Mathematical Modelling and Simulation of Adsorptive Moving Bed Reactor for Claus Process

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Abstract. Fixed bed reactors are widely used in desulfurization processes. However, this kind of reactors has an obvious disadvantage leading to discontinuous operation that the catalysts and adsorbents must be regenerated periodically. As a continuous operated reactor, moving bed reactor can let both gas and solids move through the reactor, making it possible to remove the saturated adsorbents as well as deactivated catalysts. Meanwhile, fresh gas and solids can be fed into the reactor. This paper builds mathematical model of adsorptive moving bed reactor based on Claus Process. The model is simulated with Aspen Custom Modeler. Simulation results show that adsorptive moving bed reactor has good performance in Claus Process. Under the reaction conditions, the adsorption ability is limited by the temperature. Adequate increment of adsorbent volume fraction in the solids can improve the reactor’s performance.

1. Introduction

In Claus Process, adsorptive fixed bed reactor utilizes adsorbents to continuously remove water generated by the reaction and thus can provide good conversion of sulfur. [1] However, this kind of traditional reactor must be shut down to reload or regenerate catalysts and adsorbents when the catalysts are deactivated or the adsorbents are saturated. Thus, fixed bed reactor can’t run continuously and has to be shut down periodically. [2] To let the process run continuously, H.Yoon, J.Wei and M.M Denn developed a model of moving bed reactor for catalyst fast-deactivated reaction such as coal gasification. [3] Z.Mu, J.Wang and T.Wang introduced a model combined with hydraulics method to find a better way to describe the behaviors of moving bed reactor and presented its potential values in process industry. [4] The reaction of Claus Process is exothermic. Heat accumulates in the reactor and affects the reaction equilibrium.

$$2\text{H}_2\text{S} + \text{SO}_2 \rightleftharpoons \frac{3}{n} \text{S}_n + \text{H}_2\text{O} \quad \Delta H = -108\text{kJ/mol} \quad (1)$$

For two-stage reaction units, the conversion of sulfur is generally between 93% and 95%. [6] This paper develops mathematical models of moving bed reactor for Claus Process. The model is then simulated with Aspen Custom Modeler with experimental data to check the reactor’s performance.
2. Reactor Model

2.1. Basic Assumptions

A one-dimensional non-isothermal dynamic model is presented to describe a gas-solid reaction in moving bed reactor. Gas flow and solids flows are moving counter-currently. The radical profiles of concentration and temperature are neglected under the reactor dimension and prevailing reaction conditions. [7] Both the gas and solid phases are plug flows. Axial velocities in both phases are uniform and the pressure drop is neglected. [8] Back-mixing in bulk gas phase flow is lumped into an axial dispersion coefficient term and the volume change is neglected because large inert is added inside the reactor. [9].

2.2. Mass Balance

Mass transfer functions are as follows. The dispersion term is very small and has little effect on the mass transfer behavior. T.Petroulas pointed out that this term is crucial when solving the problem numerically. [7] Both the gas and solid phases are plug flows. Axial velocities in both phases are uniform under the reactor dimension and prevailing reaction conditions. [9].

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Due to that reason, this term is still kept in the equation. Global linear dispersion model and Langmuir isotherm are employed. [11].

\[ \frac{\partial C_{\text{gas},i}}{\partial t} = \frac{D_{\text{ax}}}{\partial z^2} C_{\text{gas},i} - u_z \frac{\partial C_{\text{gas},i}}{\partial z} - \text{Reaction} - \text{Adsorption} \quad (2) \]

\[ \text{Reaction} = \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \varphi_{\text{cat}} \left( \frac{6k_l}{d_{\text{cat}}} (C_{\text{gas},i} - C_{\text{cat},i}) \right) \quad (3) \]

\[ \text{Adsorption} = \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \varphi_{\text{ads}} \left( \frac{6k_l}{d_{\text{ads}}} (C_{\text{gas},i} - C_{\text{ads},i}) \right) \quad (4) \]

The mass balance equations of the catalyst and adsorbent are with reaction term and adsorption term respectively. They are listed as follows.

\[ \frac{\partial C_{\text{cat},i}}{\partial t} = u_1 \frac{\partial C_{\text{cat},i}}{\partial z} + \varphi_{\text{cat}} \frac{6k_l}{\varepsilon_{\text{cat}}} (C_{\text{gas},i} - C_{\text{cat},i}) + \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \eta u_1 R_{\text{cat},i} \quad (5) \]

\[ \frac{\partial C_{\text{ads},i}}{\partial t} = u_1 \frac{\partial C_{\text{ads},i}}{\partial z} + \varphi_{\text{ads}} \frac{6k_l}{\varepsilon_{\text{ads}}} (C_{\text{gas},i} - C_{\text{ads},i}) + \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) R_{\text{ads}} \quad (6) \]

\[ R_{\text{ads}} = k_{\text{LDF}, \text{H}_2O} \left( q_{\text{H}_2O} - q_{\text{H}_2O, \text{ads}} \right) \quad (7) \]

Elsner represented the reaction kinetics regarding to the partial pressure of each component. Employing partial pressure offers an easier way to measure and calculate than using concentration. [12]

\[ R_{\text{cat},i} = k_1(T)p(H_2S)p^b(SO_2) - k_2(T)p^b(H_2O) \quad (8) \]

2.3. Heat Balance

Heat transfer of moving bed reactor mainly includes: heat conduction, heat convection, heat radiation and heat generated by particle collision. According to W.J. Yang’s study, heat produced by radiation and collision can be neglected. [13] Among gas, catalysts and adsorbents, heat balance is calculated respectively. Both reaction heat and adsorption heat are considered.

Heat balance in gas phase:

\[ \frac{\partial T_g}{\partial t} = \frac{\lambda}{\rho c_{\text{pg}}} \frac{\partial^2 T_g}{\partial z^2} - u_z \frac{\partial T_g}{\partial z} - \frac{h_L}{\rho c_{\text{pg}}} \frac{3}{\varepsilon_{\text{cat}}} (T_g - T_{\text{cat}}) - \frac{h_L}{\rho c_{\text{pg}}} \frac{3}{\varepsilon_{\text{ads}}} (T_g - T_{\text{ads}}) \quad (9) \]

Heat balance in solid phases:

\[ \rho_{\text{cat}} c_{\text{p}, \text{cat}} \left( \frac{\partial T_{\text{cat}}}{\partial t} + u_1 \frac{\partial T_{\text{cat}}}{\partial z} \right) = \frac{6h_{i_1}}{d_p} (1 - \varepsilon_b) (T_g - T_{\text{cat}}) + \varphi_{\text{cat}} \rho_{\text{cat}} R_{\text{cat}} \Delta H_r \quad (10) \]

\[ \rho_{\text{ads}} c_{\text{p}, \text{ads}} \left( \frac{\partial T_{\text{ads}}}{\partial t} + u_1 \frac{\partial T_{\text{ads}}}{\partial z} \right) = \frac{6h_{i_1}}{d_p} (1 - \varepsilon_b) (T_g - T_{\text{ads}}) + \varphi_{\text{ads}} (1 - \varepsilon_b) R_{\text{ads}} \Delta H_{\text{ads}} \quad (11) \]
2.4. Simulation Conditions
The gas phase and solid phase are fed counter-currently into the reactor. Gas is fed at the bottom while solids are fed from the top. The filling time and heating time are ignored. Reactor is assumed to be fully fulfilled and well heated at the beginning. Catalysts’ volume fraction in solid phase is 0.53. All the equations are solved with Danckwert’s boundaries.

| Term       | Temperature | Pressure | Reactor Length | Velocity | H₂S | SO₂ | N₂ |
|------------|-------------|----------|----------------|----------|-----|-----|----|
| Unit       | K           | Bar      | m              | m/s      | mol/m³ | mol/m³ | mol/m³ |
| Value      | 523.15      | 1.01426  | 1              | 0.178    | 2.3296 | 1.1648 | 19.8015 |

2.5. Model Symbols

| Symbol | Name                       | Symbol | Name | Symbol | Name                  |
|--------|----------------------------|--------|------|--------|-----------------------|
| Dₓ     | Dispersion Coefficient     | φ      | Volume Fraction | η | Effectiveness factor |
| k      | Mass Transfer Coefficient  | ε      | Porosity | ρ | Density               |
| T      | Temperature                | r      | Radius | c_p | Heat Capacity         |
| hₜ     | Heat Transfer Coefficient  | u      | Velocity | p | Partial Pressure      |
| C      | Concentration              | q      | Loading | ΔH | Enthalpy              |

3. Simulation Results and Discussion
The reaction takes about 50min to reach dynamic equilibrium. When equilibrium is reached, the concentration profiles of each component in gas phase are shown in Figure 1. It can be seen that the reaction mainly happens in the first half part of the reactor, which is called the main reaction region. In this region, reaction dominates the mass change of each component. H₂S and SO₂ are significantly consumed and water amount increases fast at the beginning and then drops quickly because water is effectively removed by the adsorbents. After leaving this region, because of the low concentration of the reactants, reaction rate becomes very low and mass transfer among components dominates in the rest of the reactor. The equilibrium conversion of H₂S is about 98.85%. Evaluating on the conversion of H₂S, it performs better than single-stage fixed bed reactor.

![Figure 1. Component Concentration Profiles in Gas Phase.](image-url)

The profiles on catalysts, as shown in Figure 2, has almost the same trend as that in the gas phase. H₂S and SO₂ drop dramatically as soon as the reaction begins. Sulfur accumulates on the catalysts and then reaches mass equilibrium between the gas phase and the solid phase. The performance of the catalysts is good enough for desulfurization in this reaction. When the catalysts are about to leave the reactor, the surface of them is covered with sulfur product. But the catalysts are sent out of the reactor in time to guarantee the equilibrium shift forward. Newly fed catalysts also ensure the reactor’s performance.
Temperature plays an important role in reaction equilibrium and affects the adsorption isotherm. The dynamic temperature profiles are shown in Figure 3. As the reaction heat accumulates, the temperature in main reaction zone increases and the final temperature increment is about 20.7K. Furthermore, the fresh solids fed from the top act as a kind of coolant to suppress the rise of temperature. This allows to keep the reaction shift forward to convert more H$_2$S.

**Figure 2.** Component Concentration Profiles on Catalysts.

**Figure 3.** Temperature of Gas Phase.

**Figure 4.** Effect of Temperature on Adsorbent Loading.

The loading of adsorbents represents how much the adsorbents can adsorb. From the figure above, it can be seen that when the partial pressure of water is fixed, the higher the temperature, the worse the adsorption ability of adsorbents. Under the reaction conditions, adsorbents’ ability decreases slowly but not that significant. Inside the reactor, water adsorption doesn’t decrease that much to hinder reaction
equilibrium. But as the catalysts are good enough to maintain the reaction rate, increasing the volume fraction of adsorbent can be beneficial to further improve the reactor’s performance. The model predicts that more adsorbents can obtain higher H$_2$S conversion as much as over 99.5%.

Figure 5. Effects of Volume Fraction of Adsorbents in Solid Phase.

4. Conclusion
In moving bed reactor, its performance in Claus Process is better than that of single-stage fixed bed reactor, due to continuously removal of product covered catalysts and saturated adsorbents. About 98.85% of H$_2$S is converted when the dynamic equilibrium is reached. Counter-currently fed solids help keep the temperature profile and the highest temperature increment is about 20.7K. Under reaction conditions, the ability of adsorbents is limited by high temperature but not that much to affect the reaction significantly. Better conversion of H$_2$S can be obtained if more adsorbents are provided in the solid phase. Moving bed reactor is a good potential choice for single-stage reactor in Claus Process.

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