Steady-state simulation of a non-isothermal hydrotreating reactor

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Abstract
A trickle-bed heterogeneous plug flow reactor for hydrotreating was modeled and simulated in steady-state conditions. The effect of important operating variables such as temperature, pressure, weight hourly space velocity (WHSV) and feed API gravity were studied over and under normal conditions ranges. Evaluation of simulated results showed that H_2, H_2S and organic sulfur (S) concentration profiles are very close in both liquid and solid phases. Thus, the differential–algebraic equations (DAEs) system were converted to particular stiff ordinary differential equations (ODEs) and solved simultaneously with simulink toolbox in MATLAB. The Simulation validation confirms good agreement with available experimental data. Furthermore, the effect of temperature and pressure on product organic sulfur content are presented. The temperature gradient obtained along the reactor bed by considering non-isothermal assumption., emphasizes necessity of using quench streams.

Keywords: Simulation, Hydrotreating, Trickle-bed reactor, non-Isothermal.

Introduction
Nowadays, crude oil is still the most important world energy source for clean fuels supplement. Furthermore, more severe environmental rules to minimize air pollution dictates refineries for upgrading fuel products yield and reducing more impurities to reach ultra clean fuels. Catalytic hydrotreating process is widely applied in the petroleum refinery industry to remove impurities, such as sulfur, nitrogen, oxygen and metal-containing compounds as well as polynuclear aromatics. One of the main purpose in hydroteating operations is removing sulfur compounds well-known as hydrodesulfurization (HDS). The HDS reactors as well as catalyst and reaction conditions used for hydrodesulfurization of various feeds (from light naphtha to heavy residue) operate in different modes including fixed-beds, moving-beds and expanded-beds. Now, most of the HDS reactors are multiphase catalytic fixed-bed classified to co-current and counter-current gas-liquid flow trickle-bed [1-3].
Modeling and simulation of HDS trickle-bed reactor is one of the interesting issue for researchers. The Korsten and Hoffmann [4], Bhaskar et al. [5], Rodríguez et al. [6] and Ancheyta [1] have presented valuable theoretical and experimental results. However, some modifications are needed in the modeling to consider various feed physical properties such as viscosity, density and other properties in wide ranges as well non-isothermal condition. In addition, more efficient algorithm should be applied for solving simultaneous governing equations to achieve appropriate steady-state simulation.

In this study , the MATLAB *simulink* toolbox is applied for simulation of the non-isothermal trickle-bed HDS reactor with co-currently downward flow. Model validation has been carried out in comparison with pilot data [4]. The predicted results show good agreement with mentioned experimental data. The temperature gradient obtained by assuming non-isothermal condition dictates necessity of using quench streams.

Reactor modelling and simulation

The presnted model is based on a three phase plug flow reactor model and governing equations are given in Table 1. This model includes correlations to calculate mass transfer coefficient, gas solubilities, hydrocarbon properties at operating conditions which had been in the literature [4, 8]. To simulate model, operating conditions were T=370 ^{o}C, P=10 bar, weight hourly space velocity (WHSV)=0.9 h^{-1} and base case feed API gravity=23.2. The major model assumptions are: Steady-state, non-isothermal reactor with constant gas and liquid velocities, non-deactivation catalyst with only chemical reactions on catalyst surface.
The model reactor is implemented in *simulink* toolbox of *MATLAB* software R2013. A part of the procedure is presented in figure 1. Evaluation of simulated results showed that H_2, H_2S and organic sulfur (S) concentration profiles are very close in both liquid and solid phases. Thus, the solid phase equation is omitted from solving procedure. Therefore, the system of differential–algebraic equations (DAEs) is simply upgrading to set of stiff ODEs.

Table 1. The main ractor model equations [4, 7].

Gaseous compounds(H_2, H_2S) in the gas phase	$\frac{u_G}{RT} * \frac{dp_i^G}{dz} + k_i^L * a_L * \left(\frac{p_i^G}{H_i} - C_i^L\right) = 0$
Gaseou s compounds(H_2, H_2S) in the liquid phase	$u_L * \frac{dC_i^L}{dz} - k_i^L * a_L * \left(\frac{p_i^G}{H_i} - C_i^L\right) + k_i^S * a_s * \left(C_i^L - C_i^S\right) = 0$
Organic sulfur in the liquid phase	$u_L * \frac{dC_1^L}{dz} + k_1^S * a_s\left(C_1^L - C_1^S\right) = 0$
Consumption on the catalyst surface	$k_i^s * a_s * \left(C_i^L - C_i^S\right) = -v_i * r_{HDS}$
HDS Reaction kinetic	$r_{HDS} = k_{app} * \rho_b * \epsilon * \eta * \frac{\left(C_S^S\right) * \left(C_{H_2}^S\right)^{0.45}}{\left(1 + K_{H_2S} * C_{H_2S}^S\right)^2}$
Energy balance equation	$\frac{dT_R}{dz} = [-\Delta H * r_{HDS}] * \frac{1}{u_L * \rho * C_p}$

Results and Discussion

The components concentration profiles along the reactor bed are shown in Figures 2a and 2b. As expected, the S concentration decreases and H_2S partial pressure increases. All of profiles exhibit steep gradient at early stage of the reactor followed by slow trend, due to decreasing in the reaction rate. As observed in figure 2b, presented results predict very good conformity between the output S concentration and H_2S partial pressure by the experimental data taken from [4]. Figure 3 shows the influence of temperature and pressure variations on the output S concentration along reactor bed in the wide ranges (under and over normal operational range for typical feed) from 340-440 ^{0}C and 4-20 MPa, respectively.

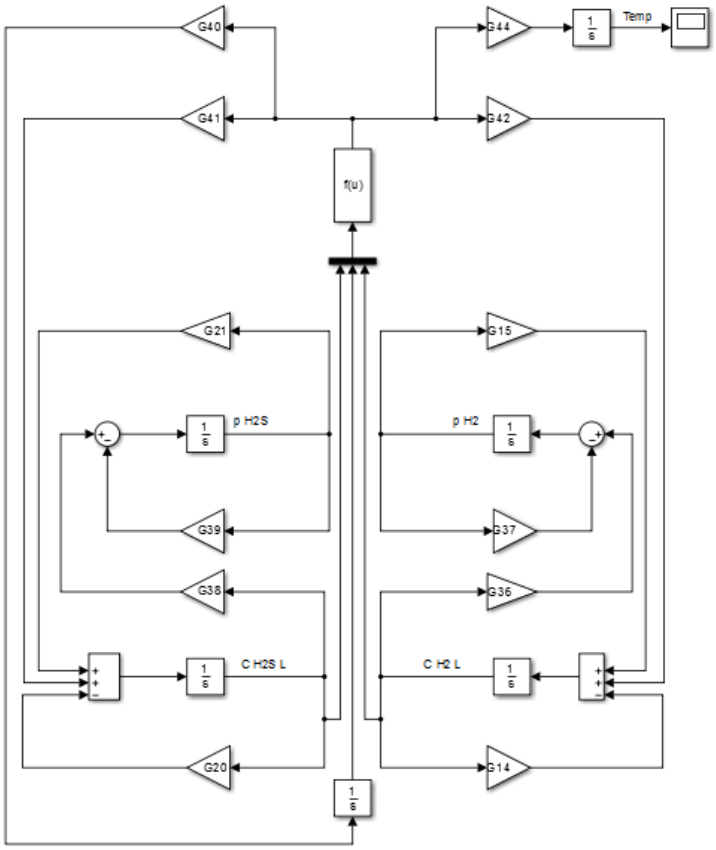
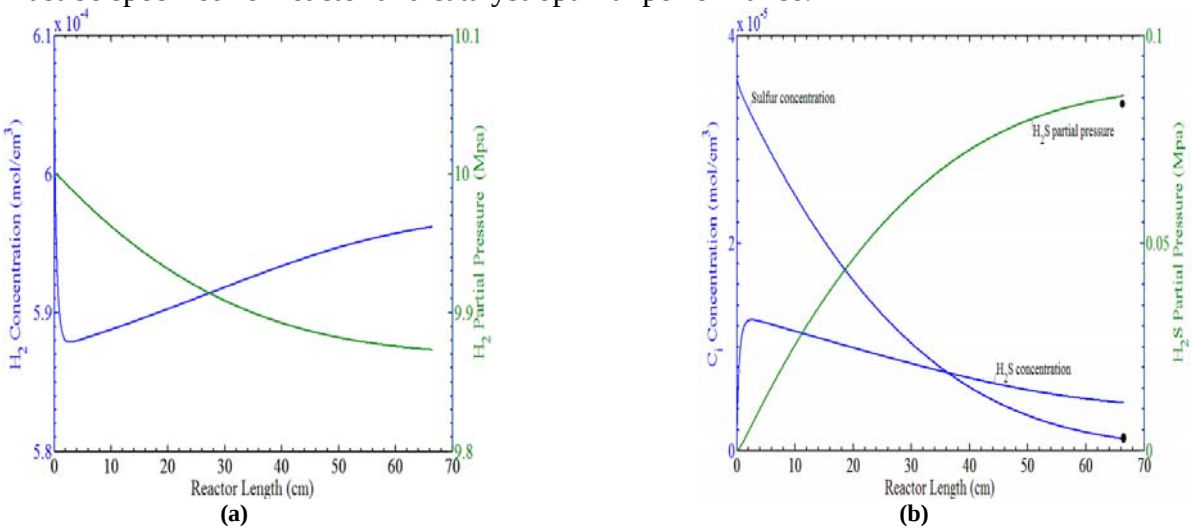


Figure 1. A part of *simulink* procedure Scheme for the presented HDS simulation.

The effect of temperature and pressure in the ranges 340-390^{o}C and 4-11 MPa is greater than their effect on 390-440 ^{o}C and 11-20 MPa. Some reasons for this event can be related to catalyst coking, damaging and other etc. On the other hand, appropriate operating conditions must be specified for reactor and catalyst optimal performance.



(a) **(b)**

Figure 2. The siumation profiles of sulfur concentration and H_2S partial pressure across yhe HDS reactor bed.

According to Figure 4, temperature increases along the reactor-bed, which is obviously due to the exothermic nature of the reaction. Since increasing in temperature can damage catalyst and equipment failure, applying quenching cooling streams ia a suitable way to control and avoid the temperature rising during catalytic bed.

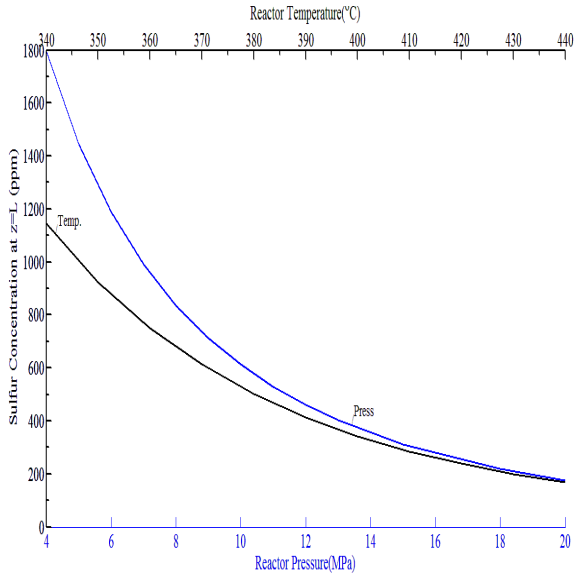


Figure 3. Effect of pressure and temperature changes on the S concentration in the HDS reactor output.

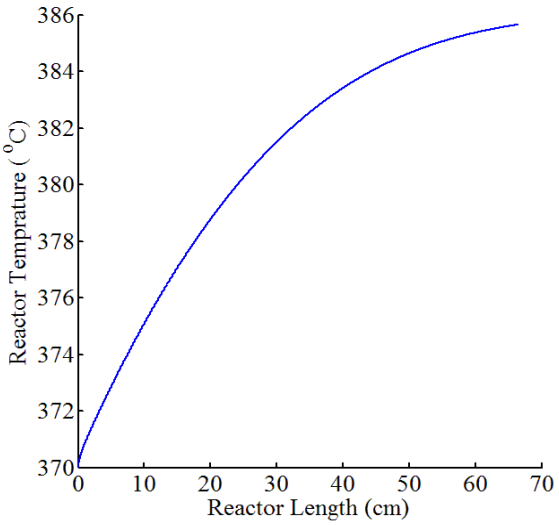


Figure 4. Predicted temperature profile during the non-isothermal HDS reactot length.

Conclusion

Modeling and simulation of the HDS trickle-bed reactor using *simulink* is presented. User friendly, flexibility and efficiency of implemented method are the most advantages in this simulation. Simulation results show good agreement with available experimental data. In addition, by increasing the temperature and pressure in the specific ranges (e.g. 340-390 ^{0}C and 4-11 MPa respectively) significant decreasing on output sulfur concentration is predicted. The non-isothermal assumption for the HDS reactor demonstrates taking quench streams for process and economic considerations is necessary.

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