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Improving Operability and Process Understanding of Sulfur Recovery Units

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Sulfur recovery units are particularly difficult to model since they are usually characterized by poor field instrumentation and the phenomena governing their main units and reactions are very complex and quite cumbersome to be explained by first-principles relationships. Specifically, the thermal reaction furnace is the key-element of these processes but there is still not full understanding on its general behavior and on the interactions of the complex phenomena that take place in it. This paper is aimed at proposing an overall sensitivity analysis of the thermal reaction furnace by means of detailed kinetics schemes (800+ reactions). The results are the essential guidelines to improve the operability and safety of sulfur recovery units.

1. Introduction

The more and more stringent European safety and environmental regulations are pushing the production sites towards the progressive rationalization of control/monitoring systems and reduction of greenhouse and pollutants emissions. These topics are well investigated for many processes and production fields through the use of process simulations (Bonet-Ruiz et al., 2010; Brinkman et al., 2009), computational fluid-dynamics studies (Kanniche, 2009), improved process understanding (Akyildiz et al., 2010; Mikulec et al., 2009; Toledano et al., 2010; Toth et al., 2010), novel technologies for sensing and measuring (Bolf et al., 2009; Ruszkowski et al., 2009) to quote a few.
This is no longer true nowadays for certain processes, which are traditionally hard to study and, therefore, to improve in terms of emissions and for several reasons:

- they have very poor field instrumentation (and so there is no way for process identification and data reconciliation)
- they are characterized by large fluctuations in the operating conditions and input variables, depending on the upstream processes (no way for comprehensive modeling that covers all the operating range)
- they have no adequate controls to manage operations (e.g. no possibility to smooth or shorten anyhow the process dynamics)

This is the typical situation of the so-called "stack processes" of oil refineries, such as sulfur recovery units (SRUs) and tail gas treatment units (TGTUs). In fact, since SRUs and TGTUs are not directly economically appealing, in the sense that they do not increase the net operating margin of the plant, they are never subject to instrumentation and control revamping to fulfill the aforementioned safety and environmental targets.

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Thus, no investments in advanced controls, instrumentations, and monitoring are available for SRU and the lack of information coming from the field is sometimes so relevant that both the field and control room operators cannot know exactly what the current plant condition is (Signor et al., 2010; Manenti et al., 2011). Nevertheless, the presence of SRU is becoming essential for oil refineries, since SRUs have the task to treat all the acid gases and tail gases of upstream processes to recover elemental sulfur and reduce the overall site emissions. Thus, oil refineries should take care about SRU performances to fulfill environmental European Community regulations, but also without lowering the process and operator safety targets. The present paper proposes an approach to improve the process understanding and hence the operability of SRUs by modeling the thermal reaction furnace via a radical kinetic scheme. To do so, a complex kinetic scheme with 800+ reactions (Ranzi et al., 2001) is adopted to get a reasonably detailed model and characterize the SRU kernel. In such a way, it is possible to have reliable predictions of the process operating conditions and final emissions. The detailed kinetic mechanisms are reported in Section 2 together with an overall sensitivity analysis of the main phenomena occurring within the furnace. Section 3 reports the validation of the kinetic model on literature data. Section 4 contextualizes the kinetic model to the thermal reaction furnace of the Claus process.

2. Kinetics

The kinetics of thermal reaction furnace of sulfur recovery units is very complex and not yet completely understood. The kinetics governing the transformations of sulfur compounds has been studied by Mueller et al. (Mueller et al., 2003), who described the main oxidation mechanisms, and Dagaut et al. (Dagaut et al., 1995), who highlighted the inhibition effects of SO_2 on the radical pool. The pyrolysis of hydrogen sulfide, H_2S, has been defined in detail by different authors (Glassmann, 1996; Binoist et al., 2003). Other authors focused their research on the formation mechanisms of single species, such as the COS (Karan et al., 1999; Clark et al., 2001) and the CS_2 (McKee and Wine, 2001; Petherbridge et al., 2003), which are particularly important in the SRUs. The abovementioned kinetic mechanisms are inserted in a complex and modular kinetic scheme containing more than 800 chemical reactions. Only a few of the reactions are discussed hereinafter in order to highlight the key-phenomena governing the furnace.

2.1 H_2S pyrolysis

Although in presence of oxygen, the pyrolysis of H_2S is particularly important in the Claus furnaces, looking forward to its high reactivity at the typical operating conditions and the non-stoichiometric inflow of combustion air. According to the Binoist's reactor and conditions (Binoist et al., 2003) the key mechanisms for the H_2S pyrolysis are:

$$H_2S + M = SH + H + M \tag{1}$$

$$H_2S + M = H_2 + S + M \tag{2}$$

Binoist kinetic parameters are used for (2), whereas the following ones are proposed for (1):

$$k_1 = 2 \cdot 10^{14} \exp\left(-\frac{66'000}{RT}\right) \tag{3}$$

Units of measure are mol/L/s for the pre-exponential factor and cal/mol for the activation energy.

2.2 H_2S oxidation

Under the combustion regime of the Claus furnace, the H_2S is partially (one third) oxidized to SO_2. The partial oxidation allows to achieve the optimal ratio in molar fractions:

$$\frac{y_{H_2S}}{y_{SO_2}} = 2 \tag{4}$$

at the catalytic reactors (Claus converters) to maximize the yield of the overall SRU:

$$2H_2S + SO_2 = \frac{3}{X}S_X + 2H_2O \tag{5}$$

and thus to maximize the sequestration of elemental sulfur. X accounts for the sulfur equilibrium ($X = 1, 2, 4, 6, 8$). More details on the Claus process can be found elsewhere (Signor et al., 2010). The oxidation of sulfur compounds can be brought back to the analysis of the H_2S explosion diagram to give SO_2. The sensitivity analyses in correspondence with the slow-oxidation region highlighted the following predominant reactions ordered by relevance:

$$SH + O_2 + M = HSO_2 + M \tag{6}$$

$$O_2 + H_2S = HO_2 + SH \tag{7}$$

$$SO + O_2 = SO_2 + O \tag{8}$$

Conversely, in the explosion region, the reaction (8) is the most important one.
The second limit in the explosion diagram defines the passage from the low to the high pressure mechanisms. It is determined by the following rival reactions:

$$SH + O_2 = SO + OH \tag{9}$$

$$SH + O_2 + M = HSO_2 + M \tag{6}$$

The ratio $r_8 / r_5 = 1$ describes the transition from low to high pressure mechanism. It is possible to evaluate the explosion diagram using the corresponding constants:

$$\frac{r_8}{r_5} = \frac{\alpha_8 [SH][O_2] \exp\left(-\frac{E_8}{RT}\right)}{\alpha_5 [SH][O_2] \frac{P}{RT} \exp\left(-\frac{E_5}{RT}\right)} = 1 \tag{10}$$

with:

$$k_8 = 10^{10} \exp\left(-\frac{12'350}{RT}\right) \tag{11}$$

$$k_5 = 3 \cdot 10^8 \tag{12}$$

The explosion diagram in the form $P(T)$ reads as follows:

$$P(T) = \frac{\alpha_8}{\alpha_5} \exp\left(\frac{E_5 - E_8}{RT}\right) RT = \frac{10^{10}}{3 \cdot 10^8} \exp\left(-\frac{12'350}{1.968T}\right) 64.2T \tag{13}$$

The sensitivity analysis performed for the upper limit showed that the reaction (8) in the ignition region is comparable to (6) in the oxidation region. Conversely, in the ignition zone, the following reactions are relevant:

$$SH + O_2 = HSO + O \tag{14}$$

$$H_2S + SO = S_2O + H_2 \tag{15}$$

The low pressure limit has poor practical relevance and it is not reported in this work for the sake of conciseness.

2.3 Effects related to SO_2

The oxidation of H_2S generates SO_2 as major compound. SO_2 is involved in many kinetic mechanisms and, specifically, it plays a key-role in the formation of SO_3 (Mueller et al., 2003):

$$SO_2 + O + M = SO_3 + M \tag{16}$$

$$SO_2 + OH + M = HOSO_2 + M \tag{17}$$

$$HOSO_2 + O = SO_3 + OH \tag{18}$$

Taking into account the typical Claus conditions, which are characterized by non-stoichiometric combustion air, SO_2 promotes or inhibits several mechanisms. For example, it is a radical pool inhibitor and reduces the oxidation rate of CO.

3. Validation

The overall model has been validated on a wide set of literature and industrial data to cover the main families of phenomena discussed above (pyrolysis, oxidation, inhibition, formation and combined effects), showing a good agreement between previsions and reality. For the sake of conciseness, we report here only a few of the trends that we used as validation cases. Figure 1 shows the fitting of Binoist's (2003) data to validate the pyrolysis mechanisms. Figure 2 is related to the Mueller's data dealing with the oxidation mechanisms. Figure 3 shows the good agreement between the model and the Dagaut's data for the inhibition effects of SO_2 on CO. At last, Figure 4 shows the good kinetic and thermodynamic prevision of the model with respect to Karan's data for the formation of COS, an important compound in SRU processes.

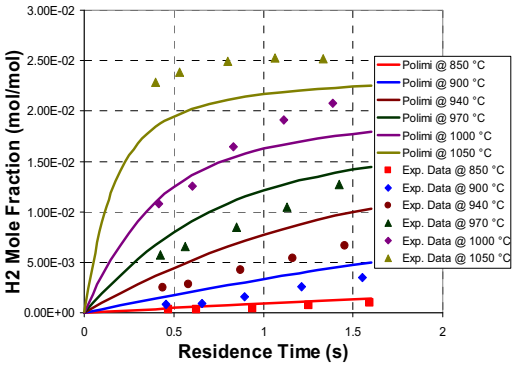

Figure 1: Pyrolysis (Experimental data from Binoist et al., 2003)

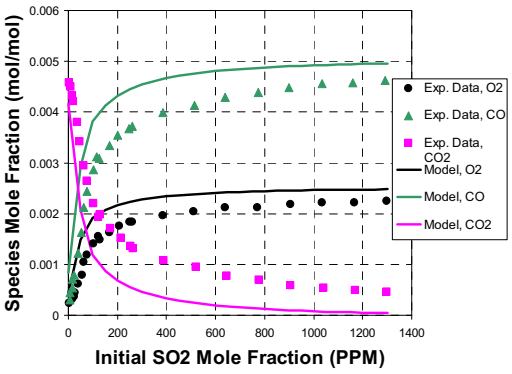

Figure 2: Oxidation (Experimental data from Mueller et al., 2003)

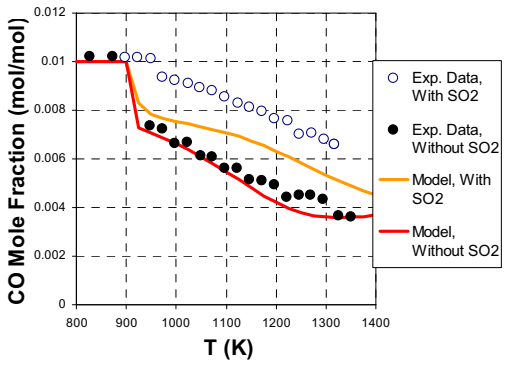

Figure 3: CO inhibition (Experimental data from Dagaut et al., 1995)

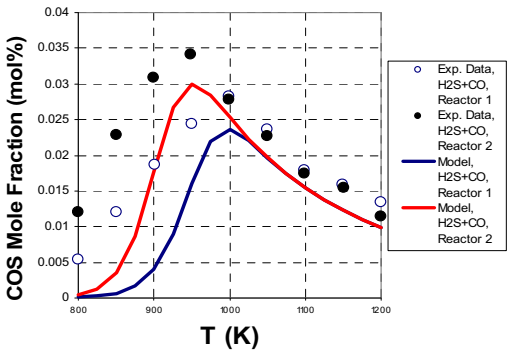

Figure 4: COS formation (Experimental data from Karan et al., 1999)

4. Contextualization: sulfur recovery units

The kinetic model has been validated at the typical Claus operating conditions (previous section). The hot zone of Claus processes consists of a thermal reaction furnace and a waste heat boiler. The furnace is usually split in two regions: the combustion mechanisms take place in the first region and the endothermic mechanisms take place in the second region. As already underlined elsewhere (Pierucci et al., 2004), contrary to methane and hydrogen, the H_2S has no induction time when mixed with

methane and hydrogen. At the Claus conditions it is possible to suppose that the oxygen is almost completely consumed by H_2S. Thus, the simulation is predisposed in order to burn only the H_2S at the beginning and to introduce the remaining species only when the oxygen is consumed. The typical Claus reaction furnace operates at 1'150-1'250 °C and 1.5 atm (151'987 Pa). The effective volume of the furnace is in the order of 3 m^3. The residence time is 1 s. The contextualization to the Claus process allows to refine certain competences for other relevant species and, therefore, to improve the overall process understanding for the process safety/operability as well as for the environmental impact and emissions.

4.1 COS formation and decomposition

A typical example is the characterization of formation and decomposition mechanisms of COS (Figure 4). COS is a relevant species in the Claus processes since it can significantly decrease the yield in elemental sulfur, but it could also be a problem for certain Claus catalysts and for environmental and health aspects. The detailed kinetic for the simulation of Claus reaction furnaces allows to realize the mechanisms behind COS generation and, then, to select the preferable operating conditions as well as to adopt several technological solutions to prevent its formation.

The final concentration of COS is the result of the combination of several formation and decomposition effects. The final concentration achieves the maximum around 1000 °C. The most relevant reactions are H_2S pyrolysis (2) and COS formation:

$$CO + S + M = COS + M \tag{19}$$

5. Conclusions

The use of detailed radical kinetic schemes allows to improve significantly the level of understanding of sulfur recovery units. In fact, using kinetic models, it is not only possible to define the best operating conditions to preserve the safety and the environmental impact, but also to investigate, as future development, possible technological solutions to make such processes as similar as possible to intrinsically green processes.

In fact, one of the main technological advances coming from an improved knowledge of the behavior of Claus thermal furnaces obtained through the detailed analysis and simulations proposed in this paper is the definition of novel operating conditions to improve the safety of common and non-conventional operations, but also to improve the overall process layout and the design of process units and reactors as well so as to reduce the environmental impact, the greenhouse emissions, and, in general, the air pollutants of these large-scale processes fully operating in the oil refineries and petrochemical plants as stack processes to clean the tail gases up.

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