Revised Kinetic Scheme for Thermal Furnace of Sulfur Recovery Units

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A revised, detailed kinetic scheme for the pyrolysis and oxidation of sulfur compounds is proposed and contextualized to thermal furnace of sulfur recovery units. The kinetic scheme differs from the literature schemes since its kinetic parameters accounts for the presence of light hydrocarbons, ammonia, and other species usually present in the feedstock of industrial sulfur recovery units. The scheme is validated on the literature as well as industrial data acquired from more than 10 different Claus processes.

1. Introduction

Claus process has been developed over 100 years ago and it is aimed at recovering elemental sulfur from oil refinery and acid gas processes. Nowadays there is a renewed interest in it, since it can play a key role in the reduction of environmental emissions, with similar environmental impact with respect to other well-established research activities applied in chemical engineering dealing with the integration of renewables, such as energy generation efficiency (Klemes et al., 2010), renewable energy and supply chain integration (Lam et al., 2010b), and concentrating solar plants (Vitte et al., 2012), or biomass valorization for biomass supply chain optimization (Cucek et al., 2010) and carbon footprint minimization (Lam et al., 2010a), and for sugar processing sustainability enhancement (Vaccari et al., 2005). As it can be seen from the scheme in Figure 1 an acid gas stream is injected in the thermal furnace together with combustion air (further details on Sulfur Recovery Units can be found in (Manenti et al., 2011), online data reconciliation and (Signor et al., 2010), adaptive simulation). The acid gas is partially oxidized in the thermal furnace at severe temperature conditions. The outflowing stream is cooled in a waste heat boiler and sent to the train of fixed-bed catalytic reactors (CR). Several reactors are required since the Claus reaction is interested by equilibrium. The number of reactors and the type of catalyst are selected according to the sulfur recovery specifications. To obtain more than 97.5% of sulfur recovery is important to take account for the hydrolysis reactions of carbon and sulfur compounds like COS and CS2. Other unit operations are the sulfur condensers for separating the elemental sulfur from the main stream and gas preheaters to refine the inlet temperature of the acid gas stream before entering each CR. After the catalytic section, the outlet gas stream is usually sent to tail gas treatment units for final combustion of remaining compounds.

Kinetics involved in the Thermal Furnace (TF) of Claus processes is very complex and quite cumbersome to model since many phenomena and reaction mechanisms occur in extremely short time. Some of them are the H2S pyrolysis and oxidation, effects related to SO2 as a radical pool inhibitor or promoter, formation of undesired compound such as COS and CS2. A detailed kinetic scheme, including more than 2300 reactions and 140 species (based on carbon, hydrogen, nitrogen, oxygen and sulfur) has been developed and honed in the last years (Manenti et al., 2013).

Some recent improvements in the kinetic parameters allow more reliable characterization of the TF behavior with the consequent possibility to deepen the understanding of the overall process and to improve safety, operations, efficiency, and sulfur removal. Claus process is a relevant application of H2S oxidation and it involves a large number of reactions and kinetic mechanisms.

Several kinetic models have been developed for describing the formation and reaction of the sulfur compounds but only very few part of them has been verified under real Claus conditions. For this reason our aim is to make a review of our kinetic model, contextualizing it to the Claus process operations. The main phenomenon occurring in the thermal stage is certainly the partial oxidation of the H_2S in the acid gas to give SO_2. The optimal ratio between H_2S and SO_2 outflowing the TF is equal to 2 as the stoichiometry of Claus reaction in the catalytic converters:

$$2H_2S + SO_2 \leftrightarrow \frac{3}{x}S_x + H_2O$$

(1)

where x takes account of the sulfur equilibrium ($x = 1, 2, 4, 6, 8$). For this reason combustion air is well balanced to obtain that ratio. Acid gas streams to be processed are often rich in CO_2 (ranging from 5% up to 70 % mol/mol basis) and with presence of ammonia and light hydrocarbons. In this context, it is therefore useful to revise some kinetic parameters with respect to the ones estimated in the literature with *relatively pure* feedstock to improve the reliability of kinetic model previsions for industrial applications.
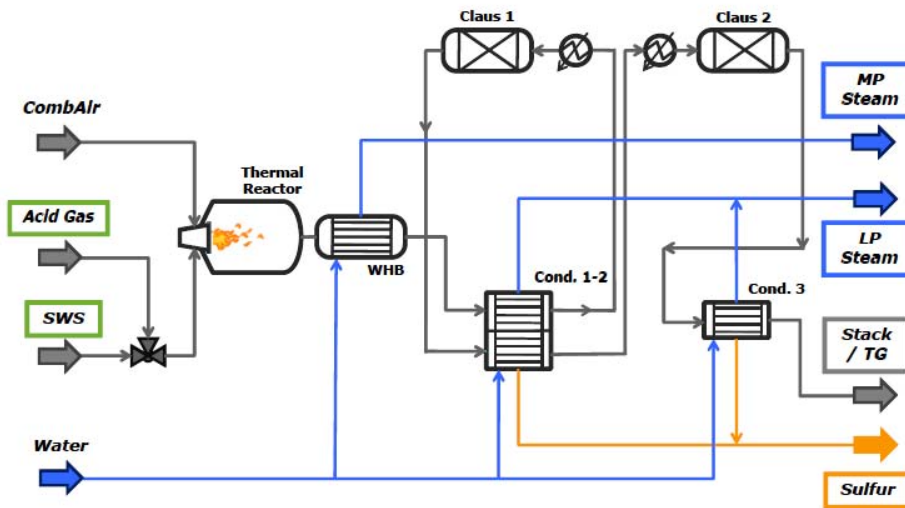

Figure 1: Basic scheme of a Sulfur Recovery Unit.

2. Description of the main phenomena

2.1 H₂S pyrolysis

An important phenomenon involved in the TF is certainly H_2S pyrolysis, due to the lean conditions of combustion air inflow in the furnace and to the high activity of H_2S at the furnace operating conditions. H_2S pyrolysis has been widely studied by Binoist et al. (Binoist et al., 2003). This reaction is subject to equilibrium limitations (42 % at 1000°C for a dilute 5 % H_2S stream, according to Binoist and co-workers). The equilibrium is achieved in few seconds at temperature above 1000 °C. The consideration of a detailed radical mechanism of the reaction is important to take account of some relevant aspects such as the auto-acceleration of H_2S pyrolysis observed experimentally.

2.2 Effects of SO₂ on radical pools

The effects of SO_2 as inhibitor and promoter of radical pools have been studied and described by Dagaut (Dagaut et al., 2003) and, with different conditions, by Mueller (Mueller et al., 2000), for CO-H_2 and CO-H_2O-O_2-NO-SO_2 mixtures, respectively. The inhibition effect on the oxidation of CO by SO_2 can be explained considering that a few percent of SO_2 reacts with radical O (third body reaction) to form SO_3. This leads to the reduction of radical pool (globally leading to O+H=OH and O+O=O₂), which obstructs CO oxidation. In addition, SO_2 reacts with H atoms

to form HOSO. This species brings to the formation of the radical HO_2 via reaction with O_2. This radical operates as inhibitor consuming H and O radicals.

2.3 COS and CS$_2$ formation

COS and CS$_2$ are produced in the furnace due to the cohabitation of (hydro)carbons and sulfur compounds. They are undesired compounds because they limit sulfur recovery and are also poisons for certain catalysts. Karan (Karan et al., 1999) has highlighted that COS is mainly formed at low temperatures (<900°C) according to the molecular reaction between CO and H_2S:

$$CO + H_2S \leftrightarrow COS + H_2 \tag{2}$$

At higher temperatures the pyrolysis of H_2S becomes relevant: the production of S_2 leads to:

$$CO + 0.5S_2 \leftrightarrow COS \tag{3}$$

An alternative path to COS is suggested by Gargurevich (Gargurevich, 2005) and involves the formation of the chemically activated adduct [S-SCH=O]* deriving from formaldehyde, obtained through the oxidation of methyl radical. Accordingly, CS$_2$ too can be produced and we remind to specific literature for the sake of conciseness (Petherbridge et al., 2003).

2.4 Oxidation

The oxidation mechanisms of hydrogen sulfide have been studied extensively by several authors. For instance, the interesting review by Selim and co-workers (Selim et al., 2012) on H_2S/O_2 reaction mechanism can be the basic starting point of our discussion, which is mainly focused on the typical phenomena of industrial processes that have less literature space than what they could deserve. Actually, the dissociation of ammonia according to the global reaction with oxygen (4) to produce nitrogen and water is one of them. It is common to have the injection of a stream deriving from sour water stripper. In this case it is necessary to have high flame temperature and quite long residence time in order to have complete conversion of ammonia.

Despite an ammonia content of less than 2 % (mol/mol basis) permits to use a straight through configuration, it is also common to have a split flow configuration when needing to remove ammonia, bringing to the possibility to manage streams with more than 2 % of ammonia (some industrial plants can manage streams with up to 20 %vol).

$$2NH_3 + 1.5O_2 \rightarrow N_2 + 3H_2O \tag{4}$$

3. Kinetic model

The detailed kinetic model for sulfur recovery units here proposed is based on the principles of hierarchy, generality, and modularity as for the previous kinetic models already developed for pyrolysis and combustion of hydrocarbons and biomasses (Ranzi et al., 1994). The sulfur subset derives from the work of Glarborg's group (Rasmussen et al., 2007), which is adapted to the typical operating conditions of sulfur recovery units so as to improve the agreement with experimental/industrial data.

3.1 H$_2$S pyrolysis

The experimental data considered for the model validation is acquired from Binoist et al. (2003). The preliminary results for H_2S pyrolysis (with and without inlet sulfur) are in *Figure 2* and *Figure 3*. The trends show that the model is in a good agreement with the data when no sulfur is fed to the system. On the other hand, when the sulfur is fed the data are systematically underestimated. For this reason a coupled sensitivity and local reaction fluxes analysis was performed and led to the identification of a few reactions whose parameters can be adjusted in order to get better data fitting. These minor adjustments are possible if considering the range of uncertainty about the kinetic parameters. The resulting kinetic scheme for pyrolysis is shown in Table 1. The trends in *Figure 2* and *Figure 3* show the better trend with the modified model. The kinetic model prevision is improved by 10-20%, depending on the operating temperature. It is useful to underline that even changing the parameters of the most sensitive reactions, the system seem not to strongly modify its behavior with respect to the other involved phenomena.

Table 1. Kinetic parameters for H2S pyrolysis. Rate eq.: $k=A.T^{\beta} .exp(-E_a/RT)$ [cm-kmol-s-K-kcal].

| n	Reactions	A	β	Ea
R1	$S+H+M=SH+M$	.62E+17	-.6	.0
R2	$S+H_2=SH+H$	.14E+15	.0	19300
R3	$S_2+M=S+S+M$	.48E+14	.0	77000
R4	$S_2+H+M=HSS+M$	.40E+15	2.84	1665
R5	$SH+SH=S_2+H_2$	.50E+12	0.0	.0
R6	$SH+S=S_2+H$	.30E+14	0.0	.0
R7	$H_2S+M=S+H_2+M$	.16E+25	2.613	89100
	$N_2/1.5 \, SO_2/10$			
	$H_2O/10$			
R8	$H_2S+H=SH+H_2$	.35E+08	1.94	904
R9	$H_2S+S=SH+SH$	.83E+14	0.0	7400
R10a	$HSS+H=SH+SH$	.97E+08	1.62	-1030
R10b	$HSS+H=SH+SH$	.11E+14	.353	210.0
R11	$HSS+H=S_2+H_2$	.12E+09	1.653	-1105.0
R12	$HSS+H=H_2S+S$	.44E+14	.000	6326.0
R13	$HSS+S=S_2+SH$	.42E+07	2.200	-600.0
R14	$HSS+SH=H_2S+S_2$	.63E+04	3.050	-1105.0
R15	$HSS+HSS=HSSH+S_2$	.96E+01	3.370	-1672.0
R16	$HSSH+M=SH+SH+M$	.14E+16	1.000	57030.0
R17	$HSSH+H=HSS+H_2$	.50E+08	1.933	-1408.0
R18	$HSSH+H=H2S+SH$	.20E+15	.000	.0
R19	$HSSH+S=HSS+SH$	.29E+07	2.310	1204.0
R20	$HSSH+SH=HSS+H_2S$	.64E+04	2.980	-1480.0
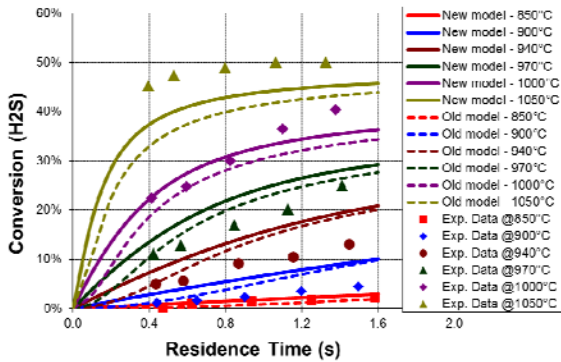
Figure 2. H2S pyrolysis without S, conversion.
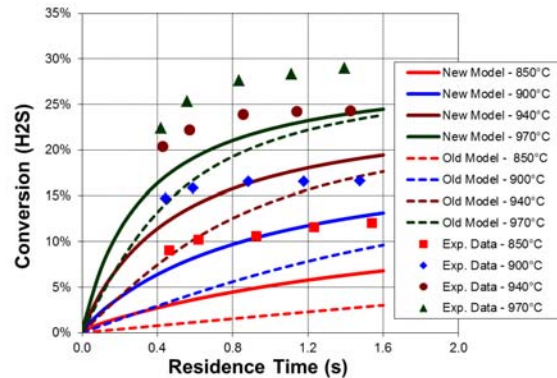
Figure 3. H2S pyrolysis with S, conversion.

3.2 COS formation

In order to simulate COS formation, Karan's data and reactor configuration have been considered. Also in this case minor adjustments to the kinetic parameters of a reaction have been proposed, analogously to the previous paragraph so as to enhance the data fitting. The model results are reported in *Figure 4*. The proposed kinetic parameters for the considered reaction are:

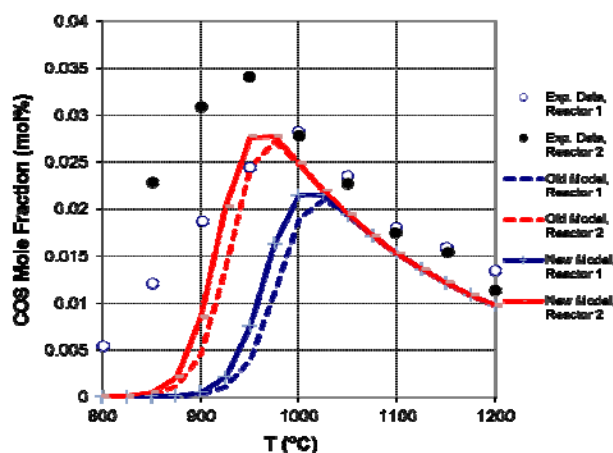$$S+COS \leftrightarrow S_2 + CO \qquad k = 2.951 \cdot 10^{16} \cdot e^{(3404/RT)} \tag{5}$$

Figure 4. COS formation: comparison of literature and proposed models.

A better agreement between data and model is obtained for temperatures higher than 1000°C with the revised parameters. Please not that model underestimation for low temperatures are not of interest since such conditions are quite far from the typical Claus conditions (950-1400°C).

3.3 CS$_2$ formation

CS$_2$ formation had not previously taken into account in the kinetic scheme. Since the purpose of this work is that of revising the scheme in order to get better results when dealing with the simulation of reacting mixtures with sulfur and carbon species, a bibliographic search has been performed for getting data, reactions and related kinetic parameters about this phenomenon.

One another paper from Karan and coworkers (Karan and Behie, 2004) has been considered to take into consideration the formation of CS$_2$ from H$_2$S and S$_2$ in presence of carbon gaseous species (e.g. methane, in this case). The author presents experimental results for the systems H$_2$S+CH$_4$ and S$_2$+CH$_4$. The experiments are carried out in a high-temperature flow reactor with pressures of 101−150 kPa, temperatures of 800−1250 °C, and residence times of 90−1400 ms. They develop also a kinetic scheme, but CS$_2$ formation seems to be taken into account as a global reaction (and not a detailed one). Due to this, the kinetic scheme proposed by (Petherbridge et al., 2003) for CS$_2$ production has been considered and inserted in our kinetic scheme. This scheme suggests that the formation of CS$_2$ follows a path from the addiction of SH radical to CH$_3$ radical, in order to form the CH$_3$SH or CH$_2$S (with H$_2$) species. These compounds later react with atomic hydrogen H to give H$_2$ and the H-C-S compound deriving from the loss of H. This can happen until the formation of CS, that can further react with SH radical to give, finally, CS$_2$. This path is briefly illustrated in the scheme in Figure 5.
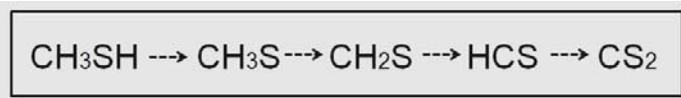

Figure 5 Path of formation of CS$_2$, consecutive reactions from CH$_3$SH

The kinetic parameters related to this scheme are reported in Table 2.

Table 2: Kinetic parameters for the CS$_2$ scheme, from (Petherbridge et al., 2003) Rate eq.: k=A.T$^\beta$ .exp(-Ea/RT) [cm-kmol-s-K-kcal].

n	Reactions	A	β	Ea
R21	H$_2$S=SH+H	7.632E+14	.0	82155.0
R22	SH+CH$_3$=CH$_3$SH	9.998E+12	.0	2969.67
R23	SH+CH$_3$=CH$_2$S+H$_2$	1.018E+12	.0	.0

R24	$H+CH_3SH=CH_3+H_2S$	6.926E+12	.0	1664.0
R25	$H+CH_3SH=CH_3S+H_2$	2.903E+12	.0	2593.0
R26	$H+CH_3S= CH_2S+H_2$	1.988E+13	.0	.0
R27	$H+CH_2S= HCS+H_2$	5.252E+12	1.77	2989.29
R28	$H+HCS=CS+H_2$	1.211E+14	.0	.0
R29	$SH+CS=H+CS_2$	3.232E+10	1.50	495.0
R30	$CH_4+S=CH_3+SH$	2.042E+14	.000	19796.0
R31	$H_2S+S=2SH$	5.704E+14	.0	15045.0
R32	$2S+M=S_2+M$	1.200E+17	-1.0	.0

In addition to the kinetic scheme, thermodynamic properties had to be found for the species not included in the previous version of the global scheme. Such properties can be given in the form of NASA-polynomials (Burcat and Ruscic, 2005), calculated starting from formulas including 7 coefficients .

$$\frac{C_p^\circ}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \tag{6}$$

$$\frac{H_T^\circ}{RT} = a_1 + \frac{a_2 T}{2} + \frac{a_3 T^2}{3} + \frac{a_4 T^3}{4} + \frac{a_5 T^4}{5} + \frac{a_6}{T} \tag{7}$$

$$\frac{S_T^\circ}{R} = a_1 \ln T + a_2 T + \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \frac{a_5 T^4}{4} + a_7 \tag{8}$$

The paper of (Petherbridge et al., 2003) proposes the coefficients for the calculation of the thermodynamic properties for species CH_3SH, CH_3S, CH_2S, HCS as reported in Table 3. Alternatively, a wide accepted source for the thermodynamic data can be found on the website of the Institute of Chemistry, Eötvös University (ELTE), Budapest, Hungary (Burcat, 2006). The corresponding data are reported in Table 4.

Table 3: Thermodynamic parameters (NASA-Polynomial form) from (Petherbridge et al., 2003)

Temperature range (K)	Coefficient	CH3SH	CH3S	CH2S	HCS
298-1000	a_1	1.8873	1.5421	2.4953	3.5537
	a_2	1.5460E-2	1.5180E-2	6.1100E-3	2.0700E-3
	a_3	-5.6022E-6	1.0000E-5	4.3754E-6	2.4041E-6
	a_4	-1.8247E-9	3.8581E-9	-9.6164E-9	-3.7711E-9
	a_5	1.5779E-12	-4.0429E-13	4.2503E-12	1.4823E-12
	a_6	-3.9260E3	1.3532E-4	1.1906E4	3.5321E4
	a_7	1.5501E1	1.6659E1	1.1629E1	7.4244
1000-5000	a_1	4.5472	3.6110	3.4681	3.7778
	a_2	1.0180E-2	8.9200E-3	6.2500E-3	2.8700E-3
	a_3	-3.7614E-6	-3.6176E-6	-2.5499E-6	-1.0604E-6
	a_4	6.3502E-10	6.8569E-10	4.8585E-10	1.7918E-10
	a_5	-4.0058E-14	-4.9459E-14	-3.5164E-14	-1.1311E-14
	a_6	-4.8540E3	1.2974E4	1.1504E4	3.5163E4
	a_7	8.9853E-1	6.4563	5.9022	5.7494

Table 4: Thermodynamic parameters (NASA-Polynomial form) from (Burcat, 2006)

Temperature range (K)	Coefficient	CH3SH	CH3S	CH2S	HCS

Temp range					
298-1000	a_1	3.7863	2.5644E+0	2.4953E+0	3.7916E+0
	a_2	3.7703E-3	1.1580E-2	6.1100E-3	-4.9480E-4
	a_3	1.9647E-5	-4.5012E-6	4.3754E-6	1.2755E-5
	a_4	-2.6573E-8	-5.0234E-10	-9.6164E-9	-1.7355E-8
	a_5	1.0529E-11	6.9525E-13	4.2503E-12	7.2053E-12
	a_6	-3.8792E+3	1.3371E+4	1.1906E+4	3.2783E+4
	a_7	7.0951	1.1250E+1	1.1629E+1	6.5058E+0
1000-5000	a_1	4.5037	4.6281E+0	3.4681E+0	4.2466E+0
	a_2	9.4987E-3	7.5024E-3	6.2500E-3	2.3582E-3
	a_3	-3.3430E-6	-2.7063E-6	-2.5499E-6	-8.2547E-7
	a_4	5.3197E-10	4.3767E-10	4.8585E-10	1.3088E-10
	a_5	-3.1516E-14	-2.6153E-14	-3.5164E-14	-7.7350E-15
	a_6	-4.4615E+3	1.2656E+4	1.1504E+4	3.2499E+4
	a_7	1.5116	4.1587E-2	5.9022E+0	3.2748E+0

Since equilibrium conditions can be reached in some of the abovementioned experiments, thermodynamic data have fundamental importance in these simulations. Thus, a comparison between the simulated trends for the reacting systems with the two different thermodynamic properties databases has been performed.

The results of this approach for the reacting mixture with H_2S and CH_4 are shown in Figure 6, Figure 7 and Figure 8, where dotted lines represent the kinetic scheme with the use of the thermodynamic data from Petherbridge et al, while the solid lines represent the results obtained with the thermodynamic coefficients from Burcat.
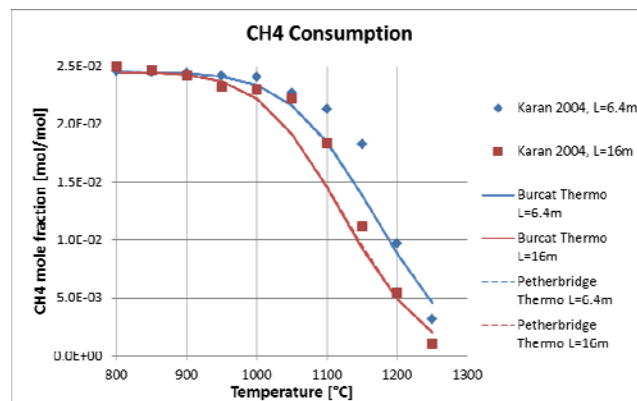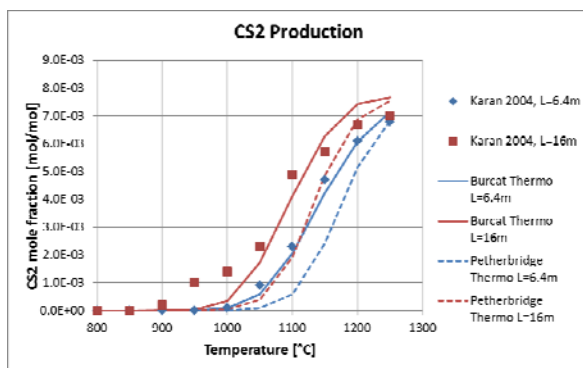

Figure 6 CH_4 consumption. Reacting mixture with CH_4 and H_2S

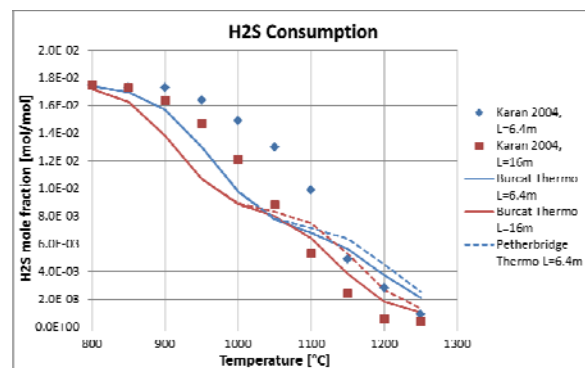*Figure 7 CS_2 production from CH_4 and H_2S*

Figure 8 H_2S consumption, mixture with CH_4 and H_2S

As one can see, the simulations follow the trend of the experimental data in both of the cases. Despite this, it seems that from 1000°C on, there is a deviation between the curves for CS_2 production and H_2S consumption.

This could be attributed to divergences in the thermodynamic data in the high temperature region. For this reason, the data set of Burcat has been considered as the better reference for our kinetic scheme.

This is evidenced also for the system initially containing CH_4 and S_2 (reported in Figure 9, Figure 10 and Figure 11), even though it has to be noted that for this case the estimated production of H_2S and CS_2 are not in good agreement with the experimental data.

This has to be certainly attributed to the problems related to H_2S formation and consequent decomposition paths, since also this time CS2 is strictly related to the H2S formed, as evidenced by the reactions from R21 to R32, with particular attention to those regarding the formation of the key unstable intermediates (CH_3SH, CH_3S, CH_2S and HCS) from H and SH radical reactions.
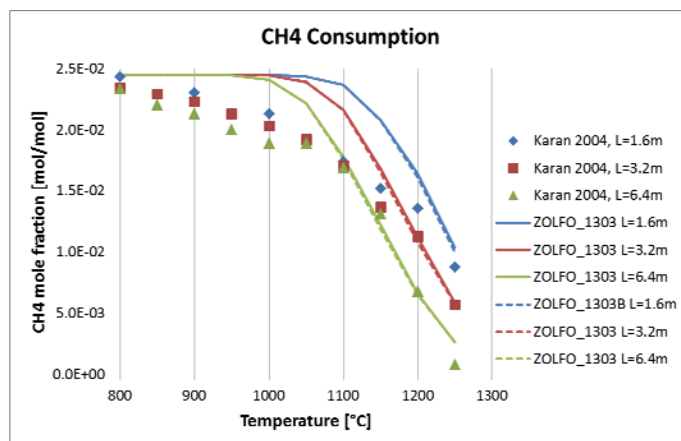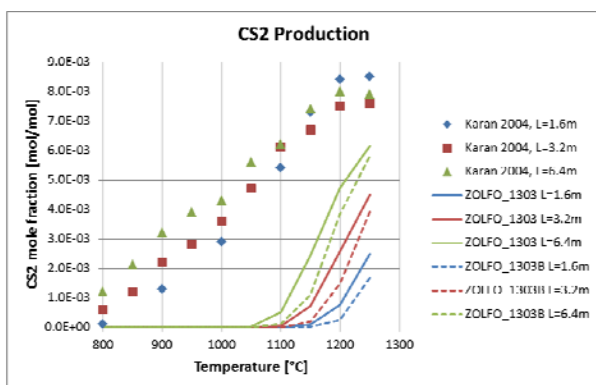

Figure 9 CH_4 consumption. Reacting mixture with CH_4 and S_2

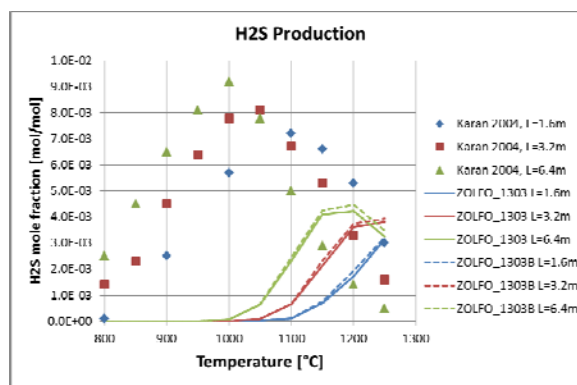Figure 10 CS_2 production from CH_4 and S_2

Figure 11 H_2S production, mixture with CH_4 and S_2

Since the present work is still in progress, the authors save the further modifications to the kinetic scheme for a future work, in order to get better results for CS_2 production from highly containing S_2 mixtures with low content of H_2S. Despite this, one can notice that in Claus conditions H_2S is in large abundance. As evidenced above, H_2S formation and decomposition reactions are limiting CS_2 production, hence in case of large H2S content, the situation appears to be associated to the first case presented (and well simulated). The impact of oxygen containing molecules has certainly to be taken into future consideration, since species as CO, CO_2 and COS could affect CS_2 formation.

4. Industrial case study

The revised kinetic scheme has been therefore applied to a set of industrial cases in order to validate it under real Claus process conditions. The TF and WHB reactor models are based on detailed reactor network analysis to characterize the non-ideal nature of the system TF-WHB, as presented in our previous work (Manenti et al., 2012a), and on the recombination effects due to the quench (an in-depth analysis can be found in the references.

See for example (Manenti, 2011) for heat transfer control and (Manenti et al., 2012b) for the analysis of the recombination reactions in waste heat boiler). The resulting system is solved using DSmoke coupled with BzzMath Library (Buzzi-Ferraris and Manenti, 2012). Axial profiles for temperature and concentrations for a selected plant (Nanjing, courtesy of Tecnimont-KT) are reported in *Figure 12* and *Figure 13*, respectively. Residuals are plotted in *Figure 14* and *Figure 15*. The kinetic scheme combined with the reactor network analysis leads to a very good agreement with the industrial data, further validating the revised kinetic model. CO only seems to be overestimated by ~20 % (relative). This is probably due to fluid-dynamics issues or from wrong CO-CO_2 inferred measurements based on inlet carbon species amount.
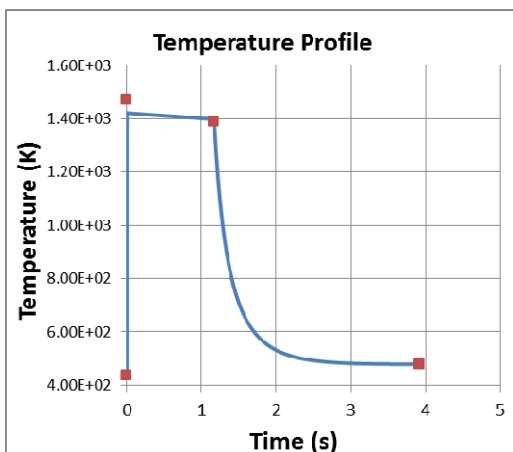

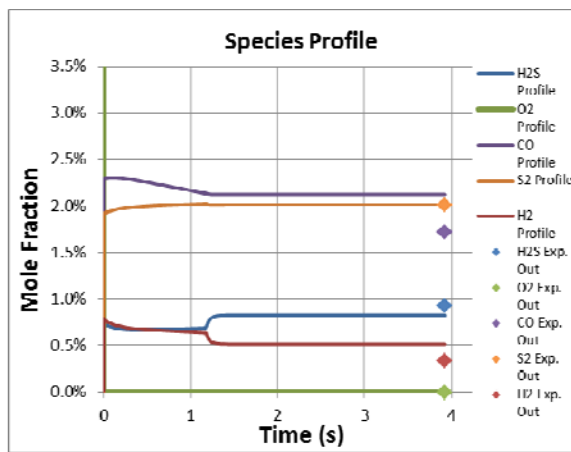Figure 12. Calculated temperature profile.

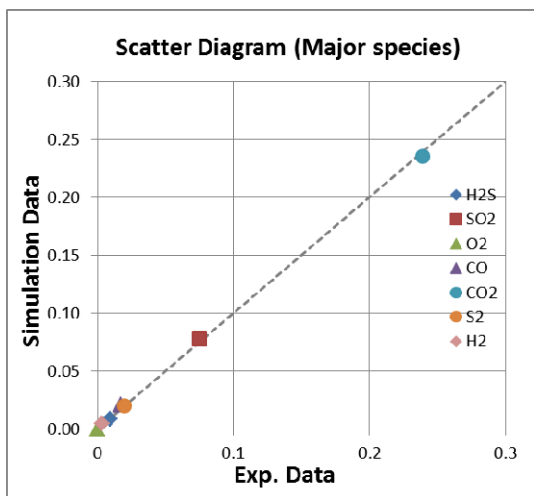Figure 13. Calculated species profile.
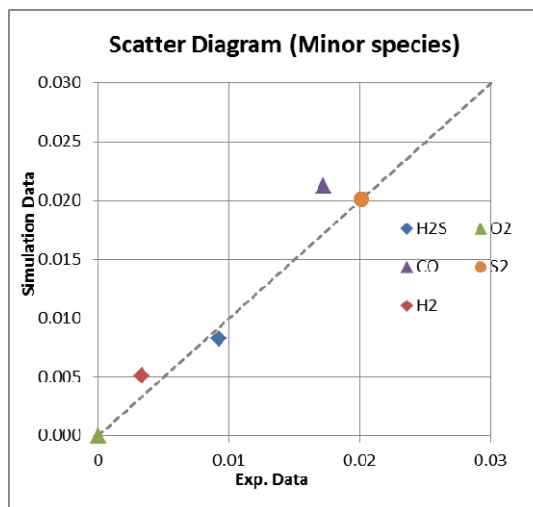

Figure 14. Residuals model-data.

Figure 15. Zoom of Figure 10.

5. Conclusions

The present work offers a review of the main phenomena involved in reacting systems which involve sulfur compounds. A detailed kinetic scheme has been presented and validated on literature and industrial basis. Some modifications on H_2S pyrolysis and COS formation have been proposed to improve the characterization of the thermal furnace and waste heat boiler at the industrial operating conditions. The revised kinetic model has been applied to several industrial cases with good agreement with respect to the industrial data.

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