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Modeling and optimization of an industrial Claus process: Thermal and catalytic section

H. Ghahraloud, M. Farsi, M.R. Rahimpour*

Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz, Iran

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ABSTRACT

The main goal of this research is modeling and optimization of an industrial modified Claus process to achieve maximum sulfur recovery. The modified Claus process consists thermal conversion in furnace and catalytic conversion in two series fixed bed reactors. The furnace and catalytic reactors are modeled based on the mass and energy conservation laws at steady state condition. To prove the accuracy of the developed mathematical model, simulation results of conventional process are compared with the available plant data. Then, the optimal condition of Claus process is calculated considering sulfur recovery as the objective function using Genetic algorithm as a useful method in global optimization. The attainable decision variables are inlet temperature of furnace and fixed bed reactors, feed distribution along the furnace and flow rate of air in the furnace. The simulation results show that sulfur recovery is improved about 4.63% in the optimized process compared to the conventional process. In addition, performance of auto-thermal reactor as a substitute for conventional adiabatic reactors is investigated to enhance sulfur recovery and reducing sulfur contaminants emission in the Claus process.

1. Introduction

Elemental sulfur is a bright yellow crystalline solid at room temperature. Under normal conditions, sulfur atoms form cyclic octatomic molecules with chemical formula S_8. It is a useful element that is used to manufacture of fertilizers with other principal users including rubber industries, cosmetics, and pharmaceuticals. The modified Claus process is the most popular method for recovery of elemental sulfur from hydrogen sulfide in oil and natural gas refinery units. The modified Claus process is suitable when hydrogen sulfide concentration and feed capacity is high.

Sulfur contaminants emission and sulfur management is an important challenges from environmental and economic viewpoints. So, a small improvement in efficiency, operational cost and energy management in sulfur recovery units is worthy. Generally, the Claus process comprises two main stages including thermal and catalytic sections. In the first stage, a part of inlet H_2S is burned in a furnace at high temperature and elemental sulfur, sulfur dioxide and water vapor are produced. After sulfur condensation, furnace effluent is fed to the catalytic stage. In the catalytic stage, un-reacted hydrogen sulfide and produced sulfide dioxide react to form elemental sulfur and vapor [1,2]. Due to importance of hydrogen sulfide as one of the main environmental pollutants, many researchers have focused on sulfur recovery from hydrogen sulfide and other sulfur contaminants. Some scholars studied kinetics of thermal conversion of hydrogen sulfide at different temperatures and residence time. Several researches have focused on identifying catalyst, mechanism of reactions, rates, and catalyst deactivation in the catalytic section. Generally, various catalysts such as metal oxides were proposed for Claus reaction and decomposition of H_2S. Between metal oxides, vanadium oxide has presented better performance and attracted more attention [3,4]. Monnery et al. modeled the thermal section and waste heat boiler of Claus process based on an equilibrium model [5]. Nasato et al. presented a mathematical model to evaluate the kinetic and thermal characteristics of waste heat boiler in modified Claus Sulfur Recovery Unit [6]. The results showed that, hydrogen production could be increased over 20% by reconfiguration of waste heat boiler tubes. Pierucci et al. developed a detail kinetic scheme based on the free radical approach to predict flame temperature and conversion of hydrogen sulfide [7]. Zarenezhad and Hosseinpour investigated some applicable techniques to increase furnace temperature [8]. The results showed that acid gas enrichment is a reliable method to create the desired furnace temperature, when a high flow of lean acid gas is processed. Manenti et al. modeled furnace and waste heat boiler based on a detailed kinetic considering 2400 reactions and 140 species. They optimized the process condition to achieve maximum elemental sulfur recovery, acid gas conversion

* Corresponding author.
E-mail addresses: rahimpor@shirazu.ac.ir, Rahimpor230000@gmail.com (M.R. Rahimpour).

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and steam generation [9,10]. Manenti et al. revised a conventional kinetic model of thermal section of sulfur recovery units to account light hydrocarbons, ammonia and other species that there are in the feedstock of industrial units [11]. Zarei et al. selected a detail kinetic model for thermal conversion of hydrogen sulfide and obtained the kinetic parameters of model [12]. Comparison between simulation results and plant data shows that the mean absolute error is about 7.6%. Elsner et al. applied the mixture of catalyst and water adsorbent in the catalytic section of Claus process as a reliable method to shift the reaction and overcome equilibrium limitations [13]. Nabikandi and Fatemi modeled the catalytic section of Claus process based on the both equilibrium and kinetic approaches [14]. The simulation results showed that although both equilibrium and kinetic models present reliable results, the kinetic model reveals more accuracy compared to the equilibrium model. Modeling of fluidized bed reactor for Claus process showed that replacing the fixed bed reactor with a fluidized bed decreases catalyst loading and pressure drop [15,16]. Abdel Fattah et al. used computational fluid dynamic tool to develop a three dimensional finite element model for catalytic section of Claus process [17]. They investigated the effect of feed temperature and composition on the specification of outlet product.

Due to importance of environmental legislation and limitations, any decrease in sulfur contaminants emission is attractive. In this study, the thermal and catalytic sections of Claus Sulfur Recovery Unit is modeled and optimal operating condition of considered process is determined to achieve maximum sulfur recovery. Then, the simulation results of optimized process are compared with the conventional system. In the recent decades, auto-thermal reactor concept for weakly endothermic or endothermic fixed-bed reactions was developed. Auto-thermal reactors consists a combination of a chemical reactor with a heat exchanger, where the generated heat by the chemical reaction(s) in the reactor is used to heat up the feed. In this research as the second goal, the efficiency of auto-thermal reactor is investigated as a substitute for conventional adiabatic reactors in Claus process.

2. Process description

The Claus process was invented in 1883 by English scientist, Carl Friedrich Claus. The Claus is the most popular sulfur recovery process to produce elemental sulfur from hydrogen sulfide. The considered Claus process in this research is Split-Flow type and consists a furnace reactor and two series adiabatic reactors. The feed is divided in two streams. The first stream is mixed with air and fed to the furnace, while the second part of feed stream is injected at the middle part of furnace. In the furnace, a part of hydrogen sulfide is converted to the sulfur and sulfur dioxide. To prevent sulfur condensation in the pipelines and heat recovery from furnace effluent, the output stream from furnace is cooled in a boiler, and the elemental sulfur is condensed and separated from furnace effluent. In addition, since the hydrogen sulfide conversion is characterized by a large number of radical reactions; therefore, it is mandatory to freeze the reactive situation to avoid recombination reactions. Usually, about 60–70% of the total amount of elemental sulfur is produced in the thermal section. Then, the stream is heated and fed to the first catalytic reactor. The outlet stream from first reactor is cooled in the boiler to separate elemental sulfur and after heating is fed to the second reactor. Generally, the catalytic recovery of sulfur consists three sub steps including heating, catalytic reaction, cooling and condensation. The outlet stream from second reactor is fed to the boiler to separate elemental sulfur and uncondensed part is sent to the separation section. Fig. 1 depicts the schematic of Claus process.

Nomenclature

a_v	specific surface area of catalyst pellet (m^2/m^3)
A_c	cross section area of each tube (m^2)
C_p	specific heat of the gas at constant pressure (J/mol/K)
C_t	total concentration ($kmol/m^3$)
D	tube diameter (m)
d_p	catalyst particle diameter (m)
E_i	activation energy for ith reaction (J/mol)
D_{ij}	binary diffusion coefficient of component i in j (m^2/s)
D_{im}	diffusion coefficient of component i in the mixture (m^2/s)
F	total molar flow rate (mol/s)
h_f	gas–solid heat transfer coefficient in reactor ($W/m^2/K$)
h_i	tube side heat transfer coefficient in reactor ($W/m^2/K$)
h_o	shell side heat transfer coefficient in reactor ($W/m^2/K$)
$\Delta H_{f,i}$	heat of reaction for reaction i (kJ/kmol)
ΔH_i	heat of adsorption of water on catalyst surface (kJ/kmol)
k_i	reaction rate constant ($mol/g_{cat}/h$)
$K_{H_2O_i}$	water adsorption equilibrium constant in the rate equation (k/Pa)
K_E	equilibrium constant ($1/kPa^{0.5}$)
L	reactor length (m)
P	total pressure (bar)
P_i	partial pressure of component i (kPa)
r_i	rate of reaction ($mol/g_{cat}/h$)
R	Universal gas constant (J/mol/K)
T^g	bulk gas phase temperature in reaction side (K)
T^c	bulk gas phase temperature in shell side (K)
T^s	solid phase temperature (K)
u_g	velocity of fluid phase (m/s)
U	overall heat transfer coefficient ($W/m^2/K$)
y_i	mole fraction of component i in the fluid phase
Z	axial reactor coordinate (m)
Greek letters	
μ	viscosity of gas phase (Pa s)
η	catalyst effectiveness factor
ρ	gas density (kg/m^3)
ρ_b	catalytic bed density (kg/m^3)
ε	porosity factor

3. Auto-thermal configuration

It is appeared that removing of the generated heat from reaction zone and decreasing reactor temperature shift thermodynamic equilibrium limitation of the reversible reactions toward the completion. Therefore, it concluded that a structure in form of a shell and tube exchanger is satiable to enhance capacity of sulfur recovery plant. The proposed reactor is a shell and tube heat exchanger that the tube side is packed with the catalyst slice. The feed stream is fed to the shell side of the reactor, receives the generated heat of reaction in tube side. Thus, the feed temperature increases along the shell side and reaction temperature decreases. Then, the preheated feed is entered to the tube side and reactions occur over the catalyst surface.