Reduced and Detailed Kinetic Models Comparison for Thermal Furnace of Sulfur Recovery Units

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Acid gas obtained from oil refineries contains large amounts of hydrogen sulfide, which are not allowed as the off-gas or burned to the atmosphere. The waste gas collected during the processes in the refineries contains a high amount of sulfur-bearing compounds, hence it should be sent to the sulfur recovery unit (SRU). Modified Claus process is the most common sulfur recovery process that is used around the world in the hydrocarbon processing industry. The thermal furnace is the most important part because the majority of the reactions occur in this unit. The aim of the current study is to investigate the possibility of using a reduced kinetic scheme in DSMOKE simulation environment. The hydrogen sulfide conversions are 75%, 80% and 86% obtained from plant data, detailed kinetic model and reduced kinetic model, respectively. Reduced kinetic model results agree with both detailed kinetic model results and plant data by 5% and 6% error.

1. Introduction

Natural gas may consist of hydrogen sulfide, which is an extremely toxic compound, up to 30% (Nabikandi and Fatemi, 2015). Global natural gas resources increase due to the occurrence of shale gas includes formations, methane, and natural gas liquids along with high amounts of acid gases (mainly CO2 and H2S) (Li et al., 2018). Though, sulfur emissions to the atmosphere are substantially limited according to recent environmental regulations. The large variations in concentrations and flows require different methods for H2S removal and sulfur recovery. In oil refineries, modified Claus is the most common sulfur recovery process, which converts toxic hydrogen sulfide to elemental sulfur from acid gas (Zarei et al., 2016).

Claus process consists of a burner, a thermal reaction furnace, a waste heat boiler, catalytic reactors and sulfur condensers (Manenti et al. 2014). While reaction furnace is the first and most important part while the majority of the reactions carried out in it, any improvement on the furnace modeling will help to optimize the efficiency of the process and operation costs. An appropriate kinetic model is required for optimization studies on the furnace. Unfortunately, the kinetics of thermal reaction furnace of SRUs is rather complex and not yet completely understood, hence kinetic modeling of SRU process is rarely found in literature, along with new studies has been done recent days.

Some researchers were interested in using a reduced kinetic model to estimate the gas concentration of reaction furnace outlet, while some of them studied with the detailed kinetic scheme. Pahlavan and Fanaei (2015) used a kinetic scheme contains fourteen reactions and developed simulation for the furnace by PROMAX V2.0. Nabikandi and Fatemi (2015) studied with both reduced kinetic and equilibrium models, then they compared the results with industrial data. The kinetic model results are more precise than the equilibrium model. Zarei et al. (2016) modeled the furnace with reduced kinetic model and the results show a good agreement with the plant data. Kazempour et al. (2017) developed another reduced kinetic model with twelve reactions and the results approached the industrial data obtained from the reaction furnace outlet. Ahmadi and Rad (2017) simulated a Claus plant, by considering only four reactions in the furnace. Ghahraloud et al.

(2017) focused on modeling and optimization of the whole Claus plant, by using reduced kinetics for furnace modeling. Zarei (2018) modified their previous work by decreasing the reaction number. On the other side, researches with detailed kinetics are available in the literature. Pierucci et al. (2004) modeled the reaction furnace as a PFR by considering more than 1500 elementary reactions with 130 species. Manenti et al. (2013a) used a detailed kinetic scheme with 146 species and 2412 reactions and they considered the reaction furnace as a combination of a PFR and a CSTR, and they studied on the industrial case (Manenti et al., 2013b). A detailed model of H2S oxidation with CO2 presence was utilized by Li et al. (2017) for modeling of the furnace as a PFR. Although there are previous studies on reduced kinetic scheme development, it hasn't been reported any reduced kinetic work by using DSMOKE simulator in the literature. The aim of the current study is to compare two different kinetic models and investigate the possibility of using DSMOKE program with the reduced kinetic scheme. For this purpose, reaction furnace was modeled by using detailed and reduced kinetic schemes in this study and the results were compared with industrial data.

2. Process description

The modified Claus process is a sulfur recovery process which is applicable for feeds with H2S concentration greater than 30% and in large scale plants which produce sulfur greater than 2 tons/day. In the Claus process, H2S is converted to elemental sulfur by the following simple overall reaction:

$$H_2S + 0.5O_2 \rightarrow 0.5S_2 + H_2O \qquad (1)$$

The modified Claus process consists of two steps: thermal and catalytic sections. The reaction furnace, which is the first equipment of the thermal section, is a huge cylindrical reactor performs at high temperatures, between 975-1400°C. One-third of hydrogen sulfide is oxidized to sulfur dioxide using air in the furnace. The oxidation of hydrogen sulfide (2) is an exothermic reaction with no thermodynamic restriction.

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O \qquad (2)$$

The remaining two-thirds of hydrogen sulfide and produced sulfur dioxide react and produce elemental sulfur at lower temperatures via Claus reaction (3).

$$2H_2S + SO_2 \leftrightarrow 1.5S_2 + 2H_2O \qquad (3)$$

Reaction (3) takes place endothermically at high temperatures in the reaction furnace or exothermically at low temperatures in the catalytic reactors. The second unit of the thermal section is the waste heat boiler (WHB). WHB is a shell and tube exchanger which cools the furnace outlet gas before catalytic step and due to the low temperatures, recombination reactions carry out inside of it. The off-gas leaving the WHB enters to the first condenser to separate the elemental sulfur. Then, the remaining gas is sent to the first catalytic converter, where Claus reaction takes place mainly. A typical modified Claus generally has two or three catalytic converters depends on the feed composition (Nabikandi and Fatemi, 2015; Manenti et al., 2014; Zarei et al., 2016; Zarei, 2018).

3. Reaction furnace modeling

3.1 Process specifications

In this study, the reaction furnace was modeled as a PFR, by considering the previous studies. Furnace geometry and inlet feed information were taken from Nabikandi and Fatemi (2015) and presented in Table 1. It's assumed that acid gas and air are mixed in the inlet of the burner. The simulations were run at the temperatures between 950 and 1200°C isothermally.

Table 1: Geometry and inlet feed information of the reaction furnace

	Acid gas	Air	Fuel gas
Components	mol%	mol%	mol%
CO_2	53.16	0.00	1.10
N_2	0.00	73.00	3.90
CH_4	0.90	0.00	95.00
H_2S	36.04	0.00	0.00
O_2	0.00	19.50	0.00
H_2O	9.90	7.50	0.00
Molar flow (mol/s)	171.11	181.50	3.05
Furnace geometry			
Length (m)		6.5	
Inside diameter (m)		3.4	

3.2 Reduced kinetic model

These reactions were selected among many other reactions so that they could present the best possible prediction of the behavior of furnace. The reactions were chosen by considering the key components, and the previous studies in the literature. The selected reactions and their kinetics are presented in Table 2 and Table 3, respectively.

Table 2: Selected reactions and kinetics for reduced kinetic scheme

No.	Reaction	Reaction kinetics	Reference
R1	$H_2S \leftrightarrow 0.5S_2 + H_2$	$r_{H_2S} = A_f e^{\frac{-E_f}{RT}} P_{H_2S} P_{S_2}^{0.5} - A_r e^{\frac{-E_r}{RT}} P_{H_2} P_{S_2}$	Hawboldt et al. (2000)
R2	$2H_2S + SO_2 \leftrightarrow 1.5S_2 + 2H_2O$	$r_{H_2S} = A_f e^{\frac{-E_f}{RT}} P_{H_2S} P_{SO_2}^{0.5} - A_r e^{\frac{-E_{ar}}{RT}} P_{H_2O} P_{S_2}^{0.75}$	Nabikandi and Fatemi (2015)
R3	$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O$	$r_{H_2S} = A_f e^{\frac{-E_f}{RT}} C_{H_2S} C_{O_2}^{1.5}$	Nabikandi and Fatemi (2015)
R4	$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S$	$r_{CS_2} = A_f e^{\frac{-E_f}{RT}} C_{CH_4} C_{S_2}$	Karan and Behie (2004)
R5	$CO_2 + H_2 \rightarrow CO + H_2O$	$r_{CO} = A_f e^{\frac{-E_f}{RT}} C_{CO_2} C_{H_2}^{0.5}$	Karan et al. (1999)
R6	$CO + 0.5S_2 \leftrightarrow COS$	$r_{COS} = A_f e^{\frac{-E_f}{RT}} C_{CO} C_{S_2} - 2k_r C_{COS} C_t$ $C_t = \frac{P_t}{RT}$	Karan et al. (1998)
R7	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$r_{CH_4} = A e^{\frac{-E_a}{RT}} C_{CH_4}^{-0.3} C_{O_2}^{1.3}$	Westbrook and Dryer (1981)
R8	$H_2 + O_2 \rightarrow H_2O + 0.5O_2$	$r_{H_2} = A_f e^{\frac{-E_f}{RT}} C_{H_2} C_{O_2}$	Kazempour et al. (2017)
R9	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	$r_{CH_4} = A_f e^{\frac{-E_f}{RT}} C_{CH_4} C_{CO_2}$	Pahlavan and Fanaei (2015)

Table 3: Kinetic parameters of the selected reactions

No.	$A_{forward}$	$E_{forward}$ (kcal/mol)	$A_{reverse}$	$E_{reverse}$ (kcal/mol)
R1	$5260 \frac{mol}{cm^3 * s * atm^{1.5}}$	45000	$14 \frac{mol}{cm^3 * s * atm^2}$	23550
R2	$15762 \frac{mol}{cm^3 * s * atm^{1.5}}$	44857	$506 \frac{mol}{cm^3 * s * atm^{1.75}}$	44827
R3	$4.728 * 10^8 \left(\frac{m^3}{mol}\right)^{0.5} * \frac{1}{s}$	11000	-	-
R4	$5.532 * 10^7 \frac{m^3}{mol * s}$	38000	-	-
R5	$3.95 * 10^{10} \frac{m^3}{kmol * s}$	54021	-	-
R6	$3.181 * 10^2 \frac{m^3}{mol * s}$	13340	$1.22 * 10^4 \frac{m^3}{mol * s}$	43000
R7	$1.3 * 10^8 \, 1/s$	22705	-	-
R8	$1.08 * 10^6 \frac{mol}{cm^3 * s}$	30000	-	-
R9	$8.06 * 10^5 \frac{m^3}{mol * s}$	4980	-	-

3.3 Detailed kinetic model

The detailed kinetic scheme developed by Manenti et al (2013a) was used in this study. The scheme consists of 146 species and 2412 elementary reactions.

3.4 Computational environment

The reactor network is performed and solved through the use of specific tools for the simulation of ideal reactors controlling large kinetic schemes that have been developed through the last 20 and more years by the research group of Politecnico di Milano. These tools benefit the coupled use of DSMOKE suite, a general tool for the simulation of reactor network using detailed ChemKin-format kinetic schemes, and BzzMath numerical library for the rapid solution of very large systems (Manenti et al., 2013a).

This tool uses standard material and energy balances of plug flow reactor, and in particular:

$$\frac{dw_i}{d\tau} = \sum_{j=1}^{NR} \vartheta_{ij}\, R_j W_i \qquad i = 1, \ldots, NC \tag{4}$$

$$c_p \frac{dT}{d\tau} = \sum_{j=1}^{NR} -\Delta H_j\, R_j + \frac{U_{ext} S}{V}(T_{ext} - T) \tag{5}$$

5. Results and discussion

The hallmark of this study is the test of the reduced kinetic scheme in DSMOKE simulation environment. In this section, the competence of reduced kinetic model usage will be discussed. Figure 1-4 show the key components profiles obtained from simulations studies.

Due to the high temperatures, from 950 to 1200°C, the oxygen reacts rapidly, and consumed immediately in the burner, the beginning point of the reaction furnace. The burner is the step that the acid gas and air meet. A typical industrial burner is no longer than 0.5 m; while the furnace length is approximately 6.5 m, it explains the rapid consumption of oxygen in both models.
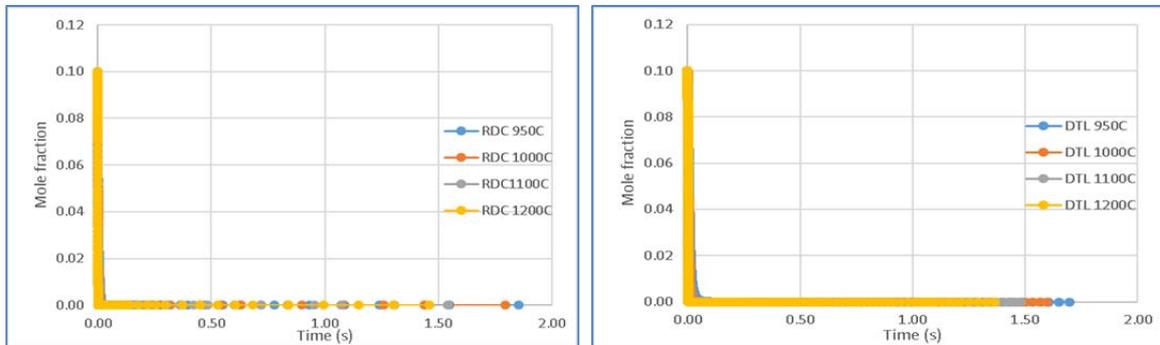

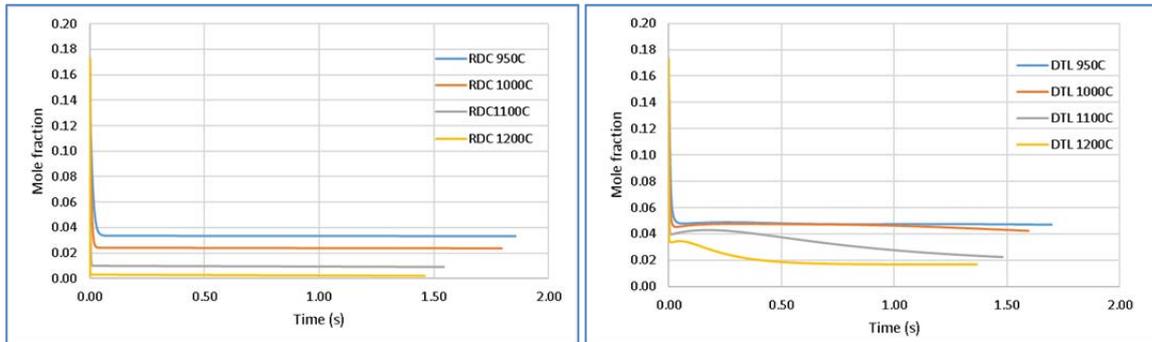Figure 1: O_2 profile at different temperatures, with (a) reduced and (b) detailed kinetics

Figure 2: H_2S profile at different temperatures, with (a) reduced and (b) detailed kinetics

As seen in general all the reactions are depended on temperature. Figure 2 shows the profiles of the hydrogen sulfide. As mentioned before, hydrogen sulfide is consumed by oxidation, decomposition and also reacting with sulfur dioxide after it is produced. The results show a significant decrease, as expected. In both two models, all oxygen is consumed in the burner which is the first part of the reactor. The trends are in good agreement at lower temperatures. By increasing the temperature, a slight difference arises due to radical species in the detailed model. The hydrogen sulfide conversions are 75%, 80% and 86% obtained from plant data, detailed kinetic model and reduced kinetic model, respectively. Hence, the reduced model result matches with both detailed kinetic model results and plant data by 5% and 6% error.

Similar to the previous one, Figure 3 shows the profiles of the sulfur which is the demanded product in the process. As expected, sulfur production increases with temperature and both kinetic scheme simulations provide sufficient results. The reason of this slight difference is possibly the reaction between hydrogen sulfide and sulfur dioxide, in the detailed model it is probably consumed via other reactions.
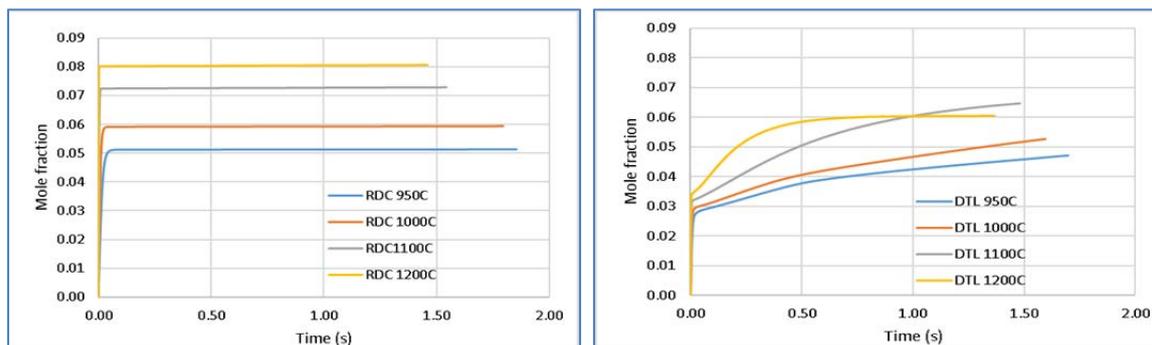
Figure 3: S$_2$ profile at different temperatures, with (a) reduced and (b) detailed kinetics

While most important reactions take place in the reaction furnace, the outlet stream is directly affected to the final composition of the whole process. The compositions at the end of the furnace were given in Table 4. This table shows that both simulation compositions are sufficient compared with the industrial data. The main target of Claus process is to reduce hydrogen sulfide substance. According to the results, the reduced model outlet stream is the one has the minimum hydrogen sulfide content.

Table 4: Mole fraction results obtained from the simulation at 1000°C compared with the industrial data

Components	Reduced model	Detailed model	Plant data
CO_2	0.240	0.265	0.232
N_2	0.368	0.373	0.373
CH_4	0.0	0.0	0.0
H_2S	0.024	0.042	0.034
COS	0.0	0.0	0.018
CS_2	0.0	0.0	0.0016
SO_2	0.028	0.023	0.027
S_2	0.059	0.053	0.045
CO	0.025	0.002	0.017
H_2	0.029	0.022	0.090
H_2O	0.227	0.218	0.241

6. Conclusions

The hallmark of this study is the use of the reduced kinetic scheme in DSMOKE simulation environment. In general, reduced kinetic model results show a good agreement with both industrial data and detailed kinetic model results. According to these results, this reduced kinetic scheme is an alternative kinetic mechanism for the reaction furnace modeling. The results also show that DSMOKE environment is capable of process simulation with reduced kinetics, along with the detailed scheme.

Acknowledgments

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