Department of Chemical Engineering

CHE 4036Z – Chemical Engineering Design

Area 5

October 2020

GROUP Q

Table of Contents

List of Illustrations

List of tables

List of figures

Glossary

Adiabatic	A process or unit operation in which no heat enters or exits the system.
Aspect ratio	The length to diameter ratio of a vessel.
AspenPlus	Flowsheet simulation software.
Axial Dispersion	Back mixing of reactants in the axial direction of a tubular reactor.
Catalyst	A substance used to increase the rate of a chemical reaction without undergoing a physical change. The catalyst increases the rate of reaction by decreasing the related activation energy.
Condensation	Change in the physical state of a substance from the gaseous phase to the liquid phase.
Chemical equilibrium	A state in which the rate of the forward and reverse reactions are equal. Therefore, there is no longer any change in the concentration of any reaction components.
Exothermic reaction	A reaction with a negative standard enthalpy. This implies that the heat is released during the reaction resulting in a temperature rise.
Mass transfer limited reaction	Reaction in which the rate of chemisorption of reactants and products onto the catalyst is slower that the rate of reaction.
Reactor	The vessel, pressurised or non-pressurised, in which a chemical reaction occurs.
Scilab	Numerical orientated programming language.

List of Symbols

BPCS	Basic Process Control System
CO_2	Carbon Dioxide
COS	Carbonyl Sulfide
H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen Sulfide
HPS	High Pressure Steam
MSDS	Material Safety Data Sheet
O_2	Oxygen
ODE	Ordinary Differential Equation
PBR	Packed Bed Reactor
PFD	Process Flow Diagram
S_2	Diatomic Sulfur
S_6	Hexasulfur
SCOT	Shell Claus Off-gas Treating
SIS	Safety Instrumented Systems

1. Design Problem Definition

Design problem definition of Area 5

The purpose of this report is to provide a detailed design of the sulfur recovery section, Area 5, in the processing of sour natural gas from the Brulpadda exploratory area, in order to determine the feasibility of the overall process. Area 5 consists of the Claus catalytic reactors used to reduce the sulfur content of the acid gas produced by the natural gas sweetening unit (Area 2). Area 5 is located onshore in Mossel Bay, on a green field site between the Gourikwa power station and the PetroSA GTL facility.

Overview and process background

The gas feeding Area 5 is the combustion product of the Claus furnace, found in Area 4, which contains a high proportion of hydrogen sulfide (H_2S), sulfur dioxide (SO_2) and carbonyl sulfide (COS). In order to abide by stringent sulfur emissions regulations, these compounds are catalytically converted to elemental sulfur (S_6) in multiple reactors. Due to the equilibrium-limited nature of the reactions occurring, S_6 is separated from the remaining gaseous species by condensation between each reactor. This results in Area 5 producing a liquid sulfur stream and an exit gas which is further processed in Area 6.

Required process functionality and area performance criteria

Area 5 is required to catalytically convert the H_2S, SO_2 and COS in the gas mixture, from Area 4, to liquid sulfur such that the exit gas stream contains less than 0.5% and 7.0% of H_2S and SO_2 respectively on a molar basis. The design of this area needs to be done in a manner which prioritises process safety while minimising the energy demand, resource consumption and total cost of the process. The environmental impact of the various chemical components and unit operations designed in the area must be considered and accordingly managed. The design of Area of 5 must be closely linked to that of Areas 4 and 6 to determine the preferred feed gas composition and pressure such that no further compression is required in Areas 5 and 6.

Objectives of the report

The objectives of this report are to:

- Provide a summary of the relevant literature pertaining to the design of this area and subsequently develop a plausible sequence of unit operations which can achieve the required area objectives.
- Conduct detailed design modelling of the first catalytic Claus reactor and provide a detailed explanation of how the model works, thermodynamic models used, and any assumptions made in the modelling process.
- Use the design model to determine the optimal number of Claus reactors, the optimal feed temperature to each reactor and the pressure drop across the entire Area 5 process.

- Determine the temperature at which sulfur separation occurs, how much sulfur is produced and how the sulfur recovery unit should be designed for start-up and shutdown.
- Conduct a sensitivity analysis and thereafter optimise the size of the equipment and operating conditions in order to present a summary of the base and optimised cases.
- Prepare a data sheet for the designed reactor and provide a detailed equipment list containing the equipment sizing required by the Layout Engineer.
- Produce the process description, plan for area interfaces, process flow diagram and stream tables required by the Process Coordinator.
- Develop a process control strategy and control diagram for the Control Engineer.
- Gather all relevant Safety and Environmental information required by the Health, Safety & Environment Officer.
- Determine the capital and operating costs related to this area and supply them to the Project Accountant.
- Calculate the energy requirements of the process and compile all necessary utility and heat integration information required by the Utilities & Heat Integration Engineer.

Scope, limitations and key issues affecting study

The gas mixture fed to the battery limits of Area 5, is the gas exiting the flash separator used to remove majority of the diatomic sulfur (S_2) from the Claus furnace in Area 4. The two streams exiting the battery limits of Area 5 are the condensed liquid S_6 and the remaining waste gas. The waste gas is sent to Area 6 for further catalytic reduction of the sulfur content and the liquid S_6 is sent to sulfur storage. The design of Area 5 includes the detailed modelling of the catalytic Claus reactors but other unit operations, such as heat exchangers and flash separators, will be design from heuristics or flowsheet simulations.

The detailed modelling of the Claus reactors found in Area 5 is based on the given reaction mechanism and kinetics. No further research into alternative reaction pathways was performed, which potentially limits the study in this manner. Another limitation of the study is the lack of thermodynamic data for S_6 in AspenPlus. This led to several property parameters being estimated for S_6 within the simulation which could potentially lead to inaccuracies regarding the units modelled using AspenPlus.

The feasibility of the design of this area is based upon the optimised case and thus includes the impact of the optimisation of any process variables. However, the feeds used for this investigation are based on the base case results from Area 4, before optimisation. Therefore, in order to determine the feasibility of the overall sour gas processing plant, the impact of using the optimised feed from Area 5 would need to be accounted for.

2. Process Development

Literature Review

The acid gas removed in the sweetening process, found in Area 2, is made-up predominantly of H_2S and CO_2 with a small proportion of hydrocarbons and water. Historically, the acid gas would be directly incinerated, with the H_2S being oxidised to SO_2, but strict emissions regulations prohibit this method of processing the acid gas. Therefore, the H_2S in the acid gas produced by natural gas sweetening must be further processed [1].

H_2S is a flammable and toxic gas unlike elemental sulfur, which can be easily stored for sale. Therefore, one option for the processing of H_2S is to convert it to elemental sulfur which is primarily used for the production of sulfuric acid. It is possible to chemical convert H_2S for disposal as solid waste but this is highly uneconomical [1]. The most commonly used method of reducing the sulfur content in acid gas is to convert H_2S and SO_2 to elemental sulfur using the Claus process [2].

The Claus process is carried out in two stages: a thermal section followed by a catalytic section. The thermal section, carried out in Area 4, comprises of a furnace which oxidises a portion of the H_2S in the acid gas to SO_2 in a highly exothermic reaction not limited by equilibrium [3]. Variations in the thermal section of the Claus process include the straight-through and split-flow processes. The main difference between these processes is that in the straight through process all of the acid gas is oxidised in the furnace compared to a split-flow process in which a portion of the acid gas bypasses the furnace and is fed directly to the catalytic section [4].

The second stage of the Claus process is the catalytic conversion of H_2S, SO_2 and other sulfur compounds (like COS) to elemental sulfur. The exothermic and equilibrium-limited reactions occur over an activated alumina catalyst in a series of catalytic reactors [1]. The catalyst used can be varied to promote COS and carbon disulfide (CS_2) destruction depending on the feed to the process [1]. The catalytic section of the Claus process, on which the design of Area 5 is based, consists of a series of catalytic reactors with sulfur removal occurring in-between each reactor [5]. This serves to drive the forward reactions occurring in each reactor which pertain to the conversion of H_2S [2]. The overall sulfur recovery of the catalytic section of the Claus process is dependent on the acid gas feed composition, age of catalyst and number of reactor stages. For Claus processes, with no recycle, sulfur recoveries of 90%-96% can be achieved for two-stage processes and 95%-98% for three reactor stages. These once through processes are limited to a maximum overall sulfur recovery of 98% [1].

The tail gas exiting the catalytic section of the Claus process invariably contains small amounts of unreacted H_2S and SO_2 regardless of the number of reactor units found in the Claus process [4]. Since sulfur emissions regulations are continuously getting stricter, it is necessary to remove the residual sulfur from the Claus process tail gas (which occurs in Area 6). The most commonly used method for tail gas treating is the Shell Claus Off-gas Treating (SCOT) process which catalytically converts all remaining SO_2 to H_2S by hydrogenation. The H_2S is then separated from the tail gas using an amine solvent and recycled back to the Claus process, increasing the overall sulfur recovery [1]. However, for the proposed design, the tail gas will be treated using a novel process (in Area 6) which converts the residual H_2S and SO_2 to elemental sulfur using methane derived syngas and air.

The literature reviewed indicates the viability of using the Claus process to remove sufficient sulfur components from an acid gas stream. The sequence of multiple catalytic Claus reactors in series with elemental sulfur removal in-between allows the tail gas exiting to Area 6 to conform to the given H_2S and SO_2 specifications.

Flowsheet development and sequence of unit operations

In order to design the process described in the literature review and to ensure it meets the required specifications, a specific sequence of unit operations is required. The stream entering Area 5, from Area 4, is the vapour product of a flash tank used to condense S_2 which contains an appreciable amount of H_2S and SO_2. Therefore, before it can be fed to the first catalytic converter it is requires heating. The temperature to which the feed is preheated must be high enough to ensure no sulfur vapour condenses within the pores of the catalyst in the reactor. In addition to this, the preheating of the reactor feed helps to promote the destruction of COS to H_2S on the surface [1].

The feed, at the desired feed temperature, is fed to the inlet of the catalytic Claus reactor. Claus reactors are packed-bed reactors which make use an activated alumina catalyst. Various other catalysts are used to promote the destruction of COS and CS_2 if the reactor feed has a high proportion of these components. Within the Claus reactor, H_2S and SO_2 are catalytically reacted to form hexasulfur (S_6) and water while COS is converted to H_2S and CO_2 using water. These exothermic reactions allow for the concentration of H_2S and SO_2 to decrease and the reaction temperature to increase along the length of the reactor. Both reactions occurring within the Claus reactor are equilibrium-limited, thus the increasing temperature profile of the reactor limits the conversion of H_2S. Similarly, the production of S_6 limits the progress of the reaction and equilibrium is reached before the desired conversion of H_2S and SO_2 is achieved. Therefore, to achieve the desired conversion of H_2S and SO_2, it is necessary to shift the equilibrium to the right by setting up multiple Claus reactors in series with the removal of S_6 occurring in-between each reactor.

The vapour pressure of S_6 is significantly lower compared to that of the other components in the gaseous reactor effluent. Hence, the removal of S_6 from the reactor effluent is possible by phase separation. Therefore, the reactor effluent is cooled to the dew point of S_6 immediately after exiting the Claus reactor using an air cooler (due to water scarcity), which causes mainly S_6 to condense. The cooled vapour-liquid mixture is then followed by a flash separator allowing the gas, lean in S_6, to exit out the top of the separator with the sellable liquid S_6 exiting out the bottom. The large difference in vapour pressure between S_6 and the other gas components of the reactor effluent allows the use of a cooler with a heat exchanger to be a viable method of removing a high proportion of S_6 while producing a liquid sulfur product of high purity.

Once the S_6 is removed from the reactor effluent the same sequence of unit operations is repeated. The gas exiting the top of the flash tank is fed to another preheater before entering a second Claus packed-bed reactor to prevent the formation of liquid sulfur within the reactor. Hence, the sequence of unit operations for any following Claus reactors follows the same sequence as the initial one, where the reactor feed is preheated before entering a Claus reactor which allows the reaction of H_2S to reach equilibrium before removing S_6 from the reactor effluent by phase separation using a cooler and a flash tank. This arrangement of unit operations can be repeated to achieve the desired conversion of H_2S until the addition of further units becomes uneconomical when comparing the increase in conversion to the capital requirements of more units. All liquid sulfur produced in this area is mixed together to form a single liquid sulfur product stream. This liquid sulfur product along with the tail gas exiting the final flash tank are sent to Area 6 for sulfur storage and tail gas clean-up respectively. A requirement of the design is that the feed entering Area 5 from Area 4 needs to be at a high enough pressure such that no further compression is required in Areas 5 and 6.

The aforementioned sequence of units makes use of only utility-based heat exchangers. However, as explained in Section 10, there is a potential for heat integration using the reactor effluents to heat other process streams which leads to a decrease in utility requirements. The effluent exiting the primary Claus reactor has a high enthalpy flow and thus is used to heat the feeds to all reactors. Hence, the previously mentioned utility-based preheaters are replaced with heat exchangers using the primary Claus reactor effluent to heat the feed to each reactor, as shown Figure A5.9.

The main units requiring design in this area are the catalytic packed-bed Claus reactors used for the conversion of H_2S, SO_2 and COS. Detailed design modelling of these reactors is required for an in-depth feasibility analysis with the design of the heat exchangers and flash tanks being heuristic based.

Assumptions made in process development

A few key assumptions were made when developing the flowsheet, shown in Figure A5.9, and corresponding mass balance. The catalytic Claus reactors are sized using the detailed modelling outlined in Section 3 whereas the sizing of heat exchangers and flash tanks is heuristic based as shown in Appendix A5-B. The pressure drop across the reactors is modelled using the Ergun shown in equation A5.12 but the pressure drop across the heat exchangers and flash tanks are assumed to 0.1 bar and 0.2 bar respectively.

In the development of a base case, the detailed reactor model was built using Scilab and the sulfur recovery units were modelled in AspenPlus. Due to the lack of thermodynamic data for elemental sulfur, S_6, the vapour-liquid equilibrium separation was modelled using AspenPlus predicted data for S_6. In addition to this, ideal gas law was assumed to hold since the process operates at high temperature and low pressure and thus the interactions between particles is minimised.

When modelling the air coolers used to cool the reactor effluents as part of the sulfur recovery system, the air used as a cooling utility was assumed to be fed at 25°C. The air exiting each air cooler was assumed to be 10°C higher than the inlet temperature, and thus hot air exits each air cooler at 35°C.

3. Detailed Design Modelling

Model development

The process objective for Area 5 is to decrease the H_2S, SO_2 and COS content of the tail gas exiting the Claus furnace, found in Area 4, and produce a liquid sulfur product stream. The tail gas exiting Area 5 is required to have a maximum concentration of H_2S and SO_2 of 0.5% and 7.0% respectively on a molar basis. As discussed in Section 2, a series of catalytic packed-bed reactors, heat exchangers and flash tanks are required to meet the outlined specifications. The performance of the catalytic Claus reactors strongly impacts the ability of the area to produce a tail gas stream conforming to the required specifications. Therefore, in order to accurately model the process occurring in Area 5, the development of a detailed design model of these packed-bed reactor is necessary.

Explanation of how the model works

The, catalytic packed-bed, Claus reactors reduce the sulfur content of the feed stream by converting H_2S and SO_2 to elemental sulfur and COS to H_2S on the metal catalyst surface, with the specific stoichiometry of each reaction show in Equations A5.1 and A5.2 respectively.

$$2H_2S + SO_2 \rightleftharpoons \frac{1}{2}S_6 + 2H_2O \tag{A5.1}$$

$$H_2O + COS \rightleftharpoons CO_2 + H_2S \tag{A5.2}$$

In order to model the change in flowrate of each component in the system as a function of the reaction volume, the detailed kinetic expressions for both exothermic reactions are required. The activated alumina catalysts used in these catalytic reactors are spherical particles with a 1 mm diameter with an assumed porosity of 0.4. The kinetic expressions shown in Equations A5.3 to A5.9 describe the rate of each reaction (in kmol/$m^3_{(void)}$s) as a function of the partial pressures of the key components at various temperatures. The given kinetics include the effectiveness factor and therefore account for the impact of any internal and external mass transfer limitations on the rate of reaction.

$$-r_{COS} = \frac{k_{COS}P_{COS}P_{H_2O}}{1 + K_i P_{H_2O}} \tag{A5.3}$$

$$-r_{H_2S} = \frac{k_{H_2S}\left(P_{SO_2}^{0.5}P_{H_2S} - \frac{1}{\sqrt{K_E}}P_{S_6}^{0.25}P_{H_2O}\right)}{(1 + K_{ii}P_{H_2O})^2} \tag{A5.4}$$

$$k_{H_2S} = 2.174\exp\left(-\frac{30770}{RT}\right) \tag{A5.5}$$

$$k_{COS} = 2.382 \exp\left(-\frac{57903}{RT}\right) \tag{A5.6}$$

$$K_i = 1.25 \exp\left(-\frac{83261}{RT}\right) \tag{A5.7}$$

$$K_{ii} = 0.338 \exp\left(-\frac{2510.4}{RT}\right) \tag{A5.8}$$

$$K_E = 9.502 \times 10^{-7} \exp\left(1.11 \times \frac{10^4}{T}\right) \tag{A5.9}$$

The temperature profile along the length of the reactor is modelled using an energy balance which models the impact of the heat released by each reaction, the enthalpy flow of all components and the heat lost by the reactor to the environment on the reaction temperature. In addition to this, the change in pressure along the length of the reactor is modelled by the Ergun equation. The modelling of the molar change of each component, temperature and pressure along the length of the reactor provides the basis for a coherent reactor model.

The mathematical modelling of the catalytic Claus reactors was completed using Scilab as it allows for a greater understanding of the design process and provides full control over the level of complexity of the model. Scilab offers the flexibility to adjust the model in order to accommodate process changes since process variables can be easily manipulated. This property of a Scliab based model is highly advantageous during the optimisation phase of the design.

Packed-bed reactor design equations

The Claus reactor is defined as packed-bed reactor (PBR) because the reactions take place on the surface of metal catalyst particles. In order to develop a model for the catalytic PBR, the change in flowrate of each component, temperature and pressure must be determined as a function of the reactor volume. A PBR has a set of differential design equations used to describe the changes in each of these reactor properties across the reactor volume. Therefore, the combination of the three design equations forms a system of ordinary differential equations which are solved simultaneously forming the basis of the PBR model.

In order to model the change in flowrate of each component as a function of the reactor volume, the mole balance design equation, shown in Equation A5.10, for a PBR is required [6]. This mole balance is based on the assumption that the system operates at steady-state and that there is no accumulation of material within the system. The mole balance accounts for both reactions occurring by considering the stoichiometry of each chemical reaction and thus models the change in flowrate of each component across the reactor volume. In completing the mole balance, it is assumed that there is no axial dispersion across the reactor.

$$\frac{dF_i}{dV} = -r_i \tag{A5.10}$$

The term $-r_i$, in Equation A5.10, indicates rate of change of component i within the reactor system, in kmol/m^{3}h. The flowrate of each component, F_i, and the reactor volume, V, have units of kmol/h and m^3 respectively. Therefore, the units of the rate of reaction of required to be kmol/m^{3}h. In order to convert the units of the given rate of reaction from per m$^3_{(void)}$ to per m^3 to the rate term is multiplied by the assumed voidage of 0.4.

The temperature profile along the reactor volume is determined using the energy balance, shown in Equation A5.11, which assumes the conservation of energy within the system and neglects enthalpy changes resulting from mixing [6].

$$\frac{dT}{dV} = \frac{\sum r_j \Delta H_{rxn,j} - Q_z}{\sum F_i C_{p_i}} \tag{A5.11}$$

Where T represents the temperature in K, r_j is the rate of reaction j in kmol/m^{3}h and $C_{p_i}$is the specific heat of component i, in J/kmolK, which varies with temperature. $\Delta H_{rxn,i}$ is the heat of reaction, in J/kmol, and is included in the energy balance to account for the change temperature as a result of the heat released or absorbed by the reactions occurring in the system. The reactor is not assumed to be adiabatic and therefore the term Q_z is included to account for the heat lost to surroundings in J/m^{3}h.

The final design equation required to model the catalytic Claus reactor is used to determine the pressure drop across the length of the reactor. Since the reactions occurring are gas phase reactions, the partial pressure of each component is proportional to the total pressure of the reactor. Thus, it is important to account for the effects of pressure drop on the rate of reaction when modelling a PBR [6]. Since the gas phase reactions are catalysed through a packed porous bed of spherical catalyst particles, the Ergun equation below is used to model the pressure drop across the reactor [6].

$$\frac{dP}{dV} = -\frac{G}{\rho_{fluid} d_p}\left(\frac{1-\phi}{\phi^3}\right)\left(\frac{150(1-\phi)\mu_{gas,mix}}{dp} + 1.75G\right)\left(\frac{1}{A}\right) \tag{A5.12}$$

Where P represents the pressure within the reaction vessel in kPa, G is the superficial mass velocity in kg/m^{2}s, ρ_{fluid} is the density of the gas flowing the reactor in kg/m^3, d_p is the diameter of the catalyst particles, ϕ is the porosity of the packed-bed, $\mu_{gas,mix}$ is the viscosity of the gas mixture in kg/ms and A is the cross-sectional area of the cylindrical reactor in m^2.

These three design equations form the basis of a complete model for the packed-bed Claus reactors. This system of ordinary differential equations was solved using Scilab ODE solver for varying reactor volumes to produce the flowrate of each component, temperature and pressure profiles for the Claus reactor. Many of the parameters found in these design equations are functions of temperature, pressure and composition which, as previously stated, vary across the length of the reactor and thus, the value of these parameters would also vary across the length of the reactor. Therefore, to adequately model the Claus reactor the change in the values of these parameters needs to be accurately modelled.

Modelling heat of reaction

The heat of reaction, ΔH_{rxn}, is included in the energy balance to account for the change in temperature as a result of the heat released by the exothermic reactions occurring within the Claus reactor. The heat released by each reaction is a strong function of temperature as, shown by Equation A5.13 below [6].

$$\Delta H_{rxn}(T) = \Delta H_{rxn}^{0}(T_R) + \int_{T_R}^{T} \Delta C_p(T)dT \qquad \text{(A5.13)}$$

The term $\Delta H_{rxn}^{0}(T_R)$, is the standard heat of reaction at the reference temperature which is 25°C. Equation A5.14 describes how the standard heat of reaction is determined [6].

$$\Delta H_{rxn}^{0}(T_R) = \sum v_i H_{f,i}^{0} \qquad \text{(A5.14)}$$

Where v_i and $H_{f,i}^{0}$ are the stoichiometric coefficient and enthalpy of formation at the reference temperature of component i in the chemical reaction respectively. The standard enthalpy of formation for each component in the reactor system was sourced from literature [7]. The $\Delta C_p(T)$ is the average change in heat capacity as the reaction progresses and determined using Equation A5.15 [6].

$$\Delta C_p(T) = \sum v_i C_{p,i}(T) \qquad \text{(A5.15)}$$

Where $C_{p,i}$ is the specific heat capacity of component i which varies with temperature. The specific heat capacity of component i is determined using Equation A5.16 below, where a, b, c, d and e are component specific constants sourced from literature [7].

$$C_{p,i} = a + bT + cT^2 + dT^3 + eT^4 \qquad \text{(A5.16)}$$

Modelling gas density

In order to determine the density of the gaseous reaction mixture, it is assumed that the gas mixture is an ideal gas. This is assumption holds because the system under investigation is at high temperature and low pressure. Thus, the interactions between the gas molecules is minimised due to the kinetic energy of the molecules being comparatively greater than the intermolecular forces between the molecules. Therefore, the effect of molecular size and intermolecular forces on the behaviour of the gas are negligible and the gas can be assumed to be ideal [8]. Hence, the initial density of the gaseous mixture entering the reactor is determined using the modified version of the ideal gas law, shown in Equation A5.17 [6].

$$\rho_{fluid,0} = \frac{\bar{M}P_0}{RT_0} \tag{A5.17}$$

Where $\bar{M}$ is the weighted average of the molar masses of the components in the gas mixture and R is the universal gas constant of 8.314 J/molK. Since, the reactor is assumed to be operating at steady state the density of the gas mixture across the length of the reactor is given by Equation A5.18 [6].

$$\rho_{fluid} = \rho_{fluid,0}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)\left(\frac{F_{T0}}{F_T}\right) \tag{A5.18}$$

Modelling gas viscosity

The viscosity of a gaseous fluid describes the gas's resistance to flow and therefore is a key parameter in the Ergun equation which models the pressure drop across the reactor. The viscosity of a gaseous mixture is dependent on the viscosity of each component in the mixture and the interactions between each component. Since the species present in the Claus reaction is a mixture of hydrocarbon and nonhydrocarbon gases at low pressures, the Bromley and Wilke correlation is used to determine the viscosity of the gaseous mixture [8].

$$\mu_{gas,mix} = \sum_{i=1}^{n} \frac{\mu_i}{\sum_{\substack{j=1 \\ j\neq i}}^{n} Q_{ij}\frac{x_i}{x_j}} \tag{A5.19}$$

Where Q_{ij} is the unitless interaction parameter between components i and j, as shown in Equation A5.20, and μ_i is the viscosity of pure component i, which is a function of temperature [8].

$$Q_{ij} = \frac{1 + \left[\left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}}\left(\frac{M_j}{M_i}\right)^{\frac{1}{4}}\right]^2}{\sqrt{8}\left[1 + \frac{M_i}{M_j}\right]^2} \tag{A5.20}$$

The viscosity of component i as a function of temperature is given in Equation A5.21 below, where A, B, C and D are component specific constants found in literature [9].

$$\mu_i = A + BT + CT^2 + DT^3 \tag{A5.21}$$

Modelling the superficial and mass velocities

The pressure drop across the reactor, as modelled by the Ergun equation in Equation A5.12, is a function of the velocity at which mass flows across the packed bed. The mass velocity is a function of the superficial velocity which is determined using Equation A5.22.

$$u_s = \frac{\dot{m}_T}{\rho_{fluid}\, A} \tag{A5.22}$$

Where $\dot{m}_T$ is the total mass flow across the bed and A is the cross-sectional area of the PBR. The superficial velocity is then used to determine the mass velocity, G, as shown in Equation A5.23 [6].

$$G = u_s\, \rho_{fluid} \tag{A5.23}$$

Modelling heat loss

Since the catalytic Claus PBR is not assumed to operate adiabatically, the impact that the heat lost from the reaction vessel to the surrounding environment has on the temperature within the reactor must be adequately modelled. The heat transfer between the fluid within the reactor and the environment occurs in four mechanistic steps [10].

The first step in the mechanism is the heat transfer from the reaction fluid to the wall of the reaction vessel, which is modelled using Equation A5.24 [10].

$$T_{fluid} - T_{rxn\, wall,ins} = q_z\left(\frac{1}{\pi\, d_{transfer}\, h_w}\right) = q_z R_1 \tag{A5.24}$$

The wall of the reaction vessel is constructed out of carbon steel due its economic attractiveness and the fact the components in the system are noncorrosive. The heat transfer coefficient between the reaction fluid, h_w, is determined using Equation A5.25 [11].

$$h_w = \frac{k_{fluid}}{d_p}\left(2.58\, Re_p^{1/3}\, Pr^{1/3} + 0.09\, Re_p^{0.8}\, Pr^{0.4}\right) \tag{A5.25}$$

Where k_{fluid} is the thermal conductivity of the reaction fluid which a function of the reaction fluid composition and temperature as shown in Equation A5.26.

$$k_{fluid} = \sum_{i=1}^{n} \frac{y_i k_i}{\sum_{j=1}^{n} y_i A_{ij}} \tag{A5.26}$$

A_{ij} accounts for the impact that the interactions between the components in the fluid have on the thermal conductivity of the reaction fluid and is determined using Equation A5.27 [8].

$$A_{ij} = \frac{1}{4}\left\{1 + \left[\frac{\mu_i}{\mu_j}\left(\frac{M_i}{M_j}\right)^{\frac{3}{4}}\left(\frac{T + 1.5T_{b,i}}{T + 1.5T_{b,j}}\right)\right]^{\frac{1}{2}}\right\}^2 \left(\frac{T + \sqrt{1.5\, T_{b,i} \cdot 1.5\, T_{b,j}}}{T + 1.5T_{b,i}}\right) \qquad \text{(A5.27)}$$

Where $T_{b,i}$ is the normal boiling point of component i at 1 atm and μ_i is the viscosity of component i which is determined using equation A5.21. The thermal conductivity of each pure component, k_i, is determined using Equations A5.28 and A5.29 for linear and non-linear molecules respectively with T_c being the critical temperature of component i, sourced from literature [7].

$$k_i(linear) = \frac{\mu_i}{M_i}\left(1.3\, C_{p,i} + 6.33 - \frac{2.9288\, T_c}{T}\right) \qquad \text{(A5.28)}$$

$$k_i(non - linear) = \frac{\mu_i}{M_i}\left(1.15\, C_{p,i} + 8.59\right) \qquad \text{(A5.29)}$$

In order to determine the heat transfer coefficient of the fluid along the length of the reactor, the Reynolds, Re_p, and Prandtl, Pr, numbers are required according to Equation A5.25. These dimensionless numbers which describe the fluid flow within the reactor and are calculated using Equations A5.30 and A5.31 respectively.

$$Re_p = \frac{\rho_{fluid}\, u_s\, d_p}{\mu_{gas,mix}(1 - \phi)} \qquad \text{(A5.30)}$$

$$\mathrm{Pr} = \frac{\overline{C_p}\, \mu_{gas,mix}}{k_{fluid}\, \overline{M}} \qquad \text{(A5.31)}$$

Where $\overline{C_p}$ and $\overline{M}$ are weighted averaged of the specific heat capacities and molar masses in each the reaction fluid. Once heat is transfer from the fluid to the inside of the carbon steel reactor wall, heat is then transferred through the reactor wall to the outside of the wall, by conduction. The change in temperature between the inside and outside of the reactor wall is given by Equation A5.32 below [10].

$$T_{rxn\, wall,ins} - T_{rxn\, wall,out} = q_z\left(\frac{1}{2\pi\, k_{cs}} \cdot \ln\frac{d_{tube}+t_{wall}}{d_{tube}}\right) = q_z R_2 \qquad \text{(A5.32)}$$

Where k_{cs} is the thermal conductivity of carbon steel of 33 W/mK, d_{tube} is the diameter of the reactor and t_{wall} is the minimum thickness of the reactor wall and is determined using Equation A5.33 below with the pressure in bar. The 0.004 m added to the wall thickness in Equation A5.33 is included to account for any corrosion that may occur over time.

$$t_{wall} = 0.022\, P\, d_{tube} + 0.004 \qquad \text{(A5.33)}$$

To reduce the amount of heat lost to the surroundings, the reactor is insulated with 85% magnesia which has a thermal conductivity, k_{ins}, of 0.01 W/mK [12]. Therefore, heat is transferred by conduction through the layer of insulation. Therefore, Equation A5.34 is used to determine the temperature at the external surface of the insulation layer.

$$T_{rxn\, wall,out} - T_{ins\, wall,out} = q_z \left(\frac{1}{2\pi\, k_{ins}} \cdot \ln \frac{d_{tube} + t_{wall} + t_{ins}}{d_{tube} + t_{wall}} \right) = q_z R_3 \qquad \text{(A5.34)}$$

Where t_{ins} is the thickness of the insulation layer around the reactor which is assumed to be 15 cm [13]. By adding Equations A5.24, A5.32 and A5.34 together, the temperature of the external surface of the reactor (which is the external temperature of the insulation) can be determined using Equation A5.35.

$$T_{ins\, wall,out} = T_{fluid} - q_z (R_1 + R_2 + R_3) \qquad \text{(A5.35)}$$

The final aspect that needs to be modelled, in order to determine the total heat lost from the reactor, is the convective heat transfer from the external surface of the reactor to the surroundings. The effect of heat loss by radiation is assumed to be negligible because the temperatures within the reactor are below 1000 K [10]. The heat loss by convective heat transfer is described by Equation A5.36 below.

$$q_{conv} = \frac{2.3613 \cdot 10^3}{\left((d_{tube} + t_{wall} + t_{ins}) \cdot 100\right)^{0.2}} \cdot \frac{(T_{ins\, wall,out} - T_{ext})}{\left(0.9(T_{ins\, wall,out} + T_{ext}) - 32\right)^{0.181}} \qquad \text{(A5.36)}$$

Where T_{ext} is the ambient temperature of the environment surrounding the reactor which is assumed to be 25°C. The total heat loss from reactor is calculated using Equation A5.37.

$$q_z = \pi (d_{tube} + t_{wall} + t_{ins})(q_{conv}) \left(\frac{1}{A} \right) \qquad \text{(A5.37)}$$

Hence Equations A5.35 and A5.37 form the basis of the model used to determine the heat loss from the reactor to the surrounding environment. The combination of these equations forms a linear system of equations which are solved simultaneously to determine the heat lost per cubic meter of reactor and the temperature of the external surface along the length of the reactor.

Summary of how the models and equations are implemented

The overall objective of the equations, which encompass the full reactor model for the Claus reactors, is to determine the dimensions of the reactor and the flowrate, temperature and pressure profiles as a function of the reactor volume.

In order to determine these profiles along the volume of the reactor, the system of differential design equations of a packed bed reactor, namely Equations A5.10, A5.11 and A5.12, are solved simultaneously using the ODE solver in Scilab. In order to use the ODE solver to determine these reactor profiles, the various parameters in the design equations are modelled, using parameter specific equations and correlations, within the same function as the design equations. Once the flowrate, temperature and pressure profiles are determined, using the ODE solver, the dimensions of the reactor which achieve the required specifications were determined.

Base case design modelling

Number of reactors and reactor sizing

In order to design the entire process found in Area 5 the operation of the heat exchangers, condensers and flash tanks are modelled using AspenPlus in tandem with the previously developed Scilab reactor model for the Claus reactors. This complete model of the Claus reactor process is then subsequently used to determine the number of packed-bed reactors required to meet the H_2S and SO_2 specifications on the exiting tail gas.

The minimum number of Claus reactors required is strongly dependent on the conversion achieved by each catalytic reactor, which is a function of reactor volume. Since the chemical reactions occurring are equilibrium reactions, the conversion achievable is limited. Therefore, the volume of the reactors needs to be of sufficient size such that equilibrium is reached but not so large that the increased capital costs outweigh the minimal conversion increase. The H_2S conversion profile for the first Claus reactor, as shown in Figure A5.1, highlights that the rate of conversion decreases as the reactor volume reaches 200 m^3 which implies that equilibrium has been reached. Hence, any further increase in the reactor volume would not result in a significant increase in conversion and thus would be economically detrimental.

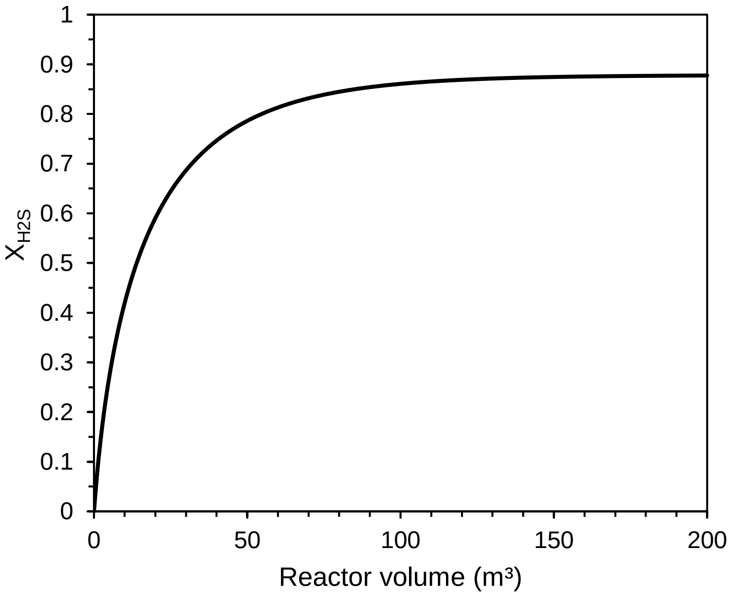


Figure A5.1: H_2S conversion profile over the volume of the primary Claus reactor

Figure A5.1 shows that the conversion of H_2S achieved by the, 200 m^3, initial Claus reactor is 87.7% which is not sufficient to meet the required H_2S specification but achieves the desired outlet concentration of SO_2, as shown in Figure A5.2. Therefore, the elemental sulfur produced in the first Claus reactor is removed using a partial condenser and a flash tank in order to shift the equilibrium in favour of the forward reaction in a second reactor. This sequence of unit operations is repeated until the outlined specifications are met. A volume of 190 m^3 for the second reactor was chosen because that is the point at which the rate of H_2S conversion begins to decrease, as shown in Figure A5.12 in Appendix A5-A. Figure A5.2 shows that the mole fraction of H_2S exiting reactor 2 is 0.7%, and thus a third reactor is necessary to produce a tail-gas with an H_2S content below 0.5% on a molar basis. Since H_2S content of the stream exiting reactor only needs to be reduced slightly, the 130 m^3 volume of the third reactor is determined at the point at which sufficient H_2S is converted. Therefore, the reactions occurring in the third reactor do not reach equilibrium, as shown by Figure A5.13 in Appendix A5-A, but the exiting tail gas contains less than 0.5% H_2S and 7.0% SO_2 on a molar basis.

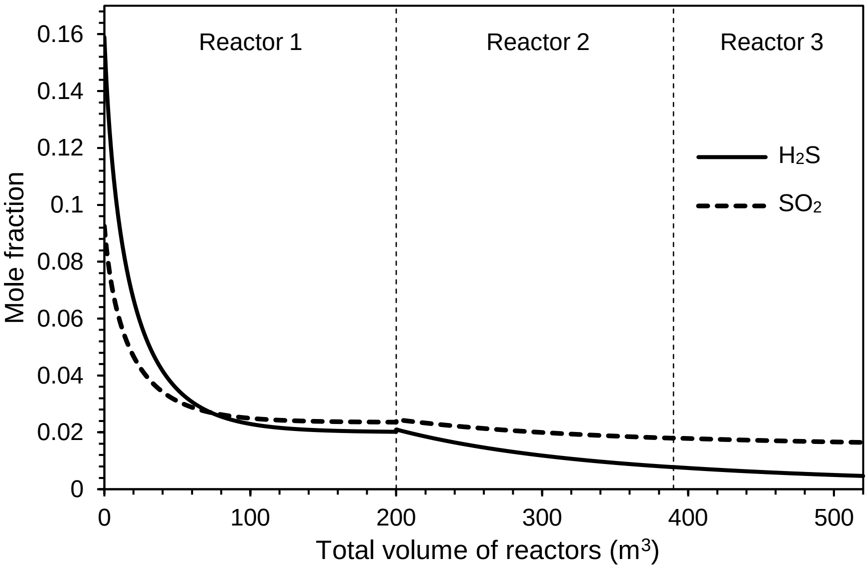


Figure A5.2: Mole fraction of H_2S and SO_2 in the reactor effluent as a function of reactor volume for the entire system

The combination of the three Claus reactors results in an overall conversion of H_2S of 97.3%, as shown in Figure A5.14 in Appendix A5-A, which is in line with results determined in literature [1]. Hence, the resulting H_2S and SO_2 mole fractions in the tail gas exiting Area 5 to Area 6 are 0.46% and 1.65% respectively.

Reactor inlet temperature

The conversion achieved by each previously mentioned reactor is highly dependent on the inlet temperature to each reactor. Since the chemical reactions, in Equations A5.1 and A5.2, occurring within the Claus reactors are equilibrium limited and exothermic, increasing the reaction temperature increases the rate the of reverse reaction resulting in a reduction in the conversion of H_2S and SO_2. This implies that the lower the temperature, the higher the achievable conversion. However, the rate of both the forward and reverse reactions decrease with temperature and thus the inlet temperature needs to be high enough to ensure a high rate of reaction is achieved. Another constraint on the inlet temperature to these Claus reactors, is that it must be high enough to ensure that the reactor effluent contains no liquid products. This is important because the formation of liquid within the reactor deactivates the activated alumina catalyst by preventing mass transfer within the system.

Literature suggests, for Claus processes with three reactors, that the inlet temperatures to the primary, secondary and tertiary reactors be 232°C, 216°C and 204°C respectively [1]. For the process feed, from Area 4, the lowest possible inlet temperature at which no liquid formed within the primary reactor was 255°C. The literature sourced inlet temperatures to the secondary and tertiary reactors were high enough to ensure that no liquid was formed within either reactor and that sufficient conversion was achieved. The exothermic nature of the reactions occurring within the Claus reactors implies that a temperature increase will occur along the volume of the reactor. However, since the reactors are not assumed to be adiabatic, the heat loss to the environments reduces the temperature rise, which increases the possibility of liquid formation within the reactor. This explains the necessity for a higher inlet temperature for the first reactor, with the temperature profile for primary reactor shown in Figure A5.3.

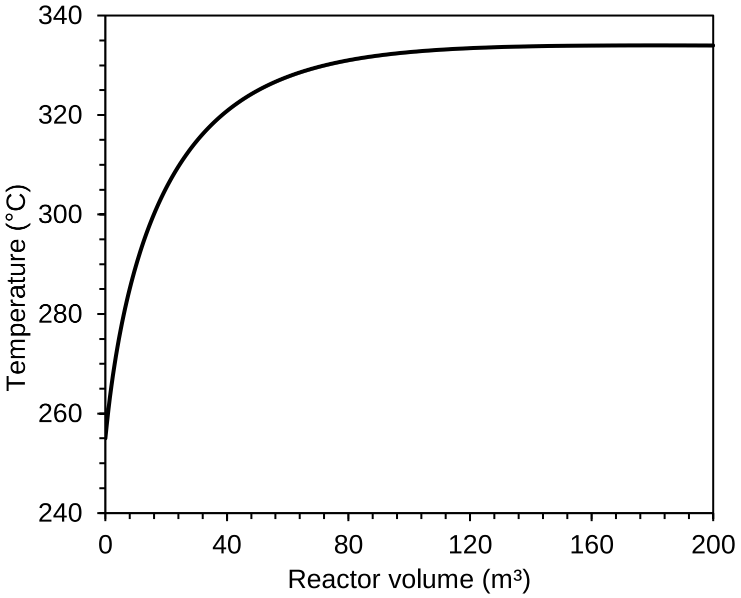


Figure A5.3: Temperature profile as function of reactor volume for the primary Claus reactor

The temperature profile for the first reactor, in Figure A5.3, shows that a maximum temperature is obtained at the same volume at which equilibrium is reached, which is depicted in Figure 1. Since the reactor is assumed not to be adiabatic, if the reactor volume is increased a significant temperature loss would be observed. The temperature profiles for the secondary and tertiary Claus reactors are shown in Figures A5.15 and A5.16 in Appendix A5.A. Similar to the first reactor, the temperature profiles of the second and third reactor mimic the respective conversion profile of each reactor which highlights the equilibrium behaviour of the reactions occurring.

Sulfur condensation

In order to recover the elemental sulfur formed in each of the Claus reactors, a sulfur recovery unit consisting of a partial condenser and a flash tank is found after each reactor. The partial condenser is used to reduce the temperature of the reactor effluent to the dew point of the elemental sulfur. This forms a vapour-liquid mixture with a sulfur rich liquid phase which is separated from the vapour in a flash tank. The flash tanks are assumed to operate adiabatically at the same temperature of the preceding flash tank. The operation of the partial condensers and flash tanks are modelled using AspenPlus. Due to the lack of thermodynamic and physical data for S_6, AspenPlus was used to predict these properties based on the molecular structure of S_6. This allows for the vapour-liquid equilibrium phenomena occurring within the condensers and flash tanks to be adequately modelled and provide reliable results.

For a Claus process containing three catalytic reactors, the operating temperature for the three partial condensers (air coolers) are 177°C, 149°C and 132°C according to literature [2]. The decreasing trend in the operating temperature for the condensers is due to the fact that the proportion of S_6 entering each subsequent condenser decreases. Using the literature specified operating temperatures for the partial condensers, the recoveries of the S_6 in the liquid stream exiting the flash are 98%, 99% and 95%. This shows that the literature determined operating temperatures achieve the desired separation. It must be noted that a small proportion of water is condensed into the liquid phase along with the elemental sulfur.

As previously shown, the conversion achieved in the primary reactor is greater than the secondary reactor which in turn is larger than the tertiary reactor. This implies that the amount of S_6 produced in each reactor follows a similar trend. Combining the S_6 produced by each reactor with the corresponding recovery of S_6 in each sulfur recovery unit results in the S_6 recovered in the first, second and third flash tanks being 34.1 kmol/h, 3.67 kmol/h and 0.880 kmol/h respectively. These predominantly sulfur streams are combined in a mixture to form the 38.6 kmol/h liquid sulfur product which contains 92% S_6 and 8% water on a molar basis. This mixed sulfur product exits Area 5 to Area 6 for storage at 173°C and 154 kPa. In order to determine the exiting temperature of the sulfur product, the flowrate and temperature of each stream being mixed is accounted for while considering the heat released due to mixing.

A key issue related to the sulfur recovery system is the solidification of sulfur within the system leading to blockages. This is problematic because it restricts the flow of material and thus reduces the economic benefit of the process and could potentially lead to various safety issues [14]. There is potential for these blockages to occur within both the partial condenser and the flash tank. Therefore, both units need to be adequately designed to prevent these blockages from occurring. For steady operation of the process, blockages are prevented by constructing the partial condensers and flash tanks on an inclined plane in order to prevent the pooling of liquid sulfur within these units.

However, the potential for the solidification of liquid sulfur during start-up and shutdown is much greater due to the unsteady state nature of the process during these times. The way to address the sulfur solidification during these periods is dependent on the time taken for start-up and shutdown. For short term start-up or shutdown (3 to 5 days), sulfur crusting is prevented by continuously blowing nitrogen through the system [15]. For long term start-up and shutdown, the sulfur present in the condensers and flash tanks is removed by blowing hot gas through the system to ensure no liquid sulfur remains in the system [15].

Pressure drop across the system

As previously outlined, the pressure drop across each reactor is determined using the Ergun equation as shown by Equation A5.12. The pressure drop across the reactor is strong function of the reactor diameter and hence the length to diameter ratio of the reactor. The optimal length to diameter ratio for all three Claus reactors is assumed to be 3:1 [16]. Therefore, the pressure drop across the primary, secondary and tertiary reactors are 0.51 kPa, 0.52 kPa and 0.69 kPa respectively. Figure A5.4 outlines the linear nature of the pressure drop across the first reactor with Figures A5.17 and A5.18, in Appendix A5.A, showing similar relationships for the second and third reactors respectively.

The pressure drop across the three heat exchangers and the partial condensers is assumed to be 10 kPa [13]. In addition to this, a 20 kPa pressure drop across the adiabatic flash tanks and the isobaric operation of the mixer are assumed [16]. This results in a total pressure drop across the overall process of 141 kPa and thus the feed, from Area 4, to the process must be 295 kPa in order to provide Area 6 with a tail gas at 154 kPa.

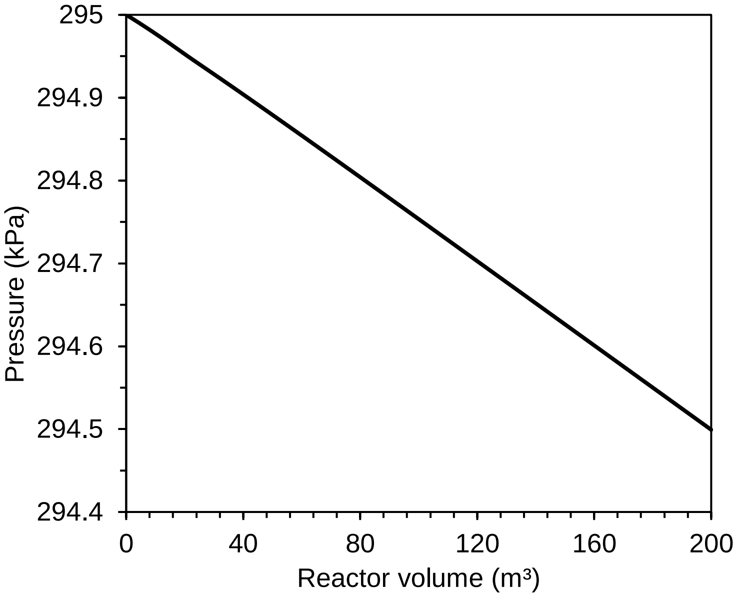


Figure A5.4: Pressure profile as a function of reactor volume for the primary Claus reactor

Catalyst end of life conditions

The aforementioned reactor model used to design the reactor makes use of the given kinetic data and rate equations. This data for the activated alumina catalyst does not account for catalyst deactivation and thus only models ideal operation of the reactor. In reality, there are several mechanisms for catalyst deactivation such as fouling, poisoning, sintering or thermal degradation [6]. Catalyst poisoning is a result of liquid sulfur condensing within the reactor and settling in the catalyst pores. This reduces the rate of mass transfer and thus reduces the catalyst activity [17]. The reactor system is designed to prevent this from occurring by ensuring the reactor effluent is a vapour. However, sulfur condensation may occur during the start-up and shutdown or any other periods of unsteady state operation.

If catalyst deactivation occurs, the conversion achieved would decrease, impacting the ability of the system to achieve the required H_2S and SO_2 content specifications. Therefore, the system needs to be adjusted to prevent the effects of catalyst deactivation negatively impacting the outputs of the process. The first option is to overdesign the reactors by increasing the volume and catalyst required by each reactor. This increases the capital investment required and does not directly address the impact of catalyst deactivation. Therefore, the regeneration of the alumina catalyst every four year is preferred, even though it requires complete shutdown of the process and purging of the reactors [18]. The regeneration of the catalyst allows the catalyst to be reused by increasing its catalyst activity [19]. Therefore, the number and volume of reactors required for end life catalyst conditions is the same as normal operating conditions. However, the economic impact of regenerating the catalyst needs to be evaluated.

4. Model Optimisation and Sensitivity analysis

Analysis of Sensitivity of Primary Claus reactor

The outputs from Section 3 describe a feasible process which achieves the design objectives for Area 5. However, many of the process variables such as the inlet temperature to each Claus reactor and the aspect ratio of each reactor were assumed from literature. In addition to this, the feed to the process was not of a specific ratio. Although the proposed base case achieves the design objectives, by using assumed literature values for various parameters, the performance of the units found in the area can be improved. In order to optimise the performance of any unit found within Area 5 a sensitivity analysis into the impact of specific parameters must be conducted.

The use of a set of sensitivity analyses is used to determine if there are any opportunities for optimisation since it will highlight specific operating conditions at which performance is optimal. This allows an economic comparison to be made between the base and optimised cases to show the potential gain of operating at optimal conditions. The main unit operations found in Area 5 are the three catalytic Claus reactors used to convert H_2S and SO_2 to elemental sulfur. As shown previously, the conversion of H_2S and SO_2 achieved by the primary Claus packed-bed reactor is significantly higher compared to the second and third reactors. Therefore, the optimisation of the first reactor would have the greatest impact the performance of the process found in Area 5.

There are multiple parameters which impact the performance of the first Claus reactor. However, the performance of the reactor is a stronger function of certain parameters and therefore the parameters required to be optimised are the inlet composition and temperature for maximum sulfur generation and the pressure drop across the reactor. The first step in the optimisation process is to determine the impact of these parameters on reactor performance in a sensitivity analysis. All sensitivity analyses are performed on the previously presented base case in order to determine the impact of the investigated parameters on the proposed system with all other parameters remaining constant.

Impact of inlet temperature

The inlet temperature to the reactor strongly impacts the conversion of H_2S which directly relates to the amount of the sulfur generated within the reactor. The exothermic and equilibrium limited nature of the chemical reactions occurring within the Claus reactor implies that an optimal inlet temperature exists at which the equilibrium conversion and rate of reaction are maximised. However, since S_6 is being produced along the reactor volume, if the reactor inlet temperature is not high enough there will be liquid formed within the reactor which decreases the activity of the catalyst. The formation of liquid within the reactor decreases catalyst activity by prohibiting the mass transfer of reactants and product within the pores of the alumina catalyst. Hence, a key aspect of this sensitivity analysis is determining the minimum inlet temperature at which no liquid formation occurs within the reactor, which was found to be

238°C. In order to determine the minimum inlet temperature it was assumed that if the reactor effluent was found to be completely vapour, there was no formation of liquid within the packed-bed reactor.

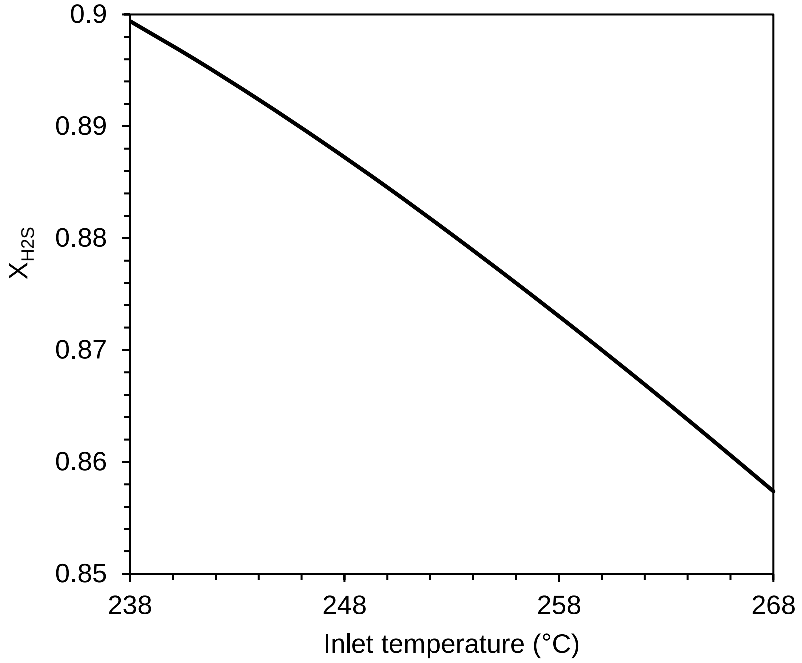


Figure A5.5: Impact of inlet temperature on the conversion of H_2S in the first Claus reactor

Figure A5.5, shows the negative impact of increasing the temperature from 238°C to 268°C on the conversion of H_2S. Figure A5.5 shows that the highest conversion of H_2S, and thus the maximum sulfur generation, occurs at the minimum inlet temperature of 238°C which is in line with operating temperatures presented in literature [1]. In addition to improving the performance of the reactor, the reduction in the feed temperature reduces the outlet temperature and therefore less cooling is required by the partial condenser found directly after the first reactor.

Impact of H_2S to SO_2 feed ratio

To ensure the tail gas exiting Area 5 conforms to the H_2S and SO_2 composition specifications, the feed is required to contain a stoichiometric excess of SO_2 in comparison to H_2S. This stoichiometric excess allows for a higher conversion of H_2S which has a tighter specification in the exiting tail gas. Therefore, the highest ratio of H_2S investigated is a 2:1 feed ratio which corresponds to a stochiometric feed, with the reaction stoichiometry shown in equation A5.1. The lowest ratio investigated is a 1.5:1 feed ratio because after this point the amount unreacted of SO_2 present in the tail gas becomes so large such that the maximum SO_2 concentration specification cannot be met. In order to vary the feed composition exiting the Claus furnace, in Area 4, the air flowrate to the furnace is varied. This impacts the performance of the furnace and thus the flowrates of other key components, such as COS and water, are altered in order to manipulate the feed ratio of H_2S to SO_2. Using multiple feeds of varying feed ratios produced by Area 4 in favour of manually manipulating the feed ratio, increases the validity of the results produced by the sensitivity study because it makes use of potential feeds. Figure A5.6 indicates that as the feed ratio of H_2S to SO_2 increases, the conversion of H_2S decreases in a generally linear trend. Additionally it shows that a feed ratio of 1.5:1 of H_2S to SO_2 yields the highest conversion of H_2S and thus the highest production rate of liquid sulfur.

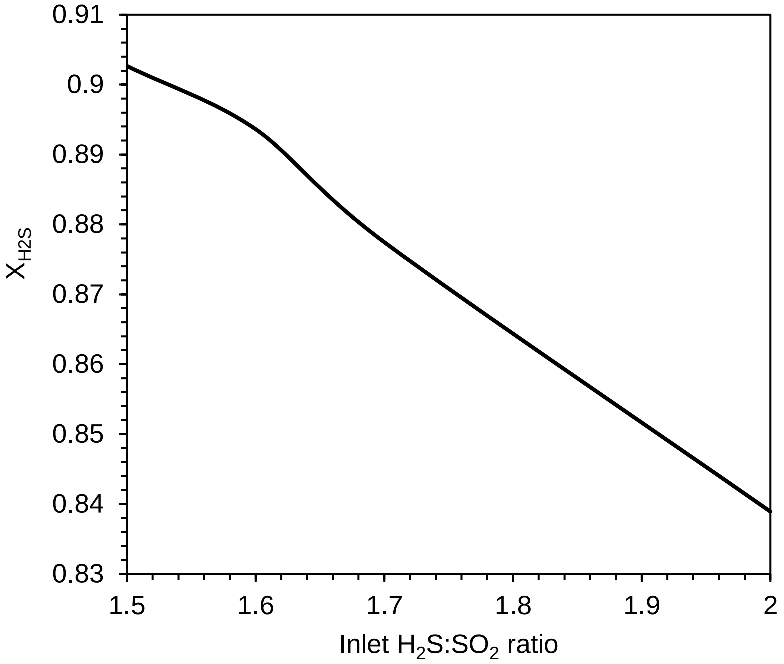


Figure A5.6: Impact of inlet H_2S to SO2 ratio on the conversion of H_2S in the first Claus reactor

Impact of aspect ratio

The final parameter which needs to be optimised is the pressure drop across the reactor. Since the reactions occurring within the Claus reactor are in the gas phase, the total pressure of the system impacts the rate of both reactions, as shown by Equations A5.3 and A5.4. The pressure drop across the reactor is modelled using the Ergun equation, shown in Equation A5.12. Equation A5.12 highlights that the parameters available to manipulate to reduce the pressure drop across the process are the cross-sectional area of the cylindrical packed-bed reactor and the superficial mass velocity. The superficial mass velocity is the total mass flowrate per area of reactor. Therefore, the cross-sectional area of the reactor strongly impacts the pressure drop across it. The cross-sectional area of the reactor is determined using the reactor diameter and thus the pressure drop across the reactor is a function of the aspect ratio of the reactor.

According to literature, the ideal length to diameter ratio for a reactor is between 2 and 6 [13]. Hence, Figure A5.7 shows the relationship between the aspect ratio and the pressure drop across the reactor for length to diameter ratios from 2 to 6. Figure A5.7 highlights that increasing the aspect ratio, and thus decreasing the reactor diameter, increases the pressure drop across the reactor. This trend is observed because by decreasing the diameter of the cylindrical reactor, the resistance of fluid flow through the packed bed increases, which leads to the pressure drop across the reactor increasing. The pressure drop across the packed bed needs to be minimised to ensure optimal performance of the reactor. Therefore, a length to diameter ratio of 2 is optimal to reduce the pressure drop across the reactor, as shown by Figure A5.7.

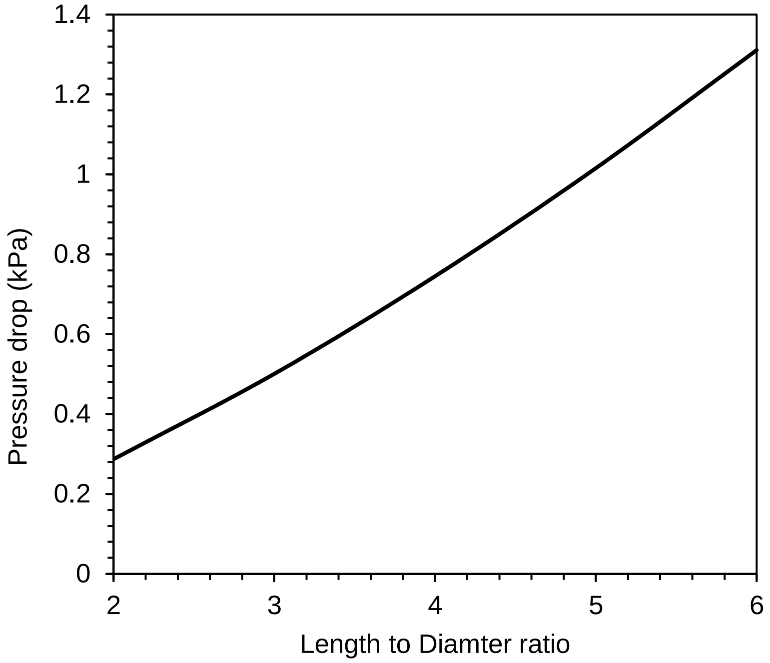


Figure A5.7: Impact of aspect ratio of the pressure drop across the first Claus reactor

Impact of sensitivity analysis on control of the Primary Claus reactor

The sensitivity analyses conducted highlights how the operating parameters can be adjusted to improve the performance of the primary Claus reactor. In addition to this, the analyses highlight how sensitive reactor performance is to the inlet temperature and composition, as shown by Figures A5.5 and A5.6 respectively. Figure A5.5 shows that if the inlet temperature to the reactor increases to 268°C from the optimal 238°C, the conversion of the reactor decreases from 89.9% to 85.7% Similarly, Figure A5.6 indicates a decrease in conversion from 90.2% to 83.9 if the feed ratio of H_2S to SO_2 is increased from 1.5:1 to 2:1. This shows that any deviation from the optimal operating conditions will strongly impact the performance of the primary Claus reactor. Therefore, in order to maintain the desired performance of the reactor the inlet composition of the primary Claus reactor need to be tightly controlled.

Optimisation of Primary Claus reactor

The optimisation of the base case primary Claus reactor was completed considering the results of the sensitivity analyses. The aim of the optimisation process was to minimise the capital and operating costs related to the primary Claus reactor while considering the safety and operability of the process. The sensitivity analyses conducted on parameters which strongly impact the operation of the reactor provides an insight into how the reactor can be improved. The optimal values for the reactor inlet temperature, inlet composition and aspect ratio determined in the sensitivity analyses are implemented within the existing base in order to develop an optimised case. The impact of implementing these changes are compared on an economic basis to determine if optimising these variables result in significant cost reductions.

The optimisation was conducted such that the conversion achieved by the first reactor would remain the same with the optimisation resulting in either a reduction in energy or material requirements. This is because the conversion achieved by the base case reactor is sufficient to meet the requirements for the tail gas exiting to Area 6. Therefore, the optimisation of the first Claus reactor would not impact the operation of the remaining two Claus reactors in the process. Therefore, to make the economic comparison between the base and optimised cases not all the equipment found in the process need to be accounted for. Only the units which are directly linked to the operation of the first Claus reactor are costed. Hence, the capital costs of the primary Claus reactor, the first heat exchanger used to heat the first reactor feed and cool the reactor effluent, the second heat exchanger which also cools the first reactor product and heats the second reactor feed, the third heat exchanger which further cools the first reactor product and heats the third reactor feed and finally the air cooler used to partially condense the first reactor product are considered. In addition to these costs, the operating cost related to the air cooler is considered since the duty required by the air cooler is impacted by the optimisation. The detailed methods used to size and cost these pieces of equipment can be found in Appendices A5-B and A5-C.

The implementation of the 238°C inlet temperature, the 1.5:1 H_2S to SO_2 feed ratio and a reactor aspect ratio of 2 strongly impacts the sizing and operability requirements of the units linked to the operation of the first Claus reactor. Table A5.1 below demonstrates the differences in the equipment specifications for the base and optimised cases.

Table A5.1: Comparison of the equipment specification required by the base and optimised cases

Unit	**Specification**	**Base case**	**Optimised Case**
RX-501	Volume (m^3)	200	94
HX-501	Heat transfer area (m^2)	218	295
HX-502	Heat transfer area (m^2)	130	168
HX-503	Heat transfer area (m^2)	183	247
HX-504	Heat transfer area (m^2)	52	10.2
HX-504	Duty (kW)	958	653

Summary of base case and optimised case

Table A5.1 shows that other than the volume of the reactor and the size and duty of the air cooler (HX-504), the equipment size requirements of the base case are lower than those for the optimised case. However, in order to determine if the optimisation of the Claus reactor has an overall favourable outcome, the related capital and operating cost for the base and optimised cases are compared in Table A5.2.

Table A5.2: Summary of capital and operating costs for the base and optimised cases

Unit	**Base case cost**	**Optimised case cost**
Capital costs (R)		
RX-501	11 800 000	4 070 000
HX-501	2 004 000	2 380 000
HX-502	1 570 000	1 760 000
HX-503	1 830 000	2 150 000
HX-504	1 140 000	93 000
TOTAL	17 200 000	10 450 000
Operating costs (R/year)		
HX-504	84 400	57 600

The summary of the base and optimised costs shows that, although the implementing the optimised variables increases the capital requirements for the first three heat exchangers, the optimisation of the previously mentioned parameters makes for a more economically feasible process. The implementation of the optimised reactor parameters resulted in a R26 800 per year reduction in operating costs as well as a R6 750 000 saving in capital costs. This shows that the initial base case can be improved upon and thus the optimised parameters will be implemented moving forward.

5. Specification of equipment

Datasheet of Primary Claus reactor

Table A5.3: Datasheet for primary Claus reactor

Group Q: Sour Natural Gas Processing							
Location: Mossel Bay, Western Cape				Equipment Item:		RX-501	
Job: Claus Reactor Datasheet				Sheet No.			
No.	Vessel Design Data		Units	Services	Schedule	Size	Units
1	Orientation	Vertical		Gas inlet	40	6	in
2	Capacity	94	m^3	Gas outlet	40	8	in
3	Diameter	3.91	m	Manhole	40	28	in
4	Length	11.7	m	Thermocouple	40	0.75	in
5	Operating Pressure	2.95	bar	Pressure gauge	40	0.75	in
6	Design Pressure	6.35	bar	Spray nozzle	40	1	in
7	Pressure Drop	0.362	kPa				
8	Operating Temperature	309	°C				
9	Design Temperature	334	°C				
10	Bed Properties						
11	H_2S to SO_2	1.5:1		Voidage		0.4	
12	Bed length	7.82	m	Catalyst density		769	kg/m^3
13	Catalyst Diameter	0.001	m	Catalyst weight		72	ton
14	Catalyst type	Activated Alumina					
15	Vapour Properties						
16	Constituents	H_2S, SO_2, S_6, H_2O, COS, CO_2, O_2, N_2, H_2					
17	Flammability	High					
18	Toxicity	High					
19	Corrosivity	Low					
20	Construction Requirements						
21	Material of Construction			Carbon steel			
22	Insulation Material			85% magnesia			
23	Wall Thickness			0.002			m
24	Insulation Thickness			0.15			m
25	End type			Hemispherical			
26	Additional notes:						

Drawing of Primary Claus reactor

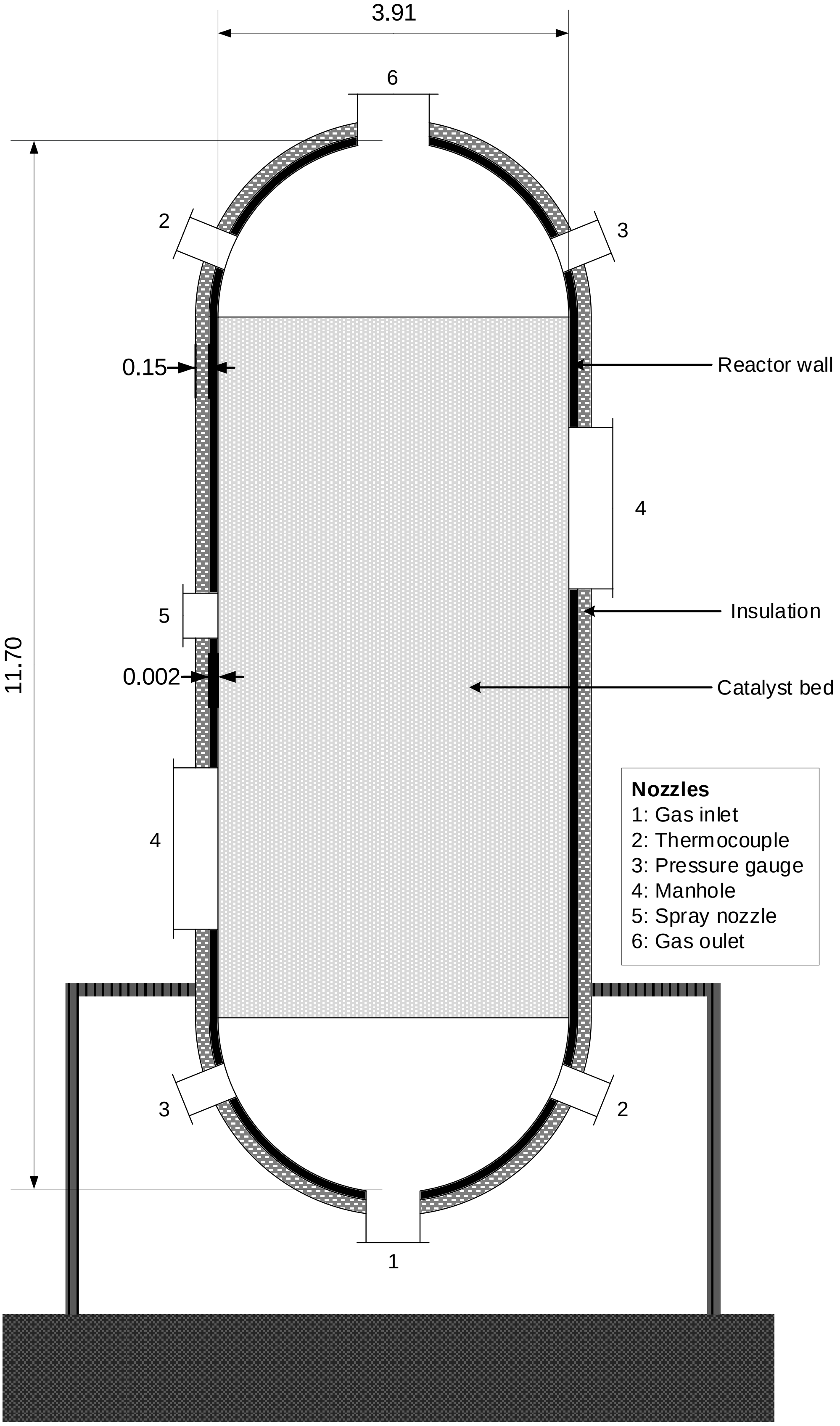


Figure A5.8: Sketch of the primary Claus reactor

Equipment list for Area 5

Table A5.4: Area 5 Equipment list

Label	Description	Specifications
Reactors		
RX-501	Primary Claus reactor	Type: Packed bed, Orientation: Vertical, Volume: 94 m^3, L: 11.7 m, Catalyst weight: 72 ton, D: 3.91 m, DP: 6.35 bar, OT: 309°C, DT: 334°C, Catalyst: Activated alumina, MOC: Carbon steel
RX-502	Secondary Claus reactor	Type: Packed bed, Orientation: Vertical, Volume: 155 m^3, L: 16.1 m, Catalyst weight: 119 ton, D: 4.04 m, DP: 5.65 bar, OT: 221°C, DT: 246°C, Catalyst: Activated alumina, MOC: Carbon steel
RX-503	Tertiary Claus reactor	Type: Packed bed, Orientation: Vertical, Volume: 130 m^3, L: 15.2 m, Catalyst weight: 100 ton, D: 3.81 m, DP: 5.24 bar, OT: 205°C, DT: 230°C, Catalyst: Activated alumina, MOC: Carbon steel
Heat exchangers		
HX-501	Primary heat exchanger	Type: Shell and tube, Area = 295 m^2, Number of tube passes: 1, Tube Inlet T: 200°C, Tube Outlet T: 235°C, Shell Inlet T: 309°C, Shell Outlet T: 283°C, Tube-side: Process fluid, DP: 6.45 bar, OT: 255 °C, DT: 280 °C, MOC: Carbon steel Shell-side: Process fluid, DP: 6.45 bar, OT: 309°C, DT: 334°C, MOC: Carbon steel Operation: Counter-current, Pressure drop: 0.1 bar, Duty: 490 kW
HX-502	Secondary heat exchanger	Type: Shell and tube, Area = 168 m^2, Number of tube passes: 1, Tube Inlet T: 177°C, Tube Outlet T: 216°C, Shell Inlet T: 283°C, Shell Outlet T: 264°C, Tube-side: Process fluid, DP: 6.25 bar, OT: 216 °C, DT: 241 °C, MOC: Carbon steel Shell-side: Process fluid, DP: 6.25 bar, OT: 283°C, DT: 307°C, MOC: Carbon steel Operation: Counter-current, Pressure drop: 0.1 bar, Duty: 315 kW
HX-503	Tertiary heat exchanger	Type: Shell and tube, Area = 247 m^2, Number of tube passes: 1, Tube Inlet T: 149°C, Tube Outlet T: 204°C, Shell Inlet T: 264°C, Shell Outlet T: 234°C, Tube-side: Process fluid, DP: 6.15 bar, OT: 204 °C, DT: 229 °C, MOC: Carbon steel Shell-side: Process fluid, DP: 6.15 bar, OT: 264°C, DT: 289°C, MOC: Carbon steel Operation: Counter-current, Pressure drop: 0.1 bar, Duty: 434 kW
HX-504	First air cooler	Type: Double pipe, Area = 10.2 m^2, Number of tube passes: 1, Tube Inlet T: 25°C, Tube Outlet T: 35°C, Shell Inlet T: 234°C, Shell Outlet T: 177°C, Tube-side: Air, DP: 6.05 bar, OT: 35°C, DT: 60°C, MOC: Carbon Steel Shell-side: Process fluid, DP: 6.05 bar, OT: 234°C, DT: 259 °C, MOC: Carbon Steel Operation: Counter current, Pressure drop: 0.1 bar, Utility: Air, Duty: 653 kW

HX-505	Second air cooler	Type: Double pipe, Area = 11.6 m^2, Number of tube passes: 1, Tube Inlet T: 25°C, Tube Outlet T: 35°C, Shell Inlet T: 221°C, Shell Outlet T: 149°C, Tube-side: Air, DP: 5.64 bar, OT: 35°C, DT: 60°C, MOC: Carbon Steel Shell-side: Process fluid, DP: 5.64 bar, OT: 221°C, DT: 246 °C, MOC: Carbon Steel Operation: Counter current, Pressure drop: 0.1 bar, Utility: Air, Duty: 652 kW
HX-506	Third air cooler	Type: Double pipe, Area = 11.8 m^2, Number of tube passes: 1, Tube Inlet T: 25°C, Tube Outlet T: 35°C, Shell Inlet T: 205°C, Shell Outlet T: 132°C, Tube-side: Air, DP: 5.23 bar, OT: 35°C, DT: 60°C, MOC: Carbon Steel Shell-side: Process fluid, DP: 5.23 bar, OT: 205°C, DT: 230 °C, MOC: Carbon Steel Operation: Counter current, Pressure drop: 0.1 bar, Utility: Air, Duty: 591 kW
Flash tanks		
FT-501	Primary flash tank	Orientation: Vertical, Length: 2.45 m, Diameter: 7.34 m, OT: 177°C, DT: 202°C, OP: 4.25 bar, DP: 5.95 bar, Pressure drop: 0.2 bar, MOC: Carbon steel
FT-502	Secondary flash tank	Orientation: Vertical, Length: 2.49 m, Diameter: 7.47 m, OT: 149°C, DT: 174°C, OP: 3.84 bar, DP: 5.54 bar, Pressure drop: 0.2 bar, MOC: Carbon steel
FT-503	Tertiary flash tank	Orientation: Vertical, Length: 2.59 m, Diameter: 7.76 m, OT: 132°C, DT: 157°C, OP: 3.43 bar, DP: 5.13 bar, Pressure drop: 0.2 bar, MOC: Carbon steel

6. Information required by the Process Coordinator

Process description

The 948 kmol/h tail gas at 200°C and 3.05 bar is fed to the primary process heat exchanger, from Area 4 and contains 14.01% and 9.51% of H_2S and SO_2 on a molar basis. The primary process heat exchanger makes use of the primary Claus reactor effluent in order to heat the feed to 235°C. The primary Claus reactor achieves an 88% conversion of H_2S and produces an effluent stream at 309°C and 2.95 bar which used to heat the reactor feed in the primary process heat exchanger. This effluent stream is then passed through the secondary and tertiary process heat exchangers, in order to heat the feeds to the secondary and tertiary Claus reactors, and exits the tertiary heat exchanger at 234°C. In order to condense the elemental sulfur formed, the effluent stream is cooled to 177°C and 2.55 bar by the primary air cooler. The vapour-liquid mixture exiting the first air cooler is fed to the primary flash tank which separates the sulfur rich liquid from the remaining tail gas. The tail gas exiting the top of the flash tank at 177°C and 2.35 bar contains 1.78% and 3.56% of H_2S and SO_2 respectively on a molar basis. This vapour is heated in the secondary process heat exchanger to 216°C before entering the secondary Claus reactor.

A 67% conversion of H_2S is achieved in this secondary Claus reactor to produce an effluent stream at 221°C and 2.24 bar. The reactor effluent is cooled to 149°C by the second air cooler with the exiting vapour-liquid mixture entering the secondary flash tank. The secondary flash tank produces a sulfur rich liquid and a vapour with both at 149°C and 1.94 bar. The vapour exiting the secondary flash tank contains 0.6% and 3% H_2S and SO_2 on a molar basis. Therefore, a tertiary Claus reactor is required to meet the process specifications and thus the vapour exiting secondary flash is heated to 204°C before entering the tertiary Claus reactor. The tertiary Claus reactor converts 51% of the H_2S in the feed to produce a 205°C reactor effluent at 1.83 bar. In order to separate any elemental sulfur present, the tertiary reactor effluent is cooled to 132°C using the third air cooler. The vapour-liquid mixture exiting the third air is fed to the tertiary flash which produces a vapour containing 0.29% and 2.84% of H_2S and SO_2 on a molar basis. This 880 kmol/h tail gas, at 132°C and 1.53 bar, is fed to Area 6 for further processing. The liquid sulfur streams exiting the primary, secondary and tertiary flash tanks are mixed together to form a 35 kmol/h liquid sulfur product at 173°C and 1.53 bar which is sent to Area 6 for storage.

Process flow diagram

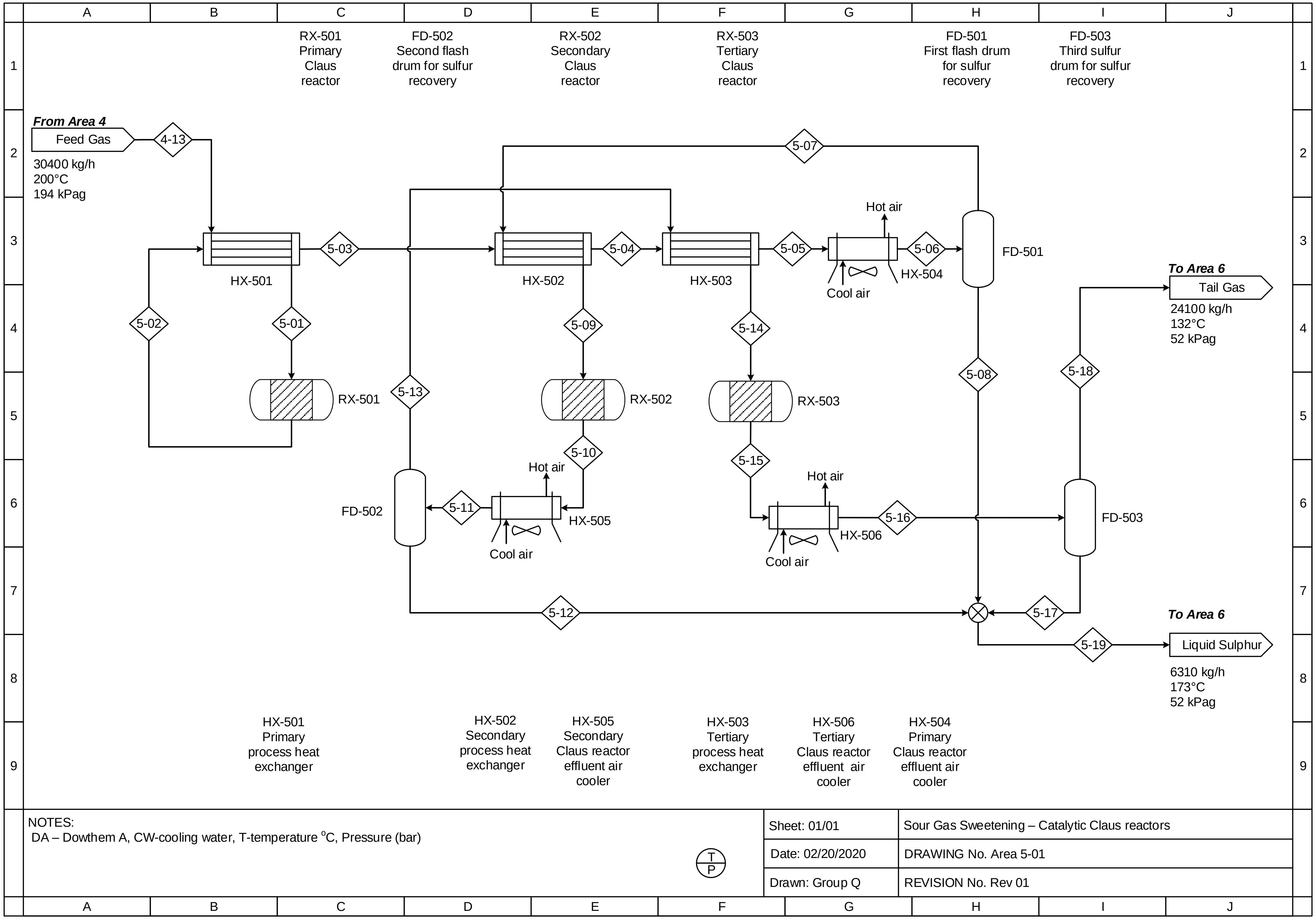


Figure A5.9: Process flow diagram for the process found in Area 5

Stream table

Table A5.5: Summary of mass flow for stream 4-13 to 5-9

Stream	**4-13**	**5-1**	**5-2**	**5-3**	**5-4**	**5-5**	**5-6**	**5-7**	**5-8**	**5-9**
Stream Descriptor										
From	Area 4	Primary heat exchanger	Primary Claus reactor	Primary heat exchanger	Secondary heat exchanger	Tertiary heat exchanger	First air cooler	Primary flash tank	Primary flash tank	Secondary heat exchanger
To	Primary heat exchanger	Primary Claus reactor	Primary heat exchanger	Secondary heat exchanger	Tertiary heat exchanger	First air cooler	Primary flash tank	Secondary heat exchanger	Liquid sulfur product mixer	Secondary Claus reactor
Pressure(bara)	3.05	2.95	2.95	2.85	2.75	2.65	2.55	2.35	2.35	2.25
Temperature(°C)	200	255	309	283	264	234	177	177	177	216
Phase	V	V	V	V/L	V/L	V/L	V/L	V	L	V
Mass Flow - kg/h (g/h) ((mg/h))										
Selexol	-	-	-	-	-	-	-	-	-	-
Oxygen	10	10	10	10	10	10	10	10	((415))	10
Nitrogen	15539	15539	15539	15539	15539	15539	15539	15539	(608)	15539
Carbon Dioxide	2469	2469	2470	2470	2470	2470	2470	2470	(329)	2470
Hydrogen Sulfide	4526	4526	540	540	540	540	540	540	(189)	540
Methane	-	-	-	-	-	-	-	-	-	-
Ethane	-	-	-	-	-	-	-	-	-	-
Propane	-	-	-	-	-	-	-	-	-	-
n-Butane	-	-	-	-	-	-	-	-	-	-
i-Butane	-	-	-	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-	-	-	-
n-Hexane	-	-	-	-	-	-	-	-	-	-
n-Heptane	-	-	-	-	-	-	-	-	-	-
n-Octane	-	-	-	-	-	-	-	-	-	-
Water	2040	2040	4147	4147	4147	4147	4147	4108	39	4108
SO_2	5775	5775	2028	2028	2028	2028	2028	2026	2	2026
Elemental Sulfur	13	13	5640	5640	5640	5640	5640	105	5535	105
Carbon Monoxide	6	6	6	6	6	6	6	6	((229))	6
COS	1	1	-	-	-	-	-	-	-	-
Hydrogen	(50)	(50)	(50)	(50)	(50)	(50)	(50)	(50)	((0))	(50)
TEG	-	-	-	-	-	-	-	-	-	-
Total	30380	30380	30380	30380	30380	30380	30380	24803	5577	24803

Table A5.6: Summary of mass composition for streams 4-13 to 5-9

Stream	**4-13**	**5-1**	**5-2**	**5-3**	**5-4**	**5-5**	**5-6**	**5-7**	**5-8**	**5-9**
Stream Descriptor										
From	Area 4	Primary heat exchanger	Primary Claus reactor	Primary heat exchanger	Secondary heat exchanger	Tertiary heat exchanger	First air cooler	Primary flash tank	Primary flash tank	Secondary heat exchanger
To	Primary heat exchanger	Primary Claus reactor	Primary heat exchanger	Secondary heat exchanger	Tertiary heat exchanger	First air cooler	Primary flash tank	Secondary heat exchanger	Liquid sulfur product mixer	Secondary Claus reactor
Pressure(bara)	3.05	2.95	2.95	2.85	2.75	2.65	2.55	2.35	2.35	2.25
Temperature(°C)	200	255	309	283	264	234	177	177	177	216
Phase	V	V	V	V/L	V/L	V/L	V/L	V	L	V
Mass Composition - wt.% [ppm] [[ppb]]										
Selexol	-	-	-	-	-	-	-	-	-	-
Oxygen	[329]	[329]	[329]	[329]	[329]	[329]	[329]	[403]	[[74]]	[403]
Nitrogen	51.15	51.15	51.15	51.15	51.15	51.15	51.15	62.65	[109]	62.65
Carbon Dioxide	8.13	8.13	8.13	8.13	8.13	8.13	8.13	9.96	[59]	9.96
Hydrogen Sulfide	14.9	14.9	1.78	1.78	1.78	1.78	1.78	2.18	[34]	2.18
Methane	-	-	-	-	-	-	-	-	-	-
Ethane	-	-	-	-	-	-	-	-	-	-
Propane	-	-	-	-	-	-	-	-	-	-
n-Butane	-	-	-	-	-	-	-	-	-	-
i-Butane	-	-	-	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-	-	-	-
n-Hexane	-	-	-	-	-	-	-	-	-	-
n-Heptane	-	-	-	-	-	-	-	-	-	-
n-Octane	-	-	-	-	-	-	-	-	-	-
Water	6.71	6.71	13.65	13.65	13.65	13.65	13.65	16.56	[7075]	16.56
SO_2	19.01	19.01	6.67	6.67	6.67	6.67	6.67	8.17	[312]	8.17
Elemental Sulfur	[430]	[430]	18.56	18.56	18.56	18.56	18.56	[4250]	99.24	[4250]
Carbon Monoxide	[188]	[188]	[188]	[188]	[188]	[188]	[188]	[230]	[[41]]	[230]
COS	[43]	[43]	-	-	-	-	-	-	-	-
Hydrogen	[2]	[2]	[2]	[2]	[2]	[2]	[2]	[2]	[[0]]	[2]
TEG	-	-	-	-	-	-	-	-	-	-
Total	100	100	100	100	100	100	100	100	100	100

Table A5.7: Summary of molar flows for streams 4-13 to 5-9

Stream	**4-13**	**5-1**	**5-2**	**5-3**	**5-4**	**5-5**	**5-6**	**5-7**	**5-8**	**5-9**
Stream Descriptor										
From	Area 4	Primary heat exchanger	Primary Claus reactor	Primary heat exchanger	Secondary heat exchanger	Tertiary heat exchanger	First air cooler	Primary flash tank	Primary flash tank	Secondary heat exchanger
To	Primary heat exchanger	Primary Claus reactor	Primary heat exchanger	Secondary heat exchanger	Tertiary heat exchanger	First air cooler	Primary flash tank	Secondary heat exchanger	Liquid sulfur product mixer	Secondary Claus reactor
Pressure(bara)	3.05	2.95	2.95	2.85	2.75	2.65	2.55	2.35	2.35	2.25
Temperature(°C)	200	255	309	283	264	234	177	177	177	216
Phase	V	V	V	V/L	V/L	V/L	V/L	V	L	V
Mole Flow -kmol/h (mol/h) ((mmol/h))										
Selexol	-	-	-	-	-	-	-	-	-	-
Oxygen	(312)	(312)	(312)	(312)	(312)	(312)	(312)	(312)	((13))	(312)
Nitrogen	555	555	555	555	555	555	555	555	(22)	555
Carbon Dioxide	56	56	56	56	56	56	56	56	((7471))	56
Hydrogen Sulfide	133	133	16	16	16	16	16	16	((5543))	16
Methane	-	-	-	-	-	-	-	-	-	-
Ethane	-	-	-	-	-	-	-	-	-	-
Propane	-	-	-	-	-	-	-	-	-	-
n-Butane	-	-	-	-	-	-	-	-	-	-
i-Butane	-	-	-	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-	-	-	-
n-Hexane	-	-	-	-	-	-	-	-	-	-
n-Heptane	-	-	-	-	-	-	-	-	-	-
n-Octane	-	-	-	-	-	-	-	-	-	-
Water	113	113	230	230	230	230	230	228	2	228
SO_2	90	90	32	32	32	32	32	32	(27)	32
Elemental Sulfur	(204)	(204)	29	29	29	29	29	(684)	29	(684)
Carbon Monoxide	(204)	(204)	(204)	(204)	(204)	(204)	(204)	(204)	((8))	(204)
COS	(22)	(22)	-	-	-	-	-	-	-	-
Hydrogen	(25)	(25)	(25)	(25)	(25)	(25)	(25)	(25)	((0))	(25)
TEG	-	-	-	-	-	-	-	-	-	-
Total	948	948	919	919	919	919	919	887	31	887

Table A5.8: Summary of molar compositions for stream 4-13 to 5-9

Stream	**4-13**	**5-1**	**5-2**	**5-3**	**5-4**	**5-5**	**5-6**	**5-7**	**5-8**	**5-9**
Stream Descriptor										
From	Area 4	Primary heat exchanger	Primary Claus reactor	Primary heat exchanger	Secondary heat exchanger	Tertiary heat exchanger	First air cooler	Primary flash tank	Primary flash tank	Secondary heat exchanger
To	Primary heat exchanger	Primary Claus reactor	Primary heat exchanger	Secondary heat exchanger	Tertiary heat exchanger	First air cooler	Primary flash tank	Secondary heat exchanger	Liquid sulfur product mixer	Secondary Claus reactor
Pressure(bara)	3.05	2.95	2.95	2.85	2.75	2.65	2.55	2.35	2.35	2.25
Temperature(°C)	200	255	309	283	264	234	177	177	177	216
Phase	V	V	V	V/L	V/L	V/L	V/L	V	L	V
Mole Composition - wt.% [ppm] [[ppb]]										
Selexol	-	-	-	-	-	-	-	-	-	-
Oxygen	[329]	[329]	[340]	[340]	[340]	[340]	[340]	[352]	[[418]]	[352]
Nitrogen	58.53	58.53	60.39	60.39	60.39	60.39	60.39	62.5	[700]	62.5
Carbon Dioxide	5.92	5.92	6.11	6.11	6.11	6.11	6.11	6.32	[241]	6.32
Hydrogen Sulfide	14.01	14.01	1.72	1.72	1.72	1.72	1.72	1.78	[179]	1.78
Methane	-	-	-	-	-	-	-	-	-	-
Ethane	-	-	-	-	-	-	-	-	-	-
Propane	-	-	-	-	-	-	-	-	-	-
n-Butane	-	-	-	-	-	-	-	-	-	-
i-Butane	-	-	-	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-	-	-	-
n-Hexane	-	-	-	-	-	-	-	-	-	-
n-Heptane	-	-	-	-	-	-	-	-	-	-
n-Octane	-	-	-	-	-	-	-	-	-	-
Water	11.95	11.95	25.06	25.06	25.06	25.06	25.06	25.69	7.06	25.69
SO_2	9.51	9.51	3.45	3.45	3.45	3.45	3.45	3.56	[875]	3.56
Elemental Sulfur	[215]	[215]	3.21	3.21	3.21	3.21	3.21	[770]	92.74	[770]
Carbon Monoxide	[215]	[215]	[222]	[222]	[222]	[222]	[222]	[230]	[[264]]	[230]
COS	[23]	[23]	-	-	-	-	-	-	-	-
Hydrogen	[26]	[26]	[27]	[27]	[27]	[27]	[27]	[28]	[[5]]	[28]
TEG	-	-	-	-	-	-	-	-	-	-
Total	100	100	100	100	100	100	100	100	100	100

Table A5.9: Summary of mass flows for streams 5-10 to 5-19

Stream	**5-10**	**5-11**	**5-12**	**5-13**	**5-14**	**5-15**	**5-16**	**5-17**	**5-18**	**5-19**
Stream Descriptor										
From	Secondary Claus reactor	Second air cooler	Secondary flash tank	Secondary flash tank	Tertiary heat exchanger	Tertiary Claus reactor	Third air cooler	Tertiary flash tank	Tertiary flash tank	Liquid sulfur product mixer
To	Second air cooler	Secondary flash tank	Liquid sulfur product mixer	Tertiary heat exchanger	Tertiary Claus reactor	Third air cooler	Tertiary flash tank	Liquid sulfur product mixer	Area 6	Area 6
Pressure(bara)	2.24	2.14	1.94	1.94	1.84	1.83	1.73	1.53	1.53	1.53
Temperature(°C)	221	149	149	149	204	205	132	132	132	173
Phase	V	V/L	L	V	V	V	V/L	L	V	L
Mass Flow - kg/h (g/h) ((mg/h))										
Selexol	-	-	-	-	-	-	-	-	-	-
Oxygen	10	10	((45))	10	10	10	10	((10))	10	((469))
Nitrogen	15539	15539	(64)	15539	15539	15539	15539	(14)	15539	(686)
Carbon Dioxide	2470	2470	(42)	2470	2470	2470	2470	(11)	2470	(381)
Hydrogen Sulfide	179	179	((8258))	179	179	88	88	((1048))	88	(198)
Methane	-	-	-	-	-	-	-	-	-	-
Ethane	-	-	-	-	-	-	-	-	-	-
Propane	-	-	-	-	-	-	-	-	-	-
n-Butane	-	-	-	-	-	-	-	-	-	-
i-Butane	-	-	-	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-	-	-	-
n-Hexane	-	-	-	-	-	-	-	-	-	-
n-Heptane	-	-	-	-	-	-	-	-	-	-
n-Octane	-	-	-	-	-	-	-	-	-	-
Water	4298	4298	8	4290	4290	4338	4338	3	4336	50
SO_2	1687	1687	(206)	1687	1687	1601	1601	(53)	1601	2
Elemental Sulfur	614	614	580	34	34	162	162	141	21	6256
Carbon Monoxide	6	6	((24))	6	6	6	6	((5))	6	((259))
COS	-	-	-	-	-	-	-	-	-	-
Hydrogen	(50)	(50)	((0))	(50)	(50)	(50)	(50)	((0))	(50)	((0))
TEG	-	-	-	-	-	-	-	-	-	-
Total	24803	24803	589	24215	24215	24214	24214	144	24071	6309

Table A5.10: Summary of mass compositions for streams 5-10 to 5-19

Stream	**5-10**	**5-11**	**5-12**	**5-13**	**5-14**	**5-15**	**5-16**	**5-17**	**5-18**	**5-19**
Stream Descriptor										
From	Secondary Claus reactor	Second air cooler	Secondary flash tank	Secondary flash tank	Tertiary heat exchanger	Tertiary Claus reactor	Third air cooler	Tertiary flash tank	Tertiary flash tank	Liquid sulfur product mixer
To	Second air cooler	Secondary flash tank	Liquid sulfur product mixer	Tertiary heat exchanger	Tertiary Claus reactor	Third air cooler	Tertiary flash tank	Liquid sulfur product mixer	Area 6	Area 6
Pressure(bara)	2.24	2.14	1.94	1.94	1.84	1.83	1.73	1.53	1.53	1.53
Temperature(°C)	221	149	149	149	204	205	132	132	132	173
Phase	V	V/L	L	V	V	V	V/L	L	V	L
Mass Composition - wt.% [ppm] [[ppb]]										
Selexol	-	-	-	-	-	-	-	-	-	-
Oxygen	[403]	[403]	[[76]]	[412]	[412]	[412]	[412]	[[70]]	[415]	[[74]]
Nitrogen	62.65	62.65	[109]	64.17	64.17	64.17	64.17	[99]	64.55	[109]
Carbon Dioxide	9.96	9.96	[71]	10.2	10.2	10.2	10.2	[74]	10.26	[60]
Hydrogen Sulfide	[7215]	[7215]	[14]	[7390]	[7390]	[3633]	[3633]	[7]	[3654]	[31]
Methane	-	-	-	-	-	-	-	-	-	-
Ethane	-	-	-	-	-	-	-	-	-	-
Propane	-	-	-	-	-	-	-	-	-	-
n-Butane	-	-	-	-	-	-	-	-	-	-
i-Butane	-	-	-	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-	-	-	-
n-Hexane	-	-	-	-	-	-	-	-	-	-
n-Heptane	-	-	-	-	-	-	-	-	-	-
n-Octane	-	-	-	-	-	-	-	-	-	-
Water	17.33	17.33	1.33	17.72	17.72	17.92	17.92	1.81	18.01	[7905]
SO_2	6.8	6.8	[350]	6.97	6.97	6.61	6.61	[369]	6.65	[317]
Elemental Sulfur	2.48	2.48	98.62	[1402]	[1402]	[6704]	[6704]	98.13	[878]	99.16
Carbon Monoxide	[230]	[230]	[[41]]	[236]	[236]	[236]	[236]	[[38]]	[237]	[[41]]
COS	-	-	-	-	-	-	-	-	-	-
Hydrogen	[2]	[2]	[[0]]	[2]	[2]	[2]	[2]	[[0]]	[2]	[[0]]
TEG	-	-	-	-	-	-	-	-	-	-
Total	100	100	100	100	100	100	100	100	100	100

Table A5.11: Summary of molar flows for streams 5-10 to 5-19

Stream	**5-10**	**5-11**	**5-12**	**5-13**	**5-14**	**5-15**	**5-16**	**5-17**	**5-18**	**5-19**
Stream Descriptor										
From	Secondary Claus reactor	Second air cooler	Secondary flash tank	Secondary flash tank	Tertiary heat exchanger	Tertiary Claus reactor	Third air cooler	Tertiary flash tank	Tertiaty flash tank	Liquid sulfur product mixer
To	Second air cooler	Secondary flash tank	Liquid sulfur product mixer	Tertiary heat exchanger	Tertiary Claus reactor	Third air cooler	Tertiary flash tank	Liquid sulfur product mixer	Area 6	Area 6
Pressure(bara)	2.24	2.14	1.94	1.94	1.84	1.83	1.73	1.53	1.53	1.53
Temperature(°C)	221	149	149	149	204	205	132	132	132	173
Phase	V	V/L	L	V	V	V	V/L	L	V	L
Mole Flow -kmol/h (mol/h) ((mmol/h))										
Selexol	-	-	-	-	-	-	-	-	-	-
Oxygen	(312)	(312)	((1))	(312)	(312)	(312)	(312)	((0))	(312)	((15))
Nitrogen	555	555	((2282))	555	555	555	555	((507))	555	(25)
Carbon Dioxide	56	56	((954))	56	56	56	56	((241))	56	((8666))
Hydrogen Sulfide	5	5	((242))	5	5	3	3	((31))	3	((5816))
Methane	-	-	-	-	-	-	-	-	-	-
Ethane	-	-	-	-	-	-	-	-	-	-
Propane	-	-	-	-	-	-	-	-	-	-
n-Butane	-	-	-	-	-	-	-	-	-	-
i-Butane	-	-	-	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-	-	-	-
n-Hexane	-	-	-	-	-	-	-	-	-	-
n-Heptane	-	-	-	-	-	-	-	-	-	-
n-Octane	-	-	-	-	-	-	-	-	-	-
Water	239	239	(433)	238	238	241	241	(145)	241	3
SO_2	26	26	((3217))	26	26	25	25	((829))	25	(31)
Elemental Sulfur	3	3	3	(312)	(312)	(980)	(980)	(734)	(246)	33
Carbon Monoxide	(204)	(204)	((1))	(204)	(204)	(204)	(204)	((0))	(204)	((9))
COS	-	-	-	-	-	-	-	-	-	-
Hydrogen	(25)	(25)	((0))	(25)	(25)	(25)	(25)	((0))	(25)	((0))
TEG	-	-	-	-	-	-	-	-	-	-
Total	885	885	3	881	881	881	881	(880)	880	35

Table A5.12: Summary of molar compositions for streams 5-10 to 5-19

Stream	**5-10**	**5-11**	**5-12**	**5-13**	**5-14**	**5-15**	**5-16**	**5-17**	**5-18**	**5-19**
Stream Descriptor										
From	Secondary Claus reactor	Second air cooler	Secondary flash tank	Secondary flash tank	Tertiary heat exchanger	Tertiary Claus reactor	Third air cooler	Tertiary flash tank	Tertiary flash tank	Liquid sulfur product mixer
To	Second air cooler	Seocndary flash tank	Liquid sulfur product mixer	Tertiary heat exchanger	Tertiary Claus reactor	Third air cooler	Tertiary flash tank	Liquid sulfur product mixer	Area 6	Area 6
Pressure(bara)	2.24	2.14	1.94	1.94	1.84	1.83	1.73	1.53	1.53	1.53
Temperature(°C)	221	149	149	149	204	205	132	132	132	173
Phase	V	V/L	L	V	V	V	V/L	L	V	L
Mole Composition - wt.% [ppm] [[ppb]]										
Selexol	-	-	-	-	-	-	-	-	-	-
Oxygen	[353]	[353]	[[402]]	[354]	[354]	[354]	[354]	[[356]]	[355]	[[415]]
Nitrogen	62.69	62.69	[660]	62.93	62.93	62.98	62.98	[576]	63.04	[693]
Carbon Dioxide	6.34	6.34	[276]	6.37	6.37	6.37	6.37	[274]	6.38	[245]
Hydrogen Sulfide	[5934]	[5934]	[70]	[5957]	[5957]	[2930]	[2930]	[35]	[2933]	[164]
Methane	-	-	-	-	-	-	-	-	-	-
Ethane	-	-	-	-	-	-	-	-	-	-
Propane	-	-	-	-	-	-	-	-	-	-
n-Butane	-	-	-	-	-	-	-	-	-	-
i-Butane	-	-	-	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-	-	-	-
n-Hexane	-	-	-	-	-	-	-	-	-	-
n-Heptane	-	-	-	-	-	-	-	-	-	-
n-Octane	-	-	-	-	-	-	-	-	-	-
Water	26.96	26.96	12.54	27.02	27.02	27.34	27.34	16.46	27.35	7.83
SO_2	2.98	2.98	[930]	2.99	2.99	2.84	2.84	[942]	2.84	[882]
Elemental Sulfur	[3763]	[3763]	87.27	[354]	[354]	[1112]	[1112]	83.36	[279]	91.97
Carbon Monoxide	[230]	[230]	[[250]]	[231]	[231]	[231]	[231]	[[219]]	[232]	[[261]]
COS	-	-	-	-	-	-	-	-	-	-
Hydrogen	[28]	[28]	[[4]]	[28]	[28]	[28]	[28]	[[3]]	[28]	[[5]]
TEG	-	-	-	-	-	-	-	-	-	-
Total	100	100	100	100	100	100	100	100	100	100

Table A5.13: Summary of overall mass balance

Flows IN		**Flows OUT**	
Stream No.	Flowrate (kg/h)	Stream No.	Flowrate (kg/h)
4-13	30380	5-18	24071
		5-19	6309
TOTAL IN	30380	TOTAL OUT	30380
Error		0.0001%	

Table A5.14: Summary of required design specifications

Specification	**Required Value**	**Value achieved**
Tail gas H_2S content	0.05%	0.029%
Tail gas SO_2 content	7.0 %	2.84 %

Table A5.15: Summary of energy usage

Electricity available	60 MVA
Electrical energy usage (MW)	1.897
Electrical energy usage (MVA)	1.897

Table A5.13 and A5.14 indicate that the mass balances across the Area 5 process which achieves the required design specification. Table A5.15 shows that the electricity required amounts to 1.897 MVA which is significantly lower than the allotted 60 MVA. Therefore, the process does not violate the given energy constraints.

7. Information required by the Control Engineer

Process control diagram

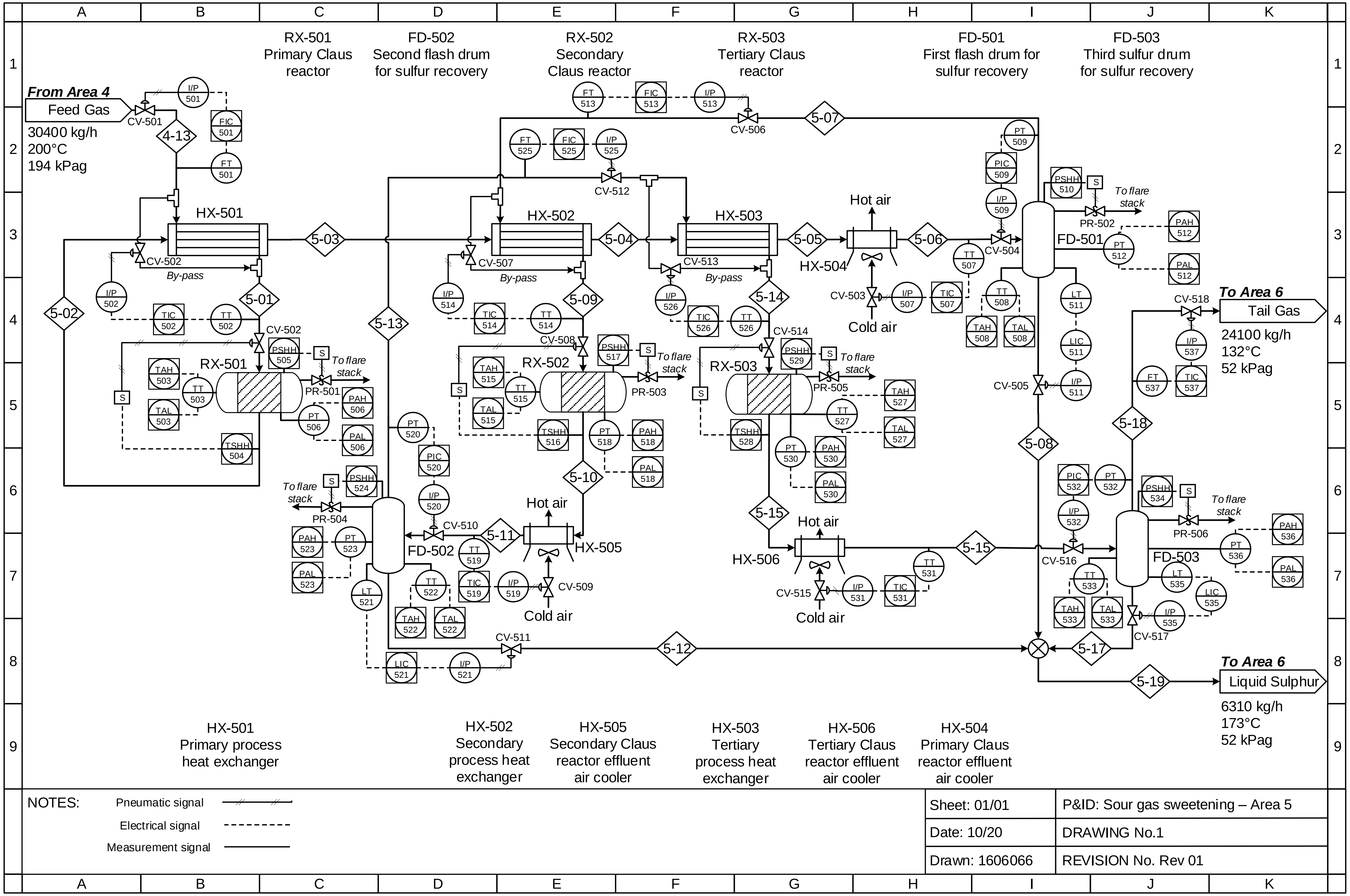


Figure A5.10: Process and instrumentation diagram for Area 5

Control objectives

The process of plantwide control consists of the systems and procedures required to control a chemical process. The development of a suitable plantwide control strategy is important to ensure that the process objectives of the plant are obtained in a safe and steady-state manner. The process objectives for Area 5 directly correlate to the objectives for the control strategy. Thus, the control objectives include producing a tail gas which contains less than 0.5% and 7.0% of H_2S and SO_2 on a molar basis in an inherently safe process. The control loops found within the plantwide control strategy are implemented to react to various disturbances in process variables [20]. Changes in feed composition, pressure and temperature are common disturbances which occur within a chemical process and the control strategy is formulated such that these disturbances are not propagated through the system. It is assumed that the utilities plant is well controlled, and therefore there are no disturbances in terms of changing utility conditions.

Control strategy discussion

In order to ensure the process objectives are met in a safe manner, the control system of the plant is designed with multiple layers of protection which include basic process control systems (BCPS), alarm system and safety instrumented system (SIS) [21]. BCPS consists of feedforward and feedback control loops used to regulate process variables and maintain steady-state operation of the process. These control loops consist of a transmitter, controller and transducer. The second layer of protection consists of alarms which are triggered to highlight abnormal operating conditions. Finally, SIS is the backup to the BCPS and is automatically started when a process variable exceeds a predetermined critical limit [21]. In order to guarantee the availability of emergency protection, process alarms and SIS function independently of BPCS and thus no instrumentation is shared between these systems [20].

The first step in developing the overall control strategy for Area 5, is to analyse each individual unit operation and determine the control loops required for the steady-state operation of each unit. In order to develop the control loops required for each unit a degrees of freedom analysis is used to determine the number of manipulated variables available to control the controlled variables [20]. The aids in developing an automatic control strategy which responds quickly to any disturbances which occur within the system.

Control of Claus reactors

The Claus reactors present in the process found in Area 5 are packed-bed reactors which are required to achieve specific conversions in order to achieve the design objectives of the process. Therefore, the control strategy related to the Claus reactor is required to control the conversion of each reactor. A shown by the sensitivity analysis in Figures A5.5 and A5.6, the conversion achieved by the Claus reactor is a strong function of the inlet temperature and composition to the reactor. Although heat loss from the reactor was modelled in Section 3, Figure A5.3 shows that for the chosen reactor volume for the first Claus reactor the temperature within the reactor does not reach a maximum and decrease. This indicates that the insulation around the reactor is sufficient and that the temperature profile approximates adiabatic operation. Therefore, the temperature rise within the reactor is not impacted by disturbances in the temperature of the surrounding environment and is only a function of the conversion achieved. Thus, the exit temperature of the reactor is a function of the conversion achieved. Therefore, in order to achieve control of the conversion, and thus the exit temperature, of the reactor the inlet temperature and composition need to be tightly controlled.

The only manipulated variable, and hence the only control valve, available for the control of the reactor is the control of the feed flowrate. This cannot be used to control either the inlet temperature or composition but is used to fix the flowrate of material entering each reactor. Figure A5.9 shows that the reactor effluent of the primary Claus reactor is used to heat the feeds of all three reactors found in the process to the required inlet temperature. This use of process streams for heat exchange reduces the utility requirements but does not allow the reactor inlet temperature to be controlled using a utility flowrate. This set up of unit operations introduces the risk achieving a high exit temperature due to the exothermic nature of the chemical reactions occurring. In order to control the inlet temperature to the reactor an additional control valve needs to be made available to do so. A portion of the feed to each reactor is by-passed around the heat exchange which impacts the temperature of the stream entering each reactor. Hence, the flowrate of the cold feed by-passing the heat exchanger can be used to control the inlet temperature to the reactor.

As previously stated, the ratio of H_2S to SO_2 in the feed to each reactor strongly impacts the conversion achieved by each reactor. However, the unit operations found in Area 5 are not capable of manipulating the feed ratio. The feed ratio to the primary Claus reactor, exiting the furnace found in Area 4, needs to be controlled within Area 4 by adjusting the air flowrate into the furnace. The feed ratio to the remaining two Claus reactor are controlled by controlling the conversion achieved by each reactor and ensuring the desired separation occurs within the flash tanks used to recover liquid sulfur which is described below.

The BPCS described above is used to maintain steady-state operation of the process and to ensure the process objectives are achieved. In order to ensure safe operation of the process, alarms are used as the second layer of protection because they signal abnormal operating conditions to operators. The key variables related to the safe operation of the Claus reactors are temperature and pressure and thus high- and low-level alarms are required for both variables. These alarms will notify plant operators of potentially dangerous events and if the process is operating outside of the optimal operating conditions. In the event that a process variable exceeds its maximum limit for safe operation, SIS loops are used to prevent hazardous situations from materialising. The first unwanted event which could occur within the Claus reactors is the pressure within the reactor becoming so high such that the reactor ruptures. In order to prevent this from materialising a pressure relief valve is interlocked to a high-high pressure switch on the reactor. The exothermic nature of the reaction leads to the potential of a runaway reaction occurring. In order to prevent this from occurring, the reactor temperature is interlocked to the feed flowrate so that if the maximum allowable temperature within the reactor is realised the feed to the reactor can be shutoff in order to prevent any further temperature increases.

Control of air coolers and flash tanks

The separation of the elemental sulfur, S_6, from the stream exiting each Claus reactor is a key operation in the process found in Area 5. Ensuring that the desired separation occurs is important because it impacts the feed entering each reactor and thus strongly influences the overall process. Since S_6 is separated from the remaining components in the reactor effluent by phase separation, which is governed by vapour-liquid equilibrium, temperature is used to control the composition of the vapour and liquid exiting the flash. Since, the flash tank is assumed to be adiabatic, the temperature of the vapour-liquid mixture entering the flash tank, exiting the preceding air cooler, determines the composition of the vapour and liquid. Therefore, the temperature of the stream exiting each air cooler needs to be tightly controlled using the air flowrate entering the cooler. The air flowrate is manipulated using the power of the fan and thus is used to control the temperature of the stream exiting the cooler.

Just as the temperature of the fluid entering the adiabatic flash is controlled, the exit pressure of the vapour is controlled because it impacts the separation achieved within the flash tank. The pressure of the vapour exiting the flash tank is function of the inlet flowrate. Therefore, the flowrate of the vapour-liquid mixture entering each flash tank is used to control the exiting pressure. The level of the liquid within the flash is controlled using the bottoms flowrate to ensure that it doesn't not overflow. The vapour exiting each flash tank is fed to either a Claus reactor or exiting to Area 6, therefore its flowrate is controlled to maintain steady-state operation.

Similar to the Claus reactors, temperature and pressure are key variables for safe operation of the flash tanks and thus high- and low-level alarms are required for both variables on each flash tank. The flash tanks are pressure vessels and thus the pressure within each tank is interlocked to a pressure relief valve which, if triggered, sends the released gas to a flare stack.

It is important to note that all BPCS control loops, alarms and SIS loop are implemented independent of one another. This ensures that these multiple layers of process safety do not interfere with each another and that if one level of safety fails it does not impact the operation of the other control systems.

Start-up and shut down procedures

An important step in the starting-up of the plant is pre-inspection of the process to determine if it is ready for start-up. This includes pre-commissioning checks such as ensuring all utilities are available at the required conditions, verifying all units operate correctly and ensuring all reaction vessels have been purged with nitrogen. The first step in developing the start-up strategy for the process is dissolving the units in the process into reversible and irreversible units [22]. A reversible unit operation is one which can be operated as an isolated process and does not require any process streams to operate. In contrast to this, irreversible unit operations require a process feed in order for production to be started. Decomposing the units found in Area 5, the Claus reactors are classed as irreversible units since they require a specific feed to start production and the flash tanks are reversible units because material can be recycled within the subsystem. The general rule in developing a start-up procedure is that the reversible units are commissioned into operation first, with independent heating and cooling units started up before the irreversible units are put into operation.

Once the pre-commissioning checks have been completed, the flash tanks are started using raw material from a crude charge tank. The air coolers preceding the flash tanks are then started up with the raw material feed and products recirculating to the charge tank until the system produces products of the required specifications. Once, this system reaches steady-state the BPCS controls are commissioned into operation before driving the unit to normal operating conditions [22].

Next, the heat exchangers used to heat the feed to each Claus reactors are started up using a pseudo-feed until the reactors are put into operation. During start-up, the steady-state energy recycle is not operational, and therefore the feeds to the Claus reactors are heated using high pressure steam in independent heat exchangers. The reactors are then started-up by supplying an adequate feed to the system. In order to obtain the required initial reactor conditions, an additional set of intermediate operating states are used. Thus, process material is recycled over the reactor to push the system to required operating conditions [22]. The use of these intermediate operating states is an important safeguarding strategy since the it allows the reactors to be put in these states during emergency situations [22]. Once the reactor has reached the desired operating conditions the effluent is instantaneously discharged to downstream units and the steady-state energy recycle is commissioned into operation [22].

The order in which units are shutoff during shutdown is the reverse of which they are started-up in. Therefore, the first units shut off are the Claus reactors by removing the feed to the system. For safety reasons, the Claus reactors are shut down using multiple intermediate states in a recycle loop, as for start-up. Once the reactors are completely shut down and are at ambient conditions, they are purged using nitrogen to remove trace amounts of components from the reactor. The heat exchangers used to heat the reactor feeds are then decommissioned from operation before the air coolers are shut off by cutting of the utility supply to these units. The feed to each flash tank is then shutoff and the vessels are drained and purged to prevent the solidification of sulfur.

It must be noted that the designed BPCS only applies during steady-state operation and not during plant start up or shut down sequences. Therefore, during start-up and shutdown only the alarms systems and SIS are operational to maintain plant safety. The steady-state BPCS should only be commissioned into operation once the plant has reached steady-state.

8. Information Required by the Health, Safety and Environmental Officer

The information provided in this section along the material safety data sheets, shown in Figures A5.19, A5.20, A5.21 in Appendix A5-E, encompass the information required by the Health, Safety and Environmental Officer.

Hazard inventory

Table A5.16: Summary of physical hazards found in Area 5

Physical Hazard		Magnitude
Noise		100 dB [23]
Electricity		60 MVA, 3 phase
High temperature	RX-501	309°C
	RX-502	221°C
	RX-503	205°C
High pressure		295 kPa

Table A5.17: Summary of chemicals found in Area 5

Process chemicals	Max Flowrate (kg/h)	Max temperature (°C)	Min temperature (°C)	Flammability data
CO_2	2470	309	132	Non-flammable, non-toxic
CO	6	309	132	Flammability limits: 12.5 – 74.2 vol%, Toxic
H_2S	4560	309	132	Flammability limits: 4.3 – 4.6 vol%, Toxicity limits: 700 mg/m^3
N_2	15500	309	132	Non-flammable, non-toxic
O_2	10	309	132	Non-flammable, non-toxic
Elemental sulfur	6260	309	132	Flammability limits: 3.3 – 46.0 vol%, Toxicity limit: 3000 mg/kg (Rat)
SO_2	5780	309	132	Non-flammable, Toxicity limits: 1260 ppm/4h
COS	1	309	132	Flammability limits: 6.5 – 29 vol%, Toxicity limits 1070 ppm
H_2O	4340	309	132	Non-flammable, non-toxic
H_2	0.050	309	132	Flammability limits: 4.0- 75 vol%, non-toxic

There are no chemicals being stored or recirculated within the process found in Area 6, and thus there are no health and safety related issues regarding storage or recirculation in Area 5.

Quantification of external resources required

Table A5.18: Summary of external resources required

External resource	Description	Magnitude
Electricity	Air cooler fan	1.9 MW
Employees	Plant operators	14

Possible unwanted event

An unwanted event, which could lead to severe economic losses, injury and death, is the rupture and explosion of any of the Claus reactors found in the process. This could be caused by the pressure within the reactor exceeding its maximum allowable value or by a runaway reaction occurring within the reactor leading to a steep increase in temperature. In order to prevent these events from materialising, two sets of SIS control loops are implemented. The first of these loops involves measuring the pressure within the reaction vessel and interlocking it to a pressure relief valve which is opened if the pressure in the vessel exceeds a pre-determined maximum value. Since the reactions occurring are exothermic, the possibility of a runway reaction is controlled by interlocking the reactor outlet temperature to the inlet flowrate. Thus, if the temperature exiting the reactor exceeds a maximum value then the feed to the reactor is shutoff in order to stop the reaction and prevent any further increases in temperature. In the event that the reactor ruptures and explodes, automatic fire hydrants need to be on hand to immediately quell the fire caused by the explosion using municipal water. In addition to this the plant would need to be immediately evacuated using predetermined plans and safety institutions, such as the fire department, must be notified in to order to manage the damage.

9. Information Required by the Project Accountant

Tables A5.19 and A5.20 below summarise the capital and operating costs related to the process found in Area 5, as required by the project accountant. All detailed calculations pertaining to the values reported below can be found in Appendices A5-C and A5-D.

Capital Cost

Table A5.19:Summary of Capital Costs in Area 5

Unit	Description	Capital Cost (R)
Reactors		
RX-501	Primary Claus reactor	5 001 408
RX-502	Secondary Claus reactor	7 759 470
RX-503	Tertiary Claus reactor	6 642 984
Heat exchangers		
HX-501	Primary process heat exchanger	2 382 250
HX-502	Secondary process heat exchanger	1 764 179
HX-503	Tertiary process heat exchanger	2 154 739
HX-504	Primary Claus reactor effluent air cooler	92 961
HX-505	Secondary Claus reactor effluent air cooler	94 810
HX-506	Tertiary Claus reactor effluent air cooler	95 012
Flash tanks		
FT-501	First flash drum for sulfur recovery	2 225 044
FT-502	Second flash drum for sulfur recovery	2 251 149
FT-503	Third flash drum for sulfur recovery	2 349 275
TOTAL BARE MODULE CAPITAL COST		32 813 280
TOTAL PLANT INVESTMENT		44 527 621

Operating Cost

Table A5.20: Summary of Operating Costs in Area 5

Description		Operating cost (R/year)
Electricity	HX-504	57 587
	HX-505	57 446
	HX-506	52 131
Operating labour		2 261 070
TOTAL OPERATING COST		2 428 234

10. Information Required by the Utilities and Heat Integration Engineer

Heat integration

The exothermic nature of the reactions occurring within in each Claus reactor implies that the temperature increases along the length of the reactor such that the outlet temperature is higher than the inlet temperature. The feed from Area 4 needs to be heated from 200°C to 255°C before entering the primary Claus reactor and the reactor effluent needs to be cooled from 309°C to 177°C. This is a favourable for steady-state heat integration since the reactor effluent can be used to heat the reactor feed in the primary heat exchanger. The heat exchanger network, shown in Figure A5.11 below, indicates that the temperature of the primary reactor effluent exiting the primary heat exchanger is 283°C and hence can be used to heat the feed to the secondary reactor exiting the primary flash tank at 177°C. Figure A5.11 shows that the temperature of the primary reactor effluent exiting the secondary heat exchanger is sufficient to heat the feed to the tertiary reactor from 149°C to 204°C. This matching of hot and cold streams allows the utilities requirements of the process to be significantly decreased but must be done while considering the pinch temperature to ensure the minimum approach temperature of 20°C is not violated. The streams, in Figure A5.11, are matched by first matching the hottest hot stream with the warmest stream in order to maximise heat exchange. The heat exchanger network shows that the hot secondary and tertiary reactor effluents were not needed for heat integration and may be used for heat integration in other area of the plant.

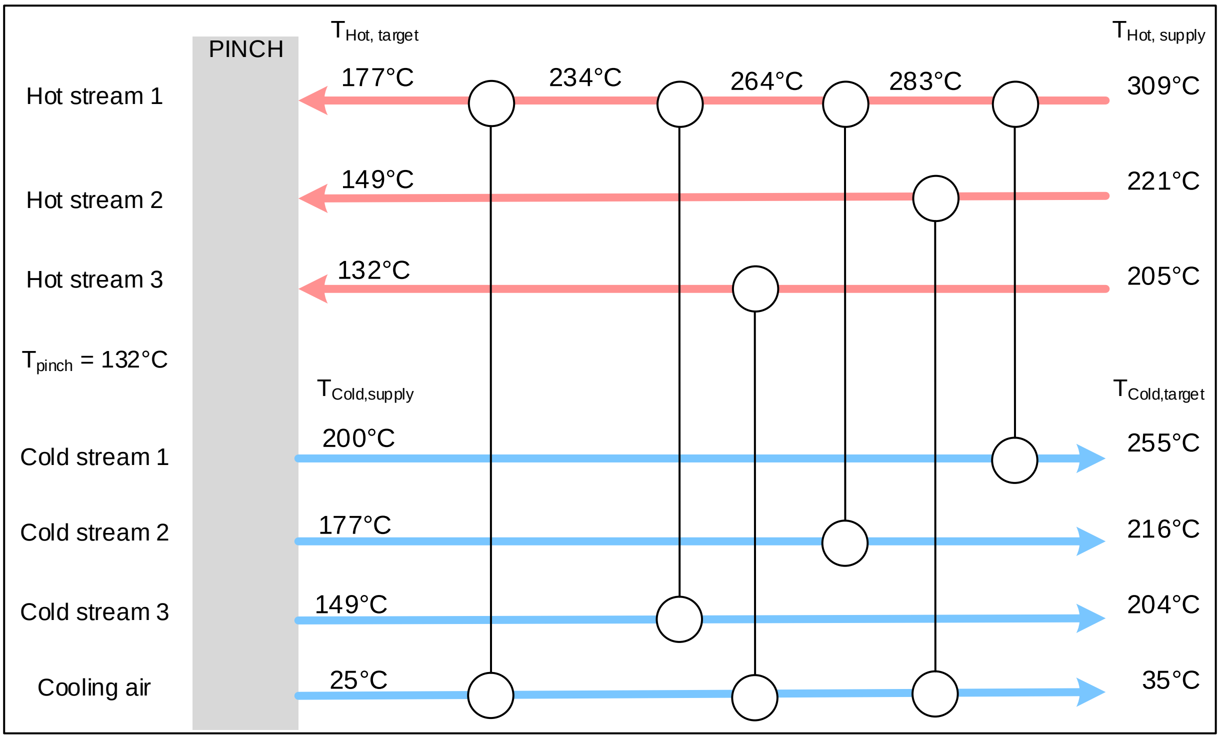


Figure A5.11: Heat exchanger network diagram

The pinch temperature is determined to be 122°C using the interval method, shown in Table A5.36 in Appendix A5-F, which aims to determine the minimum utility requirement [21]. Table A5.37 confirms that heat integration allows the process to not require any hot utility in the form of high-pressure steam. Heat integration also decreases the cooling requirements of the first air cooler since its feed is at a lower temperature. Table A5.21 outlines the reduction in utility requirements due to the implementation of heat integration.

Table A5.21: Comparison of heating and cooling requirements before and after heat integration

	Before Energy Recycle	**After Energy Recycle**
Heating Duty requirement (MW)	1.06	0
Cooling Duty requirement (MW)	3.14	1.90
Total energy requirement (MW)	4.20	1.90

The results shown in Table A5.21 highlight the potential savings for using heat integration within Area 5. Table A5.21 shows that if the heat integration is implemented no high-pressure steam is required and a 57% reduction in electricity requirement is observed. This configuration of heat exchangers only applies to the steady-state operation of the process and not during start-up and shut-down because during these unsteady-state phases the reactor effluent is not available to heat the reactor feed. Therefore, during start-up and shut down it is necessary to switch the heat exchangers from using process fluids to utility-based heat exchangers until steady-state operation of the plant is achieved. Hence, during start-up and shutdown Area 5 requires high pressure steam and more electricity to power the fans. The economic impact of this needs to be evaluated in conjunction with the start-up and shut down strategies.

Utilities requirements

Table A5.22: Utilities list for Area 5

Equipment No	**Duty (kW)**	**Electricity demand (kWh/year)**
Electricity		
HX-504	653	67749
HX-505	652	67584
HX-506	592	61331
TOTAL	1897	196664

Streams available for further heat integration

There are three remaining streams which can be used for further heat integration across different areas. These streams include, the primary reactor effluent exiting the tertiary heat exchanger, the secondary reactor effluent and the tertiary reactor effluent. Table A5.23 provides the stream information required by the Utilities and Heat Integration engineer to complete plantwide heat integration.

Table A5.23: Summary of streams available for heat integration

Stream number	**5-5**	**5-10**	**5-15**
Type	Hot	Hot	Hot
Molar flowrate (kmol/s)	0.255	0.246	0.245
Temperature (°C)	234	221	205
C_p (J/mol.K)	37052	32916	32504
mC_p (W/K)	9448	8097	7963

11. References

[1] S. Mokhatab, W. A. Poe, and J. Y. Mak, *Handbook of natural gas transmission and processing: Principles and practices*. 2018.

[2] A. L. Kohl and R. B. Nielsen, *Gas Purification*, vol. 72, no. 10. 1977.

[3] J. H. Gary and G. E. Handwerk, *Petroleum Refining: Technology and Economics.*, vol. 49, no. 16. 1994.

[4] A. J. Kidnay, A. J. Kidnay, W. R. Parrish, and D. G. McCartney, “Fundamentals of Natural Gas Processing,” *Fundam. Nat. Gas Process.*, 2011.

[5] J. K. Laursen and A. N. Karavanov, “Processes for sulfur recovery, regeneration of spent acid, and reduction of NO x emissions,” *Chem. Pet. Eng.*, vol. 42, no. 5–6, pp. 229–234, 2006.

[6] H. S. Fogler, “Essentials of chemical reaction engineering,” 2004.

[7] C. L. Yaws, *Yaws’ Handbook of Thermodynamic Properties for Hydrocarbons and Chemicals*. 2009.

[8] R. H. Perry and D. W. Green, *Perry’s Chemical Engineering Handbook*. 2007.

[9] C. L. Yaws, *Yaws’ Handbook of Thermodynamic and Physical Properties of Chemical Compounds*. 2003.

[10] W. L. McCabe, J. C. Smith, and P. Harriot, *Unit Operations of Chemical Engineering*. 2005.

[11] J. Beek, “Design of Packed Catalytic Reactors,” *Adv. Chem. Eng.*, 1962.

[12] “Thermal Conductivity of selected Materials and Gases,” *The Engineering ToolBox*. [Online]. Available: https://www.engineeringtoolbox.com/thermal-conductivity-d_429.html. [Accessed: 15-Oct-2020].

[13] A. K. Coker, “Ludwig’s Applied Process Design for Chemical and Petrochemical Plants,” vol. 1 (4th Edi, p. 41, 2007.

[14] S. B. Roscoe and W. G. Muller, “United States Patent (19) 11 Patent Number : Primary Examiner Mark L . Bell,” no. 19, 2000.

[15] P. E. Haêne, “SULFUR PLANT and TAIL GAS TREATING UNIT - STARTUP and SHUTDOWN,” 2011.

[16] R. Turton, R. C. Bailie, W. B. Whiting, and J. A. Shaeiwitz, *Analysis, Synthesis and Design of Chemical Processes*. 2009.

[17] C. H. Bartholomew, “Mechanisms of catalyst deactivation,” *Appl. Catal. A Gen.*, vol. 212, no. 1–2, pp. 17–60, 2001.

[18] A. Piéplu, O. Saur, J. Lavalley, O. Legendre, A. Pieplu, and O. Saur, *Claus Catalysis and H , S Selective Oxidation*, vol. 4940. 2006.

[19] P. N. Kalinkin, O. N. Kovalenko, and O. I. Platonov, “Analysis of the deactivation of claus alumina catalyst during its industrial exploitation,” *Catal. Ind.*, vol. 3, no. 2, pp. 183–188, 2011.

[20] W. L. Luyben, B. D. Tyreus, and M. L. Luyben, *Plantwise Process Control*. 1998.

[21] W. D. Seider, J. Seader, D. R. Lewin, and S. Widagdo, *Product and Process Design Principles*. 2009.

[22] J. W. Verwijs, P. H. Kosters, and H. Van Den Berg, “Reactor Operating Procedures for Startup of Continuously-Operated Chemical Plants,” vol. 41, no. 1, 1995.

[23] “Sound Power,” *The Engineering ToolBox*. [Online]. Available: https://www.engineeringtoolbox.com/sound-power-level-d_58.html. [Accessed: 22-Oct-2020].

[24] R. K. Sinnott, *Coulson and Richardson’s Chemical Engineering Volume 6 - Chemical Engineering Design (4th Edition)*. 2005.

[25] S. Jenkins, “2019 CHEMICAL ENGINEERING PLANT COST INDEX ANNUAL AVERAGE,” *Chemical Engineering*, 2020. [Online]. Available: https://www.chemengonline.com/2019-chemical-engineering-plant-cost-index-annual-average/. [Accessed: 22-Oct-2020].

[26] “Rand Dollar Exchange Rate,” *Moneyweb*, 2020. [Online]. Available: https://www.moneyweb.co.za/tools-and-data/currency-markets/. [Accessed: 22-Oct-2020].

[27] Afrox, “Material Safety Data Sheet Carbon Monoxide,” no. January. pp. 1–2, 2015.

[28] Airgas, “SAFETY DATA SHEET - Carbonyl Sulfide,” vol. 4, no. 2. pp. 8–10, 2012.

[29] ThermoFischer Scientific, “Safety Data Sheet - Sulfur,” vol. 4, no. 2. pp. 8–10, 2018.

Area 5 Appendices

A5-A. Reactor modelling

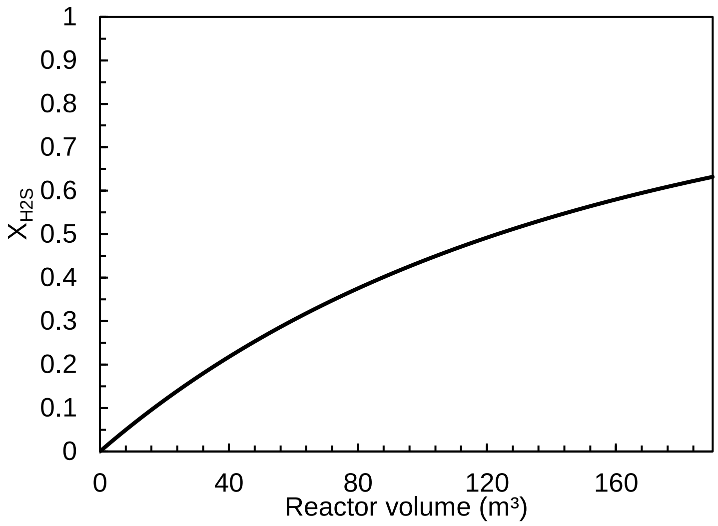


Figure A5.12: H_2S conversion profile over the volume of the secondary Claus reactor

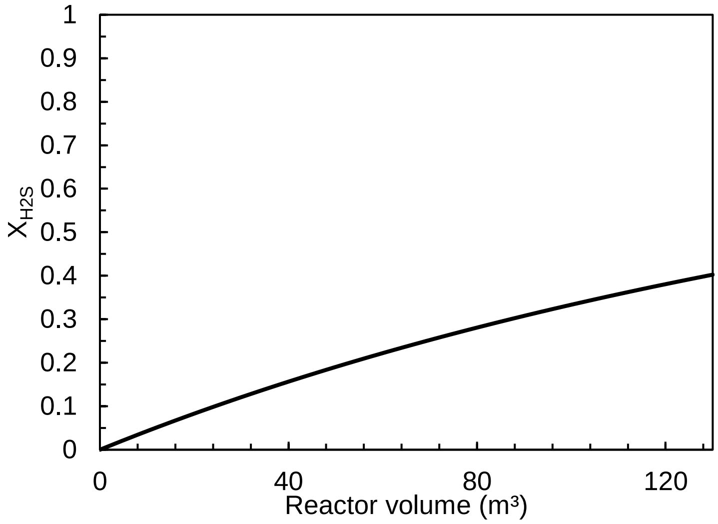


Figure A5.13: H_2S conversion profile over the volume of the tertiary Claus reactor

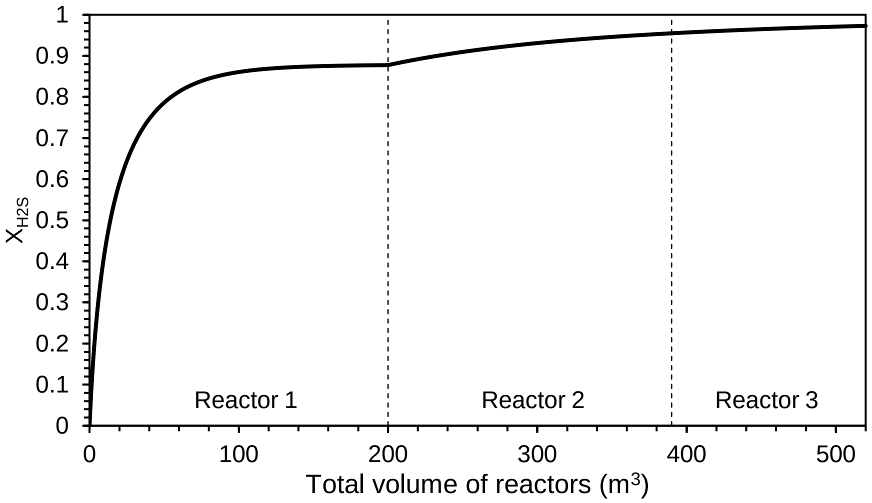


Figure A5.14: Overall conversion of H_2S over the entire system

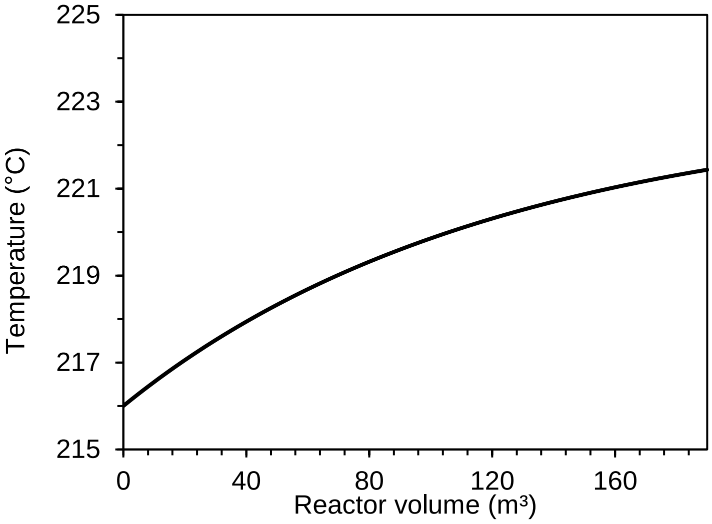


Figure A5.15: Temperature profile as a function of reactor volume for the secondary Claus reactor

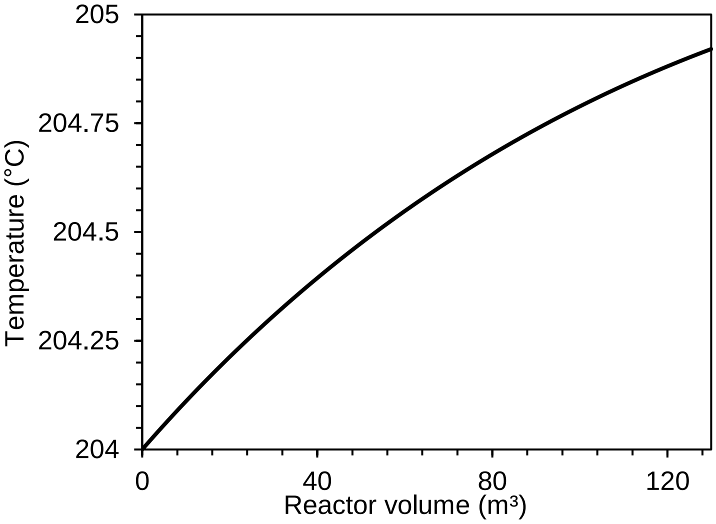


Figure A5.16: Temperature profile as a function of reactor volume for the tertiary Claus reactor

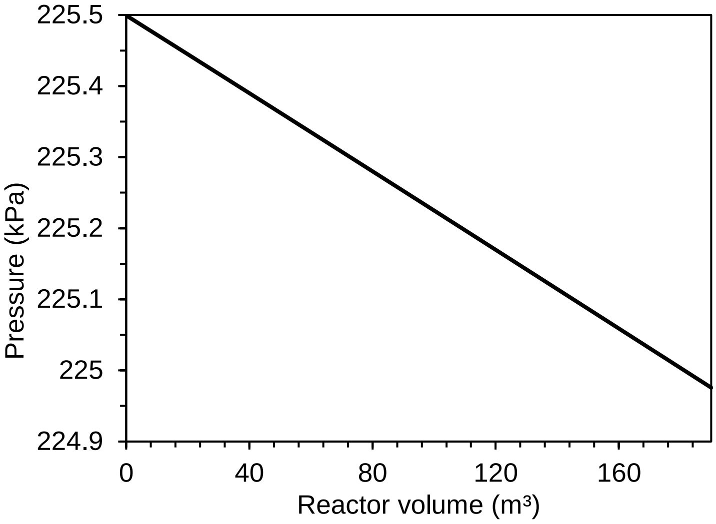


Figure A5.17: Pressure profile as a function of reactor volume for the secondary Claus reactor

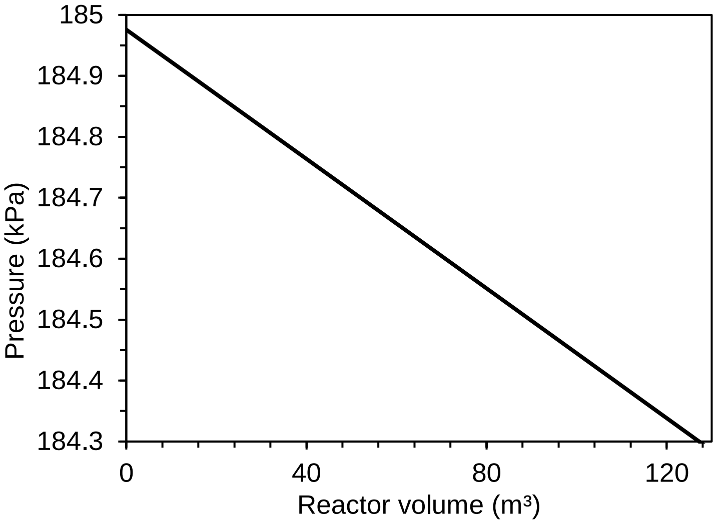


Figure A5.18: Pressure profile as a function of reactor volume for the tertiary Claus reactor

A5-B. Equipment Sizing

Sizing of flash tanks

The calculations used to determine the size of the flash tanks in the process are as follows [16] [13]. A sample calculation for the size of the primary flash tank (FT-501) is shown below with a summary of the results shown in Table A5.25.

Table A5.24: Information required to size a flash tank

Equipment No.	FT-501	Inlet liquid density (kg/m^3)	2155
Inlet vapour flow (kg/h)	24803	Inlet Temperature (°C)	177
Inlet vapour density (kg/m^3)	1.903	Inlet Pressure (bar)	2.54
Inlet liquid flow (kg/h)	5576	Mesh entrainer present	No

$$u = k\sqrt{\frac{\rho_{liq}}{\rho_{vap}} - 1} = 0.0305\sqrt{\frac{2155}{1.903} - 1} = 1.025\frac{m}{s} \quad \text{(A5.38)}$$

Where u is the gas velocity in m/s and $k = 0.11$ if a mesh entrainer is used and $k = 0.0305$ is not. Therefore, since mesh entrainers are not used $k = 0.0305$.

Good performance of the flash tank is assumed to occur at 75% of the gas velocity. The volumetric flowrate of the gas is given by Equation A5.39 below.

$$\dot{V}_{gas} = \frac{v_{in}}{\rho_{vap}} = \frac{24803}{1.903} \times \frac{1}{3600} = 3.62\frac{m^3}{s} \quad \text{(A5.39)}$$

The volumetric flowrate of the gas and the actual gas velocity are used to determine the cross-sectional area of the flash tank which is used to determine the diameter of the tank, as shown in Equations A5.40 and A5.41below.

$$A_{CS} = \frac{\dot{V}_{gas}}{0.75\,u} = \frac{3.62}{0.75(1.025)} = 4.71\,m^2 \quad \text{(A5.40)}$$

$$D = \sqrt{\frac{4A_{CS}}{\pi}} = \sqrt{\frac{4(4.71)}{\pi}} = 2.45\,m \quad \text{(A5.41)}$$

In order to determine the length of the flash tank a hold-up time of 5 minutes is assumed, which is based on the half volume of the tank. The volumetric flowrate of liquid in the tank, as determined in Equation A4.42, is then combined with this hold-up time, in Equation A5.43, to determine the liquid volume in the flash tank.

$$\dot{V}_{liquid} = \frac{l_{in}}{\rho_{liq}} = \frac{5576}{2155} \times \frac{1}{60} = 0.043 \frac{m^3}{min} \tag{A5.42}$$

$$V_{liquid} = 5 \cdot \dot{V}_{liquid} = 0.22\, m^3 \tag{A5.43}$$

Since the liquid hold used is based on half the volume of the tank, half the area available is taken up and is determined in Equation A5.44. This area is then used to determine the length of the flash tank in Equation A5.45.

$$Area = \left(\frac{1}{2}\right)\sqrt{\pi\left(\frac{D}{2}\right)^2} = \left(\frac{1}{2}\right)\sqrt{\pi\left(\frac{2.45}{2}\right)^2} = 1.09\, m^2 \tag{A5.44}$$

$$L = \frac{V_{liquid}}{Area} = \frac{0.22}{1.09} = 0.201\, m \tag{A5.45}$$

The length to diameter ratio is then determined to be 0.082. If the length to diameter ratio of the flash tank is found to be less than 2.5 or greater than five a length to diameter ratio of 3 must be used. Therefore the length of the flash tank is equivalent to 7.34 m.

The design temperature for the flash tank is assumed to be 25°C above the normal operating temperature, as shown in Equation A4.46.

$$Design\ T = Operating\ T + 25℃ = 177 + 25 = 202℃ \tag{A5.46}$$

The operating pressure of the flash tank is assumed to be 1.7 bar above the inlet temperature. If the inlet pressure to the flash tank is less than 0.69 bar, the design pressure of the tank is assumed to be 3.77 bar. Otherwise, the design pressure of the flash tank is largest value between the operating pressure multiplied by 1.1 or the operating pressure plus 1.7. For the first flash tank, the design pressure is determined to be 5.95 bar.

Table A5.25: Summary of flash tank specifications

Equipment No.	**FT-501**	**FT-502**	**FT-503**
Length (m)	2.45	2.49	2.59
Diameter (m)	7.34	7.47	7.76
Operating temperature (°C)	177	149	132
Design temperature (°C)	202	174	157
Operating pressure (bar)	4.25	3.84	3.43
Design pressure (bar)	5.95	5.54	5.13

Sizing of heat exchangers

The calculations used to determine the size of the heat exchangers in the process are as follows [16] [24]. It is important to note that the method of sizing heat exchangers using process stream and air coolers is the same. A sample calculation for the size of the primary heat exchanger (HX-501) is shown below with a summary of the results shown in Table A5.27.

Table A5.26: Summary of information required to size a heat exchanger

Equipment No.	HX-501	Hot stream temperature out (°C)	283
Heat duty (kW)	490	Cold stream temperature in (°C)	200
Heat transfer coefficient (W/m^2°C)	30	Cold stream temperature out (°C)	255
Hot stream temperature in (°C)	309	Pressure (bar)	3.05

The step in determining the area of a heat exchanger is to determine the log mean temperature difference, shown in Equation A5.49 below.

$$\Delta T_1 = T_{C,out} - T_{H,in} = 255 - 309 = -54 \quad \text{(A5.47)}$$

$$\Delta T_2 = T_{C,in} - T_{H,out} = 200 - 283 = -83 \quad \text{(A5.48)}$$

$$LMTD = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} = \frac{-54 + 83}{\ln\left(\frac{54}{83}\right)} = 67.6 \quad \text{(A5.49)}$$

A safety factor of 1.1 is multiplied by the heat duty of each heat exchanger and the LMTD correction factor, F, is estimated to 0.9. These, along with the heat transfer coefficient, both used to determine the heat exchange area for the heat exchanger. The heat transfer coefficient is 30 W/m^2°C for gas to gas heat exchange and 450W/m^2°C for air coolers.

$$A_{HX} = \frac{(1.1 \cdot Q)}{U \cdot F \cdot LMTD} = \frac{1.1(490)(1000)}{(30)(0.9)(67.6)} = 295\ m^2 \quad \text{(A5.50)}$$

If the area of the heat exchanger is between 9.3-18.6 m^2, a double pipe heat exchanger is used. Otherwise a shell and tube heat exchanger is chosen. Therefore, HX-501 is a shell and tube heat exchanger.

Similar to the flash tank, the design temperature for the hot and cold side of reactor is assumed to be 25°C above the operating temperature. Therefore the design temperature for the hot and cold sides are 334°C and 280°C respectively.

The operating pressure of the heat exchanger is assumed to be 1.7 bar above the inlet temperature. If the inlet pressure to the heat exchanger is less than 0.69 bar, the design pressure of it is assumed to be 3.77 bar. Otherwise, the design pressure of the heat exchanger is largest value between the operating pressure multiplied by 1.1 or the operating pressure plus 1.7. Hence, for the primary heat exchanger then design pressure is 6.45 bar.

For Shell and tube heat exchangers, with an area greater than 101 m^2, the shell diameter of the heat exchanger is determined using Equation A5.51 below[16].

$$Shell\ diameter(cm) = \frac{Area + 43.2}{1.545} = \frac{295 + 43.2}{1.545} = 219\ cm \qquad \text{(A5.51)}$$

Table A5.27: Summary of heat exchanger specifications

Equipment No	**HX-501**	**HX-502**	**HX-503**	**HX-504**	**HX-505**	**HX-506**
Type	Shell & tube	Shell & tube	Shell & tube	Double pipe	Double pipe	Double pipe
Area (m^2)	295	168	247	10.2	11.6	11.8
Duty (kW)	490	315	434	653	652	591
Hot side fluid	Process	Process	Process	Process	Process	Process
Cold side fluid	Process	Process	Process	Air	Air	Air
Hot side operating temperature (°C)	309	283	264	234	221	205
Cold side operating temperature (°C)	255	216	204	35	35	35
Hot side design temperature (°C)	334	307	289	259	246	230
Cold side design temperature (°C)	280	241	229	60	60	60
Design pressure (bar)	6.45	6.25	6.15	6.05	5.64	5.23
Shell diameter (cm)	219	137	189	N/A	N/A	N/A
Tube OD	1.90	1.90	1.90	N/A	N/A	N/A
Triangle spacing	2.54	2.54	2.54	N/A	N/A	N/A
Tube length (m)	4.90	4.90	4.90	N/A	N/A	N/A

Sizing of reactors

The volume of each of the Claus reactors found in the process is determined using the detailed model described in Section 3 of this report. Using the volume and the chosen aspect ratio, the diameter and length of each reactor is determined. The reactor ends are assumed to be hemispherical, which is accounted for in the reactor length.

Similar to heat exchangers and flash tanks, the design temperature of the reactors is determined by adding 25°C to the operating temperature of the reactor. The operating pressure of each reactor is assumed to be 1.7 bar above the inlet temperature. If the inlet pressure to the reactor is less than 0.69 bar, the design pressure of the reactor is assumed to be 3.77 bar. Otherwise, the design pressure of the reactor is largest value between the operating pressure multiplied by 1.1 or the operating pressure plus 1.7.

Table A5.28: Summary of reactor specifications

Equipment No	**RX-501**	**RX-502**	**RX-503**
Volume (m^3)	94	155	130
Bed Length (m)	7.82	12.1	11.4
Length (m)	11.7	16.1	15.2
Diameter (m)	3.91	4.04	3.81
Operating temperature (°C)	309	221	205
Design temperature	334	246	230
Operating pressure (bar)	2.95	2.25	1.84
Design pressure (bar)	6.35	5.65	5.24

A5-C. Equipment Capital Costing

The heuristic methods used to determine the capital costs of each piece of equipment in the Area 5 process are outlined below [21]. The CEPCI values for 2006 and 2019, which are used to account for increase in capital costs over time, are 499.6 and 619.2 respectively [25]. The rand to dollar conversion used is R16.72 per dollar [26].

Capital costing of flash tanks and reactor shells

The calculations used to determine the capital cost of each flash tank and shell of the reactors are as follows [16]. Sample calculations for the primary flash tank, FT-501, are shown below.

Table A5.29: Summary of information required to determine the capital cost of a flash tank

Diameter (inches)	96.5	Diameter (m)	2.45
Length (inches)	289	Length (m)	7.34
Design Pressure (psig)	71.6	Design Pressure (bar)	5.95
$\rho_{\text{carbon steel}}$ (lb/inch^3)	0.284		

The first steps in the determining the capital requirements of the flash, is to determine the wall thickness and then the weight of the vessel.

$$t_{wall} = 0.022\,P(bar)D(m) = \frac{0.022(5.95)(2.45)(39.3301)}{1000} = 0.013\,m \qquad \text{(A5.52)}$$

$$W = \pi(D + t_{wall})(L + 0.8D)t_{wall}\rho_{cs} \qquad \text{(A5.53)}$$

$$W = \pi(96.5 + 0.013)\big(289 + (0.8)(96.5)\big)(0.013)(0.284) = 397\,lb \qquad \text{(A5.54)}$$

Since the flash tanks are vertical vessels, the C_v value can be determined using Equation A5.55.

$$C_v = \exp\{7.0132 + 0.18255\ln(W) + 0.02297[\ln(W)]^2\} \qquad \text{(A5.55)}$$

$$C_v = \exp\{7.0132 + 0.18255\,ln(397) + 0.02297[ln(397)]^2\} = 9802 \qquad \text{(A5.56)}$$

$$C_{pl} = 361.8\left(\frac{D}{12}\right)^{0.73960}\left(\frac{L}{12}\right)^{0.70684} \qquad \text{(A5.57)}$$

$$C_{pl} = 361.8\left(\frac{96.5}{12}\right)^{0.73960}\left(\frac{289}{12}\right)^{0.70684} = 16008 \qquad \text{(A5.58)}$$

Since carbon steel is the material of construction, the material factor, F_m, is 1 and bare module factor, F_{BM}, of 4.16. Hence the cost of the flash is found in Equation A5.59.

$$C_{BM} = F_{BM}\big(C_vF_m + C_{pl}\big)\left(\frac{CEPCI(2019)}{CEPCI(2006)}\right)(RD) \qquad \text{(A5.59)}$$

Where RD is the rand to dollar exchange rate of R16.72 per dollar.

$$C_{BM} = 4.16\big((9802)(1) + 16008\big)\left(\frac{619.2}{499.6}\right)(16.72) = R2\ 225\ 044 \qquad \text{(A5.60)}$$

Table A5.30: Summary of the capital costs for the flash tanks and the reactor shells

Equipment No	Capital cost (R)
FT-501	2 225 044
FT-502	2 251 149
FT-503	2 349 275
RX-501	4 066 314
RX-502	6 217 564
RX-503	5 349 772

Capital cost of catalyst in each reactor

The capital cost for the reactors includes the cost of the reactor shell, as shown above, as well as the cost of the activated alumina catalyst required for each reactor. Sample calculations to the capital cost of catalyst and total reactor cost are shown for the primary Claus reactor, RX-501.

Table A5.31: Information required to determine the capital cost of catalyst in the Claus reactors

Catalyst density (kg/m^3)	769	Volume (m^3)	94
Catalyst price (R/kg)	21.56	Voidage	0.4

$$m_{catalyst} = V(1-\phi)\rho_{cat} = 94(1-0.4)(769) = 43372 \qquad \text{(A5.61)}$$

Using the mass of catalyst, determined in Equation A5.61, and the catalyst price the cost of catalyst can be determined in Equation A5.62.

$$Catalyst\ cost = m_{catalyst} \times Catalyst\ price \qquad \text{(A5.62)}$$

$$Catalyst\ cost = (43372)(21.56) = R935\ 092 \qquad \text{(A5.63)}$$

Table A5.32: Summary of capital costs for each Claus reactor

Equipment No	Catalyst cost (R)	Total Capital cost (R)
RX-501	935 092	5 001 406
RX-502	1 541 907	7 759 470
RX-503	1 293 212	6 642 984

Capital cost of heat exchangers

The calculations used to determine the capital cost of each heat exchanger are as follows [16]. Sample calculations for the primary heat exchanger, HX-501, and first air cooler, HX-504, are shown below.

Table A5.33: Summary of information required to determine the capital cost for each heat exchanger

Equipment No	HX-501	HX-504
Area (ft^2)	3179	110
Design pressure (psig)	78.9	73.0

The material factors,a and b, are both zero since carbon steel is chosen as the material of construction for all parts of the heat exchanger. The F_d value is assumed to be 1 for all heat exchangers.

$$F_m = a + \left(\frac{Area}{100}\right)^b = 0 + \left(\frac{3179}{100}\right)^0 = 1 \qquad \text{(A5.64)}$$

The method used to cost to determine the base cost, C_b, differs for shell and tube and double pipe heat exchangers. Sample calculations for shell and tube and double pipe exchangers are shown for HX-501 and HX-504 respectively.

For shell and tube heat exchangers C_b and F_p are determined using Equations A5.65 and A5.67 below with a bare module factor, F_{BM}, of 3.17.

$$C_b = \exp\left(11.667 - 0.8706\ln(Area) + 0.09005[\ln(Area)]^2\right) \qquad \text{(A5.65)}$$

$$C_b = \exp\left(11.667 - 0.8706\ln(3179) + 0.09005[\ln(3179)]^2\right) = 36316 \qquad \text{(A5.66)}$$

$$F_p = 0.8510 + 0.1292\left(\frac{P}{600}\right) + 0.0198\left(\frac{P}{600}\right)^2 \qquad \text{(A5.67)}$$

$$F_p = 0.8510 + 0.1292\left(\frac{78.9}{600}\right) + 0.0198\left(\frac{78.9}{600}\right)^2 = 0.996 \qquad \text{(A5.68)}$$

For double pipe heat exchangers C_b and F_p are determined using Equations A5.69 and A5.71 below with a bare module factor, F_{BM}, of 1.80.

$$C_b = \exp\left(7.1460 + 0.16\ln(Area)\right) \qquad \text{(A5.69)}$$

$$C_b = \exp\left(7.1460 + 0.16\ln(3179)\right) = 2691 \qquad \text{(A5.70)}$$

$$F_p = 0.9803 + 0.018\left(\frac{P}{100}\right) + 0.0017\left(\frac{P}{100}\right)^2 \qquad \text{(A5.71)}$$

$$F_p = 0.9803 + 0.018\left(\frac{73.0}{100}\right) + 0.0017\left(\frac{73.0}{100}\right)^2 = 0.867 \qquad \text{(A5.72)}$$

Therefore, the total capital cost for each heat exchanger is given by Equation A5.73.

$$C_{BM} = C_b\left(F_{BM} + F_d F_p F_m - 1\right)\left(\frac{CEPCI(2019)}{CEPCI(2006)}\right)(RD) \qquad \text{(A5.73)}$$

Table A5.34: Summary of capital costs for all heat exchangers

Equipment No	Type	Capital Cost (R)
HX-501	Shell and tube	2 382 250
HX-502	Shell and tube	1 764 179
HX-503	Shell and tube	2 154 739
HX-504	Double pipe	92 961
HX-505	Double pipe	94 810
HX-506	Double pipe	95 012

Total capital investment for the plant

The total bare module cost of the plant is equivalent to the sum of the capital cost of all pieces of equipment found in the process, which is R 32 813 280. The total capital investment for the entire plant, accounting for site and building costs, is determined using Equation A5.74 below.

$$C_{TPI} = 1.18(C_{BM} + 0.05C_{BM} + 0.1C_{BM}) \qquad \text{(A5.74)}$$

Therefore, the total capital investment for the plant is R 44 527 621.

A5-D. Process Operating Costs

The only operating costs related to the process found in Area 5 are the electricity required to blow air through the air coolers and the operating labour related to the process.

Electricity cost required for air coolers

The air coolers found in the Claus process require a fan to blow the air required for heat exchange. The calculations used to determine the annual cost of electricity for the first air cooler are shown below [13].

The only input required to determine the electricity cost in the cooler duty in MJ/h. The electricity price is given as 0.85 kW/h with the time on stream being 8000 h/year. The energy demand required by the fan is determined using Equation A5.75 below.

$$Energy\ Demand = IF \cdot Duty \cdot TOS \qquad \text{(A5.75)}$$

Where IF is the input factor, 0.0036 kWh/MJ, which is used to account for the energy losses occurring in the systems [13]. Therefore, the energy demand for the fan for the first air cooler is 67749 kWh/year. Using the given electricity price the electricity cost for the first air cooler is R57 587 per year.

Table A5.35: Summary of electricity costs for air coolers

Equipment No	Electricity cost
HX-504	57 587
HX-505	57 446
HX-506	52 131

Operating labour costs

In order to determine the operating labour costs, the yearly wage of R161 505 and number of operators are used. Equation A5.76 below describes how to determine the minimum number of operators per shift, with N_{np} being the number of unit operations in the process.

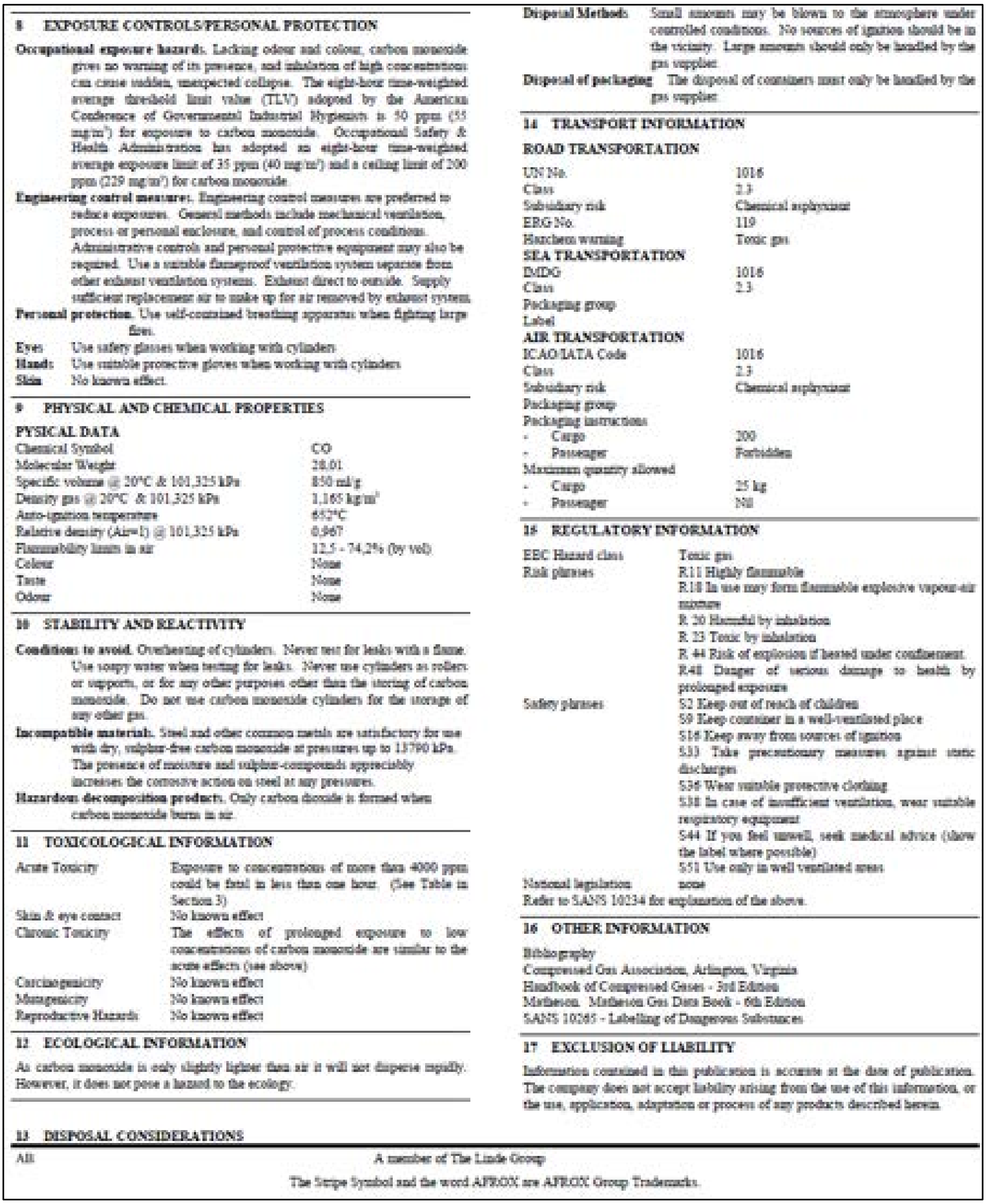
$$N_{OL} = (6.29 + 0.23N_{np})^{0.5} = (6.29 + 0.23(12))^{0.5} = 3 \qquad \text{(A5.76)}$$

However, four and half operators are hired per operator need at any time and thus the number of operators required is 14 [16].

Therefore the annual operating labour cost amounts to R2 261 070 per year.

A5-E. Material Safety Data Sheets

The following material safety data sheets (MSDS), Figures A5.19, A5.20 and A5.21 were obtained for CO, COS and S_6 as per the request of the Health, Safety and Environmental Specialist [27] [28] [29].



8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Occupational exposure hazards. Lacking odour and colour, carbon monoxide gives no warning of its presence, and inhalation of high concentrations can cause sudden, unexpected collapse. The eight-hour time-weighted average threshold limit value (TLV) adopted by the American Conference of Governmental Industrial Hygienists is 50 ppm (55 mg/m³) for exposure to carbon monoxide. Occupational Safety & Health Administration has adopted an eight-hour time-weighted average exposure limit of 35 ppm (40 mg/m³) and a ceiling limit of 200 ppm (229 mg/m³) for carbon monoxide.

Engineering control measures. Engineering control measures are preferred to reduce exposures. General methods include mechanical ventilation, process or personal enclosure, and control of process conditions. Administrative controls and personal protective equipment may also be required. Use a suitable flameproof ventilation system separate from other exhaust ventilation systems. Exhaust direct to outside. Supply sufficient replacement air to make up for air removed by exhaust system.

Personal protection. Use self-contained breathing apparatus when fighting large fires.

Eyes	Use safety glasses when working with cylinders
Hands	Use suitable protective gloves when working with cylinders
Skin	No known effect.

9 PHYSICAL AND CHEMICAL PROPERTIES

PYSICAL DATA

Chemical Symbol	CO
Molecular Weight	28,01
Specific volume @ 20°C & 101,325 kPa	850 ml/g
Density gas @ 20°C & 101,325 kPa	1,165 kg/m³
Auto-ignition temperature	652°C
Relative density (Air=1) @ 101,325 kPa	0,967
Flammability limits in air	12,5 - 74,2% (by vol)
Colour	None
Taste	None
Odour	None

10 STABILITY AND REACTIVITY

Conditions to avoid. Overheating of cylinders. Never test for leaks with a flame. Use soapy water when testing for leaks. Never use cylinders as rollers or supports, or for any other purposes other than the storing of carbon monoxide. Do not use carbon monoxide cylinders for the storage of any other gas.

Incompatible materials. Steel and other common metals are satisfactory for use with dry, sulphur-free carbon monoxide at pressures up to 13790 kPa. The presence of moisture and sulphur-compounds appreciably increases the corrosive action on steel at any pressures.

Hazardous decomposition products. Only carbon dioxide is formed when carbon monoxide burns in air.

11 TOXICOLOGICAL INFORMATION

Acute Toxicity	Exposure to concentrations of more than 4000 ppm could be fatal in less than one hour. (See Table in Section 3)
Skin & eye contact	No known effect
Chronic Toxicity	The effects of prolonged exposure to low concentrations of carbon monoxide are similar to the acute effects (see above)
Carcinogenicity	No known effect
Mutagenicity	No known effect
Reproductive Hazards	No known effect

12 ECOLOGICAL INFORMATION

As carbon monoxide is only slightly lighter than air it will not disperse rapidly. However, it does not pose a hazard to the ecology.

13 DISPOSAL CONSIDERATIONS

Disposal Methods	Small amounts may be blown to the atmosphere under controlled conditions. No sources of ignition should be in the vicinity. Large amounts should only be handled by the gas supplier.
Disposal of packaging	The disposal of containers must only be handled by the gas supplier.

14 TRANSPORT INFORMATION

ROAD TRANSPORTATION

UN No.	1016
Class	2.3
Subsidiary risk	Chemical asphyxiant
ERG No.	119
Hazchem warning	Toxic gas
SEA TRANSPORTATION	
IMDG	1016
Class	2.3
Packaging group	
Label	
AIR TRANSPORTATION	
ICAO/IATA Code	1016
Class	2.3
Subsidiary risk	Chemical asphyxiant
Packaging group	
Packaging instructions	
- Cargo	200
- Passenger	Forbidden
Maximum quantity allowed	
- Cargo	25 kg
- Passenger	Nil

15 REGULATORY INFORMATION

EEC Hazard class	Toxic gas
Risk phrases	R11 Highly flammable R18 In use may form flammable explosive vapour-air mixture R 20 Harmful by inhalation R 23 Toxic by inhalation R 44 Risk of explosion if heated under confinement. R48 Danger of serious damage to health by prolonged exposure
Safety phrases	S2 Keep out of reach of children S9 Keep container in a well-ventilated place S16 Keep away from sources of ignition S33 Take precautionary measures against static discharges S36 Wear suitable protective clothing S38 In case of insufficient ventilation, wear suitable respiratory equipment S44 If you feel unwell, seek medical advice (show the label where possible) S51 Use only in well ventilated areas
National legislation	none

Refer to SANS 10234 for explanation of the above.

16 OTHER INFORMATION

Bibliography
Compressed Gas Association, Arlington, Virginia
Handbook of Compressed Gases - 3rd Edition
Matheson. Matheson Gas Data Book - 6th Edition
SANS 10265 - Labelling of Dangerous Substances

17 EXCLUSION OF LIABILITY

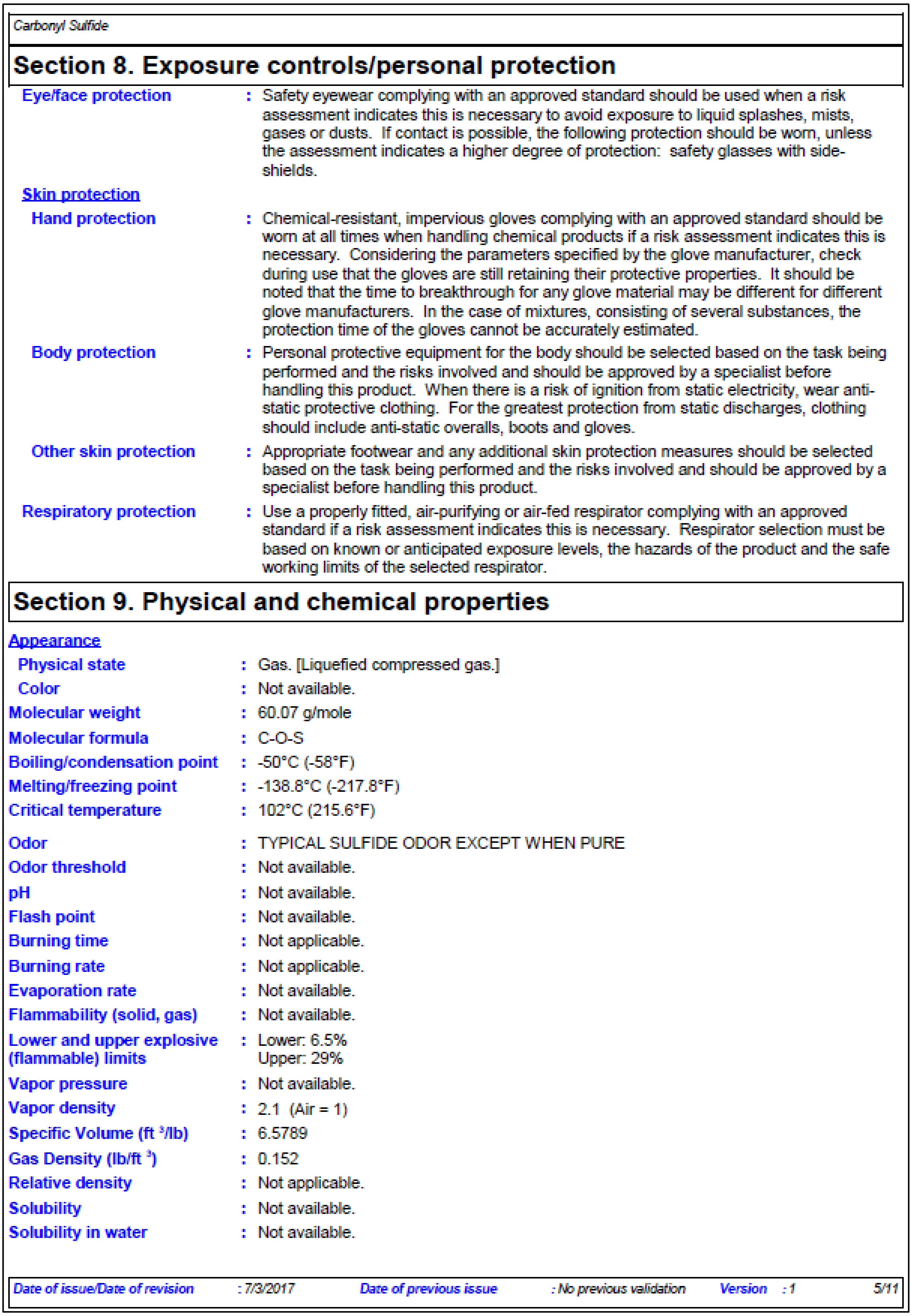
Information contained in this publication is accurate at the date of publication. The company does not accept liability arising from the use of this information, or the use, application, adaptation or process of any products described herein.

All

A member of The Linde Group

The Stripe Symbol and the word AFROX are AFROX Group Trademarks.

Figure A5.19: MSDS for carbon monoxide [27]



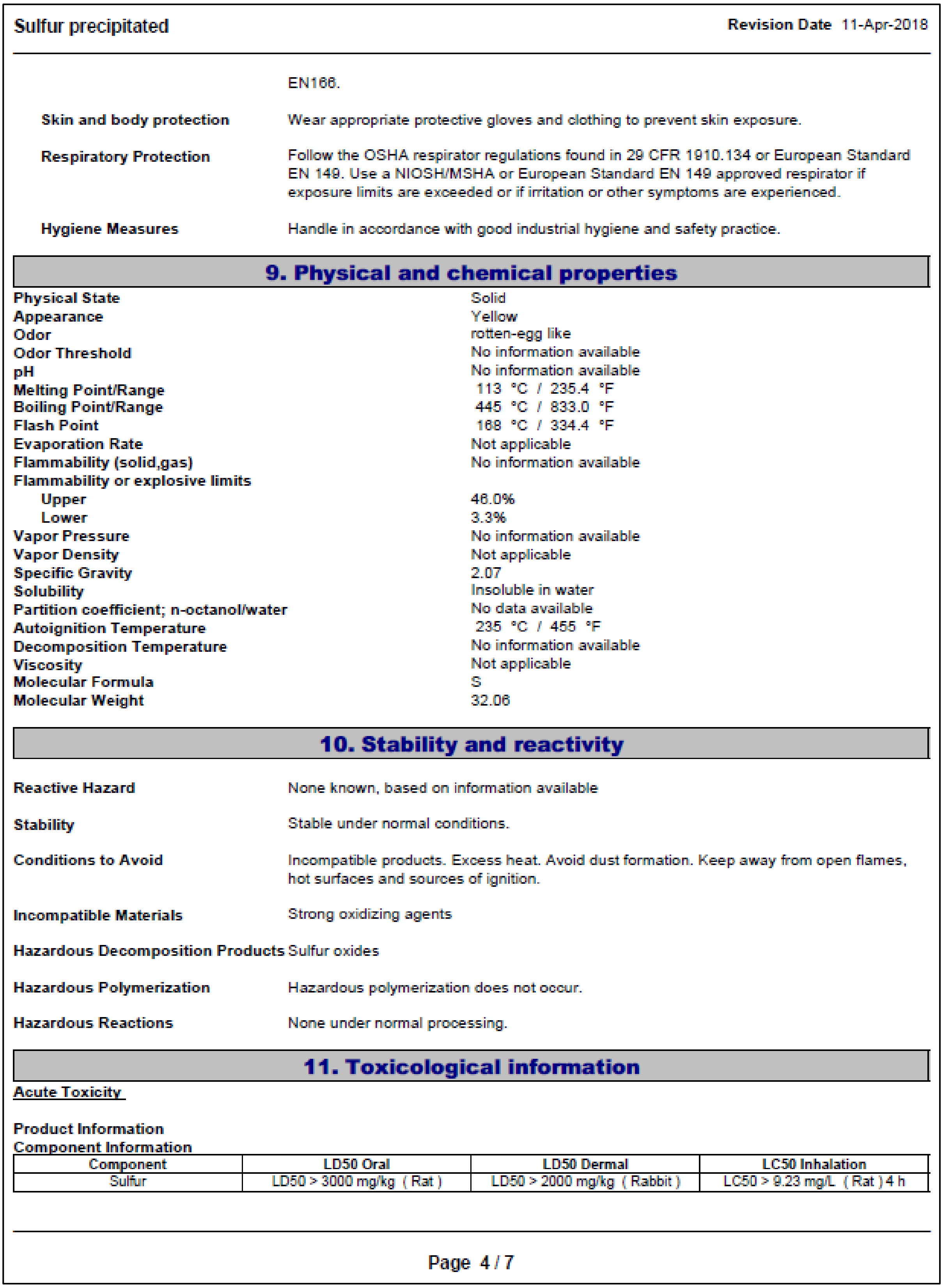
Section 8. Exposure controls/personal protection

Eye/face protection	Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists, gases or dusts. If contact is possible, the following protection should be worn, unless the assessment indicates a higher degree of protection: safety glasses with side-shields.
Skin protection	
Hand protection	Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary. Considering the parameters specified by the glove manufacturer, check during use that the gloves are still retaining their protective properties. It should be noted that the time to breakthrough for any glove material may be different for different glove manufacturers. In the case of mixtures, consisting of several substances, the protection time of the gloves cannot be accurately estimated.
Body protection	Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product. When there is a risk of ignition from static electricity, wear anti-static protective clothing. For the greatest protection from static discharges, clothing should include anti-static overalls, boots and gloves.
Other skin protection	Appropriate footwear and any additional skin protection measures should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.
Respiratory protection	Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.

Section 9. Physical and chemical properties

Appearance	
Physical state	Gas. [Liquefied compressed gas.]
Color	Not available.
Molecular weight	60.07 g/mole
Molecular formula	C-O-S
Boiling/condensation point	-50°C (-58°F)
Melting/freezing point	-138.8°C (-217.8°F)
Critical temperature	102°C (215.6°F)
Odor	TYPICAL SULFIDE ODOR EXCEPT WHEN PURE
Odor threshold	Not available.
pH	Not available.
Flash point	Not available.
Burning time	Not applicable.
Burning rate	Not applicable.
Evaporation rate	Not available.
Flammability (solid, gas)	Not available.
Lower and upper explosive (flammable) limits	Lower: 6.5% Upper: 29%
Vapor pressure	Not available.
Vapor density	2.1 (Air = 1)
Specific Volume (ft ^{3}/lb)	6.5789
Gas Density (lb/ft ^{3})	0.152
Relative density	Not applicable.
Solubility	Not available.
Solubility in water	Not available.

Figure A5.20: MSDS for carbonyl sulfide [28]



	EN166.
Skin and body protection	Wear appropriate protective gloves and clothing to prevent skin exposure.
Respiratory Protection	Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.
Hygiene Measures	Handle in accordance with good industrial hygiene and safety practice.

9. Physical and chemical properties

Physical State	Solid
Appearance	Yellow
Odor	rotten-egg like
Odor Threshold	No information available
pH	No information available
Melting Point/Range	113 °C / 235.4 °F
Boiling Point/Range	445 °C / 833.0 °F
Flash Point	168 °C / 334.4 °F
Evaporation Rate	Not applicable
Flammability (solid,gas)	No information available
Flammability or explosive limits	
Upper	46.0%
Lower	3.3%
Vapor Pressure	No information available
Vapor Density	Not applicable
Specific Gravity	2.07
Solubility	Insoluble in water
Partition coefficient; n-octanol/water	No data available
Autoignition Temperature	235 °C / 455 °F
Decomposition Temperature	No information available
Viscosity	Not applicable
Molecular Formula	S
Molecular Weight	32.06

10. Stability and reactivity

Reactive Hazard	None known, based on information available
Stability	Stable under normal conditions.
Conditions to Avoid	Incompatible products. Excess heat. Avoid dust formation. Keep away from open flames, hot surfaces and sources of ignition.
Incompatible Materials	Strong oxidizing agents
Hazardous Decomposition Products	Sulfur oxides
Hazardous Polymerization	Hazardous polymerization does not occur.
Hazardous Reactions	None under normal processing.

11. Toxicological information

Acute Toxicity

Product Information

Component Information

Component	LD50 Oral	LD50 Dermal	LC50 Inhalation
Sulfur	LD50 > 3000 mg/kg (Rat)	LD50 > 2000 mg/kg (Rabbit)	LC50 > 9.23 mg/L (Rat) 4 h

Figure A5.21: MSDS for elemental sulfur [29]

A5-F. Pinch analysis and minimum utility requirements

Table A5.36: Determining the pinch temperature using the temperature interval method

T_{mod} (°C)	Hot 1	Hot 2	Hot 3	Cold 1	Cold 2	Cold 3	Σmc_p (kW/°C)	ΔT (°C)	ΔH (kW)	ΣΔH (kW)	$\Sigma\Delta H_{mod}$ (kW)
299							0				-2076
245	14.3						14.3	54	775	775	-1301
226	14.3			-8.88			5.5	19	104	879	-1197
214	14.3			-8.88	-8.09		-2.6	12	-31	847	-1229
211	14.3			-8.88	-8.09	-7.91	-10.5	3	-32	816	-1260
210	14.3	9.05		-8.88	-8.09	-7.91	-1.5	1	-1	814	-1262
195	14.3	9.05			-8.09	-7.91	7.4	15	111	925	-1151
187	14.3	9.05	8.10		-8.09	-7.91	15.5	8	124	1049	-1027
167	14.3	9.05	8.10			-7.91	23.6	20	472	1521	-555
159		9.05	8.10			-7.91	9.2	8	74	1595	-481
139		9.05	8.10				17.2	20	343	1938	-138
122			8.10				8.1	17	138	2076	0

Table A5.37: Summary of results of pinch analysis and utility requirements

$T_{p,mod}$ (°C)	122	Minimum hot utility (kW)	0
$T_{p,mod\ (Hot)}$ (°C)	132	Minimum cold utility (kW)	2076
$T_{p,mod\ (Cold)}$ (°C)	112		