit. Figure 13-4 shows the effect of CHRN on LPS total production in Claus unit after the optimisation.

LPS total production has dramatically declined from 11260 kg/hr at HCRN=1 to almost 11060 kg/hr at HCRN= 7 which means as HCRN increases the total LPS total production decreases. However, LPS total production jumped from 7665 kg/hr in the real Claus unit to 11171 kg/hr at HCRN=1.

2. HCRN & unit Conversion ratio

The unit overall conversion ratio is one the important variables that must be respected in Claus unit process analysis because it determines if the unit is running normally with high productivity or not. Generally, HCRN can increase the plant productivity and overall conversion ratio as far as it is close to 2. It is acceptable to be between 2 to 5 but 2, but the
best value is 2 which leads to Claus unit Conversion ratio over 97.6%. Figure 14-4 represents the change in Claus unit overall conversion ratio caused by the change in HCRN. As shown in Figure 4-14 Claus unit is close to the highest conversion ratio when the HCRN is close to 2. In addition, it means the reactions are shifted to the right-hand side and the yield is at the highest rate.

![Figure 4-15 HCRN & Claus unit conversion ratio at 65% load](image)

However, Claus unit conversion ratio is important the HCRN is important as well because it is not possible to develop an indication in such chemical plant that helps to determine if the plant running normally or not. Claus unit overall conversion ratio has jumped from 97.57% at HCRN=1 to 97.62% at HCRN= 1.28 then it reached a peak at HCRN= 2 of 97.63% and remained steady until HCRN=2.35 after that the efficiency has decreased sharply to reach 97.31% at HCRN= 7.125. It clear that the efficiency of the unit increases with HCRN and reach the maximum at HCRN=2 when the Claus unit at optimum feed combination of combustion air and AAG.
### 4.1.4 Scenario 4 88% Claus unit load

<table>
<thead>
<tr>
<th>Air Flow at AAG Flow of 40950 kg/hr in Kg/hr</th>
<th>Total Sulphur Product in kg/hr</th>
<th>HPS production kg/hr</th>
<th>kmol/hr</th>
<th>LPS Production kg/hr</th>
<th>kmol/hr</th>
<th>H$_2$S mole fraction in tail gas</th>
<th>O$_2$ mole fraction in tail gas</th>
<th>HCRN H$_2$S/SO$_2$</th>
<th>Conversion ratio</th>
</tr>
</thead>
<tbody>
<tr>
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<td>26030</td>
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<td>15082</td>
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<td>0.0057</td>
<td>0.0008</td>
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<td>97.32% H$_2$S Base</td>
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<td>22300</td>
<td>9922.6</td>
<td>26060</td>
<td>1447</td>
<td>15109</td>
<td>838.7</td>
<td>0.0052</td>
<td>0.0010</td>
<td>5.2</td>
<td>97.44% H$_2$S Base</td>
</tr>
<tr>
<td>22400</td>
<td>9930.3</td>
<td>26100</td>
<td>1449</td>
<td>15146</td>
<td>840.5</td>
<td>0.0047</td>
<td>0.0012</td>
<td>3.9</td>
<td>97.56% H$_2$S Base</td>
</tr>
<tr>
<td>22500</td>
<td>9942</td>
<td>26140</td>
<td>1451</td>
<td>15173</td>
<td>842.5</td>
<td>0.0043</td>
<td>0.0015</td>
<td>2.87</td>
<td>97.61% H$_2$S Base</td>
</tr>
<tr>
<td>22600</td>
<td>9951.7</td>
<td>26170</td>
<td>1453</td>
<td>15209</td>
<td>844.3</td>
<td>0.0040</td>
<td>0.0017</td>
<td>2.35</td>
<td>97.63% H$_2$S Base</td>
</tr>
<tr>
<td>22650</td>
<td>9951.7</td>
<td>26190</td>
<td>1454</td>
<td>15227</td>
<td>845.2</td>
<td>0.0038</td>
<td>0.0019</td>
<td>2</td>
<td>97.63% H$_2$S Base</td>
</tr>
<tr>
<td>22700</td>
<td>9951.7</td>
<td>26210</td>
<td>1455</td>
<td>15245</td>
<td>846</td>
<td>0.0037</td>
<td>0.0020</td>
<td>1.85</td>
<td>97.63% H$_2$S Base</td>
</tr>
<tr>
<td>22800</td>
<td>9943</td>
<td>26240</td>
<td>1457</td>
<td>15271</td>
<td>847.8</td>
<td>0.0034</td>
<td>0.0023</td>
<td>1.48</td>
<td>97.62% H$_2$S Base</td>
</tr>
<tr>
<td>22900</td>
<td>9943</td>
<td>26280</td>
<td>1459</td>
<td>15306</td>
<td>849.5</td>
<td>0.0032</td>
<td>0.0026</td>
<td>1.23</td>
<td>97.58% H$_2$S Base</td>
</tr>
<tr>
<td>23000</td>
<td>9942.5</td>
<td>26310</td>
<td>1461</td>
<td>15331</td>
<td>851.3</td>
<td>0.0030</td>
<td>0.0029</td>
<td>1.034</td>
<td>97.53% H$_2$S Base</td>
</tr>
</tbody>
</table>

Table 4-5Scenario 4 at 88 % Claus unit load
Claus Unit load has been increased from 65% to 88% to investigate Claus unit efficiency at high load. Claus unit real outputs at this load which is normal operation load is as follow total sulphur production 5765 kg/hr, HPS total production 22650 kg/hr, and LPS total production 10450 kg/hr. the results have shown a low conversion ratio of 60.57% that must be optimised to meet the plant maximum allowable production. The results of the unit output are analysed with different factors to improve the conversion and recover more energy. Here below the factors which have been taken into consideration in the process analyses:

1. **Combustion Air flow rate & HCRN**

O₂ to H₂S ratio is one of the important factors that must be considered in the Claus unit process analysis because this shall enhance the reactions which take place on the thermal and catalytic reactors and it should be as close as possible to ½ which represents the optimum ratio.

![Combustion air flow rate & HCRN](image)

**Figure 4-16 Combustion air flow rate & HCRN Claus unit load 88%**
Figure 4-16 shows the effect of O₂ on Claus unit HCRN in tail gas. It shows that the HCRN has declined sharply from 7 to 2.5 as the combustion air flow rate increased from 22200 kg/hr to 22600 kg/hr. The figure after HCRN 2.5 is degreasing as well but not as sharp as it was before, in other words, the graph can be divided into two parts the first part show an increase of combustion air flow rate by 400 kg/hr resulted a decrease in HCRN by 4.5 when the second part has shown an increase by 400 kg/hr which has met by decrease in HCRN by 2.5. To conclude, the combustion flow rate has significate effect on HCRN before 2.5 then its effect is less where we must be able to keep the unit at this ratio.

2. **HCRN & S₂ Total production**

Sulphur total production is the main product of Claus unit, as the unit produce more the profit increases in respect of the utility consumption. An investigation has been made to see if the total sulphur production has increased or not.

![HCRN & S₂ total Production](image)

Figure 4-17 HCRN & S₂ total production in Claus unit with 88% load

Total sulphur production has shown an increase after a short stability from HCRN 1 to 1.5 with a value of almost 9943 kg/hr of total sulphur production then it reached the maximum value of 9951.7 kg/hr of total sulphur production at HCRN 2 and remained steady until HCRN

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2.35 afterwards it decreased dramatically to reach the lowest value at HCRN 7 which is 9903.2 kg/hr of total sulphur production.

3. HCRN & HPS total production

HPS total production is produced from the waste heart recovered in WHB where the BFW is heated up to produce HPS at 46 barg and 260°C. The process is enhanced as the rate of the reactions mentioned in chapter 2 is increased to produce a significant quantity of heat which is enough to heat up the BFW and produce HPS. Figure 4-18 shows the effect of HCRN over HPS total production, HPS is decreased as the HCRN increases. Figure 4-18 shows a gradual decrease from 26300 kg/hr at HCRN 1 to reach 26030 Kg/hr at HCRN 7. However, total HPS has gradually decreased. The total of HPS production is greater than HPS production with the same AAG feed at real Claus unit which was 22650 kg/hr.
4. **HCRN & LPS Total production**

LPS is produced in Claus unit (HA005 and HA006) where the sulphur vapour is condensed by means of heating up low pressure boiler feed water with almost 5 barg and 157°C. To analyse the relation between HCRN and LPS total production.

![Figure 4-19 HCRN & LPS total production at 88% Claus unit load](image)

**Figure 4-19** HCRN & LPS total production at 88% Claus unit load

Figure 4-19 shows the effect of HCRN on LPS total production in Claus unit. LPS total production has shown a dramatic decrease from 15331 kg/hr to 15082 kg/hr during an increase of HCRN from 1 to 7. It is a fact that the HCRN is showing a decrease as the HCRN is increasing but it almost 1.5 times from LPS total production at real Claus unit with the same AAG flow rate and concentration which means the combustion air flow rate was not optimum.

5. **HCRN & Claus unit conversion rate at 88% load**

Claus unit conversion ratio has shown a significant increase at this step because the HCRN has reached the optimum range where the overall sulphur production is a maximum value and both HPS and LPS total production has increased 1.5 times than it was at the same AAG flow rate and H₂S concentration.
Figure 4-20 Claus unit conversion ratio rose sharply from 97.53% when HCRN=1 to reach 97.62% at HCRN= 1.48 then it reached a peak of 97.63% at HCRN= 2 and remain steady until HCRN 2.35. The last part of the Figure shows a gradual decline in Claus unit overall conversion ratio from 97.63% to 97.325% at HCRN=5. In conclusion, the highest overall conversion was at HCRN=2 but the range of HCRN from 1.5 to 2.5 has shown an acceptable overall conversion ratio which is higher than 97.62%.
4.1.5 Scenario 5 100% Claus unit load
To confirm that the work is done properly the final step of process analysed carried out with Claus unit full load, to confirm that the same HCRN is applicable with full Claus unit load. Clause unit AAG flow rate at full load is 46410 kg/hr and combustion air flow rate is 14090 kg/hr which do not give the required O\textsubscript{2}/H\textsubscript{2}S ratio. The model has used again to find out the optimum quantity and the rustles were as follow:

<table>
<thead>
<tr>
<th>Air Flow at AAG Flow of 46410 Kg/hr</th>
<th>Total Sulphur Product in Kgs/hr</th>
<th>HPS Production Kg/hr</th>
<th>LPS Production Kg/hr</th>
<th>H\textsubscript{2}S mole fraction in tail gas</th>
<th>SO\textsubscript{2} mole fraction in tail gas</th>
<th>H\textsubscript{2}S/SO\textsubscript{2}</th>
<th>Conversion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>251150</td>
<td>11311</td>
<td>29500</td>
<td>1637</td>
<td>17083</td>
<td>984.4</td>
<td>0.0057</td>
<td>0.0008</td>
</tr>
<tr>
<td>25250</td>
<td>11243</td>
<td>29530</td>
<td>1639</td>
<td>17120</td>
<td>950.2</td>
<td>0.0052</td>
<td>0.0010</td>
</tr>
<tr>
<td>25350</td>
<td>11262.5</td>
<td>29570</td>
<td>1641</td>
<td>17147</td>
<td>952.1</td>
<td>0.0048</td>
<td>0.0011</td>
</tr>
<tr>
<td>25450</td>
<td>11262.4</td>
<td>29600</td>
<td>1643</td>
<td>17190</td>
<td>953.9</td>
<td>0.0045</td>
<td>0.0014</td>
</tr>
<tr>
<td>25550</td>
<td>11272.2</td>
<td>29640</td>
<td>1645</td>
<td>17220</td>
<td>955.7</td>
<td>0.0041</td>
<td>0.0016</td>
</tr>
<tr>
<td>25675</td>
<td>11273</td>
<td>29680</td>
<td>1648</td>
<td>17256</td>
<td>957.9</td>
<td>0.0038</td>
<td>0.0019</td>
</tr>
<tr>
<td>25750</td>
<td>11273</td>
<td>29710</td>
<td>1649</td>
<td>17283</td>
<td>959.3</td>
<td>0.0036</td>
<td>0.0021</td>
</tr>
<tr>
<td>25850</td>
<td>11273</td>
<td>29740</td>
<td>1651</td>
<td>17308</td>
<td>1260.9</td>
<td>0.0034</td>
<td>0.0023</td>
</tr>
<tr>
<td>25950</td>
<td>11263.6</td>
<td>29780</td>
<td>1653</td>
<td>17344</td>
<td>962.8</td>
<td>0.0032</td>
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<td>11255</td>
<td>29830</td>
<td>1656</td>
<td>17386</td>
<td>965.4</td>
<td>0.0029</td>
<td>0.0030</td>
</tr>
</tbody>
</table>

Table 4-6 Scenario 5 100% Claus unit load
As the results of scenario 5 is similar to the previous four scenarios it is not necessary to be concluded in this chapter and all the figures and tables will be added to the appendixes of this thesis.
4.2 Results and discussion
Claus unit model in HYSYS 8.6 process software has given a great result that shows a significant increase in the unit overall production of \(S_2, HPS, LPS\). A comparison has been made between current Claus unit overall production in \(S_2, HPS, LPS\) and the Clause unit simulation prediction in five different scenarios.

4.2.1 \(S_2\) overall Claus unit production
Total sulphur overall production has shown a significant increase in the five scenarios particular in HCRN range between 2-5 and the maximum total sulphur production was at HCRN=2.

![S\textsubscript{2} Production in real Claus unit and the Model result](image)

**Figure 4-21 Total \(S_2\) production in the real Claus Unit and the Model Prediction in five different scenarios**

Chart 4-21 represents the total sulphur production in real Claus unit and the results of the model. The production of sulphur has increased by 1.726 times in each scenario, for example in the first scenario, sulphur total production was 2690 kg/hr in real Claus unit and increased
to reach 4642.6 kg/hr and this was the highest production in this scenario where HCRN=2. The same with all other four scenarios that means the highest Sulphur production can only be achieved when the $\text{H}_2\text{S}/\text{SO}_2=2$ in tail gas, as it is not possible to keep the HCRN at 2 continuously, therefore it can be kept in a range of 1.5-3 as shown in Figure 4-22.

4.2.2 Clause unit conversion
Claus unit overall conversion ratio has shown a significant increase after the process optimisation as the overall conversion ratio has been increased from 60.57% on the real Claus unit to reach 97.63% as maximum overall conversion ratio after the optimisation and this value can only be reached if HCRN=2. Figure 4-22 shows the effect of HCRN on overall Claus unit conversion ratio:

![Figure 4-22 Overall Conversion Ratio & HCRN in Clause Unit](image)

As the Figure 4-22 shows the highest conversion is at HCRN=2 and in HCRN from 1.5 to 3 are acceptable because Claus unit conversion ratio is higher than 97.6% which is a very good value.
5 Energy Recovery

The energy consumption is one of the significant factors in Claus unit operation because it is almost 70% of the operation coast (Mellitah Oil & Gas, 2006). Energy is mainly consumed as LPS and HPS and both are used to heat up the system during plant operation. Increasing Claus unit overall LPS and HPS total production shall reduce Claus unit operating cost. Therefore, improving the conversion produces more energy in a form of heat as Claus reactions are exothermic.

5.1 HPS total production

In general, Claus unit HPS production increases as the combustion air flow rate increases because the heat transfer rate increases and it will decline as the HCRN increase Equation 5-1 shows the relation between gases mass flow and overall heat transfer at the WHB:

\[ Q = m c_p \Delta T \]

\[ Q = \text{overall heat transfer kJ} \]
\[ m = \text{mass flow rate of the combustion zone outlet gases kg/hr} \]
\[ C_p = \text{FV001 outlet gases specific heat kJ/kg. } ^\circ C \]
\[ \Delta T = \text{Differential temperature } ^\circ C \]

Equation 5-1 is the simplest equation that can help to understand the energy saving in this study. It represents the main three factors that shall effect the process of heat transfer. The recovered heat Q shall increase as the mass flow rate of the gases (the carrier of the heat form the combustion chamber to WHB, 1st and 2nd condensers) increases because the higher conversion leads to an increase of O₂.

HPS total production in Claus unit is effected by combustions air flow. It increases when the combustion air flow rate increases at constant AAG flow rate and concentration which means HPS total production is decreasing as the HCRN increases as shown in the Figures 4-4, 4-8, 4-13, 4-17. In addition, Figure 5-1 shows the output of Claus unit and the model results in term of HPS total production.
Figure 5-1 HPS total production in Existing Claus unit and HPS in Model Prediction in five different scenarios
5.2 LPS total production
Low pressure steam is generated at the LPS boilers by means of recovering the latent heat that result from the sulphur vapour condensation in the 1st and 2nd sulphur condensers and heat low pressure boiler feed water as equation one state. The quantity of sulphur vapour increase as the conversion increases and consequently heat transfer shall increase in order to heat low pressure boiler feed water and produce LPS in the low pressure boilers. Figure 5-2 shows the increase in LPS total production resulted from Process simulation and the current Claus total production.

![Figure 5-2 Total H.P.S Production in different five scenarios in real Claus unit output and Model Prediction](image)

Figure 5-2 Total H.P.S Production in different five scenarios in real Claus unit output and Model Prediction
LPS total production has shown an increase of almost 1.5 times of the real Claus unit total LPS production which means that LPS production has increased by 50%.

5.3 Conclusion

The process analysis has shown an improvement in energy recovery as shown in Figures 5-1, 5-2. HPS and LPS total production has increased by 50% by mean of more energy has been recovered in a form of heat which leads to decrease in utility consumption and the Claus unit operational coast.
6 Conclusion and Recommendations

6.1 Overview
Claus unit is the famous sulphur recovery unit that has been used since 1883 until today and Mellitah gas complex is using this type of technology to recover sulphur from natural gas. The overall efficiency of Clause unit in Western Libya Gas Project (Mellitah Complex) has decreased as the raw gas concentration and composition has changed in order to cope with this problem a step forward has been taken to perform process analysis and improvement in order to reduce utility losses and increase profit by recovering more energy and enhance the chemical reactions. Claus unit analysis has been achieved through HYSYS 8.6 process software which is one of the common software used in such application and the result was reliable.

6.2 Conclusion
Existing sulphur recovery facilities often be modified to increase sulphur recovery due to increasingly stringent sulphur emissions regulations. The changes in the rate of sulphur recovery were studied with respect to the oxygen concentration in the intake air into the Claus unit. The overall efficiency of the unit is related to the HCRN in tail gas, for the instant, it is related to the control of the acid gas flow rate, the combustion airflow rate and the ratio between the two variables (O₂ /H₂S). That means the HCRN in tail gas shall be fixed by the optimal equal 2. in order to not changing the HCRN and being constant in 2.0 in all input concentrations of H₂S and the ratio is controlled by manipulating the flow rate of inlet air from the blower to Claus unit.

The result is analysed to find out the optimum combustion air flow rate to AAG ratio (O₂/H₂S) and its effect on Claus unit outputs. In order to do this, a common factor must be developed to join all the process variables, the variable is HCRN (High Conversion Ratio Number). The HCRN represents the H₂S/SO₂ ratio in tail gas and give an indication if the process is in normal and optimum run or not. The flow of the combustion air was not enough to oxidise the required amount of H₂S that results in low H₂S conversion in the thermal reactor section. Therefore, the reaction in the catalytic reactors has slow rate and low conversion that led to
Claus unit overall conversion of 61%, resulting in low productivity in S2, HPS, and LPS. According to the results of the simulation, the best HCRN is 2 where Claus unit can achieve its maximum productivity and highest overall conversion ratio. Due to the variation of the feed streams, it is impossible to keep the HCRN at 2, a range of 1.5 to 3 is acceptable where the overall conversion ratio is over 97.6%.

6.3 Recommendation

Claus unit control system shall be improved using the model that has been developed during this project to control the process with a feedback control loop. The control loop must be linked to an online analyser in order to measure the flue gases such as H2S, SO2, COS, SC2, NOX. The development of the control loop of Claus unit shall help the operator to trace the H2S/SO2 ratio during normal Claus unit operation and maintaining it at the recommended range.
REFERENCES


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APPENDICES

Appendix A

Data Used In Model Validation

1. Scenario 1

AAG=19110 kg/hr  O2= 5800kg /hr

Table A-1 Model Validation Scenario 1

<table>
<thead>
<tr>
<th>No</th>
<th>Parameters</th>
<th>Plant Data</th>
<th>Model Prediction</th>
<th>Difference %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Conversion ratio</td>
<td>61%</td>
<td>60.57%</td>
<td>0.7%</td>
</tr>
<tr>
<td>2</td>
<td>Total $S_2$ production</td>
<td>2710</td>
<td>2690</td>
<td>0.75%</td>
</tr>
<tr>
<td>3</td>
<td>Total HPS production</td>
<td>10650</td>
<td>10570</td>
<td>0.75%</td>
</tr>
<tr>
<td>4</td>
<td>Total LPS production</td>
<td>4912</td>
<td>4877</td>
<td>0.71%</td>
</tr>
</tbody>
</table>

2. Scenario 2

AAG=24570 kg/hr  O2=7465 kg/hr

Table A-2 Model Validation Scenario 2

<table>
<thead>
<tr>
<th>No</th>
<th>Parameters</th>
<th>Plant Data</th>
<th>Model Prediction</th>
<th>Difference %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Conversion ratio</td>
<td>61%</td>
<td>60.57%</td>
<td>0.7%</td>
</tr>
<tr>
<td>2</td>
<td>Total $S_2$ production</td>
<td>3482</td>
<td>3458</td>
<td>0.69%</td>
</tr>
<tr>
<td>3</td>
<td>Total HPS production</td>
<td>13682</td>
<td>13590</td>
<td>0.67%</td>
</tr>
<tr>
<td>4</td>
<td>Total LPS production</td>
<td>6317</td>
<td>6270</td>
<td>0.74%</td>
</tr>
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</table>
3. Scenario 3
AAG = 30030 kg/hr  O2 = 9121 kg/hr

Table A-3 Model Validation Scenario 3

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<th>Plant Data</th>
<th>Model Prediction</th>
<th>Difference%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Conversion ratio</td>
<td>61%</td>
<td>60.57%</td>
<td>0.70%</td>
</tr>
<tr>
<td>2</td>
<td>Total $S_2$ production</td>
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<td>4227</td>
<td>0.68%</td>
</tr>
<tr>
<td>3</td>
<td>Total HPS production</td>
<td>16720</td>
<td>16610</td>
<td>0.66%</td>
</tr>
<tr>
<td>4</td>
<td>Total LPS production</td>
<td>7719</td>
<td>7665</td>
<td>0.70%</td>
</tr>
</tbody>
</table>

4. Scenario 4
AAG = 40950 kg/hr  O2 = 12440 kg/hr

Table A-4 Model Validation Scenario 4

<table>
<thead>
<tr>
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<th>Parameters</th>
<th>Plant Data</th>
<th>Model Prediction</th>
<th>Difference%</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Conversion ratio</td>
<td>61%</td>
<td>60.57%</td>
<td>0.70%</td>
</tr>
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<td>2</td>
<td>Total $S_2$ production</td>
<td>5804</td>
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</tr>
<tr>
<td>3</td>
<td>Total HPS production</td>
<td>22800</td>
<td>22650</td>
<td>0.66%</td>
</tr>
<tr>
<td>4</td>
<td>Total LPS production</td>
<td>10530</td>
<td>10450</td>
<td>0.76%</td>
</tr>
</tbody>
</table>
### Scenario 5

AAG = 46410 kg/hr  O2 = 14090 kg/hr

Table A-5 Model validation Scenario 5

<table>
<thead>
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<th>Model Prediction</th>
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</thead>
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<td>1</td>
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<td>61%</td>
<td>60.57%</td>
<td>0.70%</td>
</tr>
<tr>
<td>2</td>
<td>Total S₂ production</td>
<td>6580</td>
<td>6533</td>
<td>0.71%</td>
</tr>
<tr>
<td>3</td>
<td>Total HPS production</td>
<td>25850</td>
<td>25670</td>
<td>0.70%</td>
</tr>
<tr>
<td>4</td>
<td>Total LPS production</td>
<td>11930</td>
<td>11841</td>
<td>0.75%</td>
</tr>
</tbody>
</table>
Case Study Scenario 5 Figures

Figure A-1 Combustion Air Flow & HCRN

Figure A-2 HCRN & S₂ Total Production
Figure A-3 HCRN & HPS Total Production

Figure A-4 HCRN & LPS Total Production
Figure A-5 HCRN & Claus Unit Conversion Ratio