

# 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 (Klemeš 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 CS<sub>2</sub>. 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 H<sub>2</sub>S pyrolysis and oxidation, effects related to SO<sub>2</sub> as a radical pool inhibitor or promoter, formation of undesired compound such as COS and CS<sub>2</sub>. 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., 2012a).

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 H<sub>2</sub>S 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:



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.

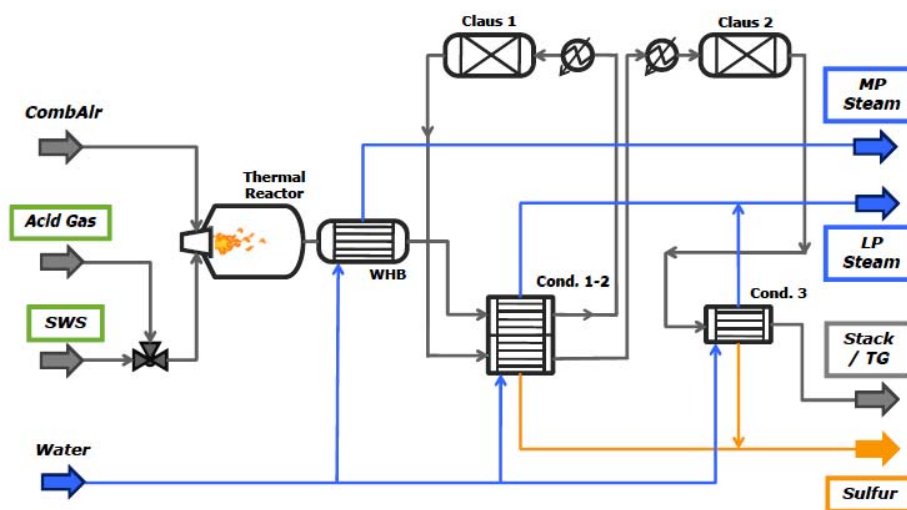


Figure 1: Basic scheme of a Sulfur Recovery Unit.

## 2. Description of the main phenomena

### 2.1 $H_2S$ 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  $1000^\circ C$  for a dilute 5 %  $H_2S$  stream, according to Binoist and co-workers). The equilibrium is achieved in few seconds at temperature above  $1000^\circ C$ . 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 $SO_2$ 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  $O+O=O_2$ ), 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 ( $<900^\circ C$ ) according to the molecular reaction between  $CO$  and  $H_2S$ :



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



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).



## 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 $H_2S$ 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  $H_2S$  pyrolysis. Rate eq.:  $k=A \cdot T^\beta \cdot \exp(-Ea/RT)$  [m-kmol-s-K].

n	Reactions	A	$\beta$	Ea	n	Reactions	A	$\beta$	Ea
R1	S+H+M=SH+M	.62E+17	-6	.0	R10b	HSS+H=SH+SH	.11E+14	.353	210.0
R2	S+H <sub>2</sub> =SH+H	.14E+15	.0	19300	R11	HSS+H=S <sub>2</sub> +H <sub>2</sub>	.12E+09	1.653	-1105.0
R3	S <sub>2</sub> +M=S+S+M	.48E+14	.0	77000	R12	HSS+H=H <sub>2</sub> S+S	.44E+14	.000	6326.0
R4	S <sub>2</sub> +H+M=HSS+M	.40E+15	2.84	1665	R13	HSS+S=S <sub>2</sub> +SH	.42E+07	2.200	-600.0
R5	SH+SH=S <sub>2</sub> +H <sub>2</sub>	.50E+12	0.0	.0	R14	HSS+SH=H <sub>2</sub> S+S <sub>2</sub>	.63E+04	3.050	-1105.0
R6	SH+S=S <sub>2</sub> +H	.30E+14	0.0	.0	R15	HSS+HSS=HSSH+S <sub>2</sub>	.96E+01	3.370	-1672.0
R7	H <sub>2</sub> S+M=S+H <sub>2</sub> +M	.16E+25	2.613	89100	R16	HSSH+M=SH+SH+M	.14E+16	1.000	57030.0
	N <sub>2</sub> /1.5 SO <sub>2</sub> /10 H <sub>2</sub> O/10				R17	HSSH+H=HSS+H <sub>2</sub>	.50E+08	1.933	-1408.0
R8	H <sub>2</sub> S+H=SH+H <sub>2</sub>	.35E+08	1.94	904	R18	HSSH+H=H <sub>2</sub> S+SH	.20E+15	.000	.0
R9	H <sub>2</sub> S+S=SH+SH	.83E+14	0.0	7400	R19	HSSH+S=HSS+SH	.29E+07	2.310	1204.0
R10a	HSS+H=SH+SH	.97E+08	1.62	-1030	R20	HSSH+SH=HSS+H <sub>2</sub> S	.64E+04	2.980	-1480.0

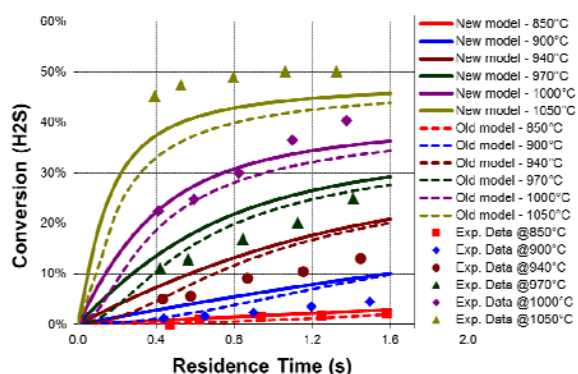


Figure 2. H<sub>2</sub>S pyrolysis without S, conversion.

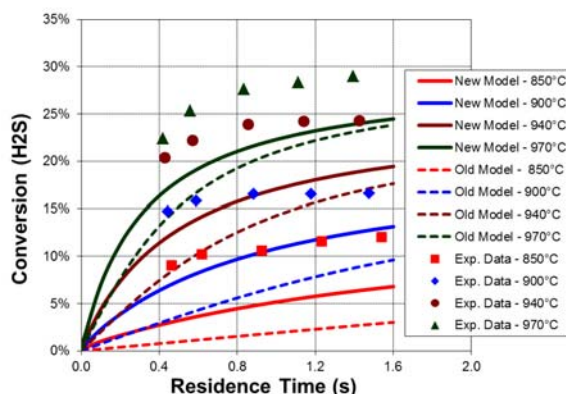


Figure 3. H<sub>2</sub>S pyrolysis with S, conversion.

### 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:



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

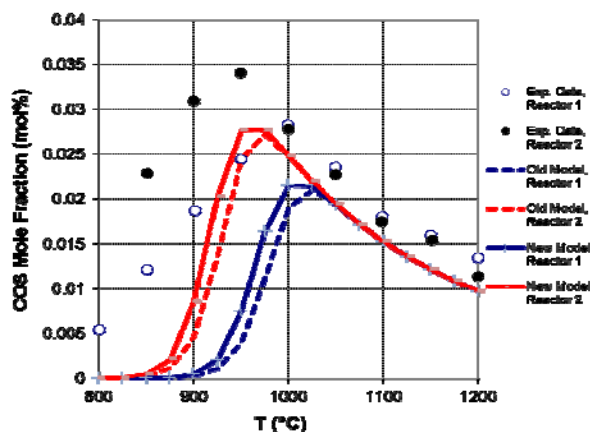


Figure 4. COS formation: comparison of literature and proposed models.

## 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 5 and Figure 6, respectively. Residuals are plotted in Figure 7 and Figure 8. 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<sub>2</sub> inferred measurements based on inlet carbon species amount.

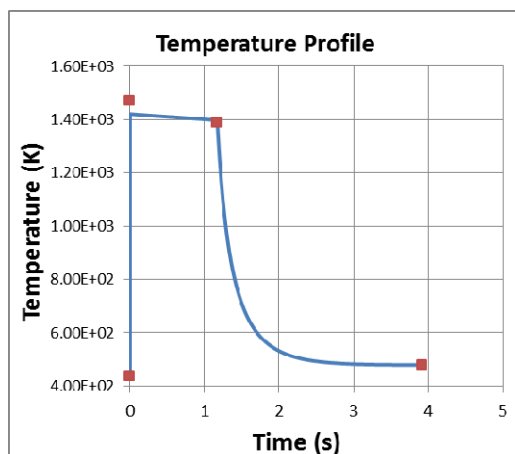


Figure 5. Calculated temperature profile.

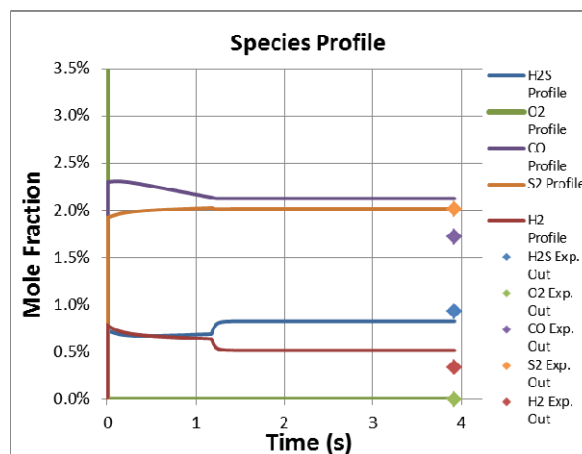


Figure 6. Calculated species profile.

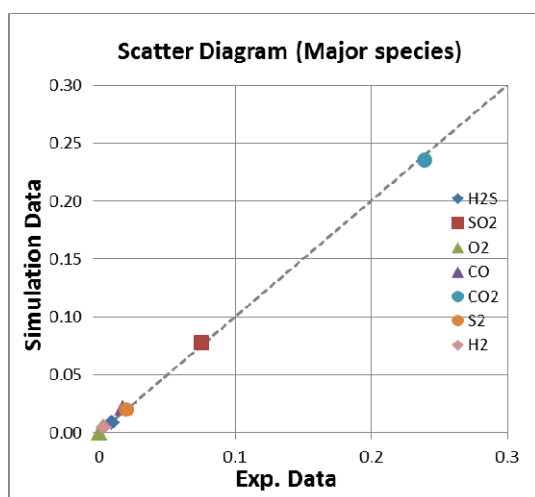


Figure 7. Residuals model-data.

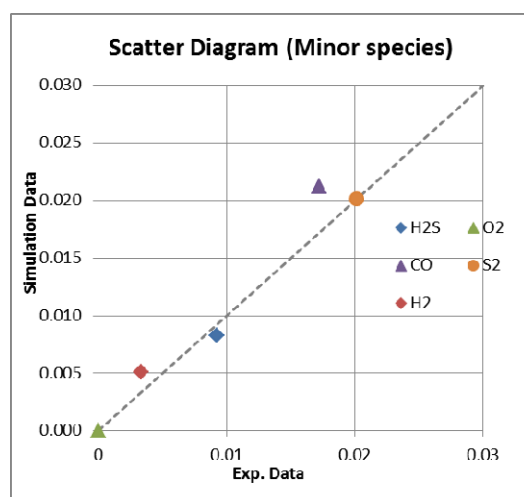


Figure 8. Zoom of Figure 10.

## 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  $\text{H}_2\text{S}$  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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