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MODELING AND SENSITIVITY ANALYSES OF HYDRODESULFURIZATION CATALYST PELLET

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Abstract
Catalyst pellets are one of the most important factors in catalytic reactor design. In this research a single catalyst pellet of hydrodesulfurization reaction have been investigated. The governing mass and energy balance equations have been solved numerically under steady state and dynamic conditions aiming to find the concentration and temperature profiles of the pelet. In order to consider the mass diffusion effect, the effectiveness factor η was introduced and solved at steady state mode.Sensitivity analysis with respect to the pellet surface conditions was studied in detail. Results showed that the effectiveness factor increases with surface concentration while it decreases as surface temperature increases. The Catalyst pellet was very sensitive to initial condition It was observed that decreasing the inlet concentration would increase the dimensionless concentration whereas the inlet concentration leads to a higher temperature.

Keywords: Catalyst Pellet; Steady And Dynamic Pellet; Reactor Design.

1. Introduction

Different parameters such as feed properties, flow rate, operating condition, reaction kinetics and catalyst pellet should be considered in designing catalytic reactors. Catalyst bed geometry and stationary spherical catalyst pellets are two design unknowns which are directly related to the conditions of individual pellets through pellet boundary conditions and effectiveness factor η in such reactors. Studies on behavior of the catalyst pellet have been reported in the literature [1-4]. Wrong information on dynamic behavior of the pellet may lead to unreal and unsafe design of the reactor. Quantifying the parameters that affect the unsteady behavior of reactor will enable engineers to describe the safety condition of their design, guarantee product quality and other operating conditions. This paper investigates the hydrodesulfurization (HDS) catalyst pellet modeling under steady and dynamic states.

2. Experimental

The experimental data published by Vishwakarma [3] have been used to validate the developed model. In that research, a reactor with the length of 240 mm and internal diameter of 14 mm has been used. The reactor was loaded with a bed of catalyst (average particle diameter ~ 1.7 mm) diluted with 90 mesh silicon carbide to minimize the axial dispersion. The setup was operated under conditions reported in table 1.

Table 1 Operating condition

Oil superficial velocity (mm/s)	0.285
Catalytic bed length (mm)	129
Internal diameter (mm)	14
LHSV (1/h)	2
H_2/Oil ratio (ml/ml)	600
Temperature, (^oC)	380
Pressure (bar)	8.9
Gas composition (mol%)	
H_2	100
H_2S	0

The feed is a type of light gas oil with the properties summarized in table 2. Also the catalyst properties are shown in that table.

Table2 The feedstock and catalyst properties

Molecular weight	233.5
Viscosity (cp)	0.282
Density (kg/m^3)	693
Total sulfur (ppmw)	15950
Total nitrogen (ppmw)	209
Catalyst Properties	
Equivalent diameter (mm)	1.7
Co content (wt %)	3
W content (wt %)	11.5
Bed porosity	0.3
Porosity catalyst pellet	0.4
Bulk density (g/cm^3)	0.918

2.1 Modeling

Mass and heat balances for catalyst pellet are developed as follow:

$$\frac{\partial C_{i,s}}{\partial t} = \frac{D^l_{e,i}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{i,s}}{\partial r}\right) \pm \rho_s r_{hds} \quad (1)$$

$$\rho_s cp_s\frac{\partial T^s}{\partial t} = \frac{\lambda^s_e}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T^s}{\partial r}\right) + \rho_s r_{hds}(-\Delta H_R) \quad (2)$$

The boundary and initial conditions for particle catalyst are:

At r=R $C_{i,s} = C^s_i$,T= T_s

At r=0 $\frac{\partial C_{i,s}}{\partial r} = 0$, $\frac{\partial T^s}{\partial r} = 0$

At t=0

$$\frac{d(\frac{T^s}{T_s})}{dt^{\acute{}}} = \frac{T_0}{T_s}, \frac{d(\frac{C_{i,s}}{C^s_i})}{dt^{\acute{}}} = \frac{C_0}{C^s_i}$$

Correlations taken from literatures were used to estimate various parameters, such as molar volume, effective diffusivity, etc [3, 7].

The rate models were developed based on the following assumptions [3]:

1- The HDS reaction is irreversible

2- Reaction rates follow a power law type equation

3- The effect of hydrocracking on HDS reaction is negligible

The HDS reaction kinetic was fitted with a power law model and the reaction was proposed to follow the form of:

$$R-S \xrightarrow{K_{hds}} product$$

$$r_{hds} = -\frac{dc_s}{dt} = K_{hds}c_s^n \quad (3)$$

Where r_{hds} is the rate of HDS reaction, K_{hds} is the apparent reaction rate constant for HDS and C_s is the concentration of total sulfur.

The values of K_{hds} and n were evaluated using non-linear regression analysis. The analyzes show that n = 0.57 gives the best fit for the experimental data and consequently the best order of reaction and K_{hds} is (7.04 $\pm$ 0.549) x 10^{-5} in reaction temperature.

The effectiveness factor (η) is expressed as the ratio of volume averaged reaction rate to the rate at surface temperature and concentration [5].

$$\eta = \frac{\int_0^1 \Phi^2 rate(\Phi,\zeta)dr^{s+1}}{\Phi^2 rate(1,1)dr^{s+1}} \quad (4)$$

3. Results and discussion

3.1. Pellet at steady state

For a non-isothermal pellet, temperature profile must be coupled with concentration profile. The system of differential equations in eqs.(1) and (2) are solved using collocation method [5,6]. We chose five collocation points to develop numerical profiles. Fig 1 shows the temperature profile in catalyst pellet and as can be seen there is no significant temperature gradient in the catalyst pellet. Fig.2 shows the radial concentration profile in catalyst pellet.

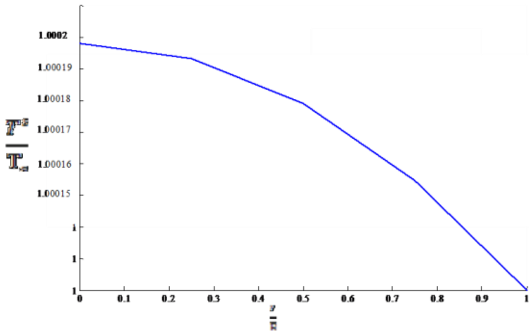


Fig. 1. Temperature profile in catalyst pellet in inlet of the reactor

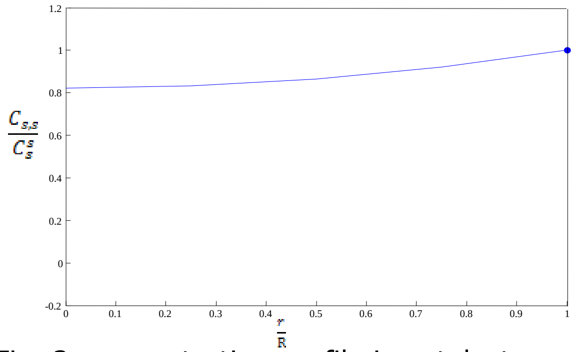


Fig. 2. concentration profile in catalyst pellet in inlet of the reactor

3.2. Sensitivity analysis of effectiveness factor

The sensitivity analysis of effectiveness factor was tested by varying surface concentration and temperature. Fig. 3 and fig. 4 show the behavior of effectiveness factor via pellet surface concentration C_S^s and surface temperature T_s respectively.

Effectiveness factor increases as surface concentration increases and decreases as surface temperature increases. This behavior is predicted from the definition of η in Eq.(1): At high temperature, diffusion effect becomes the limiting factor toward the conversion rate and thus increases the denominator of η. Increasing the surface concentration minimizes diffusion and effectiveness factor will be increased correspoundingly.

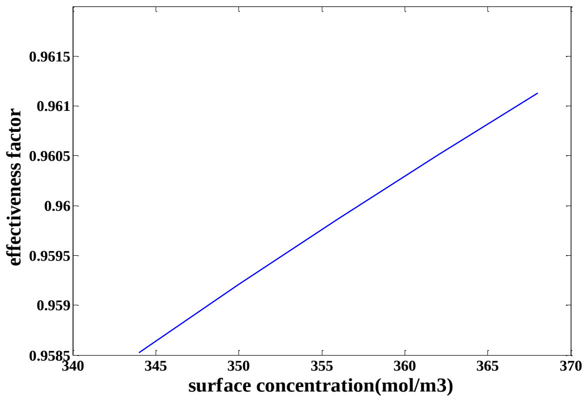


Fig. 3 Variation of effectiveness factor with surface concentration

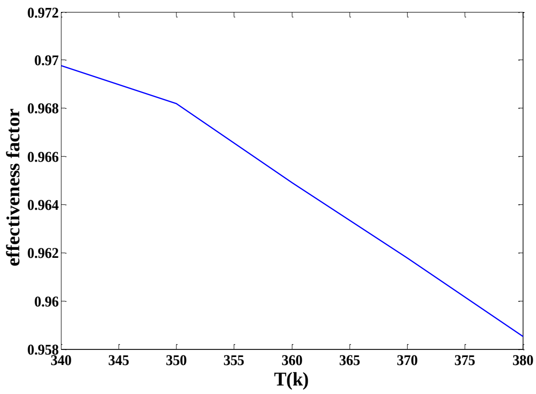


Fig. 4 Variation of effectiveness factor with surface temperature

3.3. Pellet at dynamic State

For dynamic condition, we need to solve Eqs. (1) and (2) with specified initial conditions. Since the convergence of solution is very sensitive to the initial conditions, we choose the initial conditions for dimensionless concentration profile to reach the steady state condition at which the dimensionless temperature profile is equal to 1. Fig. 5 and fig. 6 show the dynamic concentration and temperature variation with respect to time for five collocation nodes.

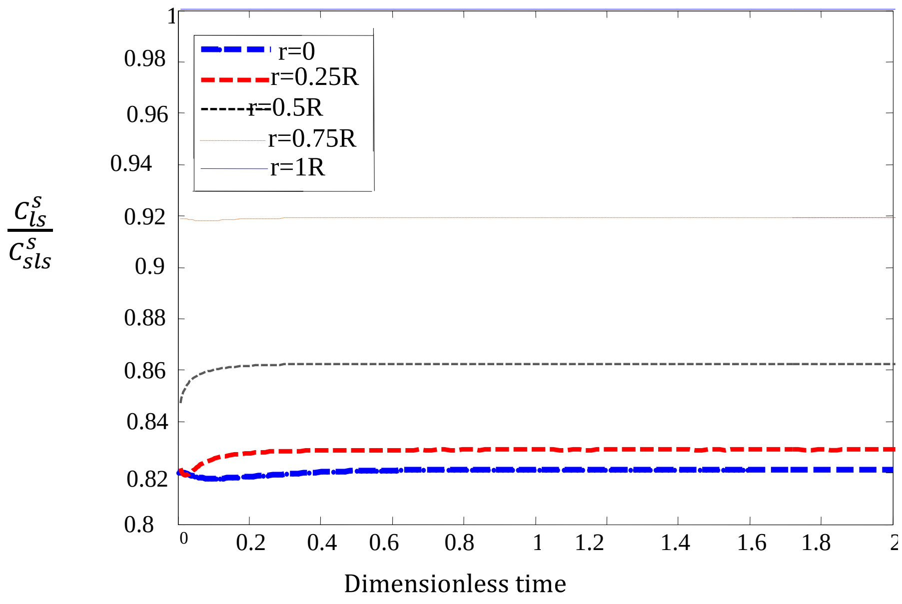
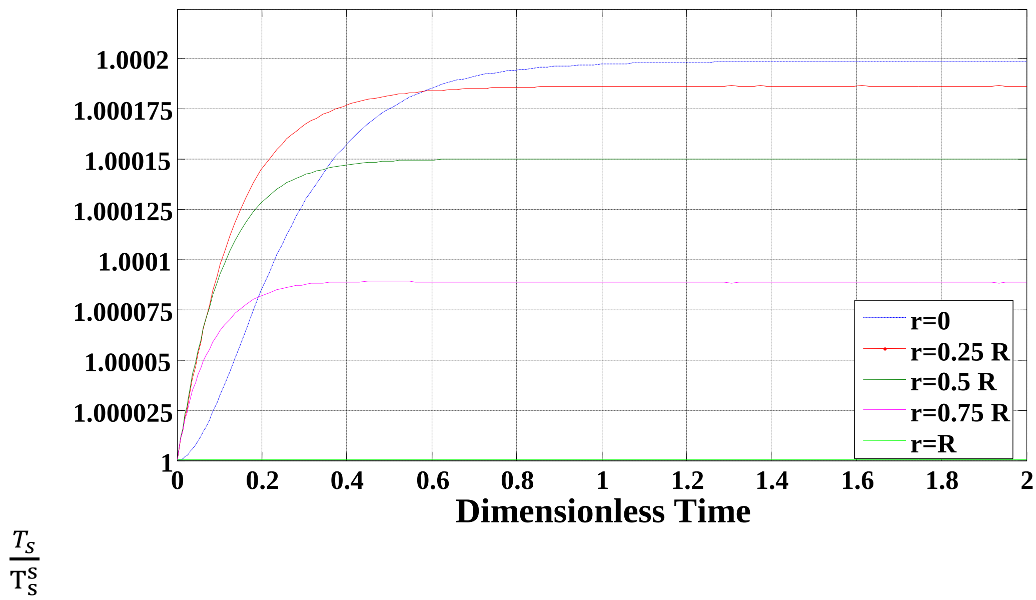


Fig.5 Concentraton profile for catalyst pellet in dynamic mode



Fiq. 6 Temperature profile for catalyst pellet in dynamic mode

3.4. Sensitivity analysis of pellet behavior in dynamic mode

For observing sensitivity of dynamic pellet we changed surface cocncentration and temperateure (C_s^s,T_s). Sensitivity of dynamic pellet with respect to surface concentration for a dimensionless radius of 0.75 are shown in Fig. 7. The spicified value for surface are: Ts=653.2 k , $C_s^s = 344\ \frac{mol}{m^3}$

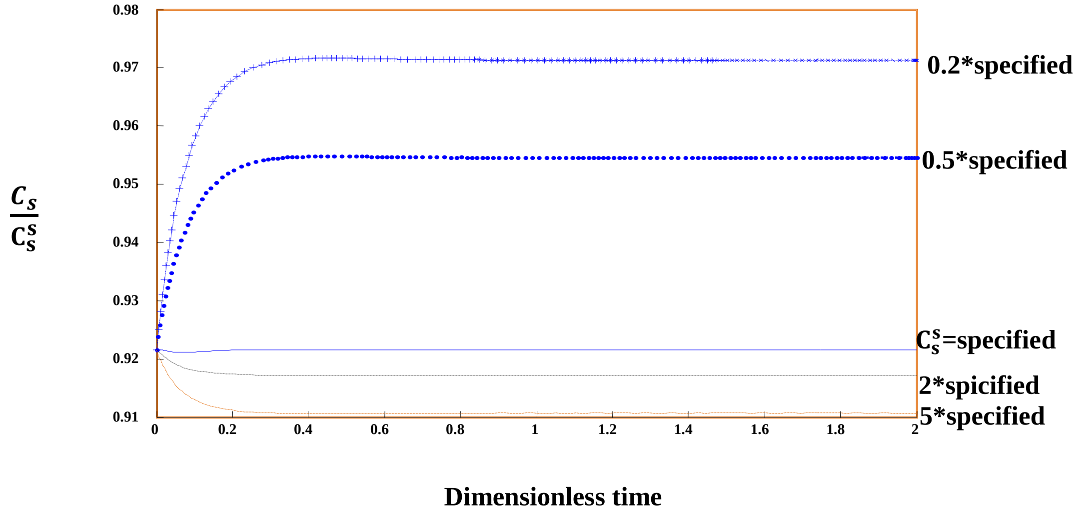
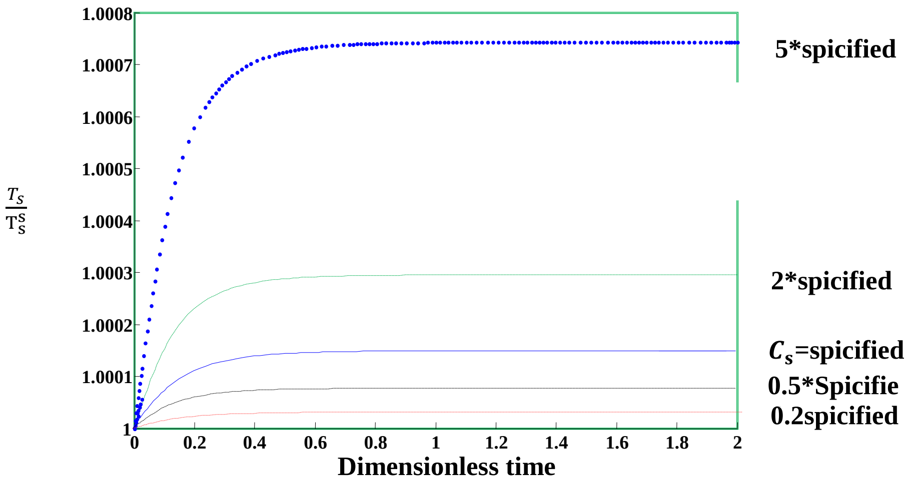


Fig. 7. Variation of pellet concentration with time

We observed that decreasing the inlet concentration increases the dimensionless concentration



Fiq. 8. Variation of pellet temperature with time

Fig. 8 showed that temperature increases when the inlet concentration increases because more reactant is entered to the reactor, more heat is released due to the exothermic of the reaction.

4. Conclusion

Designing a catalytic reactor requires engineers to accurately predict the mass and heat transfer phenomena occurring both inside an individual pellet and within the entire reactor. Having the information for individual pellets known, effectiveness factor (η) can then be evaluated. In this research the HDS catalyst pellet has been modeled at steady and unsteady States and the sensitivy analysis of effectiveness factor at steady state has been studied. It was observed that the effectiveness factor increases with surface concentration while it decreases as surface temperature increases. The Catalyst pellet was very sensitive to initial condition and results showed that decreasing the inlet concentration would increase the dimensionless concentration whereas the inlet concentration leads to a higher temperature.

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