

Article

Using Reduced Kinetic Model for the Multi-Objective Optimization of Thermal Section of the Claus Process Leading to a More Cost-Effective and Environmentally Friendly Operation

Ecem Muge Andoglu Coskun ^{1,*} , Suleyman Kaytakoglu ², Flavio Manenti ³  and Alessandro Di Pretoro ⁴ ¹ Department of Food Processing, Bilecik Seyh Edebali University, Bilecik 11230, Turkey² Department of Chemical Engineering, Eskisehir Technical University, Eskisehir 26555, Turkey; skaytako@eskisehir.edu.tr³ Dipartimento di Chimica, Materiali e Ingegneria Chimica “G. Natta”, Politecnico di Milano, 20133 Milan, Italy; flavio.manenti@polimi.it⁴ Laboratoire de Génie Chimique à Toulouse, Institut National Polytechnique de Toulouse, 31432 Toulouse, France; alessandro.dipretoro@ensiacet.fr

* Correspondence: muge.andoglu@bilecik.edu.tr

Abstract: The Claus process is a sulfur recovery unit wherein hydrogen sulfide is converted into the elemental sulfur. This study aims to model the thermal section of the Claus process, which consists of a reaction furnace and a waste heat boiler, as a configuration of two reactors, and subsequently optimize the entire section. Two different reduced kinetic schemes were provided for both units. Using the validated kinetics, mathematical models were developed. The waste heat boiler was modeled as a plug flow reactor with heat transfer, instead of a heat exchanger. The main objective was to maximize the amount of elemental sulfur at the end of the thermal section. Additionally, maximizing the amount of steam generated in the WHB was considered as a secondary objective, and the multi-objective optimization problem was solved. The sulfur production was improved 14.1% and 30% as a result of single- and multi-objective optimization studies. In addition, as an alternative, the Taguchi method was also used for optimization studies, and optimum values were determined. Using the Taguchi method, we determined that an increase in sulfur production by 24% is possible.

Keywords: process optimization; kinetic modeling; Claus process; hydrogen sulfide; reduced kinetic model; reaction furnace; waste heat boiler



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1. Introduction

The petrochemical industry is an important industry that meets the needs of the whole world. It is inevitable that various waste gases will be released from this industry, as it uses crude oil and natural gas as resources. One of these gases is hydrogen sulfide, which is a poisonous gas and is found in high concentrations in refinery acid waste gases. Due to its high abundance, H₂S removal takes place in the Claus sulfur recovery unit in refineries. The Claus unit is a part of the refinery that does not attract attention and is not studied much as long as it operates properly. However, since this unit is controlled by strict environmental regulations, its failure to operate efficiently could lead to the closing down of the refinery. For this reason, every improvement that can be made to this unit will contribute to the efficiency of refineries, increase financial gains, reduce losses, and limit the negative impact on the environment by providing the conditions determined by the regulations.

The Claus is a recovery process in which some of the hydrogen sulfide oxidizes and turns into sulfur dioxide, and then the remaining H₂S reacts with the SO₂ to form hydrogen gas and elemental sulfur. Depending on the process conditions and feed gas composition, sulfur recovery efficiency will be 94–98%; if the residual gas is sent to the incineration unit, sulfur recovery efficiency may rise up to 99.99% [1,2]. Approximately 60–70% of the hydrogen sulfide conversion in the process occurs in the thermal step [3].

In order to increase the sulfur recovery efficiency, many researchers have studied thermal furnace modeling, and in the first of these modeling studies, constrained equilibrium models were used to predict product distribution from the Claus reaction furnace. Bennett and Meisen evaluated 36 chemical species, including nitrogen compounds and radicals, and reported equilibrium calculations in the H₂S–air system at temperatures up to 2000 K [4]. Khudenko et al. performed a Claus reaction furnace equilibrium calculation under oxygen-rich conditions using the Gibbs energy minimization method [5]. As a result, they found that the oxygen-based Claus process could reduce equipment dimensions. Monnery et al. [6] applied various methods such as Gibbs energy minimization, Fisher monograph and Western Research correlations to determine the reaction furnace's output, and they determined that the results of these methods were not compatible with the results obtained before and after the waste heat boiler was applied. Selim et al. investigated the critical roles of other gases besides H₂S in determining the optimum operating temperature required for maximum sulfur recovery [7]. ZareNezhad and Hosseinpour presented a general formulation for determining the Claus reaction furnace temperature, equilibrium compositions and optimum air ratio using the Gibbs free energy minimization method [8].

Up to today, the research has evolved to focus on kinetic model-based studies. Since 1999, both simplified and detailed kinetic models have begun to be developed for the reaction furnace. Dowling and Clark aimed to apply a more stringent reversible kinetic model and use a more robust data regression technique [9]. Monnery et al. carried out laboratory and modeling studies together; they compared the separation of HS and sulfur conversion as a result of the second Claus reaction with that occurring under furnace conditions by combining their results with the results of previous studies [6]. Pierucci et al. modeled a thermal reactor with a detailed kinetic design based on an approach that included 130 species and more than 1500 elementary reactions. They aimed to present a meaningful phenomenological furnace model based on the non-equilibrium approach in order to achieve a detailed kinetic design [10]. Jones et al. defined a reaction set including independent reactions and used a four-step method to determine the product distribution of the measured waste heat boiler output. Their study was limited to the waste heat boiler output [11]. Manenti et al. modeled the thermal step of a sulfur recovery unit including the reaction furnace and waste heat boiler using a kinetic model containing 146 species and 2412 reactions [12]. In another study in the same year, they aimed to develop their own kinetic models by considering the Claus process' conditions. Unlike in the literature, their kinetic parameters explain the presence of light hydrocarbons, ammonia and other species. The work provides a review of the major phenomena involved in reacting systems containing sulfur compounds [13]. In another study, Manenti et al. used a kinetic model with 140 species and 2400 reactions to optimize elemental sulfur recovery and steam production [14].

In another study, an industrial sulfur recovery unit reaction furnace was modeled using equilibrium and combined modeling [15]. Nabikandi and Fatemi modeled and simulated an industrial Claus sulfur recovery process. Furnace and Claus reactors were comparatively modeled with two different approaches: the equilibrium and the kinetic method [16]. Zarei et al. modeled reaction furnace and waste heat boiler methods separately and together, using two different reaction schemes containing the same reaction rate expressions [17]. A dynamic model was introduced for the reaction furnace simulation, and all the existing kinetic information was used in this model, but complex reactions with free radicals were neglected Pahlavan and Fanaei [18] in order to prevent complexity. Adewale et al. examined the hydrogen and sulfur degradation of H₂S using the process simulator [19]. Andoglu et al. developed a reduced kinetic model for a reaction furnace and compared the results with detailed kinetic mechanism [20]. In the study of Fazlollahi et al., using both numerical modeling and simulation, the effects of oxygen and acid gas enrichment on the reaction furnace temperature and sulfur recovery were studied [21]. Mahmoodi et al. developed a CFD model for a thermal furnace using the reduced kinetic model [22]. Dell'Angelo et al.

proposed a machine learning method to determine the mechanisms of their reduced kinetic model for the reaction furnace [23].

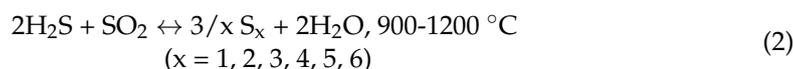
Recently, optimization studies on Claus process units have been encountered. Researchers used different algorithms and methods for optimization. Kazempour et al. detailed the multi-objective optimization of modeling and the thermal part of the Claus process with a kinetic model utilizing a response surface method (Central Composite Design). Sensitivity analysis was performed with a simulator software to investigate the effects of fuel and air inlet flow rates, steam inlet temperature, oven pressure and waste heat boiler (WHB) output temperature on sulfur recovery efficiency, steam production and H₂S/SO₂ ratio [3]. Ghahraloud et al. aimed to model and optimize an industrial modified Claus process in order to achieve maximum sulfur recovery using a genetic algorithm. The decision variables here were the inlet temperatures of the oven and fixed bed reactors, the distribution of feeding throughout the oven and the air flow rate in the furnace [24]. Zarei performed optimization work with the fmincon function in Matlab for maximizing the sulfur conversion and reducing total emissions from the thermal furnace, with the temperature, pressure, and oxygen amount in the feed as control variables [25]. Rahman et al. simulated the thermal part in Chemkin Pro and the catalytic part in Aspen Hysys using a detailed kinetic model; they performed optimization studies using a genetic algorithm and artificial neural networks in Matlab [26]. Zahid et al. modeled the Claus process, validated it with industrial data and performed an optimization study using pinch analysis [27]. Johni and OmidbakhshAmiri simulated SRU using the Aspen HYSYS, and environmental, energy, and economic features of the process based on special criteria (profit, weighted global warming potentials, and energy consumption) were analyzed. After the sensitivity analysis of the process, single- and multi-objective optimizations were carried out using genetic algorithm [28].

In the optimization studies, the reaction furnace was considered alone as the only reactor in the thermal step; the waste heat boiler was not taken into account, or it was considered as a simple heat exchanger. This assumption ignores the reformation of hydrogen sulfide with a sudden temperature drop in the waste heat boiler, where the gas mixture leaving the furnace at high temperatures is cooled before entering the catalytic reactors, thus introducing an error into the calculation of amounts of components at the end of the thermal step. This study aims to optimize the thermal section of the Claus process by considering the waste heat boiler as a reactor with heat exchange instead of a basic heat exchanger. As the first step, the reaction furnace and the waste heat boiler will be modeled as reactors on a kinetic basis using reduced kinetic models with 11 and 2 global reactions, respectively. As the second step, both units will be optimized together in the thermal section of the Claus process to maximize the sulfur and steam production using a genetic algorithm and statistical analysis.

2. Methodology

2.1. Description of the Process

The Claus process is a sulfur recovery unit in which some of the hydrogen sulfide is oxidized and forms sulfur dioxide, while some of it reacts with SO₂ and turns into elemental sulfur:



A typical Claus process consists of two main parts: the thermal part and the catalytic part. The thermal part consists of a burner, a thermal reactor and a waste heat boiler. This is also where the destruction of pollutants that may damage the system or cause calcification in the equipment, the production of sulfur through thermal decomposition, and the production of steam in the waste heat boiler occur. The catalytic part is where

elemental sulfur is produced by the Claus reaction, which involves a reaction between the SO_2 produced in the thermal part and unreacted H_2S . It usually consists of two or three catalytic reactors, the input of which is the output of the thermal part. The degree of hydrogen sulfide removal at the Claus process exit reaches 98%. An incinerator is added at the end of the process to reach 99% H_2S removal [3,5].

Thermal Section of Claus Process

A schematic representation of the thermal part, where approximately 60–70% of the hydrogen sulfide conversion takes place, and which therefore constitutes the most important part of the process, can be seen in Figure 1. Besides allowing reactions to occur, the thermal section has other functions, such as the disposal of contaminants that may accumulate and cause damage to the equipment, and the formation of steam in the waste heat boiler [3].

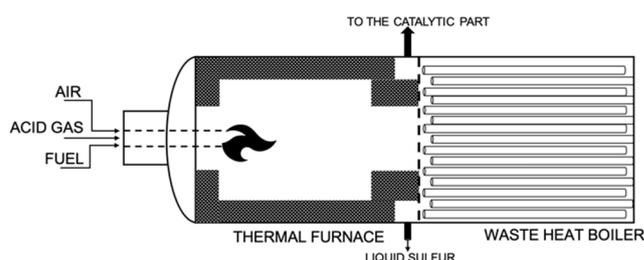


Figure 1. Schematic representation of Claus process reaction furnace and waste heat boiler.

The reaction furnace (RF) is a cylindrical boiler lined with refractory material. The thickness of the refractory lining is chosen to maintain a room temperature above the acid gas dew point temperature, which may cause undesirable corrosion. The thermal reaction furnace is a critical piece of equipment; it affects the efficiency and operation of the unit as it is the source of key components. The reaction furnace consists of two zones: the flame zone (or oxygen-rich zone) and the post-flame (oxygen-free) zone. The free flame zone (burner, oxygen-rich zone) located at the front end of the furnace is characterized by high temperatures and very fast reactions. The flame zone contains oxygen, and the temperature here can reach up to 2000 °C. Acid gas is fed to the burner located in the center of the furnace, generally at a pressure range of 130–180 kPa, along with enough air to keep the $\text{H}_2\text{S}:\text{SO}_2$ ratio at the furnace exit at 2:1. The pressure drop is 3 kPa, and air enters the burner through the ring housing and maintains the flame 0.2 to 0.3 m behind the burner mouth. Here, the oxygen content is rapidly consumed by the species with the highest reactivity. H_2S is often involved in this reaction pathway; its oxidation begins in the burner flame and continues adiabatically throughout the furnace until it reaches a thermodynamic equilibrium temperature. Reactions occur at lower temperatures and speeds in the oxygen-free zone behind the flame in the furnace. The combustion of acid gas in the furnace takes place in the range of 975–1300 °C. While the residence time in the flame zone is as short as milliseconds, in the oxygen-free zone it varies between 0.5 and 2.0 s depending on the flow rate and temperature. The temperature rises rapidly in the initial section of the thermal furnace, where one-third of the H_2S is oxidized; the temperature then decreases slowly (by about 100 °C) in the rest of the furnace due to the endothermic nature of the reactions taking place here and all the thermal losses. The pyrolysis of H_2S starts above 850 °C and reaches 50% conversion at 1050 °C. Since the combustion process in the thermal reaction furnace provides significant sulfur recovery, any development in the reaction furnace directly affects the reduction in the amount of hydrogen sulfur released into the atmosphere [10,13,14,17].

The products burned in the thermal reaction furnace are cooled from 926–1300 °C to 230–370 °C in the waste heat boiler (WHB). Since the furnace is extremely exothermic, a significant amount of high-pressure steam is generated in the subsequent waste heat boiler. A typical waste heat boiler is a shell-and-tube-type heat exchanger with one or two tube

passages directly connected to the furnace; the gas is evenly distributed in the horizontal tubes, and the water is kept at boiling conditions on the side of the body. Reforming reactions possibly occur until the relevant quenching temperatures are reached and the gas composition freezes; generally, reforming reactions occur below 900–1000 °C. The waste heat boiler model can also be defined by the presence of a PFR which the outer surface is kept at a constant temperature by the tube containing the boiling feed water [10,14,17,18].

2.2. Modeling and Simulation of Reaction Furnace

2.2.1. Process Specifications

In this study, the reaction furnace was modeled as a PFR, with reference to previous studies. The furnace geometry and inlet feed information were taken from Nabikandi and Fatemi [16], and are given in Table 1.

Table 1. Inlet conditions and furnace geometry.

	Acid Gas	Air	Fuel
Pressure (Pa)	177,000	168,000	600,000
Temperature (°C)	218	220	40
Components	Mole%	Mole%	Mole%
CO ₂	53.16	0.00	1.03
N ₂	0.00	73.00	3.68
CH ₄	0.90	0.00	89.46
H ₂ S	36.04	0.00	0.00
O ₂	0.00	19.50	0.00
H ₂ O	9.90	7.50	0.00
C ₂ H ₆	0.00	0.00	5.66
C ₃ H ₈	0.00	0.00	0.17
Molar flow rate (mol/s)	171.11	181.50	3.24
Furnace specifications			
Furnace length (m)		6.5	
Furnace inside diameter (m)		3.4	
Residence time in furnace(s)		2.0	
Operating pressure (Pa)		160,000	

2.2.2. Reduced Kinetic Model

The Claus process reaction furnace is a high-temperature reactor in which oxidation, cracking and Claus reactions mainly take place. The total reaction that characterizes the process includes the combustion reaction of hydrogen sulfide ($2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O}$), where elemental sulfur is produced, and there are complex kinetic mechanisms that describe this. Sulfur recovery plant thermal reaction furnace kinetics are complex and not yet fully understood.

It is not reasonable to consider all of the reactions, since the formation and consumption of some of the components occur in negligible amounts, meaning cumbersome computational efforts are rendered unnecessary. Therefore, in addition to the decomposition, oxidation and reaction of hydrogen sulfide, which are the main reactions assessed in this study, the reactions involving the components H₂S, S₂, CO₂, O₂ and H₂O, which are critical for the system being discussed, are found in high amounts in the feed streams, and their reactions directly affect the compositions at the furnace exit.

In this study, a reduced kinetic model was proposed and used in the following steps. The time of calculation using the reduced scheme is lower than that when using the detailed kinetic model, and easier to modify. H₂S pyrolysis and oxidation, H₂S and CH₄ pyrolysis with CS₂ formation, COS and CS₂ oxidation, and the effects on SO₂ radicals are taken as the base reactions. Another important criterion in these choices is that the reaction kinetics are well-known and can be easily found in the literature. In addition, they are homogeneous gas phase reactions and occur between 900 and 1200 °C. It is also desirable for the reaction to proceed to a significant degree during the retention time in the reactor, so that products can be obtained in measurable concentrations. The proportions of ammonia and hydrocarbons in the feed that are less than 1% are given in the literature; therefore,

reactions including ammonia and hydrocarbons are not included in the kinetic scheme. The reactions and rate expressions of the proposed reduced kinetic model are shown in Table 2. The reaction parameters are given Table 3.

Table 2. Reduced kinetic model reactions and reaction rate expressions for the thermal furnace.

Reaction No.	Reaction Equation	Reaction Rate Expression	Ref.
RF-1	$\text{H}_2\text{S} \leftrightarrow 1/2 \text{S}_2 + \text{H}_2$	$r_{\text{H}_2\text{S}} = A_f e^{\left(\frac{-E_f}{RT}\right)} P_{\text{H}_2\text{S}} P_{\text{S}_2}^{0.5} - A_r e^{\left(\frac{-E_r}{RT}\right)} P_{\text{H}_2} P_{\text{S}_2}$	[29]
RF-2	$2\text{H}_2\text{S} + \text{SO}_2 \leftrightarrow 3/2 \text{S}_2 + 2\text{H}_2\text{O}$	$r_{\text{H}_2\text{S}} = A_f \exp\left(\frac{-E_f}{RT}\right) P_{\text{H}_2\text{S}}^2 P_{\text{SO}_2}^{0.5} - A_r \exp\left(\frac{-E_r}{RT}\right) P_{\text{H}_2\text{O}}^2 P_{\text{S}_2}^{0.75}$	[30]
RF-3	$\text{H}_2\text{S} + 3/2 \text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$	$r_{\text{H}_2\text{S}} = A_f \exp\left(\frac{-E_f}{RT}\right) P_{\text{H}_2\text{S}} P_{\text{O}_2}^{1.5}$	[29]
RF-4	$\text{CH}_4 + 2\text{S}_2 \rightarrow \text{CS}_2 + 2\text{H}_2\text{S}$	$r_{\text{CS}_2} = A_f \exp\left(\frac{-E_f}{RT}\right) C_{\text{CH}_4} C_{\text{S}_2}$	[31]
RF-5	$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$	$r_{\text{CO}} = A_f \exp\left(\frac{-E_f}{RT}\right) C_{\text{CO}_2} C_{\text{H}_2}^{0.5}$	[32]
RF-6	$\text{CO} + 1/2 \text{S}_2 \leftrightarrow \text{COS}$	$r_{\text{COS}} = A_f \exp\left(\frac{-E_f}{RT}\right) C_{\text{CO}} C_{\text{S}_2} - 2A_r \exp\left(\frac{-E_r}{RT}\right) C_{\text{COS}} C_f$	[33]
RF-7	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$	$r_{\text{CH}_4} = A_f * \exp\left(-\frac{E_f}{RT}\right) C_{\text{CH}_4}^{0.7} C_{\text{O}_2}^{0.8}$	[34]
RF-8	$\text{CO} + 1/2 \text{O}_2 \leftrightarrow \text{CO}_2$	$r_{\text{CO}} = A_f * \exp\left(-\frac{E_f}{RT}\right) C_{\text{CO}} C_{\text{H}_2\text{O}}^{0.5} C_{\text{O}_2}^{0.25}$ $r_{\text{CO}_2} = A_r \exp\left(\frac{-E_r}{RT}\right) C_{\text{CO}_2}$	[35]
RF-9	$\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$	$r_{\text{H}_2} = A_f * \exp\left(-\frac{E_f}{RT}\right) C_{\text{H}_2} C_{\text{O}_2}$	[36]
RF-10	$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	$r_{\text{CH}_4} = A_f * \exp\left(-\frac{E_f}{RT}\right) C_{\text{CH}_4} C_{\text{CO}_2}$	[37]
RF-11	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	$r_{\text{CH}_4} = A_f * \exp\left(-\frac{E_f}{RT}\right) C_{\text{CH}_4} C_{\text{H}_2\text{O}}$	[37]

Table 3. Reaction parameters.

Reaction No.	A_f	E_{af} (J/mol)	A_r	E_{ar} (J/mol)
RF-1	$5263 \times 10^6 \text{ mol}/(\text{m}^3 \cdot \text{s} \cdot \text{atm}^{1.5})$	1.88×10^5	$13.6 \times 10^6 \text{ mol}/(\text{m}^3 \cdot \text{s} \cdot \text{atm}^2)$	9.8×10^4
RF-2	$15,762 \times 10^6 \text{ mol}/(\text{m}^3 \cdot \text{s} \cdot \text{atm}^{1.5})$	2.08×10^5	$506 \times 10^6 \text{ mol}/(\text{m}^3 \cdot \text{s} \cdot \text{atm}^{1.75})$	1.879×10^5
RF-3	$13.6 \times 10^6 \text{ mol}/(\text{m}^3 \cdot \text{s} \cdot \text{atm}^{2.5})$	4.60×10^4	-	-
RF-4	$5.53 \times 10^7 \text{ m}^3/(\text{mol} \cdot \text{s})$	1.6×10^5	-	-
RF-5	$1.249 \times 10^9 (\text{m}^3/\text{mol})^{0.5}/\text{s}$	2.59×10^5	-	-
RF-6	$3.18 \times 10^2 \text{ m}^3/(\text{mol} \cdot \text{s})$	5.57×10^4	$2.18 \times 10^6 \text{ m}^3/(\text{mol} \cdot \text{s})$	1.8×10^5
RF-7	$1.58 \times 10^{10} (\text{m}^3/\text{mol})^{0.5}/\text{s}$	2.2×10^5	-	-
RF-8	$1.26 \times 10^{10} \left[\left(\frac{\text{m}^3}{\text{mol}} \right)^{0.75} \frac{1}{\text{s}} \right]$	1.67×10^5	$5.0 \times 10^8 \text{ 1/s}$	1.67×10^5
RF-9	$1.08 \times 10^{10} \text{ m}^3/(\text{mol} \cdot \text{s})$	1.25×10^5	-	-
RF-10	$8.06 \times 10^8 \text{ m}^3/(\text{mol} \cdot \text{s})$	2.084×10^4	-	-
RF-11	$4.56 \times 10^9 \text{ m}^3/(\text{mol} \cdot \text{s})$	2.137×10^4	-	-

2.2.3. Mathematical Modeling of Thermal Furnace

In this study, a horizontal furnace was simulated in the MATLAB environment using the following assumptions [3,12,17,18]:

- If concentration and temperature gradients in the radial direction are neglected, one-direction plug flow can be assumed in thermal reaction furnace modeling;
- The reaction furnace is a plug flow reactor (PFR);
- The furnace is well insulated, conditions are adiabatic and pressure drop is neglected;
- The unit is in a steady-state operating condition;
- Due to the high temperature and low pressure, ideal gas assumption is valid;
- In turbulent flow, dispersion in the axial direction is neglected;
- In all kinetics stated, elemental sulfur is given as S_2 ;
- Since the feed temperature is higher than the storage temperature, direct flow configuration was used.

Mole and energy balances and equations based on reaction rate expressions were established using Fogler [38]. The energy balance for a single reaction occurring in a PFR is given by the equation below:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)[-ΔH_{Rx}(T)]}{\sum_{i=1}^m F_i C_{P_i}}, \quad (3)$$

If q reactions occur and there are m species, the equation can be generalized as follows:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum_{i=1}^q (-r_A)[-ΔH_{Rx}(T)]}{\sum_{j=1}^m F_j C_{P_j}}, \quad (4)$$

If it is accepted that the process occurs adiabatically, the $Ua(T_a - T)$ term is neglected and the equation turns into the following form:

$$\frac{dT}{dV} = \frac{\sum_{i=1}^q (-r_A)[-ΔH_{Rx}(T)]}{\sum_{j=1}^m F_j C_{P_j}}, \quad (5)$$

N_2 , which has a high mole fraction, was included in the calculations as inert. Heat capacity values were calculated according to the equation

$$C_{P_i} = a_i + b_i * \frac{T}{1000} + c_i * \left(\frac{T}{1000}\right)^2 + d_i * \left(\frac{T}{1000}\right)^3, \quad (6)$$

using a , b , c and d values taken from JANAF tables.

2.3. Modeling and Simulation of Waste Heat Boiler

2.3.1. Process Specifications

To propose and validate a kinetic model for the waste heat boiler, it was considered as a single unit. Hence, the inlet conditions were required, and Data Set 2 from Manenti et al. [12] was used to infer the boiler conditions (Table 4).

Table 4. Inlet conditions and geometry of waste heat boiler.

Component	mol%	Component	mol%
S ₂	0.09200	CO	0.00019
COS	0.00028	CO ₂	0.00604
H ₂ S	0.06023	N ₂	0.53539
SO ₂	0.03025	H ₂	0.01899
H ₂ O	0.25664		
Flow rate (kg/s) (/tube)			0.0361
Temperature (°C)			1351
Pressure (atm)			1.6
WHB tube diameter (m)			0.048
WHB tube length (m)			9.15
Number of tubes			470
Cooling water temperature (°C)			201.2

2.3.2. Reduced Kinetic Model

The waste heat boiler is a shell-and-tube-type heat exchanger that cools the gases coming out of the furnace at temperatures of 900–1300 °C to the range of 250–300 °C, with one or two tube passages, and releases high-pressure steam. Since the waste heat boiler is directly connected to the reaction furnace, the boiler inlet stream is the gas that leaves the furnace. There is no other current fed to the boiler. Therefore, the boiler is an oxygen-free zone with no combustion reactions. Besides this, in the first part of the boiler, where the gases have not yet had the opportunity to cool, furnace reactions continue to

occur. However, when the temperature decreases below 1000 °C, which is now considered a low temperature for these reactions, reformation reactions are observed; the H₂S and COS concentrations increase while S₂, H₂ and CO concentrations decrease. When the temperature of the gas mixture cools down to below 500 °C, no reaction occurs. Very little research has been done on the reactions taking place in the boiler. However, boiler behavior should be well understood, as it affects the total efficiency, and the amount of waste heat collected here is important because it is used in the catalytic part of the Claus process and other parts of the plant [12,39]. Based on this information, the reactions expected to take place in the boiler, the reaction rate expressions and the kinetic parameters of these reactions are given in Tables 5 and 6.

Table 5. Selected reactions for the waste heat boiler.

Reaction No.	Reaction Equation	Reaction Rate Expression	Ref.
RW.1	$1/2 S_2 + H_2 \leftrightarrow H_2S$	$r_{H_2S} = A_f e^{-\frac{E_f}{RT}} P_{H_2S} P_{S_2}^{0.5} - A_r e^{-\frac{E_r}{RT}} P_{H_2} P_{S_2}$	[29]
RW.2	$CO + 1/2 S_2 \leftrightarrow COS$	$r_{COS} = A_f e^{-\frac{E_f}{RT}} C_{CO} C_{S_2} - 2k_r C_{COS} C_t, C_t = \frac{P_t}{RT}$	[33]

Table 6. Reaction parameters.

Reaction No.	A _f	E _f (kcal/kmol)	A _r	E _r (kcal/kmol)
RF-1	$5263 \times 10^6 \text{ mol}/(\text{m}^3 \cdot \text{s} \cdot \text{atm}^{1.5})$	1.88×10^5	$13.6 \times 10^6 \text{ mol}/(\text{m}^3 \cdot \text{s} \cdot \text{atm}^2)$	9.8×10^4
RF-2	$15,762 \times 10^6 \text{ mol}/(\text{m}^3 \cdot \text{s} \cdot \text{atm}^{1.5})$	2.08×10^5	$506 \times 10^6 \text{ mol}/(\text{m}^3 \cdot \text{s} \cdot \text{atm}^{1.75})$	1.879×10^5

2.3.3. Mathematical Modeling of Waste Heat Boiler

In this study, a waste heat boiler was simulated in MATLAB software 2015a using the following assumptions [12,39]:

- Since the waste heat boiler is a multi-tube shell-and-tube heat exchanger and reactions continue to occur within the tubes, each tube is considered a plug flow reactor with heat transfer;
- Modeling is performed for a single tube;
- The unit is under steady-state operating conditions;
- Pressure drop is neglected;
- Due to the high temperature and low pressure, the ideal gas assumption is valid;
- In turbulent flow, dispersion in the axial direction is neglected;
- In all the kinetics stated, elemental sulfur is given as S₂;
- It is assumed to be a fully developed flow;
- Fouling in the tubes is neglected;
- The total heat transfer coefficient is assumed to be constant ($U = 35 \text{ W}/\text{m}^2/\text{K}$);
- The cooling water temperature is assumed to be equal to the wall temperature and constant.

Mole and energy balances and equations based on velocity expressions were established using [38] on a control volume (Figure 2). The heat transfer term ($Ua(T_a - T)$) has been added to the reactor energy balance, where U is the total heat transfer coefficient, a is the heat transfer area per unit reactor, and T_a is the wall temperature.

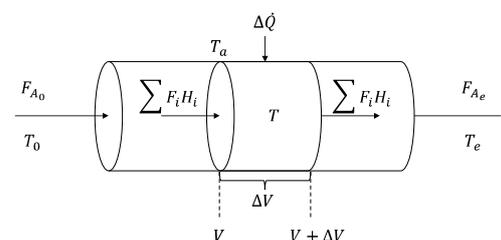


Figure 2. A tubular reactor with heat transfer and control volume.

Energy balance for volume ΔV (Since no work is done, $W_s = 0$):

$$\Delta \dot{Q} + \sum F_i H_i|_V - \sum F_i H_i|_{V+\Delta V} = 0, \quad (7)$$

$$\Delta \dot{Q} = U * \Delta A * (T_a - T) = U * a * \Delta V * (T_a - T), \quad (8)$$

$$\frac{dT}{dV} = \frac{r_A \Delta H_{Rx} - Ua(T_a - T)}{\sum F_i c_{p_i}} = \frac{r_A \Delta H_{Rx} - Ua(T_a - T)}{F_{A_0} (\sum \theta_i c_{p_i} + \Delta c_{p_x})}, \quad (9)$$

The total heat transfer coefficient is defined by the following equation:

$$\frac{1}{U} = ff_i + \frac{1}{h_i} + \frac{x_w D}{k_m D_{Lt}} + \frac{D}{D_o h_o} + \frac{D ff_o}{D_o}, \quad (10)$$

ff_i and ff_o are the pollution factors and are given as 1.77×10^{-4} and $8.81 \times 10^{-5} \text{ m}^2 \cdot \text{K}/\text{W}$, respectively. Therefore, the U value is in the range of 30–40 $\text{W}/(\text{m}^2 \cdot \text{K})$, and uncertainties in contamination factors are insignificant. For steam formation, the heat transfer coefficient outside the tube (h_o) is considered to be very large compared to the heat transfer coefficient inside the tube (h_i), so the fourth term in the equation is neglected [39]. For this reason, in this study, the U value was taken as 35 $\text{W}/(\text{m}^2 \cdot \text{K})$.

2.4. Optimization of Thermal Part of Claus Process

Constrained single-objective and multi-objective non-linear optimization problems have been discussed in optimization studies using different methods.

2.4.1. Objective Functions

The main goal of the Claus process is to eliminate H_2S by as much as possible, which is subject to restrictions by certain laws. In general, it is desired to be no less than 96% in the entire process output. Approximately 60–70% of the H_2S conversion takes place in the thermal section, especially in the furnace; therefore, changes to be made in this section have significant effects on the process. Accordingly, in this study, the objective was set as maximizing the amount of S_2 at the outputs of the units.

A waste heat boiler is a piece of equipment in which the high-temperature gas mixture coming out of the furnace is cooled before being sent to the catalytic reactor. The temperature difference here is around 700–1000 °C. This high temperature causes steam production at the high pressure and temperature in the boiler. This steam is used in the heaters in the Claus process and in other equipment that requires heating within the refinery. As the amount of steam produced increases, the energy and expenses involved in heating will be reduced by the refinery. Therefore, the amount of steam produced in the boiler was set as a secondary objective.

2.4.2. Decision Variables

Many different decision variables can be selected for this process; however, within the scope of this study, parameters that do not require large investment costs and can be altered immediately were considered. In this context, no changes in equipment design were investigated, and the furnace and boiler lengths and diameters were kept constant. In addition, the gas flow rates of air, fuel and acid fed to the furnace were determined as decision variables. As another decision variable, the temperature of feed to the furnace, which is known to have a significant effect on the entire process, was chosen. The lower and upper limits of the decision variables used are combinations of various Claus process thermal step input values found in the literature.

2.4.3. Constraints

The most important constraint that can be applied to the Claus process thermal step is the ratio of hydrogen sulfide to sulfur dioxide at the boiler exit. Due to the reaction's

stoichiometry, if this ratio is 2, unreacted hydrogen sulfide from the thermal step will be eliminated by reacting with sulfur dioxide in the catalytic part.

2.4.4. Optimization Problem

The decision variables (x_i , $i = 1, 2, 3, 4$) are furnace inlet temperature (K), inlet molar flow rate of air (mol/s), inlet molar flow rate of fuel (mol/s) and inlet molar flow rate of acid gas (mol/s);

$$\text{Maximize } f_m(x) \text{ s. t. } \begin{cases} 430 \leq x_1 \leq 570 \\ 150 \leq x_2 \leq 300 \\ 2 \leq x_3 \leq 5 \\ 150 \leq x_4 \leq 255 \\ 1.9 \leq R \leq 2.1 \end{cases}, \quad m : 1, 2$$

Here, the objective functions are $f_1(x)$ are the amount of elemental sulfur produced at the boiler outlet (mol/s) and $f_2(x)$ the amount of steam produced in the boiler (mol/s).

$$f_1(x) = F_{S_2, out} - F_{S_2, in} \quad (11)$$

$$f_2(x) = \frac{U * A * \Delta T_{ln}}{c_{P_{H_2O}} * (T_0 - T)} \quad (12)$$

where $F_{S_2, out}$ is the amount of sulfur at the boiler outlet, $F_{S_2, in}$ is the amount of sulfur at the boiler inlet, A is the heat transfer area, ΔT_{ln} is the logarithmic mean of temperatures in the boiler, $c_{P_{H_2O}}$ is the heat capacity of water, T_0 is the inlet temperature of the boiler, and T is the temperature at any point in the boiler.

$R = F_{H_2S} / F_{SO_2}$ is the ratio of the molar flow rates of hydrogen sulfide and sulfur dioxide, and should be close to 2.

2.4.5. Tools and Methods

There are different methods available to solve an optimization problem, and these can be divided into two types. Classical methods include the analytical method and the trial and error method. On the other side, intelligent optimization techniques include global optimization techniques and local optimization techniques [26]. In this study, intelligent optimization techniques were used due to their advantages, such as giving solutions in a short time and being able to work within a relatively small memory space.

In the pre-trials, four different solvers were considered for the optimization. At first, "fmincon", which is a MATLAB solver that finds the minimum of a single-optimization problem with constraints, was examined [40]. fmincon is fast, but it gets stuck in the local minima, so it was concluded that it is not suitable for use in the optimization of the thermal part of the Claus process. Another option could be MATLAB's "particleswarm" solver, which uses the Particle Swarm Optimization (PSO) algorithm. PSO is a heuristic optimization method inspired by the fact that animals such as birds and fish that move in flocks often act collectively in situations, such as searching for safe places and food [41]. Although particleswarm solver is very capable of finding global optima, it fails because it does not feature an option to add any constraints. Besides this, genetic algorithm solvers in MATLAB, with the ability to solve constrained single- and multi-objective optimization problems and find global optima, fit very well with the aim of the optimization work. Therefore, two MATLAB solvers, "ga" and "gamultiobj", were used to optimize the system. These are based on the genetic algorithm, which is a heuristic method for finding global minima [42].

As an alternative to the heuristic approach, the Taguchi method, which is an experimental design and process optimization technique that uses orthogonal arrays and signal-to-noise ratios [43], was used as a second optimization technique, as long as the

boundaries' ranges were not wide. The results of the Taguchi method were analyzed using the Minitab statistical software tool.

3. Results

3.1. Validation of Reduced Kinetic Models

The proposed reduced kinetic models were validated by comparison with the detailed kinetic model that was previously developed by Politecnico di Milano Chemical Engineering Department SuPER (Sustainable Process Engineering Research) Team researchers over many years [10]. The final version of the detailed model consists of 2400 elemental reactions and 140 types of chemical components [44]. H₂S pyrolysis and oxidation, H₂S and CH₄ pyrolysis with CS₂ formation, COS and CS₂ oxidation, and all their effects on SO₂ radicals, are considered. The models were validated by performing DSMOKE simulations.

3.1.1. Validation of Reduced Kinetic Model for Thermal Furnace

The reduced kinetic model was simulated isothermally in the DSMOKE software and compared with the detailed model. In Figure 3, the results of the DSMOKE simulation of the hydrogen sulfide, sulfur, water and oxygen profiles, which are the key components of the system, at 1000 °C with two different kinetic models are given by comparing them with industrial data [16]. The burner is the part of the reaction furnace where the acid gas mixture meets air. Here, oxygen is consumed very quickly by other components, and this causes the temperature inside the furnace to rise rapidly. Generally, an industrial Claus reaction furnace is 6.5 m long, the first 0.5 m of which is the burner.

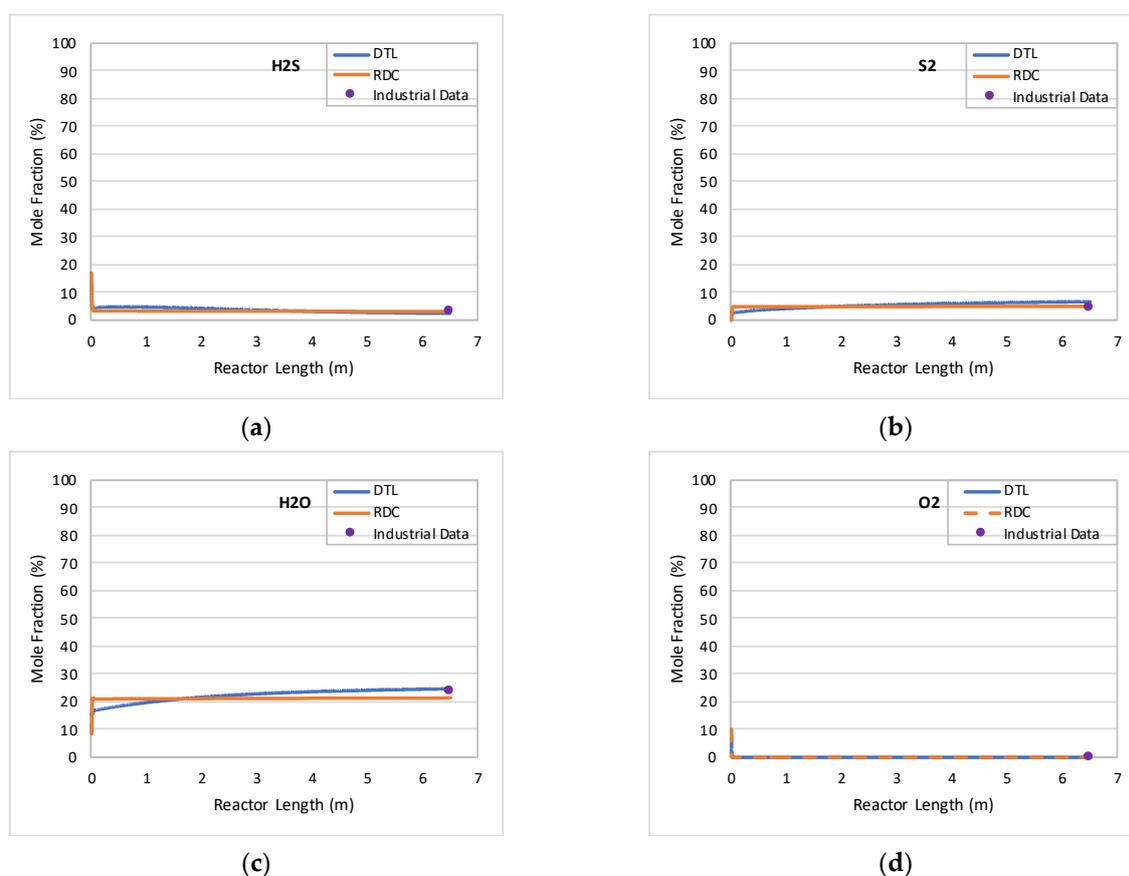


Figure 3. Comparison of mole fraction profiles of (a) H₂S, (b) S₂, (c) H₂O, and (d) O₂.

Oxygen profiles for the detailed and kinetic model are given in Figure 3. It is seen that the oxygen was completely consumed in the first half-meter of the furnace under both models.

The rapid consumption of oxygen shows that hydrogen sulfide, methane, carbon monoxide and hydrogen combustion reactions occur according to equations RF-3 and RF-8-10, given in Table 2. Hydrogen sulfide profiles are given in Figure 3, and it is seen that the component concentrations show parallel trends. The differences in the mole fractions given by the two kinetic models versus the reduced kinetic model and industrial data are 0.65% and 0.24%, respectively. In the figure, it can also be seen that both the kinetic models and industrial data are significantly close to each other.

3.1.2. Validation of Reduced Kinetic Model for Waste Heat Boiler

In Figure 4, the changes in the mole fractions of critical components throughout the waste heat boiler are presented. The trends obtained as a result of the study are compatible with the reference values.

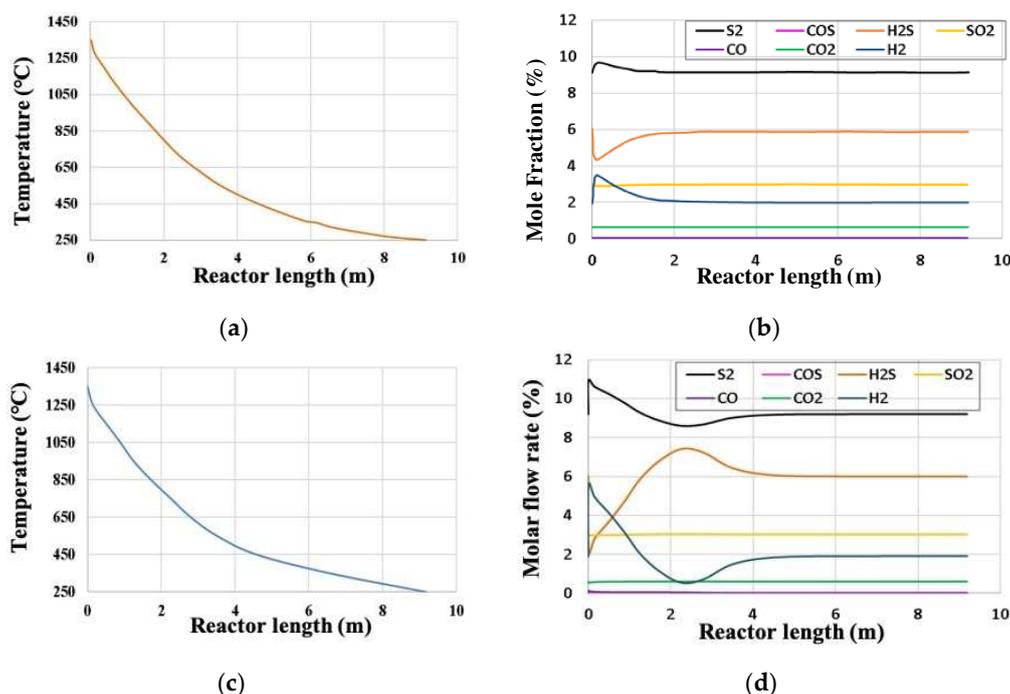


Figure 4. (a) Temperature of the detailed kinetic model; (b) mole fractions of components of the detailed kinetic model; (c) temperature in the reduced kinetic model; (d) mole fractions of components in the reduced kinetic model in the waste heat boiler.

As seen in the figures, the temperature profile fits the reference curve almost completely. Both mole fractions are compatible; their curves are slightly different due to the reaction mechanisms. The context of hydrogen sulfide started to elevate again in relation to the temperature reduction, as expected; therefore, sulfur and hydrogen were consumed (RW-1). By comparison, the H₂S outlet value reached the reference value with a difference of 3.0%.

3.2. Simulation Results

3.2.1. Thermal Furnace Simulation

The mathematical model developed was coded in the MATLAB environment considering specific assumptions, and changes in temperature and concentrations throughout the reactor were observed, while the output values were compared with those in the industrial data [16].

As shown in Figure 5, the temperature increased rapidly up to 1180 °C in the first half-meter of the furnace, which is the burner, and this provided the temperature for the furnace reactions. Then, the temperature remained constant at around 1040 °C, before reaching the industrial value. It can be seen in the figure that the changes in the molar

flow rates gave the same results as in the refinery. As the temperature reached high values, the hydrogen sulfide started to decompose (RF-1); therefore, the amounts of sulfur and hydrogen increased. In the meantime, the carbon monoxide produced reacted with sulfur, and carbonyl sulfide was formed (RF-6). The outlet values of the reaction furnace fit with those in the industrial data, and can be observed from the changes in molar flow rate that the expected reactions took place. Hence, it can be said that the model worked effectively.

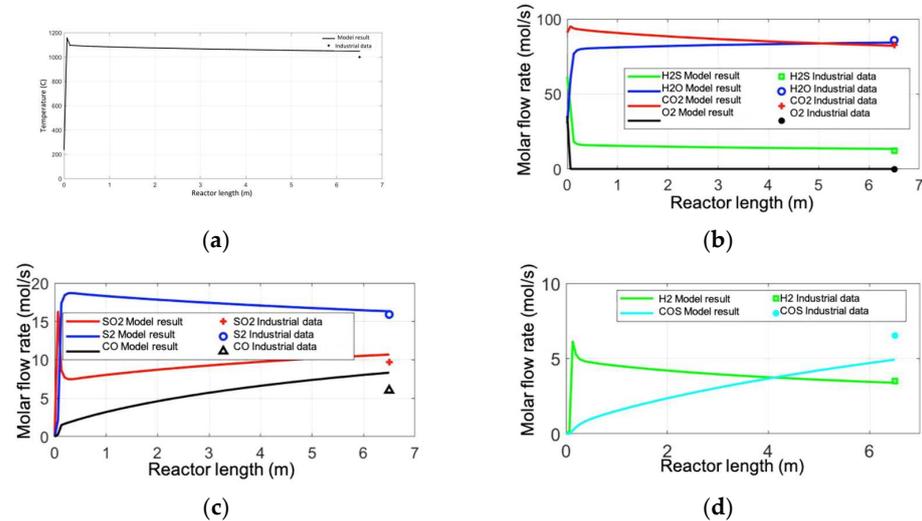


Figure 5. (a) Temperature change; (b–d) mole fractions of components in the thermal furnace.

3.2.2. Waste Heat Boiler Simulation

Modeling and simulation studies were performed in MATLAB software using the assumptions mentioned in the experimental section, and the results are given in Figure 6. Because the simulation was run for the whole thermal section, the inlet compositions and conditions of the waste heat boiler were taken as the outlet compositions and conditions of the furnace. The reference data refer to the industrial values obtained by Manenti et al. [12].

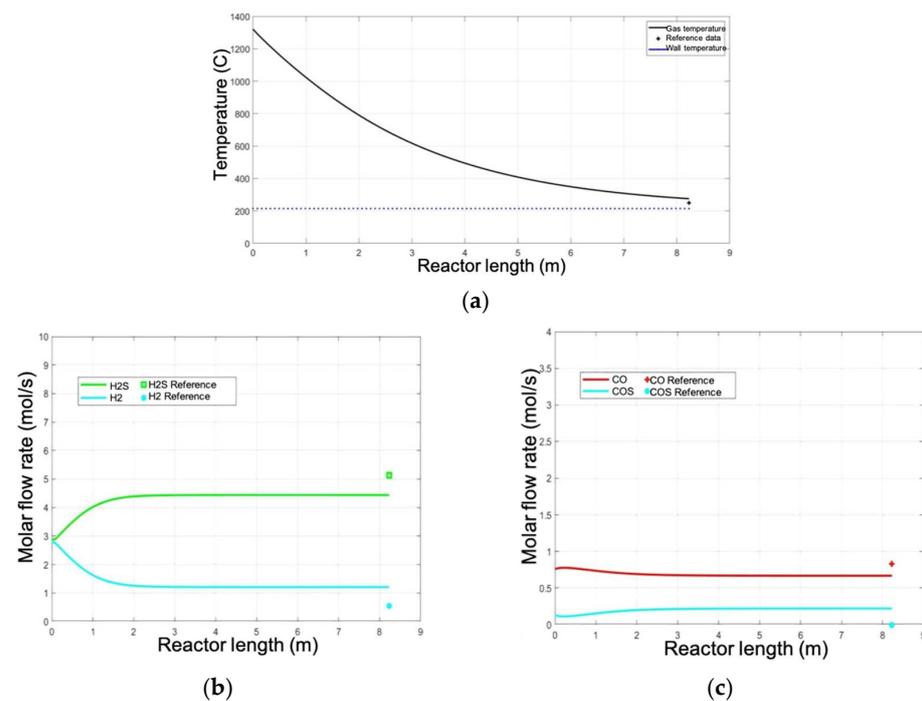


Figure 6. (a) Temperature change; (b,c) mole fractions of components in waste heat boiler.

The temperature was compatible with the wall temperature and the reference value; at the same time, it can be observed that the molar flow rates of the key components changed in accordance with the reactions predicted to occur. Thus, it can be said that the recommended model for the waste heat boiler is suitable.

3.3. Optimization Results

3.3.1. Taguchi Method

Since this study addresses a maximization problem, a policy of “the larger the better” was chosen. The selected values are 420/470/520/570 K for the temperature, 150/200/250/300 mol/s for the air feed rate, 2/3/4/5 mol/s for the fuel feed rate, and 150/185/220/255 mol/s for the acid gas feed rate. The parameters and levels determined are given in Table 7. After the parameters and levels were determined, the most suitable orthogonal array was selected using the Taguchi method. With four parameters and four levels, L16 was chosen from the Taguchi orthogonal array.

Table 7. Parameters and levels for the Taguchi method [45].

Parameter/Level	1	2	3	4
A: Temperature (K)	420	470	520	570
B: Air (mol/s)	150	200	250	300
C: Fuel (mol/s)	2	3	4	5
D: Acid gas (mol/s)	150	185	220	255

Sixteen simulations were performed using different parameters and levels. The amounts of sulfur obtained from the simulations were input into the program in response. Using these values, S/N ratios and graphs were obtained using the Minitab program, and predictions were formed as regards the highest points. The combination of values yielding the highest S/N ratio for each parameter is 4 2 1 3; that is, 570 K for temperature, 200 mol/s for air feed rate, 2 mol/s for fuel feed rate, and 220 mol/s for acid gas feed rate.

When the program predicted these levels, the S/N ratio was 31.2336, the mean value was 13.1842 mol/s and the standard deviation was 5.075. In this case, the simulation result was expected to be in the range of 8.1092–18.2592 mol/s. When the simulation was run with this specified combination, the result of 16.4755 mol/s was obtained. Since this value is within the desired range, Taguchi’s suggestion is confirmed. Although the hotspot in the furnace was 0.195 m, the temperature approached 1100 °C. In addition, the boiler outlet temperature also coincided with that in the data in the literature.

3.3.2. Single-Objective Optimization

As mentioned previously, the gas mixture from the thermal step is sent to the catalytic section after being cooled in the boiler. In catalytic reactors, unreacted H₂S reacts with SO₂, and hydrogen sulfide removal proceeds. F_{H_2S} and F_{SO_2} are the molar flow rates of hydrogen sulfide and sulfur dioxide, respectively, and the constraint is given as follows:

$$\frac{F_{H_2S}}{F_{SO_2}} \approx 2 \rightarrow 1.9 \leq \frac{F_{H_2S}}{F_{SO_2}} \leq 2.1, \quad (13)$$

According to reaction stoichiometry, when the ratio of hydrogen sulfide to sulfur dioxide is closer to 2, the degree of conversion in the catalytic step is higher. Thus, a value of this ratio in the range of 1.9 and 2.1 was used as a constraint to the single-objective optimization problem. The constrained optimization problem was solved using the genetic algorithm via the MATLAB GA solver. The decision variables and objective function values are given in Table 8.

Table 8. Optimum conditions obtained by the GA solver.

	GA Solver Results	Industrial Data
Furnace inlet temperature (K)	569.9997	513.00
Air molar flow rate (mol/s)	196.0000	181.50
Fuel molar flow rate (mol/s)	4.9999	3.24
Acid gas molar flow rate (mol/s)	254.7070	171.11
Produced S ₂ (mol/s)	14.3359	12.5533
Hotspot (m)	0.26	0.975

The amount of sulfur at the boiler outlet was 14.3359 mol/s, and it was determined that there was an increase of 12.4% compared to industrial data. The increase in the amount of produced sulfur was calculated by $\left[\frac{(V_{observed} - V_{real})}{V_{real}} * 100 \right]$.

The results show that to obtain an improvement in sulfur production, which means a decrease in hydrogen sulfide content in the gas leaving the thermal section, the inlet temperature of the thermal furnace should be higher; it can be said that higher inlet temperatures encourage the hydrogen sulfide decomposition reaction.

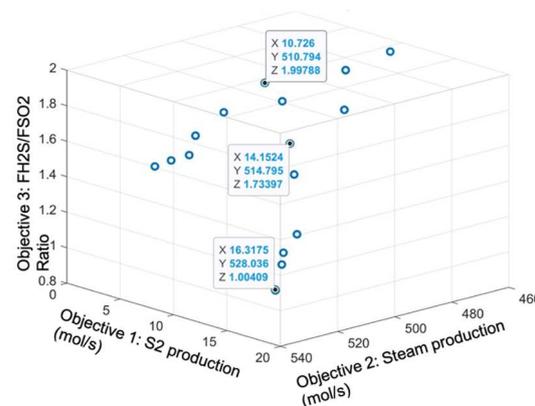
3.3.3. Multi-Objective Optimization

In this section, the constraint is considered as an objective, and is added to the objective function file in order to see the effects of changing the $R = F_{H_2S}/F_{SO_2}$ ratio on the main objectives of sulfur and steam production. The mathematical expression, as the objective function of the constraint, can be given as follows:

$$\min. \left(\frac{F_{H_2S}}{F_{SO_2}} - 2 \right)^2$$

Here, F_{H_2S} and F_{SO_2} denote the molar flow rates of hydrogen sulfide and sulfur dioxide, respectively.

Figure 7 shows how all three objectives affect each other. Although the R ratio is generally around 2, the amount of steam produced increases as it exceeds this value. Three points were chosen for analysis. Point (a) contains a solution where R is very close to 2 but the amount of sulfur is low, and it seems to be a suitable solution for a plant with an efficient catalytic part. Point (c) seems to be a suitable choice in terms of sulfur and steam production; it may be preferred for a sulfur recovery plant with three or more catalytic reactors. Point (b) is a solution where all three objectives have average values.

**Figure 7.** Pareto solution for the three-objective optimization problem.

In Table 9, the degree of improvement that can be achieved in sulfur and steam production with reference to industrial data (12.5522 mol/s and 373.6898 mol/s, respectively) for the three points examined above is given as a percentage.

Table 9. Improvement percentage for selected points as given by the multi-objective optimization problem solution.

Point	R	Sulfur Production (mol/s)	Improvement on Sulfur Production (%)	Steam Production (mol/s)	Improvement in Steam Production (%)
a	1.99788	10.7260	−14.5	510.794	36.7
b	1.73397	14.1524	12.7	514.795	37.8
c	1.00409	16.3175	30.0	528.036	41.3

Decision variables for the selected multi-objective optimization solutions are given in Table 10. The results show that it is possible to achieve relatively higher sulfur production values with lower inlet temperatures when inlet flow rates increase. It can be said that the acid gas inlet flow rate and fuel inlet flow rate should be increased in any case. If the furnace inlet temperature and inlet air flow rate are kept lower, it leads to an R ratio maintained close to 2. Another good achievement is the improvement of steam production. Any changes applied to the system according to the optimization study's results will increase steam production in the waste heat boiler.

Table 10. Decision variables of selected points as given by the multi-objective optimization problem solution.

Point	Furnace Inlet Temperature (K)	Air Molar Flow Rate (mol/s)	Fuel Molar Flow Rate (mol/s)	Acid Gas Molar Flow Rate (mol/s)
a	430.0150	258.1191	4.9800	254.9963
b	529.3669	296.1340	4.9779	254.6409
c	441.6331	286.2771	4.9788	254.4132
Industrial data	513.0000	181.50000	3.2400	171.1100

4. Conclusions

This study aimed to model and optimize the thermal section of the Claus process. At first, reduced kinetic models were proposed for the reaction furnace and waste heat boiler, and these models were validated with the detailed kinetic scheme shown in the literature. Thus, it has been demonstrated that instead of a detailed kinetic model including more than 2000 elemental reactions, which is cumbersome when applied to the ensuing calculations and is difficult to modify, a reduced kinetic model with 11 global reactions can be used.

A waste heat boiler is generally considered as a simple heat exchanger in the literature; instead, it is here modeled as a plug flow reactor with heat transfer. The simulation results show that recombination reactions cannot neglect the hydrogen sulfide ratio and temperature. Modeling the boiler as a reactor instead of a heat exchanger was a more realistic and revelatory approach.

After the modeling and simulation studies, single-objective and multi-objective optimizations were carried out on the Claus thermal step in the MATLAB environment. The aim was to maximize the sulfur production at the exit of the thermal section, which is the main goal of using sulfur recovery units. First, the simulation of the thermal step was considered as the experimental setup; simulations were carried out according to Taguchi's suggestions and the results were analyzed, and a 24% increase in sulfur production was achieved. In the second step, a single-objective optimization problem was studied, wherein the objective was to maximize the sulfur production and the constraint was to keep the ratio of hydrogen sulfide to sulfur dioxide at around 2. The genetic algorithm (ga) solver was used, and the improvement in the objective function was 14.1%. In the third step, maximizing the steam produced in the waste heat boiler was included as a secondary objective, and the constraint was considered as the third objective, using the gamultiobj solver to solve it. The results of the multi-objective optimization problem show increases of up to 30% and 41% in sulfur production and steam production, respectively, as the conditions changed.

As a result of the improvements in the operating parameters of the Claus process revealed by the model employed in this study, the process can be rendered more cost-effective and environmentally friendly.

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