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Model-based optimization of sulfur recovery units

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ABSTRACT

Multi-scale process modeling is very appealing methodology for process optimization since it highlights certain issues that remain unexplored with conventional methodologies and debottlenecks certain potentialities that remain unexploited in chemical plants. In this work, a kinetic model with 2400 reactions and 140 species is implemented in a proper reactor network to characterize the thermal furnace and the waste heat boiler of sulfur recovery units; the network with detailed kinetics is the kernel of a Claus process simulation that includes all the unit operations and the catalytic train. By doing so, reliable estimation of acid gas conversion, elemental sulfur recovery, and steam generation is achieved with the possibility to carry out an integrated process-energy optimization at the total plant scale.

1. Introduction

The modeling and optimization of sulfur recovery units (SRUs) is an environmentally relevant and quite cumbersome problem since it involves different modeling scales such as the kinetic/molecular micro-scale, the reactor design meso-scale, and the chemical process macro-scale. This work is the extension to the total plant modeling and optimization of our previous contributions on the micro-scale and meso-scale modeling and industrial data fitting (Manenti, Grottoli, & Pierucci, 2011; Manenti, Papasidero, Cuoci, et al., 2012; Signor, Manenti, Grottoli, Fabbri, & Pierucci, 2010). This work illustrates the paramount benefits in production efficiency and steam generation coming from the use of an integrated multi-scale approach to optimize the SRU. Actually, the multi-scale modeling allows to take advantage of the specific detailed simulations for each scale as well as to account for the imposition of the correct boundaries for each scale involved, dealing with environmental laws, safety regulations, experience-driven decisions.

The present work takes advantage of the methodology for the simulation of chemical reactors with detailed kinetics developed in the past forty years by the chemical reaction engineering group of Politecnico di Milano. The works of professor Mario Dente (Dente, Ranzi, & Goossens, 1979), Eliseo Ranzi (Ranzi, 2006) and Sauro Pierucci (Klemes & Pierucci, 2002; Pierucci, Faravelli, & Brandani, 1994) have been pioneer in the field, and have been followed by several others in the field of combustion modeling, process simulation, plant optimization, applied to several different processes. One of the highlight of the current approach is that of using detailed kinetics: this makes the difference with the simple use of actual process simulators (Pro/II, Aspen Hysys, Unisim), that are not able to easily manage simulations with large number of species. Simulations with detailed kinetics (as required for several combustion processes) need then specific tools like the one here used (or dedicated user added routines/unit operations) to manage that gap.

This approach to plant simulation has been joined to plant optimization with very robust and efficient solvers of the library BzzMath (Buzzi-Ferraris & Manenti, 2013), able to solve very complex systems.

The work of Manenti et al. (2011) demonstrated that online reconciliation poor redundancy systems can be feasible by adding some adaptive parameters with detailed process simulation. Claus process is one of these systems, since it is usually present in every refinery for sulfur recovery purposes, dealing more with environmental regulations than to effective economic appeal. This work's aim is to model and optimize that process to increase economical appeal, trying also to get the process energy integration. This latter solution is well known and discussed in literature, and has been proposed, for instance, in analyzing the effects of the impurities on Claus plants heat recovery (Haimour & El-Bishtawi, 2007), in the investigation of SRU-IGCC plant integration (Jones, Bhattacharyya, Turton, & Zitney, 2012), and evaluation and modeling of a whole gas treatment plant with heat recovery steam generator (HRSG) and a combined cycle (CC) (Perez-Fortes, Bojarski, Velo, Nougues, & Puigjaner, 2009). Optimizing different levels simultaneously, it is possible to further improve some solutions that are already considered optimal from the single-scale point of view. The optimization

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of elemental sulfur recovery and the integrated optimization of sulfur recovery and steam generation are then considered and compared in this work. A sensitivity analysis on the most effective variables on the process performance in terms of recovered sulfur and steam produced has been performed in order to identify the right optimization variables, avoiding to build a too big optimization problem.

2. Description of sulfur recovery unit

Task of the Claus process is to recover the elemental sulfur from the hydrogen sulfide and, more generally, from the by-product gases originated by physical and chemical gas and oil treatment units in refineries, natural gas processing, amine scrubbers, sour water strippers (SWS). It consists of a thermal reaction furnace, a waste heat boiler, and a series of catalytic (Claus) reactors and sulfur condensers (Fig. 1).

The overall reaction characterizing the process is $2H_2S + O_2 \rightarrow S_2 + 2H_2O$ and, behind it, certain complex kinetic mechanisms take place (Alzueta, Bilbao, & Glarborg, 2001; Glarborg, Kubel, Dam-Johansen, Chiang, & Bozzelli, 1996) in the thermal reactor furnace at high temperatures, in the waste heat boiler as recombination effects and in the catalytic reactors at low temperature. In the thermal furnace, one third of hydrogen sulfide is oxidized to sulfur dioxide using air. Temperatures are usually in the order of 1100–1400 °C. The oxidizing reaction (1) is exothermic and without any thermodynamic restriction.

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \quad (1)$$

The two thirds of the unreacted hydrogen sulfide react with the sulfur dioxide to produce elemental sulfur through the so-called Claus reaction:

$$2H_2S + SO_2 \leftrightarrow \frac{3}{2}S_2 + 2H_2O \quad (2)$$

This reaction takes place at high temperatures in the thermal furnace with an endothermic contribution or at low temperatures in the catalytic converters with an exothermic contribution. The off-gas leaving the thermal furnace enters the waste heat boiler, where it is quenched (by heat exchange with boiler feed water, BFW) to about 300 °C to prevent recombination reactions; then, before entering the catalytic region, the first separation of liquid elemental sulfur is carried out in the first condenser. The hydrogen sulfide conversion (3) goes on in the catalytic region.

$$2H_2S + SO_2 \leftrightarrow \frac{3}{8}S_8 + 2H_2O \quad (3)$$

A condenser is installed downstream each catalytic reactor to condensate and make feasible the separation of the elemental sulfur before entering the next catalytic reactor, with the twofold advantage of preventing the sulfur condensation into the downstream catalytic reactor and to shift the equilibrium of the Claus reaction toward the products side. In addition, the hydrolysis reactions of COS and CS_2 take place in the catalytic region according to the following reactions: $COS + H_2O \leftrightarrow CO_2 + H_2S$ and $CS_2 + 2H_2O \leftrightarrow CO_2 + 2H_2S$. It is important to reach high performances in the hydrolysis of COS and CS_2 because these species affect the global sulfur recovery. High sulfur recovery have to be obtained due to the increasingly strict environmental regulations. The most important key performance indicator is the molar ratio H_2S/SO_2 exiting the waste heat boiler. It should be as close as possible to the value of 2 in order to get the maximum conversion in sulfur (Karan, Mehrotra, & Behie, 1994; Monnery, Svrcek, & Behie, 1993; Nasato, Karan, Mehrotra, & Behie, 1994).

3. Multi-scale approach

Usually, commercial package for process simulation include global model of unit operations (UO) to be interconnected in order to obtain a numerical plant reproduction for the purpose of development, analysis, design and optimization of technical processes. Often, these UO models are not detailed enough to represent several aspects of the real UO, considering in particular the behavior of combustion processes that often needs detailed kinetic model to be developed. The multi-scale approach includes models at different scales to overcome possible limitations of conventional models. To do so, a full object-oriented model of the UOs dealing with SRU has been developed in this research activity and UOs have been interconnected in a multi-scale simulation. Specifically, the reaction scheme described in (Manenti, Papasidero, Cuoci, et al., 2012) is adopted. It consists of more than 2400 chemical reactions with 140 molecular and radical species involved (sulfur compounds, hydrocarbons, typical acid gas compounds). The scheme is the base for the reactor network analysis used to simulate the thermal reaction furnace with combustion flame accuracy. The same kinetic scheme is also adopted to account for the relevant recombination effects that take place in the first part of the waste heat boiler with consequent variation of the outlet molar fraction of the main compounds as well as of the steam generation (Manenti, Papasidero, Manenti, Bozzano, & Pierucci, 2012). At last, the catalytic converters are characterized by means of the kinetic model proposed by Abedini, Kooliv& Salooki, and Ghasemian (2010) with re-estimation of parameters using very robust algorithms and available data. Thanks to the high level of detail of models and the good agreement with the field data, it is possible to perform a reliable total plant optimization in terms of efficiency of the elemental sulfur recovery and generation of both the medium pressure steam generated at the waste heat boiler and the low pressure steam generated at the sulfur condensers. The resulting large-scale nonlinear programming problem is solved by means of nonlinear system solvers and optimizers belonging to BzzMath library and exploiting parallel computing and object-oriented philosophy (Buzzi-Ferraris & Manenti, 2012; Manenti, 2011).

4. Modeling

4.1. Thermal section

Thermal section consists of a burner, a reaction furnace (RF) and an associated waste heat boiler (WHB). In this section acid gases are partially oxidized at a temperature ranging from about 1000 to over 1400 °C, depending on the gas composition. Highest temperature is reached in the first part of the RF, close to the burner. Then, it slowly decreases along the RF for thermal losses and the flow enters the WHB where flow is quenched to 300–350 °C and medium pressure (MP, from 10 up to 40 bar) steam is produced. RF and WHB can be opportunely modeled using a non-ideal reactor network as discussed in our previous work (Manenti, Papasidero, Cuoci, et al., 2012). In this way burner could be represented by a perfectly stirred reactor and the RF and WHB as plug flow reactors. The acid gas stream entering the reactor network is characterized by high Reynolds and Peclet numbers, so diffusive terms can be neglected. The fluid-dynamics can be considered axial-symmetric due to the assumption of fully developed flow both in the RF and WHB with flat profiles across the sections. Due to the refractory covering it internally, the RF is characterized by very small heat exchange coefficient and can thus be modeled as a plug flow with constant thermal losses assumed to be in the order of 3 KW/m^2 (or adiabatic for some SRU). When the RF consists of two separate combustion chambers (split-flow configuration), each chamber can be represented by a plug flow reactor. This can be useful, for instance,