

Modeling and Simulation of Claus Unit Reaction Furnace

Maryam Pahlavan¹ and Mohammad Ali Fanaei^{2*}

¹M.S. Student, Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

²Assistant Professor, Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

Received: August 19, 2015; *revised:* November 28, 2015; *accepted:* December 21, 2015

Abstract

Reaction furnace is the most important part of the Claus sulfur recovery unit and its performance has a significant impact on the process efficiency. Too many reactions happen in the furnace and their kinetics and mechanisms are not completely understood; therefore, modeling reaction furnace is difficult and several works have been carried out on in this regard so far. Equilibrium models are commonly used to simulate the furnace, but the related literature states that the outlet of furnace is not in equilibrium and the furnace reactions are controlled by kinetic laws; therefore, in this study, the reaction furnace is simulated by a kinetic model. The predicted outlet temperature and concentrations by this model are compared with experimental data published in the literature and the data obtained by PROMAX V2.0 simulator. The results show that the accuracy of the proposed kinetic model and PROMAX simulator is almost similar, but the kinetic model used in this paper has two importance abilities. Firstly, it is a distributed model and can be used to obtain the temperature and concentration profiles along the furnace. Secondly, it is a dynamic model and can be used for analyzing the transient behavior and designing the control system.

Keywords: Claus Process, Reaction Furnace, Kinetic Modeling, Simulation

1. Introduction

Natural gas is a source of energy, which is widely used as an industrial, commercial, and domestic fuel. To make natural gas suitable for using, it is important to purify it from all impurities such as acid gases. The acid gases of hydrogen sulfide (H₂S) and carbon dioxide (CO₂) are common impurities existing in the natural gas (Al-Lagtah et al., 2015). Usually the acid gases are separated from natural gas in the gas treating unit (GTU) and the separated acid gas stream is sent into the sulfur recovery unit (SRU). Sulfur recovery unit is one of the basic units of gas refineries; this unit is very important in economic and environmental issues.

There are several configurations for sulfur recovery unit. A proper technology or configuration for sulfur recovery unit strongly depends on H₂S concentration of inlet acid gas stream (Garmroodi and Shamsavand, 2014). Most commonly used method for rich acid gas and high capacity sulfur production is the Claus process. Claus process consists of two parts, namely thermal section and

* Corresponding author:

E-mail address: fanaei@ferdowsi.um.ac.ir

catalytic section. The thermal section includes reaction furnace and waste heat boiler, while the catalytic section consists of catalyst beds, heaters, and condensers. Figure 1 shows a conventional Claus sulfur recovery unit. The acid gas stream and the amount of air required to burn almost one-third of the hydrogen sulfide to sulfur dioxide are fed through the reaction furnace. In the reaction furnace, about 60-70% of the H_2S in the feed gas stream is converted to the elemental sulfur. As the furnace reactions are highly exothermic, valuable steam can be generated in the waste heat boiler that locates after the furnace. The sulfur produced in the reaction furnace and each catalytic reactor is condensed, separated, and sent to the sulfur collector. The gases leaving the sulfur condensers are reheated and fed to the catalytic reactors, where more sulfur is produced. Finally, the exhaust outlet gas from the final stage is sent to an incinerator or tail gas clean up unit (Al-Lagtah et al., 2015).

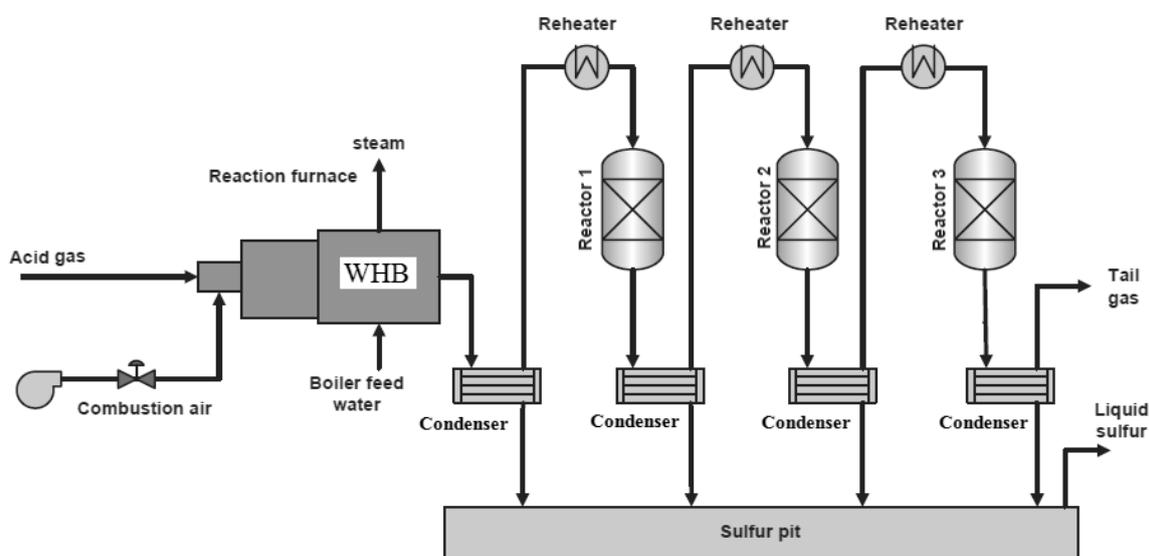


Figure 1

A schematic of Claus process.

The feed gas composition to the Claus unit consists of a number of cases. The designed process must be able to operate in all of these cases with a stable operation, at acceptable performance, and according to environmental regulations (Santo and Rameshni, 2014). Often to improve the Claus process, various technologies are used such as acid gas enrichment, air enrichment, feed preheat, etc.

Nowadays, simulation software is one of the most powerful tools in improving the operating conditions of industrial units. Software packages which are typically used in the simulation of sulfur recovery units (such as PROMAX and SULSIM) are not comprehensive and just simulate this process in steady state and ideal conditions, so it is necessary to improve these software packages or use a better method. Reaction furnace has an essential role in Claus unit and its performance affects process efficiency and other equipment performance, so, in the current work, furnace simulation is discussed. Usually one of two ways, namely an empirical model or an equilibrium model, is used for the simulation of reaction furnace. Empirical models are simple equations; for example, Western empirical model includes some equations used to predict the outlet of reaction furnace based on the mole fraction of H_2S in the feed. Empirical models are highly dispersed and are not compatible with each other; however, between empirical models, Western model gives better results (Monnery et al., 1993). Equilibrium models are not very accurate because the previous studies have shown that the output of reaction furnace is not in equilibrium conditions and furnace reactions are controlled by

kinetic laws. The simulation of the reaction furnace based on the kinetic model is an appropriate method, but, due to high complexity, is not commonly used. Reactions that occur in the furnace are very complex and, after many studies over the years, still further information is required. Some references have considered furnace with over 1500 chemical reactions and 130 molecules and free radicals (Manenti et al., 2012).

In the current study, a dynamic model is used for the reaction furnace simulation. In this model, the maximum amount of available kinetics information has been used, but, to prevent the complexity of the model, free radicals and complex reactions have been ignored.

2. Modeling of the reaction furnace

Reaction furnace is considered to be an adiabatic plug flow reactor. Reactor length is broken into small elements (finite difference method) and mass and energy balances are written for each element as shown in Figures 2 and 3.

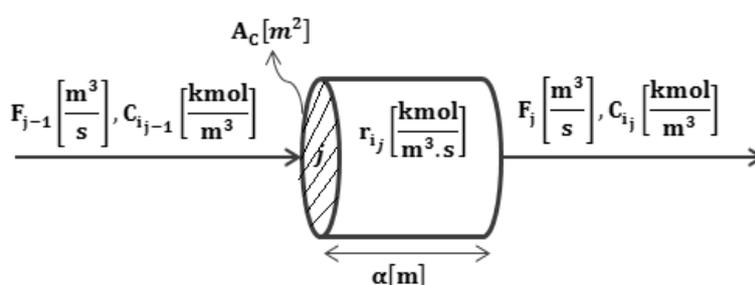


Figure 2

A mass balance element.

The mass balance of component i in element j is given by:

$$\frac{d(\alpha A_c C_{i,j})}{dt} = (FC_i)_{j-1} - (FC_i)_j + r_{i,j} \alpha A_c \quad \text{for } i=1 \text{ to } NC \quad \text{and } j=1 \text{ to } N \quad (1)$$

where, NC is the number of components and N represents the number of reactor elements.

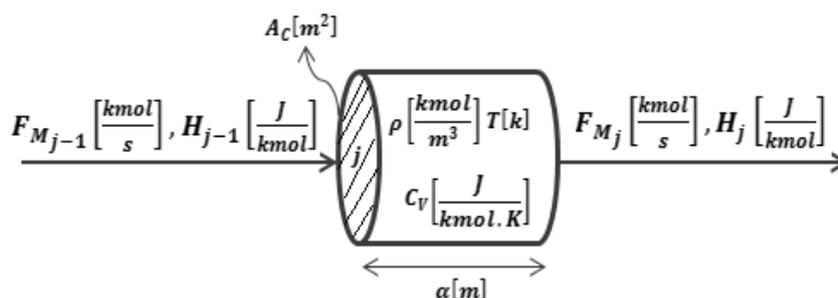


Figure 3

An energy balance element.

Energy balance in element j is defined by:

$$\frac{d(\rho C_v \alpha A_c T_j)}{dt} = (F_M H)_{j-1} - (F_M H)_j \quad \text{for } j=1 \text{ to } N \quad (2)$$

After simplification, the above equations are reduced to:

$$\frac{dC_{i,j}}{dt} = \frac{(FC_i)_{j-1} - (FC_i)_j}{\alpha A_c} + r_{i,j} \quad \text{for} \quad i=1 \text{ to } NC \quad \text{and} \quad j=1 \text{ to } N \quad (3)$$

$$\frac{dT_j}{dt} = \frac{(F_M H)_{j-1} - (F_M H)_j}{\rho C_v \alpha A_c} \quad \text{for} \quad j=1 \text{ to } N \quad (4)$$

Based on the NC components and N reactor elements, there exist $N \times (NC + 1)$ ordinary differential equations (ODE). These sets of ODE are solved simultaneously with *ode15s* function in MATLAB software. At time zero, it is assumed that air at a temperature of 25 °C exists in the furnace. Any other values of temperature and component concentrations along the furnace such as steady state values can also be used as initial conditions. The inputs to the first elements ($C_{i,0}$ and T_0), which are the boundary conditions of the problem, are known from the operating conditions of the feed gas. It should be noted that in defining the enthalpy of the gas mixture, the enthalpy of the formation of the components is considered in addition to the enthalpy of ideal gas, so it is not required to consider a separate term for the reaction enthalpy in the energy balance equation. The gas mixture enthalpy is calculated according to Equation 5.

$$H = \sum_i y_i \left[\Delta_f H_i^{ig} + \int_{T_{ref}}^T C_{p,i}^{ig}(T) dT \right] \quad (5)$$

The number of reactions that occur in the furnace is very high and it is difficult to consider all of them; in addition, the kinetics of some reactions is not known. After reviewing many related works and extracting the kinetics of the reactions, a kinetic model with fourteen important reactions was selected (Monnery et al., 1993; Howboldt, 1998; Monnery et al., 2000; Karan et al., 1998; Karan and Behie, 2004; Jones, 2011; Jones et al., 2012). In this model, the maximum amount of available kinetics information has been used, but, to prevent the complexity of the model, free radicals and complex reactions have been ignored. Tables 1 and 2 show the list of these reactions and their kinetics respectively.

Table 1
List of the furnace reactions.

$H_2S + 1.5O_2 \rightarrow SO_2 + 2H_2O$	R.1	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	R.8
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	R.2	$CO + 0.5S_2 \rightarrow COS$	R.9
$H_2 + 0.5O_2 \rightarrow H_2O$	R.3	$CO + H_2S \rightarrow COS + H_2$	R.10
$CO_2 + H_2 \rightarrow CO + H_2O$	R.4	$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S$	R.11
$H_2S + 0.5SO_2 \rightarrow 0.75S_2 + H_2O$	R.5	$H_2S + SO_2 + H_2 \rightarrow S_2 + 2H_2O$	R.12
$H_2S \rightarrow H_2 + 0.5S_2$	R.6	$NH_3 + 0.75O_2 \rightarrow 1.5H_2O + 0.5N_2$	R.13
$CH_4 + S_2 + H_2O \rightarrow COS + H_2S + 2H_2$	R.7	$NH_3 + 0.75SO_2 \rightarrow 0.375S_2 + 1.5H_2O + 0.5N_2$	R.14

Table 2
Kinetics of the furnace reactions.

Number	Kinetic	Reference
R.1	$r = A \exp(-E/RT) P_{H_2S} P_{O_2}^{1.5}$ $A = 1.4 \times 10^9, E = 11$	Jones, 2011
R.2	$r = A \exp(-E/RT) C_{CH_4}^{0.62} C_{O_2}^{0.51}$ $A = 348, E = 3.77$	Jones, 2011
R.3	$r = A \exp(-E/RT) C_{H_2}^{0.229} C_{O_2}^{0.771}$ $A = 7.63 \times 10^{10}, E = 48.2$	Jones, 2011
R.4	$r = A \exp(-E/RT) (C_{CO_2} C_{H_2}^{0.5} - \exp(-4.72 + 4800/T) C_{CO} C_{H_2O} / C_{H_2}^{0.5})$ $A = 3.95 \times 10^{10}, E = 62.03$	Jones, 2011
R.5	$r = A_1 \exp(-E_1/RT) P_{H_2S} P_{SO_2}^{0.5} - A_2 \exp(-E_2/RT) P_{H_2O} P_{S_2}^{0.75}$ $A_1 = 1.57 \pm (0.12) \times 10^7, E_1 = 49.9 \pm (0.3)$ $A_2 = 5 \pm (0.5) \times 10^5, E_2 = 44.9 \pm (0.5)$	Monnery et al., 2000
R.6	$r = A_1 \exp(-E_1/RT) P_{H_2S} P_{S_2}^{0.5} - A_2 \exp(-E_2/RT) P_{H_2} P_{S_2}$ $A_1 = 5.263 \pm (0.26) \times 10^6, E_1 = 45 \pm (0.3)$ $A_2 = 13.6 \pm (1) \times 10^3, E_2 = 23.4 \pm (0.2)$	Howboldt, 1998
R.7	$r = A \exp(-E/RT) C_{CH_4} C_{S_2}$ $A = 5.53 \times 10^{10}, E = 38.7$	Jones, 2011
R.8	$r = A \exp(-E/RT) C_{CH_4} C_{CO_2}$ $A = 8.06 \times 10^5, E = 4.98$	Jones, 2011
R.9	$r = A_1 \exp(-6700/T) C_{CO} C_{S_2} - A_2 \exp(-21630/T) C_{COS} C_I$ $A_1 = 3.18 \times 10^5, A_2 = 4.36 \times 10^9$	Karan et al. 1998
R.10	$r = A \exp(-E/RT) (C_{CO} C_{H_2S}^{0.5} - \exp(3.12 + 334.47/T) C_{COS} C_{H_2} / C_{H_2S}^{0.5})$ $A = 1.59 \times 10^5, E = 26.5$	Jones, 2011
R.11	$r = A \exp(-19320/T) C_{CH_4} C_{S_2}$ $A = 5.53 \times 10^{10}$	Karan and Behie, 2004
R.12	$r = A \exp(-E/RT) (P_{H_2S} P_{SO_2} P_{H_2} - 1/K_{eq} P_{S_2} P_{H_2O}^2)$ $A = 3.583 \times 10^7, E = 26$	Jones et al., 2012
R.13	$r = A \exp(-E/RT) P_{NH_3} P_{O_2}^{0.75}$ $A = 4.43 \times 10^6, E = 40$	Jones et al., 2012
R.14	$r = A \exp(-E/RT) C_{NH_3}^{0.25} C_{SO_2}^{0.5}$ $A = 2.286 \times 10^4, E = 27.5$	Jones et al., 2012

3. Results and discussion

For model validation, the experimental data of Sames and his colleagues at Ultramar refinery in 1990 have been used (Sames et al., 1990). Table 3 shows the flow rate of the input streams to the furnace in each experiment and Table 4 lists the analysis of these streams.

Table 3
Flow rate of input streams to the furnace in each test (Sames et al., 1990).

Molar flow (kmol/hr) test↓	Acid gas	Sour water stripper gas	Oxygen	Air
1	81.44	35.26	9.86	168.89
2	68.71	31.52	0	189.37
3	59.77	0	0	112.06
4	83.32	0	6.96	123.59
5	92.94	51.39	25.66	139.14

Table 4
Analysis of input streams to the furnace in each test (Sames et al., 1990).

Mole % test→	Acid gas		Sour water stripper gas		Air
	1, 2	3, 4, 5	1, 2	3, 4, 5	
H ₂ S	88.799	89.161	58.708	54.477	0
CO ₂	10.567	10.554	2.31	1.759	0
NH ₃	0	0	37.967	43.221	0
Hydrocarbon	0.155	0.12	0.434	0.266	0
N ₂	0.479	0.0165	0.581	0.277	79.05
O ₂	0	0	0	0	20.95
T (°C)	32.2	32.2	84.1	87.7	21.1
P (kPa)	182.3	183.8	176.9	175.7	99.9
Humidity	100%	100%	100%	100%	75%

Figure 4 shows the mole percent of key components in the furnace outlet stream. Vertical axis is the experimental data and the horizontal axis represents the results of the proposed kinetic model.

The results indicate some deviation from the experimental data. Most deviation occurs in the mole percent of hydrogen. For further investigation, the simulations were performed with PROMAX V2.0 software too, the results of which are shown in Figure 5.

The results of PROMAX V2.0 software such as kinetic model have also some deviation. Figure 6 compares the PROMAX V2.0 results with the kinetic model and confirms that the results of the two methods are almost in agreement.

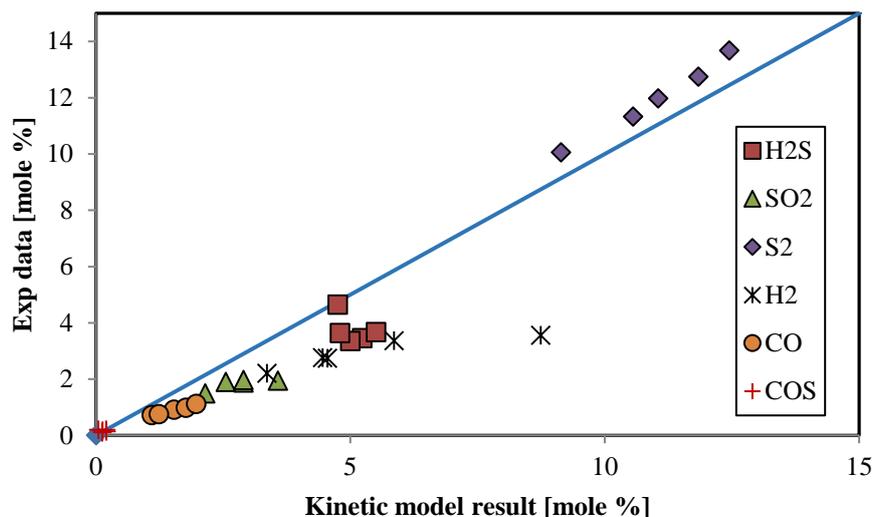


Figure 4

Mole percent of key components in furnace outlet stream (comparison of the experimental data of Sames et al., 1990 and the proposed kinetic model).

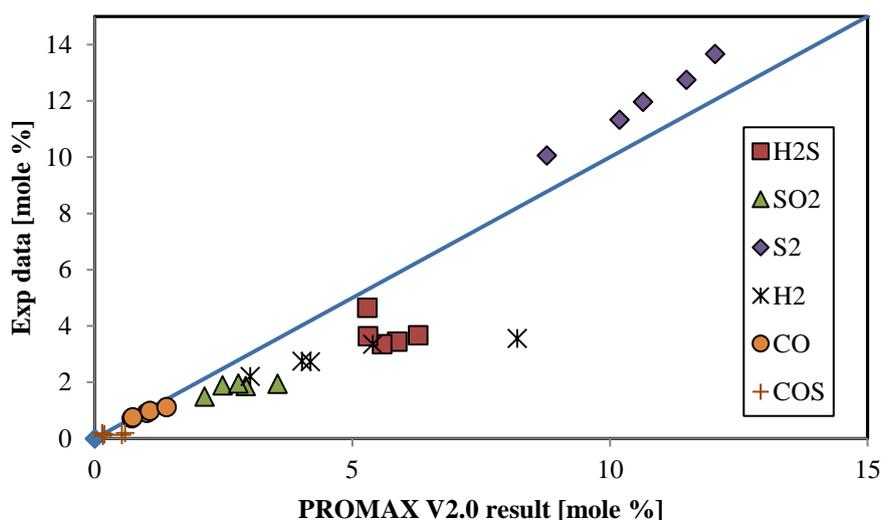


Figure 5

Mole percent of key components in furnace outlet stream (comparison of the experimental data of Sames et al., 1990 and PROMAX V2.0 software).

The simulation results show that the accuracy of the kinetic model and PROMAX V2.0 software are almost similar. PROMAX is a useful tool for Claus unit simulation and is often used in refinery simulations. The main advantages of the proposed kinetic model compared to the PROMAX software are that it can simulate reaction furnace dynamically and obtain temperature and component concentration profiles along the reaction furnace, while PROMAX software does not have provide these capabilities. For example, component concentration and temperature profiles along the reaction furnace for the first case of Table 3 are shown in Figures 7 and 8. As can be seen, combustion

reactions occur at the front of furnace and rate of changes in this location is high; the rate of changes then become slower along the furnace and the profiles move toward the equilibrium conditions.

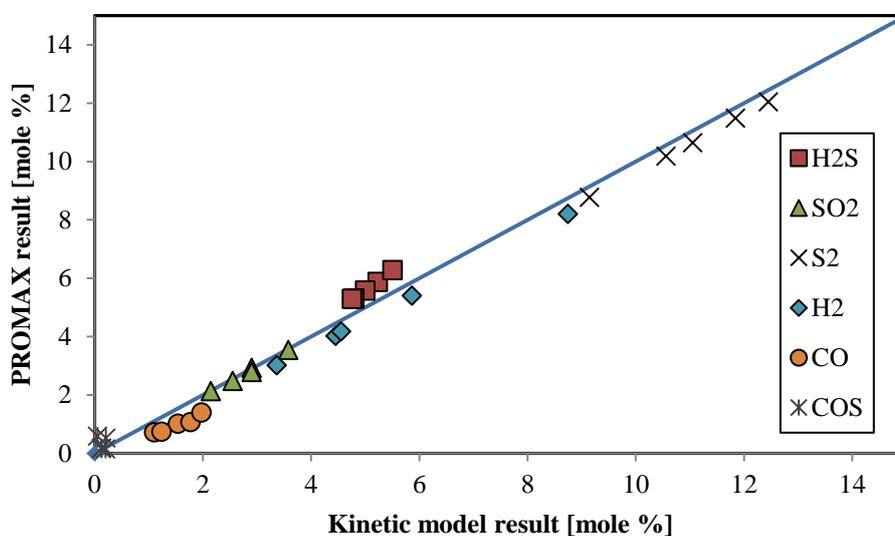


Figure 6

Mole percent of key components in furnace outlet stream (comparison of the results of PROMAX V2.0 software and the kinetic model).

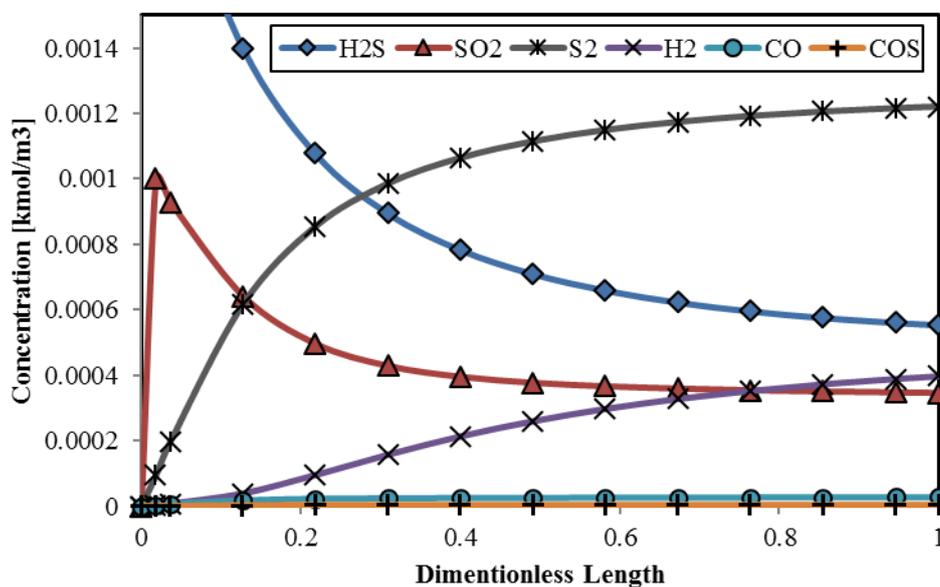


Figure 7

Component concentration profiles along the reaction furnace for the first case of Table 3.

In addition, the mole percent of S_2 , H_2S , and SO_2 at different residence times for feed gas temperatures of 350 and 550 K are shown in Figures 9 and 10. These figures show that at the same residence time, S_2 production and H_2S consumption are higher at a higher feed gas temperature.

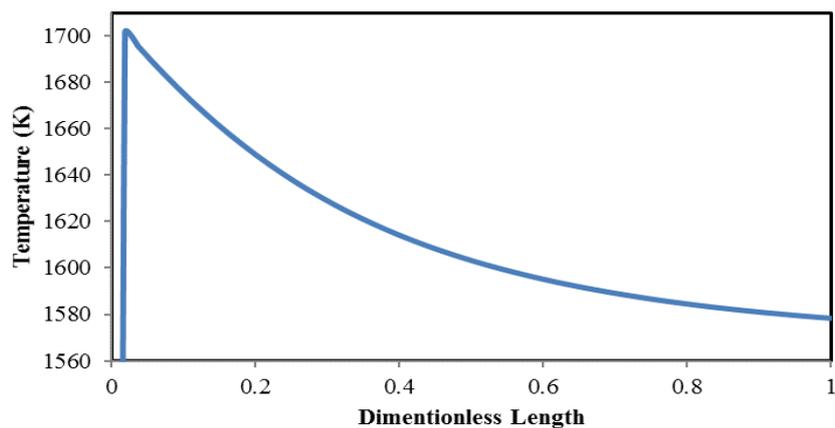


Figure 8

Temperature profile along the reaction furnace for the first case of Table 3.

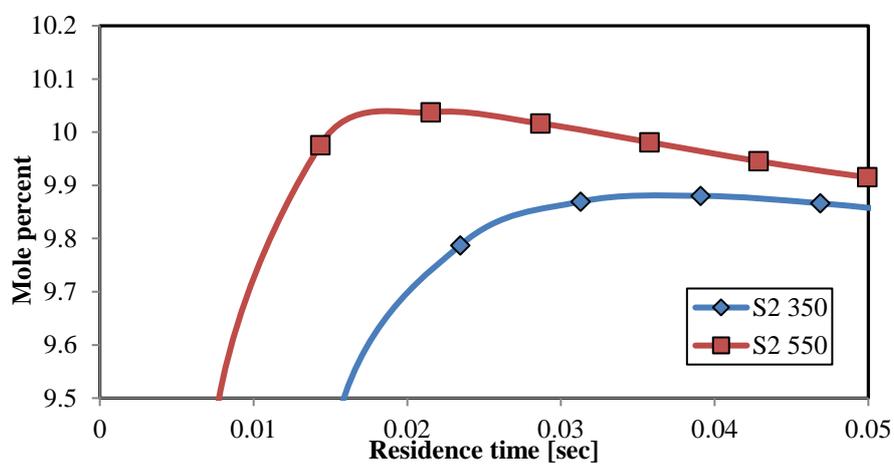


Figure 9

Mole percent of S_2 at different residence times and feed gas temperatures (350 and 550 K).

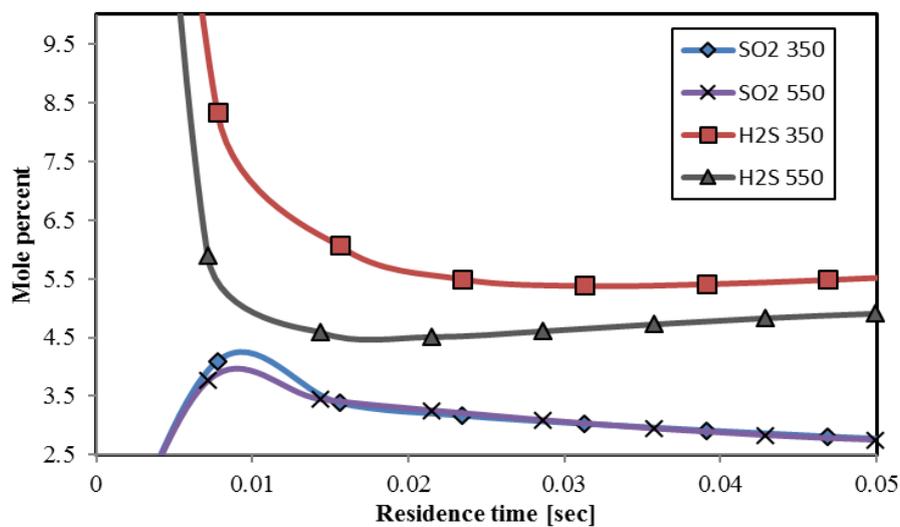


Figure 10

Mole percent of H_2S and SO_2 at different residence times and feed gas temperatures (350 and 550 K).

4. Conclusions

Reaction furnace plays an essential role in the sulfur recovery unit. Many studies on the modeling of reaction furnace have been conducted so far. Studies show that the furnace reactions are controlled by the kinetic laws; therefore, the best way to simulate the reaction furnace is using kinetic models. The kinetic model proposed in this paper includes fourteen most important reactions of the furnace. Although the results of this model are similar to the results obtained from PROMAX V2.0 software, the proposed kinetic model can simulate reaction furnace dynamically and obtain temperature and component concentration profiles along the reaction furnace. Moreover, unlike the previous works, the proposed model in this paper has a simple structure and can be used for analyzing the transient behavior and designing a control system.

Nomenclature

A_C	: Reactor cross section area [m ²]
C_i	: Concentration of component i [kmol/m ³]
$C_{i,j}$: Concentration of component i in element j [kmol/m ³]
C_t	: Total concentration [kmol/m ³]
C_V	: Heat capacity in constant volume [J/(kmol.K)]
$C_{p,i}^{ig}$: Ideal gas heat capacity in constant pressure for component i [J/(kmol.K)]
F	: Volumetric flow rate [m ³ /s]
F_M	: Molar flow rate [kmol/s]
H	: Gas mixture enthalpy [J/kmol]
$\Delta_f H_i^{ig}$: Ideal gas formation enthalpy of component i in the reference temperature [J/kmol]
K_{eq}	: Reaction equilibrium constant
N	: Number of reactor elements along the length
NC	: Number of components
R	: Universal gas constant [J/(kmol.K)]
$r_{i,j}$: Reaction rate of component i in element j [kmol/(m ³ .s)]
t	: Time [s]
T_j	: Temperature in element j [K]
T_{ref}	: Reference temperature [K]
y_i	: Mole fraction of component i in gas stream
Greek	
α	: Step size of reactor length [m]
ρ	: Molar density [kmol/m ³]

References

- Al-Lagtah, N. M. A., Al-Habsi, S., and Onaizi, S. A., Optimization and Performance Improvement of Lekhwaier Natural Gas Sweetening Plant using Aspen Hysys, Journal of Natural Gas Science and Engineering, Vol. 26, p. 367-381, 2015.
- Garmroodi Asil, A. and Shahsavand, A., Reliable Estimation of Optimal Sulfinol Concentration in Gas Treatment Unit via Novel Stabilized MLP and Regularization Network, Journal of Natural Gas Science and Engineering, Vol. 21, p. 791-804, 2014.

- Howboldt, K. A., Kinetic Modeling of Key Reaction in the Modified Claus Plant Front End Furnace, Ph.D. Thesis, Department of Chemical and Petroleum Engineering, University of Calgary, 1998.
- Jones, D., Steady State and Dynamic Modeling of the Modified Claus Process as Part of an IGCC Power Plant, M.S. Thesis, Department of Chemical Engineering, West Virginia University, 2011.
- Jones, D., Bhattacharyya, D., Turton, R., and Zitney, S. E., Rigorous Kinetic Modeling and Optimization Study of a Modified Claus Unit for an Integrated Gasification Combined Cycle (IGCC) Power Plant with CO₂ Capture, *Industrial & Engineering Chemistry Research*, Vol. 51, No. 5, p. 2362-2375, 2012.
- Karan, K. and Behie, L. A., CS₂ Formation in the Claus Reaction Furnace: A Kinetic Study of Methane-Sulfur and Methane-Hydrogen Sulfide Reactions, *Industrial & Engineering Chemistry Research*, Vol. 43, No. 13, p. 3304-3313, 2004.
- Karan, K., Mehrotra, A. K., and Behie, L. A., COS-Forming Reaction between CO and Sulfur: A High-temperature Intrinsic Kinetics Study, *Industrial & Engineering Chemistry Research*, Vol. 37, No. 12, p. 4609-4616, 1998.
- Manenti, G., Papisidero, D., Menenti, F., Bozzano, G., and Pierucci, S., Design of SRU Thermal Reactor and Waste Heat Boiler Considering Recombination Reactions, *Procedia Engineering*, Vol. 42, p. 376-383, 2012.
- Monnery, W. D., Howboldt, K. A., Pollock, A., and Svrcek, W. Y., New Experimental Data and Kinetic Rate Expression for the Claus Reaction, *Chemical Engineering Science*, Vol. 55, No. 21, p. 5141-5148, 2000.
- Monnery, W. D., Svrcek, W. Y., and Behie, L. A., Modeling the Modified Claus Process Reaction Furnace and the Implications on Plant Design and Recovery, *The Canadian Journal of Chemical Engineering*, Vol. 71, No. 5, p. 711-724, 1993.
- Sames, J. A., Paskall, H. G., Brown, D. M., Chen, M. S. K., and Sulkowski, D., Field Measurements of Hydrogen Production in an Oxygen Enriched Claus Furnace, *Proceeding of Sulfur 1990 International Conference*, Alberta, Canada, 1990.
- Santo, S. and Rameshni, M., The Challenges of Designing Grass Root Sulfur Recovery Units with a Wide Range of H₂S Concentration from Natural Gas, *Journal of Natural Gas Science and Engineering*, Vol. 18, p. 137-148, 2014.