

A Modified Kinetic Reaction Scheme for Claus Reaction Furnaces in Oil Refineries

Samane Zarei*

Research Institute of Petroleum Industry (RIPI), Tehran, Iran

Abstract

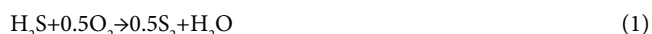
In this study, one of the recently published the kinetic models for the Claus reaction furnace was modified through utilizing a wide experimental data from the Claus reaction furnace of oil refineries and applying a novel two-step optimization approach. The Claus reaction furnace of oil refineries was modeled using the detailed kinetic model. The Mean Absolute Percentage Errors (MAPE) of the modified kinetic model for H_2S , SO_2 , H_2O and H_2 are 3.04%, 2.28%, 4.66% and 5.90%, respectively. The mean absolute percentage errors of the validated tests for H_2S , SO_2 , H_2O and H_2 are 6.72%, 5.74%, 4.74% and 7.98%, respectively. A multi-objective optimization study was carried out to examine the operating condition of the Claus reaction furnace in order to maximize reaction furnace temperature while maintaining H_2S to SO_2 flow ratio to a constant value of two. Three correlations were obtained with MAPEs 1.83%, 4.66% and 16.52% for reaction furnace temperature, sulfur conversion efficiency percentage and COS conversion percentage, respectively.

Keywords: Kinetic modeling; Optimization; Reaction furnace; Oil refineries; Claus unit

Introduction

Acid gas was mainly composed of carbon dioxide (CO_2) and hydrogen sulfide (H_2S) [1]. These two problematic compounds must be removed from natural gas in order to appropriate it for further usages as fuel and other applications. Sulfinol, Rectisol, Selexol, Flour and amine extraction processes are some methods of sweetening acid gas [2]. Processing of acid gas in an amine extraction process is one of the important processes for carbon dioxide and hydrogen sulfide removal. In amine treatment unit, absorption of CO_2 and H_2S is conducted through passing the acid gas over alkanolamine solutions [3]. Sweetened acid gas, due to stringent environmental regulations must be processed to reduce further hydrogen sulfide. Sulfreen, Unisulf, Takahax, and modified Claus processes are some options to reduce hydrogen sulfide contents of acid gases [4]. Nowadays, a new technology to convert acid gas to syngas (AG2STM) is proposed [5], but the modified Claus process is still more common than others due to higher sulfur conversion and operation at higher H_2S concentration and capacity [6]. This implies the importance of declaring a kinetic model for its description and optimization of its operation for better performance and higher conversion, consequently lower sulfur emissions.

Elements of sulfur are produced by the partial oxidation of H_2S in simple overall reaction as follows [1]:



The modified Claus process is conducted at two steps named thermal and catalytic stages. The thermal stage includes conversion of one-third of H_2S in acid gas feed to sulfur elements. This step is conducted at Reaction Furnace (RF) and Waste Heat Boiler (WHB). The Partial combustion of hydrogen sulfide and the conversion to sulfur dioxide occur in the RF that is made as a refractory lined cylindrical vessel. Inlet acid gas to the RF has a 130-180 kPa pressure and is oxidized with an appropriate quantity of air. The required air is determined based on a 2:1 ratio of $\text{H}_2\text{S}:\text{SO}_2$ in the reactor effluent. The combustion of acid gases in the RF is performed at the temperature ranges of 975°C -1300°C and gas residence times of 0.5-2.0 s [7]. Combustion products of the RF enter the WHB, equipment after the RF. The WHB is a shell and tube heat exchanger cooling hot gases of the RF to approximately

230°C-370°C and generating high pressure steam on the shell side [7]. Occurrence of recombination reactions is one of the main features of the WHB from a reaction chemistry viewpoint [8].

The following reaction for the partial oxidation of one-third of input H_2S and producing sulfur dioxide (SO_2) can be described the chemistry in this stage:



The high temperatures and rapid oxygen depletions resulted from combustion are characteristics of the thermal stage. On the catalytic stage, the reaction between the remaining two-thirds of H_2S and produced SO_2 at lower temperatures is as follows:



Some other reactions such as carbonyl sulfide (COS) and carbon disulfide (CS_2) hydrolysis also occur in catalytic convertors [1].

The RF is the first section of the modified Claus process and its operations affect the operation of downstream equipment. Any deficiency in its operation and inappropriate combustion significantly influence combustion products, leading to increasing undesirable components, mainly in form carbonyl sulfide, carbon disulfide and unburned hydrocarbon. COS and CS_2 tie up sulfur element in their structure and if they don't hydrolyze in catalytic stage, remain unconverted. Therefore, these components play a significant role in sulfur emission to the atmosphere via an incinerator. On the other hand, sulfur dioxide emissions to atmosphere are dedicated by increasingly stringent emission control regulations. Any modification in the RF affects sulfur conversion and emissions from Claus plant [7]. One of the main strategies for reducing sulfur emissions is to increase

*Corresponding author: Samane Zarei, Research Institute of Petroleum Industry (RIPI), Tehran, Iran, Tel: +98 21 4473 9650; E-mail: s.zarei.m.a@gmail.com

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the performance of the Sulfur Recovery Units (Sru) through optimizing operating conditions of the Claus reaction furnace. Optimization of the modified Claus process for further sulfur recovery and lower emissions requires a reliable kinetic model for the RF [9].

The RF of the Claus unit was modeled by equilibrium assumption in several researches. Bennett et al. [10] calculated equilibrium mole percentages of the mixtures of hydrogen sulfide and air for the temperature ranges of 600-2000 K. Khudenko et al. [11] modeled the Claus reaction furnace under oxygen enrichment conditions utilizing Gibbs energy minimization method. Monnery et al. [7] compared the Gibbs energy minimization method, Fisher monograph and western research correlations to model the reaction furnace effluents. They concluded that the results of these various methods were not in agreement with plant data collected after and before the waste heat boiler. Selim et al. [3] computed the optimum operating temperatures of H₂S streams containing different components such as CO₂ and N₂ in the modified Claus process.

Zare Nezhad et al. [12] studied methods of increasing the RF temperature of Claus units. Zarei et al. [6] combined the equilibrium and kinetic approaches in thermal stage modeling. A number of researchers have studied the effects of acid gas feed composition on Claus process experimentally [13-19]. They investigated the sulfur chemistry with acid gas additions in the hydrogen/air [13] and methane/air flames [17,18], and with oxygen [15], N₂ and CO₂ additions [19] in the acid gas feed. Gupta et al. [20] reviewed some of the advances in sulfur chemistry in the treatment of acid gases from experimental and design aspects.

Some researchers investigated the modified Claus reaction furnace through detailed kinetic modeling [8,21-24]. In the detailed kinetic modeling, the effluents of reaction furnaces are computed by utilizing reaction schemes consisting of radical, intermediate and molecular reactions.

Pierucci et al. [22] modeled the RF with plug flow assumption (PFR) and considering a detailed kinetic scheme with 130 species and more than 1500 elementary reactions. The detailed kinetic scheme utilized by Manenti et al. [24] consisted of 146 species and 2412 reactions. Their model was a combination of continuous stirred tank (CSTR) and plug flow reactors. In a recent study, Li et al. [25] applied a detailed kinetic modeling of H₂S oxidation with the presence of CO₂ under rich conditions utilizing the PFR reactor.

Some researchers are interested in developing a kinetic scheme with a limited number of reactions for the RF modeling [26-29]. The first attempt at this field was made by Jones et al. [26] who identified a reaction set to describe the WHB effluents. Javanmardi Nabikandi et al. [27] compared the kinetic and equilibrium approaches to model sulfur recovery unit. Their results show that the kinetic model yields more accurate results than equilibrium model.

Pahlavan et al. [28] simulated a Claus reaction furnace by PROMAX V2.0 simulator. Zarei et al. [29] developed a kinetic scheme to model reaction furnace and validated the model results with the experimental data. The model results were in good agreement with the experimental measured plant data. The mean absolute error of the RF was reported as 7.62%.

Among the mentioned researches, only few studies considered the optimization of the operating conditions of the modified Claus process. Manenti et al. [23] used a kinetic model with 2400 reactions and 140 species in a proper reactor network to optimize elemental sulfur recovery and steam generation. In another work, Manenti et al. [30]

conducted an integrated process-energy optimization at the total plant scale. Jones et al. [26] conducted two optimization studies and showed that there existed an optimal steam pressure and H₂S/SO₂ ratio in the WHB balancing hydrogen yield, oxygen demand, and power generation. Zarei et al. [29] maximized the reaction furnace temperature and optimized the operation of the WHB through maintaining the H₂S/SO₂ ratio at a constant of two, minimizing COS emission and maximizing sulfur production from the WHB using the developed kinetic scheme.

As previously mentioned, an optimization study requires a suitable kinetic model for Claus reaction furnace, being applied to wider operating conditions and different situations. Previous studies on modeling the RF represented inadequacy of the equilibrium model in predicting the RF effluents [7,27]. In comparison to detailed kinetic studies, kinetic studies with a limited number of reactions estimate the RF and WHB effluents with lower reaction numbers and calculation operation accompanying the acceptable error [26,29]. Among all limited reaction number studies [26,29], the reaction scheme developed by Jones et al. [26] described the WHB effluent. The kinetic model developed by Zarei et al. [29] for Claus reaction furnace provides a good approximation of reactor effluents. It is obtained from experimental data set of single reaction furnace. The research by Zarei et al. [29] was focused on developing a kinetic reaction scheme for specific single furnace by examining different reaction schemes.

However, in the current study, it is attempted to generalize the kinetic reaction network, developed by Zarei et al. [29] for industrial Claus reaction furnaces operated in oil refineries. This work requires further experimental data sets from industrial Claus reaction furnaces operating in oil refineries. The mentioned items are the main differences between the current work and the study by Zarei et al. [29]. A wide plant set obtained from industrial reaction furnaces of operating oil refineries was applied in performing a kinetic model for the RF. The above-mentioned plant data sets include different operating conditions such as different initial concentrations of H₂S and CO₂, residence times, feed temperatures and pressures. Our analyses showed that at most industrial Claus plants, operations of WHB assumed ideal. In another word, the high quenching rate of WHB did not provide situations for recombination reactions which led to lower sulfur efficiency. It is assumed that the RF and WHB have similar component compositions at different temperature. Therefore, in following work, quenching role of WHB was ignored and only the RF was considered.

Subsequently, a kinetic model to describe experimental data was developed. For this purpose, the reaction scheme introduced in the study by Zarei et al. [29] was used and its kinetic parameters were fitted by applying the data sets of industrial RFs of oil refineries. The adjustment work of the kinetic parameters was conducted by a novel two-step optimization method. The modified kinetic model was validated with experimental plant data. The case studies were performed in which the effects of increasing the air to acid gas flow ratio and feed temperature are investigated in the temperature, sulfur conversion efficiency percentage, H₂ and COS molar flow rates of reaction furnace.

The second objective of the current study is to apply the modified kinetic model by optimizing the operating conditions of the Claus reaction furnace of oil refineries. In this study, operating conditions, including reaction furnace temperature and H₂S/SO₂ ratio at Claus reaction furnace were optimized utilizing the modified kinetic model. A multi-objective function utilized in optimization studies provides solutions without interference of objectivities. The optimization work was conducted by setting the reaction furnace feed temperature and the air to acid gas flow ratio.

Moreover, three correlations are introduced to calculate reaction furnace temperature, sulfur conversion efficiency percentage and the COS conversion percentage. The correlations are obtained by utilizing the modified kinetic model for the Claus reaction furnaces in oil refineries. In developed correlations, effect of air to acid gas flow ratio, residence time, and carbon dioxide to the hydrocarbon content of feed are considered.

Model

Reactor model

Several researchers modeled Claus reaction furnace by considering a single PFR or CSTR reactor, or a combination of CSTR and PFR reactors. Pierucci et al. [22] utilized a single PFR for modeling the RF. Schöneberger et al. [21] proposed a CSTR reactor for computing the RF effluents. Manenti et al. in several works [23,24,31] considered a series of CSTR and PFR reactors for the RF modeling.

Zarei et al. [29] investigated the effect of considering different reactor networks such as PFR, CSTR and the two combinations of CSTR and PFR in kinetic modeling of the RF and showed that the single PFR reactor is suitable for describing the reaction furnace. In the present study because of cylindrical shape and considering previous works, the reaction furnace was modeled assuming the adiabatic plug flow reactor. Considering adiabatic plug flow assumption and negligible pressure drop, the following ordinary differential equations including mass and energy balance and actual mean residence time equations, should be solved simultaneously [29].

$$\frac{dF_j}{dz} = A \sum_i v_{ij} r_{ij} \quad j = 1, \dots, n_c \quad i = 1, \dots, n_R \quad (4)$$

$$\frac{dT}{dz} = A \sum_j h_j \sum_i v_{ij} r_{ij} \quad (5)$$

$$\frac{dt_R}{dz} = (AP)(RT)^{-1} \left(\sum_j F_j \right)^{-1} \quad (6)$$

The above equations can be rearranged and the mass and energy balance equations can be written based on residence time as follows:

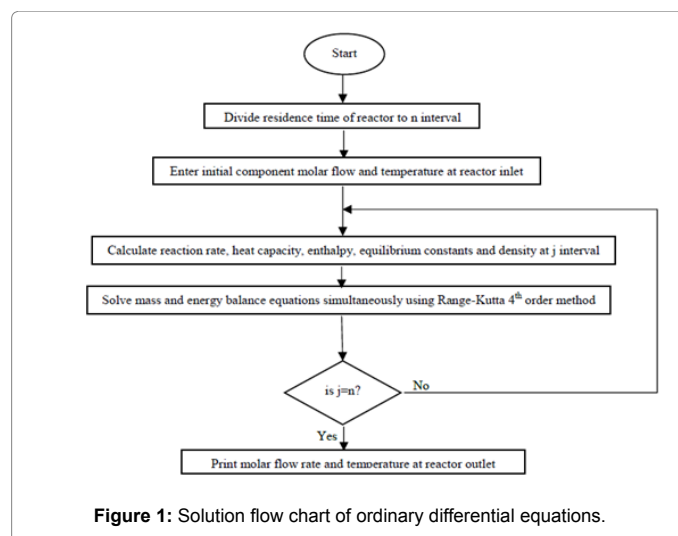
$$\frac{dF_j}{dt_R} = \frac{RT \sum_j F_j}{P} \sum_i v_{ij} r_{ij} \quad j = 1, \dots, n_c \quad i = 1, \dots, n_R \quad (7)$$

$$\frac{dT}{dt_R} = \frac{RT \sum_j F_j}{P} \sum_j h_j \sum_i v_{ij} r_{ij} \quad (8)$$

The above ordinary differential equations were solved using Runge-Kutta order 4. The numerical algorithm was written in MATLAB programming software. Figure 1 shows the solution flow chart of ordinary differential equations.

Kinetic model

Zarei et al. [29] introduced a reaction scheme for describing what actually happens in the reaction furnace. The proposed reaction scheme and their rate expressions are presented in Table 1. Their reaction scheme was obtained by considering experimental data of a single reaction furnace. One feature of the kinetic reaction scheme is thermodynamically consistency of the proposed reactions [29]. In this work, a readjusting work of kinetic parameters of the reaction scheme



in Table 1 was done by applying a novel two-step optimization method and utilizing several experimental data of different oil refineries.

Fitting Parameter Procedure

A modified kinetic model was obtained by adjusting kinetic parameters of the reaction scheme utilizing the experimental plant data-sets of Claus reaction furnaces of oil refineries. In the first step of fitting procedure, an experimental data set is required to adjust tuning parameters and usually is named train data. A test data set must be considered to avoid over fitting. Test data set is not applied in determining unknown parameters and only utilized in evaluating model performance for unfitted data. In the current study, about 70% of the experimental data considered as the train data, and the remaining data (30%) are test data (or validation data). Afterward, a two-step approach was applied to the adjusting work of kinetic parameters. Different order magnitudes of mole percentages for the Claus reaction furnace effluents that cannot be properly depicted in one objective function, is the main reason for considering the two-step approach. Two Objective Function (OB) utilized in the fitting procedure of the two-step approach are as follows:

$$OB = \sum_i \left| \frac{x_{i,cal} - x_{i,exp}}{x_{i,exp}} \right| \quad i = H_2S, SO_2, H_2O \text{ and } H_2 \quad (9)$$

$$OB = \sum_i |x_{i,cal} - x_{i,exp}| \quad i = CO_2, CO \text{ and } COS \quad (10)$$

The procedures of adjusting kinetic parameters in the two-step approach are as follows:

1. The Kinetic parameters of reactions relating to H_2S , SO_2 , H_2O and H_2 components, i.e. hydrogen sulfide decomposition, second Claus reaction and hydrogen sulfide oxidation, were fitted with the experimental oil refineries data and the objective function in accordance with equation 9.

2. After the modification of the adjusted kinetic parameters in the previous step, the kinetic parameters of reactions relating to CO_2 , CO and COS components, i.e. the COS recombination reaction, reaction between CO and H_2S , methane oxidation and water-gas shift reaction, were adjusted with equation 10 for the objective function.

Results and Discussions

The reactions and the adjusted kinetic parameters of the modified

Reaction	Rate Expression	Reference
$H_2S \leftrightarrow H_2 + 0.5S_2$	$-r_{H_2} \left(\frac{mol}{m^3 \sec} \right) = 4.3 \times 10^6 \exp\left(-\frac{26}{RT} \left(\frac{kcal}{mol} \right)\right) C_{H_2} P_{S_2} (atm) - 3.6 \times 10^8 \exp\left(-\frac{48}{RT} \left(\frac{kcal}{mol} \right)\right) C_{H_2S}$	[32]
$CO + 0.5S_2 \leftrightarrow COS$	$-r_{CO} \left(\frac{kmol}{m^3 \sec} \right) = 3.18 \times 10^5 \exp\left(-\frac{55.8}{RT} \left(\frac{kJ}{mol} \right)\right) C_{CO} C_{S_2} - 4.36 \times 10^9 \exp\left(-\frac{180}{RT} \left(\frac{kJ}{mol} \right)\right) C_{COS} C_{total}$	[33]
$CO_2 + H_2 \leftrightarrow CO + H_2O$	$-r_{CO_2} \left(\frac{kmol}{m^3 \sec} \right) = 8.59 \times 10^{10} \exp\left(-\frac{270.5}{RT} \left(\frac{kJ}{mol} \right)\right) \left(C_{CO_2} C_{H_2}^{0.5} - \frac{1}{K_{eq}} \frac{C_{CO} C_{H_2O}}{C_{H_2}^{0.5}} \right)$	[9]
$CO + H_2S \leftrightarrow COS + H_2$	$-r_{CO} \left(\frac{kmol}{m^3 \sec} \right) = 1.59 \times 10^5 \exp\left(-\frac{110.91}{RT} \left(\frac{kJ}{mol} \right)\right) \left[C_{CO} C_{H_2S}^{0.5} - \frac{C_{COS} C_{H_2}}{C_{H_2S}^{0.5} K_{eq}} \right]$	[34]
$H_2S + 0.5SO_2 \leftrightarrow H_2O + 0.75S_2$	$-r_{H_2S} \left(\frac{mol}{m^3 \sec} \right) = 3.18 \times 10^6 \exp\left(-\frac{14.3}{RT} \left(\frac{kcal}{mol} \right)\right) C_{H_2S} C_{SO_2}^{0.5} - 31081 \exp\left(-\frac{8.5}{RT} \left(\frac{kcal}{mol} \right)\right) C_{H_2O} C_{S_2}^{0.75}$	[35]
$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$	$-r_{CH_4} \left(\frac{mol}{cm^3 \sec} \right) = 10^{13.2} \exp\left(-\frac{48.4}{RT} \left(\frac{kcal}{mol} \right)\right) C_{CH_4}^{0.7} C_{O_2}^{0.8}$	[36]
$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O$	$-r_{H_2S} \left(\frac{mol}{cm^3 \sec} \right) = 14 \exp\left(-\frac{11}{RT} \left(\frac{kcal}{mol} \right)\right) P_{H_2S} (atm) P_{O_2}^{1.5}$	[37]
$NH_3 \rightarrow 0.5N_2 + 1.5H_2$	$-r_{NH_3} \left(\frac{mol}{cm^3 \sec} \right) = 0.00842 \exp\left(-\frac{16.5}{RT} \left(\frac{kcal}{mol} \right)\right) P_{NH_3}^{1.25} (atm)$	[38]

Table 1: Rate expressions of the chosen kinetic scheme in Zarei et al. [29]

Reaction	Forward Rate		Backward Rate	
	k	E	k	E
$H_2S \leftrightarrow H_2 + 0.5S_2$	7.64×10^8	206.85	7.81×10^6	132.89
$CO + 0.5S_2 \leftrightarrow COS$	4.80×10^5	54.38	4.95×10^7	152.62
$CO_2 + H_2 \leftrightarrow CO + H_2O$	4.75×10^{10}	279.37	5.89×10^8	233.59
$CO + H_2S \leftrightarrow COS + H_2$	2.03×10^5	132.61	3.10×10^6	107.76
$H_2S + 0.5SO_2 \leftrightarrow H_2O + 0.75S_2$	2.51×10^6	14.62	4.28×10^4	8.69
$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$	2.23×10^{13}	46.72	-	-
$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O$	14.85	10.65	-	-

Table 2: The reactions and adjusted kinetic parameters of modified kinetic scheme.

Components	Train	Test
H2S	3.039	6.719
SO2	2.285	5.739
H2O	4.665	4.739
H2	5.905	7.981

Table 3: The MAPEs for H_2S , SO_2 , H_2O and H_2 components for train and test data sets.

kinetic scheme are presented in Table 2. The adjusted kinetic parameters include forward and backward activation energies and rate constants. The modified kinetic model was validated with the reaction furnaces effluents of oil refinery data (test data).

Table 3 shows the Mean Absolute Percentage Errors (MAPE) for H_2S , SO_2 , H_2 and H_2O components for oil refinery data used in optimizing (train data) and validating (train data) of the modified kinetic model. Based on Table 3 for H_2S , SO_2 , H_2 and H_2O components, maximum MAPEs for both train and test data set with values 5.905%

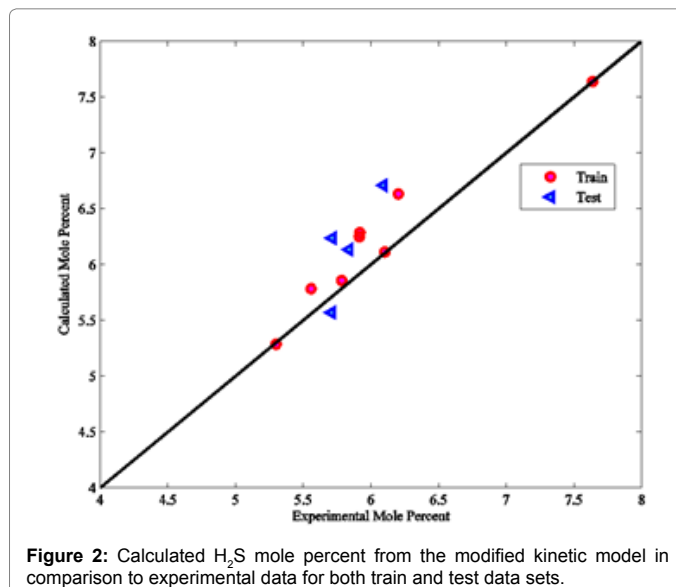


Figure 2: Calculated H_2S mole percent from the modified kinetic model in comparison to experimental data for both train and test data sets.

and 7.981%, respectively belong to H_2 .

Coefficients of determinations for CO_2 , CO and COS are 0.9989, 0.9805 and 0.9873, respectively. Use of the coefficient of determination for CO_2 , CO and COS is due to their low concentrations in the Claus reaction furnace effluents. Figures 2-8 compare the calculated mole percentages of the reaction furnace effluents with experimental data for

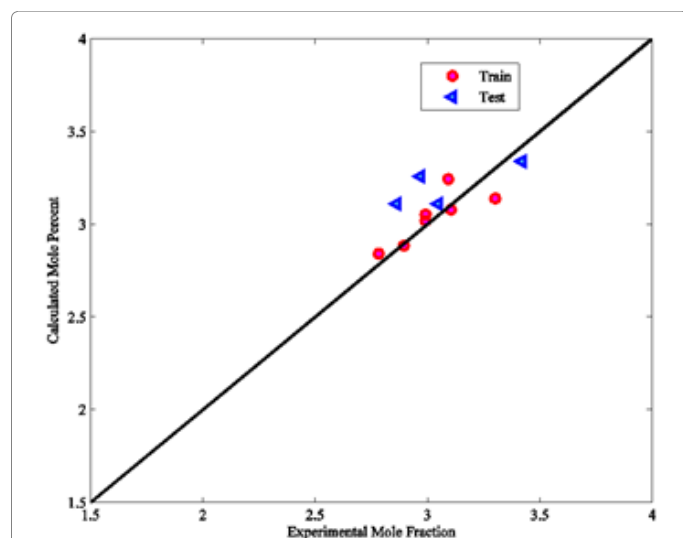


Figure 3: Calculated SO_2 mole percent from the modified kinetic model in comparison to experimental data for both train and test data sets.

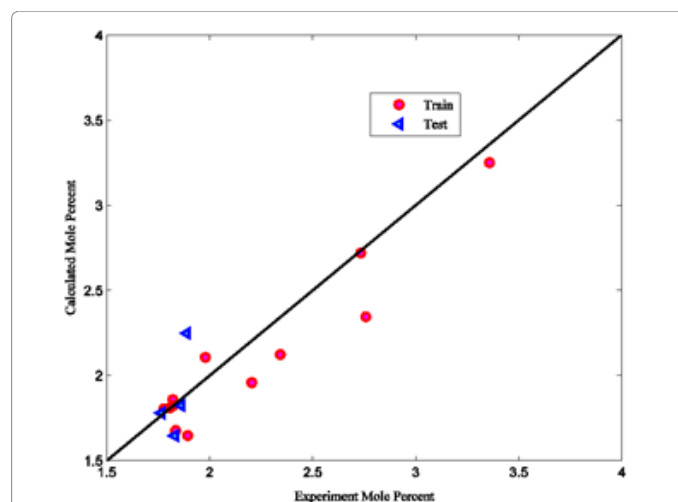


Figure 5: Calculated H_2 mole percent from the modified kinetic model in comparison to experimental data for both train and test data sets.

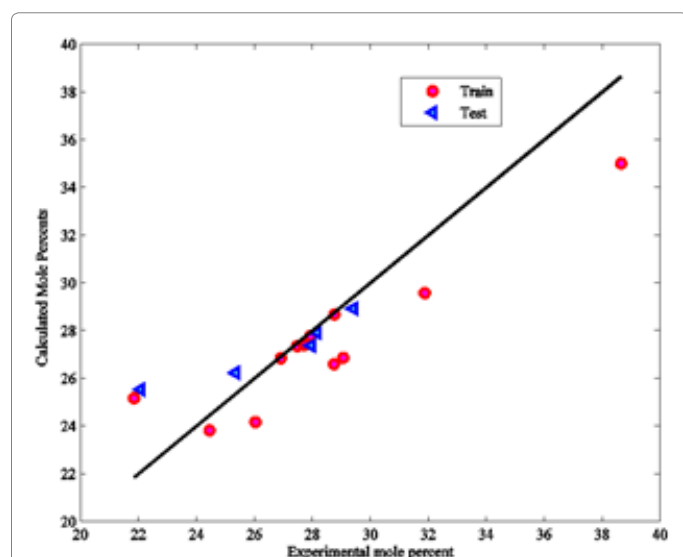


Figure 4: Calculated H_2O mole percent from the modified kinetic model in comparison to experimental data for both train and test data sets.

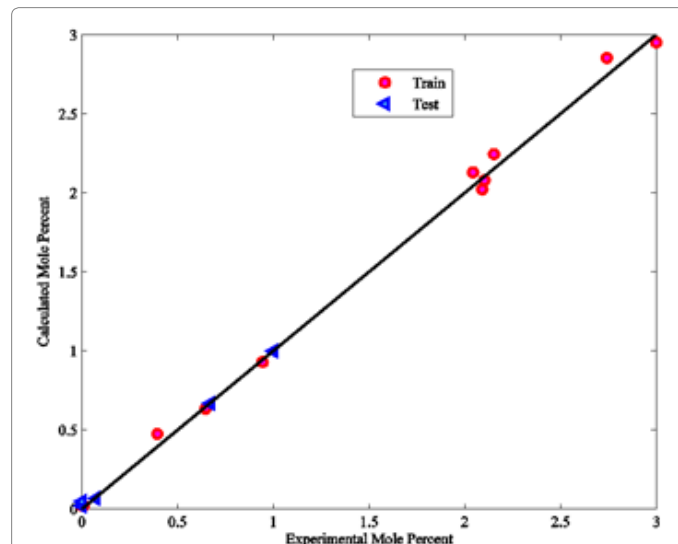


Figure 6: Calculated CO_2 mole percent from the modified kinetic model in comparison to experimental data for both train and test data sets.

both train and test data-sets. According to Figures 2-5 and Table 3 for H_2S , SO_2 , H_2O and H_2 , a good agreement is seen between experimental and calculated mole percentages for both test and train data set. Figures 6-8 and the mentioned coefficient of determinations show the goodness of fit for CO_2 , CO and COS compounds. A good agreement between the calculated mole percentage from the modified kinetic scheme and experimental mole percentages in Figures 6-8 ensure its precision in different situations and operating conditions.

Case studies

Effect of air to acid gas flow ratio: In the following section, the effect of increasing the air to acid gas flow ratio on the sulfur conversion efficiency percentage, H_2 and COS molar flow rates from the reaction furnace effluent and the reaction furnace temperature is studied. Based on the initial air to acid gas flow ratio, the limits 1.5-3 for the air to acid gas flow ratio were chosen. It must be ensured that the whole

oxygen combusts at the reaction furnace and no unburned oxygen percolates to downstream waste heat boiler and catalytic stages, to remains unconverted. Oxygen breakthrough is a serious problem for the sulfur catalyst resulting in a deactivation by a mechanism thought to be sulphation. Figure 9 shows the effect of increasing the air to acid gas flow ratio on the reaction furnace temperature and the sulfur conversion efficiency percentage.

According to Figure 9, increasing the air- to- acid -flow ratio generally results in riser reaction furnace temperature and lower sulfur conversion efficiency percentage. These outcomes can be discussed with higher oxygen available for combustion of hydrogen sulfide and other impurities such as ammonia and hydrocarbons. The combustion of hydrogen sulfide and other impurities are exothermic reactions liberating heat that result in higher reaction furnace temperature. Incremental reaction furnace temperature due to higher air to acid gas flow ratio prepares situations for the decomposition reactions. According to Figure 9, conversion efficiency percentages of sulfur increases, because of the higher conversion of hydrogen sulfide as the

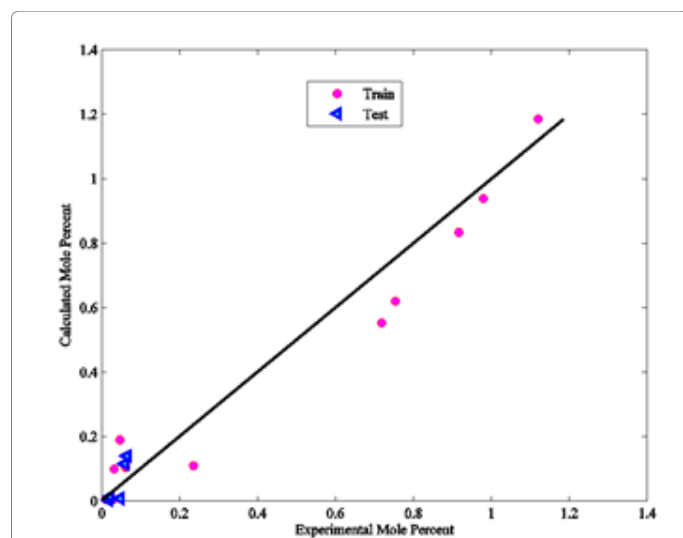


Figure 7: Calculated CO mole percent from the modified kinetic model in comparison to experimental data for both train and test data sets.

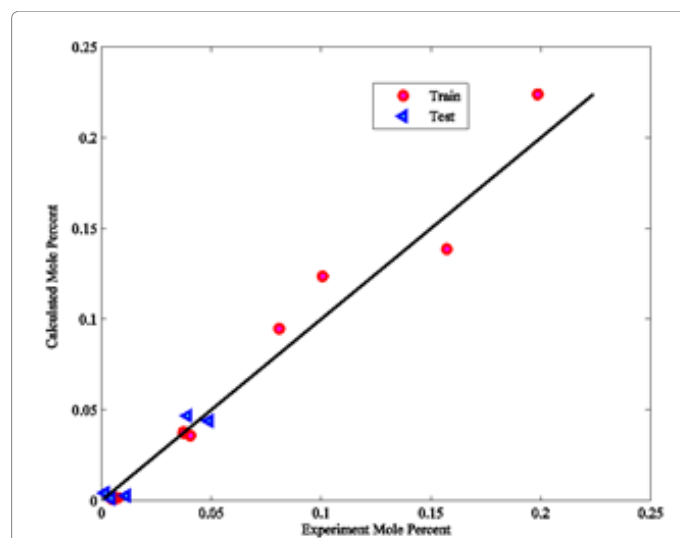


Figure 9: Effect of increasing air to acid gas flow ratio on sulfur conversion efficiency percentage and reaction furnace temperature (K).

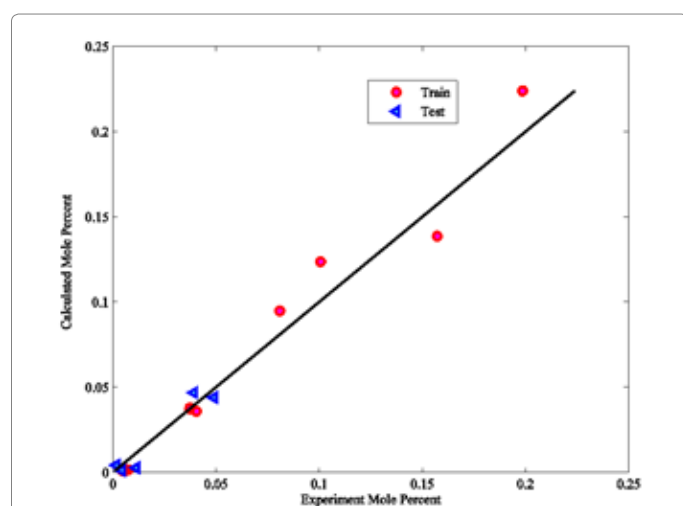


Figure 8: Calculated COS mole percent from the modified kinetic model in comparison to experimental data for both train and test data sets.

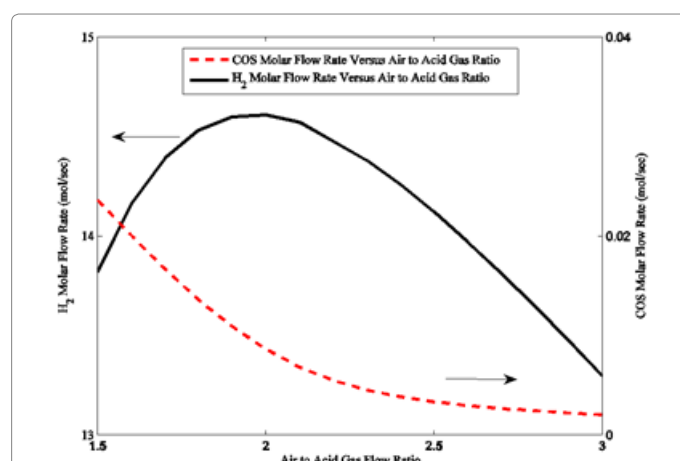


Figure 10: Effect of increasing air to acid gas flow ratio on H_2 and COS molar flow rate (mol/sec).

result of higher reaction furnace temperature, which is suitable for hydrogen sulfide decomposition reaction and, subsequently, more sulfur and hydrogen production. Gradually decrement of sulfur conversion efficiency percentages can be interpreted with higher conversion of hydrogen sulfide as the result of more oxygen consumption. Therefore, hydrogen sulfide with decomposition capability, instead of decomposition reaction, combusts, and SO_2 is produced. Consequently, lower sulfur and hydrogen is composed.

As more hydrogen sulfide is consumed in the combustion reaction than decomposition reaction, hydrogen content is decreased. The effects of increasing air to acid gas flow ratio on the H_2 and COS molar flow rates are presented in Figure 10. As the figure shows, the H_2 molar flow rate first raises with the air to acid gas flow ratio increment. Afterward, its quantity decreases. The observed H_2 trend with the air to acid gas flow ratio justifies the above mentioned statements about lower hydrogen sulfide decomposition reaction. Figure 10 shows decreasing trend of COS as a function of the air to acid gas ratio. At

higher temperature situations, the COS decomposition reaction takes place and lower COS is maintained in the system.

Effect of reaction furnace feed temperature: In addition to air to acid gas flow ratio, reaction furnace temperature is one of the important operating variables influencing operating conditions of the reaction furnace. In this section, the effects of reaction furnace feed temperature are investigated in the reaction furnace temperature, sulfur conversion efficiency percentage, COS and H_2 molar flow rates from reaction furnace effluent and are depicted in Figures 11 and 12.

The reaction furnace temperature ranges from 300-500 K. Figure 11 shows the increase in the reaction furnace temperature results in higher reaction furnace temperature due to higher enthalpy of inlet material. A 150 degree increase in reaction furnace temperature is observed because of rising feed temperature from 300 to 500 K. Incremental reaction furnace temperatures promotes hydrogen sulfide decomposition reaction. Because of more hydrogen sulfide decomposition reaction, the amount of sulfur and hydrogen are raised. Incremental conversion efficiency percentage of sulfur is explained by higher decomposition reaction due to higher resultant reaction furnace temperature. A 200

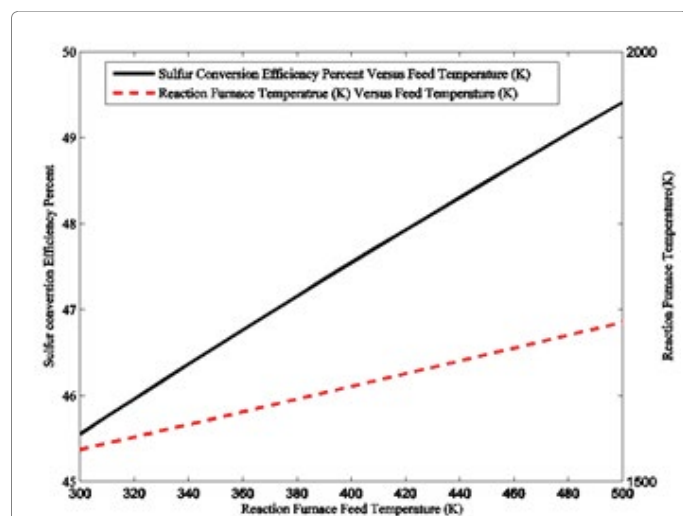


Figure 11: Effect of increasing feed temperature (K) on sulfur conversion efficiency percent and reaction furnace temperature (K).

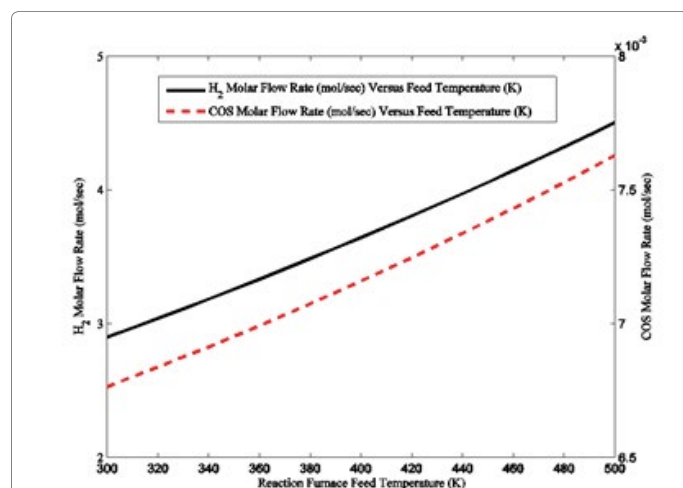


Figure 12: Effect of increasing feed temperature (K) on H₂ and COS molar flow rate (mol/sec).

degree increment of reaction furnace temperature increase sulfur efficiency percentage (3.86%) which is unusable.

Effects of increasing reaction furnace temperature on molar flow rates of H₂ and COS are demonstrated in Figure 11. According to Figure 11, molar flow rates of H₂ and COS at the reaction furnace outlet have negligible increments with the reaction furnace feed temperature. At high temperature of the reaction furnace, decomposition reactions are favorable; the higher amount of the hydrogen sulfide decomposes and higher amount of hydrogen produces. The above statement confirms the observed trend of hydrogen molar flow rate along with the increase in the reaction furnace feed temperature [32,33].

Experimental studies conducted by Karan et al. [34] showed that following reaction between CO and H₂S is favorable at high temperature situations faced in the Claus reaction furnace:



The increasing feed temperature and the resulting raised reaction furnace temperature lead to higher quantity of decomposition

reaction and reaction in accordance with equation 9. Decomposition reaction and reaction 11 proceed in such a way that reaction 11 for COS production overtakes COS consumption reaction, i.e. COS decomposition reaction, and result in production of higher quantity of COS. A comparison between Figures 9 and 11 demonstrates that the air to acid gas ratio has a more considerable effect on the operating conditions of the Claus reaction furnace.

Modification of correlations

Paskall et al. [1] proposed a set of correlation for calculating CO, H₂, COS, CS₂ and S at the reaction furnace outlet. In their correlations, mole composition of inlet flow was a variable, but the effect of reactor residence time wasn't considered. It is the main reason of deficiency of correlations in predicting reactor outlet [7]. Agreement between experimental data and model prediction encouraged to develop a set of correlations for reaction furnace temperature at the outlet, sulfur conversion efficiency percentage and COS conversion percentage. The sulfur conversion efficiency percentage and reaction furnace temperature are utilized in evaluating reaction furnace and overall process performances.

The concentration of COS determines the performance of the reactor in impurity destruction. These correlations make simple performance evaluations without requiring to run the kinetic model. In order to modify the correlations, air to acid gas flow ratio was changed and model predictions were correlated. The correlations for reaction furnace temperature and sulfur conversion efficiency percentage are as follows:

$$T_{RF} (K) = 783.97 + 528.94 (F_{Air} / F_{Acid Gas}) - 74.2260 (F_{Air} / F_{Acid Gas})^2 \quad (12)$$

$$R_{S_2} = \frac{\text{mole of S in S for effluent}}{\text{mole of S in feed}} \times 100 \quad (13)$$

$$R_{S_2} = (36.4840 - 7.0443 (F_{Air} / F_{Acid Gas})) (F_{Air} / F_{Acid Gas}) (t_R^{0.0714}) \quad (14)$$

The mean absolute percentage errors for reaction furnace temperature and the sulfur conversion efficiency percentage are 1.83% and 4.66%.

Based on the mole of carbon dioxide to mole of carbon in hydrocarbons in the feed (x), were set two correlations for COS conversion percentages (RCOS). Definitions of x and RCOS are as follows:

$$x = \frac{\text{mole C in CO}_2}{\text{mole C in hydrocarbon}} \quad (15)$$

$$R_{COS} = \frac{\text{mole of COS in effluent}}{\text{mole of C in feed}} \times 100 \quad (16)$$

$$R_{COS} = 0.00056322 (F_{Air} / F_{Acid Gas})^3 (t_R^6) \quad (17)$$

The mean absolute percentage errors of the correlations are 15.54% and 16.52%, respectively.

Optimization

In this study, operation conditions of the industrial reaction furnaces of the Claus sulfur recovery unit were optimized. In this regard, the reaction furnace temperature is maximized and the H₂S to SO₂ ratio at the reaction furnace effluents was maintained at optimal value 2 to maximize hydrogen sulfide conversion [12].

Operating variables that can be adjusted in order to maintain the H₂S/SO₂ ratio in the Claus reaction furnace at constant two and

maximize reaction furnace are the reaction furnace feed temperature and the ratio of air to acid gas flow. The variation ranges of adjusting operating variables are chosen as follows:

1. 1.5-3 for the ratio of air to acid gas flow based on initial air to acid gas ratio.
2. 150°C-300°C for the reaction furnace feed temperature.

The gamultiobj code of MATLAB programming software was used in optimization work. In former single objective function methods, such as utility theory, weighted sum method, etc., determination of a single objective function is possible. However, the problem lies in the proper selection of the weights or utility functions [39]. Scaling amongst objectives is needed and small perturbations in the weights can sometimes lead to quite different solutions [39]. Therefore, an optimization method would return a single solution rather than a set of solutions that can be examined for trade-offs. For this reason, a set of solutions considering the multiple objectives is preferred [39]. A multi-objective problem investigates a set of solutions, which satisfies the objectivities at an acceptable level without being dominated problem by any other solutions [39].

The optimal operating conditions leading to maximum reaction furnace temperature while maintaining H_2S to SO_2 ratio at constant two are listed in Table 4. The reaction furnace temperature and absolute difference of H_2S to SO_2 ratio from constant 2 before and after optimization work are presented in Table 5. As can be seen in Table 5, the reaction furnace temperature is maximized and the ratios of H_2S to SO_2 are close to constant two. The energy required for increasing feed temperature can provide inside the thermal stage from the steam produced in the WHB.

Conclusion

In this study, a modified kinetic scheme was performed for the description of the Claus reaction furnace of oil refineries. The modified kinetic scheme can be applied in wider operating conditions and different situation such as: initial concentration, feed temperature and pressure. The modified kinetic scheme is developed by a novel two-step optimization method. According to the calculated mole percentages from the modified kinetic model and experimental data set of plants, H_2 component has the maximum mean percentage errors in accordance with 5.905 and 7.981% for the train and test data sets. Coefficients of determinations (R) for CO_2 , CO and COS are 0.9989, 0.9805 and 0.9873, respectively. A good match is observed between the results of the kinetic model with the experimental reaction furnace. Validation of the modified kinetic model with test data sets shows the admissibility and precision of the model in wide operating conditions.

Air to acid gas flow ratio and the reaction furnace feed temperature are two operating variables of the Claus reaction furnace that influence the operating conditions of Claus reaction furnace. The author investigated the changes of temperature, sulfur conversion efficiency percentages, H_2 and COS molar flow rates of Claus reaction furnace along with the above mentioned operating variable. It is concluded that both reaction furnace feed temperature and air to acid gas flow ratio have an increasing effect on the reaction furnace temperature. A comparison between the results of air to acid gas flow ratio and reaction furnace feed temperature showed that the air to acid gas ratio have more notable effects on the operating conditions of the Claus reaction furnace.

Three correlations were introduced for calculating reaction

Reaction Furnace	Feed Temperature (K)	Air to Acid Gas Ratio
1	567.87	2.3551
2	578.19	2.6938
3	534.5	2.4317

Table 4: Adjusted operating parameters of optimized Claus reaction furnaces in oil refineries.

Reaction Furnace	Before Optimization		After Optimization	
	abs (H_2S/SO_2-2)	TRF (K)	abs (H_2S/SO_2-2)	TRF (K)
1	0.15745	1553.1	0.0052812	1764.9
2	0.11778	1544.7	0.041752	1770.5
3	0.030745	1603.9	1.38E-07	1750.7

Table 5: Values of objective functions before and after optimization.

furnace temperature, sulfur conversion efficiency percentage and COS conversion percentage. Air to acid gas ratio, residence time, and mole of carbon dioxide to mole of carbon in hydrocarbons were considered in the correlations.

An optimization study was conducted to investigate the optimum operating condition of the reaction furnace including maximum reaction furnace operating temperature and maintaining the H_2S/SO_2 ratio at a constant of two. The reaction furnace feed temperature and air to acid gas flow ratio parameters were optimized using a multi-objective optimization method.

Nomenclature

- A: Cross-sectional area (m^2)
- C: Concentration (mol/m^3 , $kmol/m^3$, mol/cm^3)
- E: Activation Energy (J/mol or Cal/mol)
- F: Molar Flow (mol/sec)
- h: Enthalpy (J/mol)
- k: rate constant (mol/m^3sec , $kmol/m^3sec$, mol/cm^3sec)
- n_c : Number of components
- n_R : Number of reactions
- P: Pressure (Pa)
- r: rate (mol-sec-m)
- R: Gas constant (8.314 J/mol K, 1.987 Cal/mol K)
- R_k : Conversion of component k
- t_R : Actual mean residence time(sec)
- T: Temperature (K)
- v_{ij} : Stoichiometric coefficient of component j in reaction i
- Subscripts
- i: Reaction number
- j: Component number

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