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Opinion

A Review of Investigations on Claus Reaction Furnace of Sulfur Recovery Unit

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Opinion

Environmental regulations have become more stringent on sulfur dioxide emissions to atmosphere. One of the main strategies of reducing sulfur emissions is to increase the performance of the sulfur recovery units (SRU). The modified Claus process is one of the major processes which convert toxic hydrogen sulfide to elemental sulfur from acid gas during sour natural gas processing and refinery upgrading [1]. Conversion of H_2S to SO_2 in the modified Claus process is conducted in the reaction furnace (RF) which is a refractory lined cylindrical vessel. Acid gas stream at a pressure typically ranging from 130 to 180 kPa is fed to the reaction furnace burner along with an appropriate quantity of air to oxidize feed contaminates and results in a 2:1 ratio of H_2S:SO_2 in the reactor effluent. The combustion of acid gases in the RF is performed at temperature ranges of 975-1300 °C and gas residence times 0.5-2.0s [2].

Since the combustion process in the RF provides substantial sulfur recovery and affects the entire plant emissions, any modification in the RF affects sulfur conversion and emissions such as COS, CS_2 and SO2 from Claus plant [2]. Therefore, any improvement in the reaction furnace has direct impact on reduction of sulfur emissions to the atmosphere. The waste heat boiler (WHB) which is a following equipment after the RF cools the combusted products of the RF from 926-1300 °C to about 230-370 °C in one or two tube passes producing steam on the shell side. Optimization of the modified Claus process for further sulfur recovery and lower emissions requires a reliable model for description of what actually happens in Claus reaction furnace.

Several researchers have investigated the modeling of the Claus plant or specific unit operations of the Claus process. These studies can be categorized in two fields, thermodynamic modeling (Gibbs free energy minimization) and kinetic modeling. In thermodynamic studies [3-11], most of these modeling efforts rely on restricted equilibrium models to predict product distribution from the Claus furnace. Thermodynamic modeling as a basic approach for modeling of Claus reaction furnace hasn't complexities of kinetic modeling. Only a list of Gibbs free energy for compounds and simple calculations are necessities of thermodynamic modeling. Researchers of thermodynamic modeling studies showed that results of Gibbs free energy minimization method do not match plant data taken both after and before the waste heat boiler [2]. Subsequently, inadequately of the Gibbs free energy method in modeling of Claus reaction furnace was concluded. Most thermodynamic studies relied on restricted equilibrium models to predict product distribution from the Claus reaction furnace but there have been no studies in the open-access literature adjusting Gibbs free energy parameters to the equilibrium modeling of the reaction furnace. Therefore, author in recent study [12] adjust Gibbs free energy parameters using the plant data set so as to achieve higher accuracy in the equilibrium modeling. In this study, the reaction furnace of Claus process was modeled using the Gibbs free energy minimization method, which involved new parameters in correlations of thermodynamic properties. Using the new parameters, a significant error reduction from 33.50% to 7.86% occurred in the prediction of molar flow rate of components.

In kinetic modeling studies, researchers [13-15] used detailed kinetic scheme (Jones et al., 2012) and global reaction scheme to predict the Claus reaction furnace effluents. In detailed kinetic scheme, different reactions including molecular, radical and intermediate species were considered. In one study [14], Claus reaction scheme was modeled with a detailed kinetic scheme based on a radical approach including 130 species and more than 1500 elementary reactions. Although a detailed kinetic mechanism is required for a comprehensive description of the chemical system by applying elementary reactions and intermediate species, a large-size mechanism reduces its applicability.

A large number of conservation equations (because of the number of species) prevents them from applying in computational fluid dynamics (CFD) codes and incorporating in unsteady, two- and three-dimensional calculations. Different time scales of the system resulting from the presence of the various chemical species increase stiffness of the system. As a result of stiffness, possibly code crash, and divergence, it is difficult to solve the problem. To enhance computational efficiency and to produce a smaller size mechanism with less stiffness, mechanism reduction methods were proposed. Results obtained from reduced mechanisms showed its validity. Literature review showed that the global reaction scheme

was successfully applied in kinetic modeling of a Claus reaction furnace (Jones et al., 2012). In order to develop a suitable kinetic model for prediction of reaction furnace and waste heat boiler effluents, several reaction schemes (168000) were tested by author and the best reaction set was selected [16]. The modified model results were in good agreement with the experimental measured plant data both before and after waste heat boiler (The mean absolute errors were 7.62% and 7.88% respectively).

The reaction furnace is composed of two zones, namely the flame or oxygen rich zone and post flame or anoxic zone. The flame zone is an oxygen consuming zone and its temperature exceeds 2000 °C. Whereas residence time of the flame zone is very short and in order of milliseconds, residence time in the oxygen deficient post flame zone may range from 0.5 to 2.0 s depending on the flow rate and temperature (Chin et al., 2001). Thus, it seems that different reactor networks such as a combination of CSTR and PFR reactors in series and parallel modes would model these two zones of RF. The WHB is made of one or two tube passes with anoxic zone nature where hot gases from RF are cooled down to 250-300 °C. Supposing negligible radial concentration and temperature gradients, one dimensional plug flow assumption can be applied in the RF and WHB modeling. Due to the completely different natures of these equipments, i.e. RF and WHB, different reaction schemes were made use of in their modeling. Author investigated different reactor networks using the optimum reaction set and concluded that single plug flow reactor can be applied in kinetic modeling [16].

The above reaction schemes were adjusted using industrial data. It was an incentive to perform a global kinetic scheme that adjusted by laboratory experimental data and validated with industrial data. The main object of another study of author was to introduce a global reaction scheme involving molecular species that completely describes the partial combustion step for feeds containing pure H_2S and the $H_2S + CH_4$ mixture. To show applicability of the proposed kinetic model in laboratory and industrial situations, validations with other experimental laboratory data and an industrial Claus reaction furnace were performed. The selected reaction schemes with optimized kinetic parameters were used to model H_2S and CH_4 partial oxidation, in which the corresponding MAPEs varied between 7.90 and 10.32%. Finally, a reaction scheme was chosen for complete description of the pure H_2S oxidation and $H_2S + CH_4$ cooxidation systems. The proposed kinetic reaction scheme was applied in the kinetic modeling of an industrial Claus reaction furnace (MAPEs of 5.59 and 15.02% for temperature and composition, respectively) and provided a satisfactory representation of the experimental data. Performances of the proposed reaction scheme were validated with comparison to the detailed reaction mechanism [17].

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