

## **Modeling and simulation of removal of sulfur component from oil in a fixed bed reactor in dynamic state**

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### **ABSTRACT**

Sulfur compounds are the most important pollutants in petroleum products and removing these compounds is a primary objective in the refining industries. In this study, the industrial unifier reactor of Shiraz refinery for hydrodesulfurization of naphtha has been simulated in dynamic conditions. The proposed model, consisting of a set of algebraic and partial differential equations, is based on a heterogeneous two-dimensional unsteady state formulation. The equations discretized in finite difference form and solved with 4<sup>th</sup> order Rung Kutta method in steady state condition and in dynamic condition, implicit finite difference method that cupped whit simple iteration method was used. Changes in concentration and temperature profiles obtained and discussed as a function of reactor axial and radial position and time. the dynamic model was applied to predict the dynamic behavior of the reactor. To verify the proposed model, the simulation results have been compared to available data from industrial reactor of the Shiraz refinery. A good agreement has been found between the simulation results and industrial data. A sensitivity analysis has been carried out to evaluate the influence of several parameters on the process. Results of simulation showed that conversion decreased from 0.9548 to 0.923 with increase in concentration of sulfur in the feed of reactor from 1500 ppm to 2000 ppm and at high temperature conversion decreased from 0.9548 to 0.91 because of coke formation on catalyst. © 2014 Trade Science Inc. - INDIA

### **KEYWORDS**

Fixed-bed reactor;  
Hydrodesulphurization;  
Sulfur compounds;  
Simulation.

### **INTRODUCTION**

The main objective of environmental legislation is to reduce sulfur dioxide, nitrogen oxides, aromatics, vapor and soot particulate emissions from both refineries and its products after combustion. Regulations on transportation fuel composition, which restricts mainly the concentration of sulfur compounds, have become stricter since environmental issues has increased in recent years<sup>[1]</sup>. The short-term goal is to reduce the sulfur concentration to 50ppmw.

In order to meet these new specifications, sulfur in transportation fuels have to decrease. Hydrodesulfurization (HDS) is a catalytic chemical process widely used to remove sulfur (S) from natural gas and from refined petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils<sup>[2]</sup>. The purpose of removing the sulfur is to reduce the sulfur dioxide (SO<sub>2</sub>) emissions that result from using those fuels in automotive vehicles, aircraft, railroad locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms

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of fuel combustion. Another important reason for removing sulfur from the naphtha streams within a petroleum refinery is that sulfur, even in extremely low concentrations, poisons the noble metal catalysts (platinum and rhenium) in the catalytic reforming units that are subsequently used to upgrade the octane rating of the naphtha streams. HDS is the process by which sulfur is removed from sulfur containing compounds by reaction with hydrogen, thereby forming  $H_2S$ . It is a catalyzed reaction usually involving a metal sulfide catalyst, in particular sulfided  $Co/Mo/Al_2O_3$  or sulfided  $Ni/Mo/Al_2O_3$ . The resultant  $H_2S$  that is produced from the hydrogenation reaction is subsequently absorbed by reaction with  $ZnO$  to form  $ZnS$  and, in this way, sulfur is removed from the hydrocarbon feedstock. HDS is effective for a range of sulfur containing compounds which exhibit varying reactivities towards desulfurization. The reactivity is dependent upon the local environment of the sulfur atom in the molecule, and the overall shape of the molecule. The HDS reaction is usually operated at moderately high temperature and pressure.

In Iran refineries, the HDS technology is used for removal of sulfur from oil. In this study the fixed bed reactor of the unifiner unit of Shiraz refinery is modeled and simulated. Simulation of packed bed reactors is not an easy task, since systems of nonlinear partial differential equations have to be solved along with nonlinear algebraic relationships<sup>[3]</sup>. Modeling and simulation of fixed bed reactors have been done for many industrial and pilot scales reactors. For instance Farsi et al. modeled and controlled the industrial reactor of dimethyl ether synthesis with the accompanying feed preheater and the controllability of the process had been investigated through dynamic simulation of the process under a conventional feedback PID controller<sup>[4]</sup>. Vargas et al. compared a light gas oil hydrodesulfurization process via catalytic distillation with a conventional process and showed that by integrating the separation and reaction into a single unit, the catalytic distillation may produce a diesel with low concentration of sulfur compounds at a lower cost than the traditional reaction/separation process<sup>[5]</sup>. Fatemi et al. studied the coking of a commercial fresh sulfide  $Ni-Mo/Al_2O_3$  catalyst in a fixed bed reactor. They derived initial activity of the catalyst by a time variable function and used this equation in dynamic model of HDS reaction in a packed bed reactor to determine the activity change of the catalyst in the reac-

tor during actual operation conditions<sup>[6]</sup>. Cheng et al. modeled a two-stage cocurrently and counter currently operated fixed bed reactors for HDS reaction. Their model and simulation revealed that low concentration at the reactor exit region under countercurrent flow is critical to the ultra low sulfur extent in the produced oil<sup>[7]</sup>.

In this paper, we develop a two-dimensional unsteady, heterogeneous and nonisothermal model for dynamic simulation of an industrial HDS reactor and compare the results of two-dimensional model with one-dimensional model.

### Reactor model

A mathematical model is a set of variables and a set of equations that build relationships among the variables for describing some aspects of the behavior of the system under investigation. Process models are very profitable. It has been employed for operator training, safety systems design, design of operation as well as operation control systems designs. The improvement of faster computer and advanced numerical methods has enabled modeling and solution of the whole process<sup>[8]</sup>.

In the present study, a two dimensional heterogeneous model has been considered for unsteady state simulation of the process. The basic structure of the model is composed of heat and mass conservation equation coupled with thermodynamic and kinetic relation as well as auxiliary correlation for prediction of physical properties.

In the dynamic modeling of the reactor the following assumptions have been considered:

- Adiabatic reactor
- plug flow pattern

To justify this two assumptions, it should be notified the industrial reactor considered in this study have insulation that causes the heat loss from the reactor wall to environment negligible in comparison to the heat release in the reactor, and also because of high Reynolds number, the assumption of plug flow is reasonable.

The mass and energy balances for the gas and solid phase are expressed by the following equations:

### Gas phase

$$\varepsilon \frac{\partial C_{i,b}}{\partial t} = -\varepsilon u_i \frac{\partial C_{i,b}}{\partial z} + \varepsilon D_{e,i} \frac{\partial^2 C_{i,b}}{\partial z^2} - \varepsilon D_{e,i} \left( \frac{\partial^2 C_{i,b}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{i,b}}{\partial r} \right)$$

$$-k_g a_v (C_{i,b} - C_{i,s}) \quad (1)$$

$$\begin{aligned} \varepsilon \rho_r c_{pf} \frac{\partial T_b}{\partial t} &= -\varepsilon \rho_r c_{pf} \frac{\partial T_b}{\partial z} \\ + \varepsilon \lambda_e \frac{\partial^2 T_b}{\partial z^2} + \varepsilon \lambda_e \left( \frac{\partial^2 T_b}{\partial r^2} + \frac{1}{r} \frac{\partial T_b}{\partial r} \right) - \end{aligned} \quad (2)$$

$$h_r a_v (T_b - T_s)$$

$i$  = didenzothiophene (DBT),  $H_2$ ,  $H_2S$ ;  $C_i$  = concentration of component  $i$  (mole/m<sup>3</sup>);  $\varepsilon$  = porosity;  $D_{ij}$  = coefficient diffusivity (m<sup>2</sup>/s);  $k_g$  = mass transfer coefficient;  $a_v$  = specific area (m<sup>2</sup>/m<sup>3</sup>)

### Solid phase

$$(1 - \varepsilon) \frac{\partial C_{i,s}}{\partial t} = k_g a_v (C_{i,b} - C_{i,s}) + \eta_i \rho_{Bs} \sum r_i \quad (3)$$

$$(1 - \varepsilon) \rho_{Bs} c_{ps} \frac{\partial T_s}{\partial t} = h_r a_v (T_b - T_s) + \eta_i \rho_{Bs} \sum (-\Delta H) r_i \quad (4)$$

The pressure drop in the bed is calculated by Ergun equation<sup>[9]</sup>:

$$-\frac{dP}{dz} = 150 \frac{(1 - \varepsilon)^2 \mu u_c}{d_p^2 \varepsilon^3} + 1.75 \frac{(1 - \varepsilon) \rho u_c^2}{d_p \varepsilon^3} \quad (5)$$

The initial and boundary conditions for these equations are given below.

### Boundary conditions

$$\begin{aligned} \text{At: } r = R \quad \frac{\partial C_{i,b}}{\partial r} \Big|_{r=R} = 0 \quad \frac{\partial T_b}{\partial r} \Big|_{r=R} = 0 \\ \text{At: } r = 0 \quad \frac{\partial C_{i,b}}{\partial r} \Big|_{r=0} = 0 \quad \frac{\partial T_b}{\partial r} \Big|_{r=0} = 0 \end{aligned} \quad (6)$$

### Initial conditions

$$\begin{aligned} \text{At } t=0 \quad C_{i,b} = C_{i,b}^0 \quad T_b = T_b^0 \\ \text{At } t=0 \quad C_{i,s} = C_{i,s}^0 \quad T_s = T_s^0 \end{aligned} \quad (7)$$

### Auxiliary equation

For prediction of the model parameters Auxiliary equations must be used. In these equations  $\eta_i$  is the effectiveness factor<sup>[10]</sup>. It can be calculated from the equation (8):

$$\eta_i = \frac{\int r_i dv_p}{v_p \cdot r_i \Big|_{\text{surface}}} \quad (8)$$

The physical properties of chemical species and

overall mass and heat transfer coefficients between two phase (solid phase of catalyst and gas phase) must be estimated. The overall mass transfer coefficient between solid and gas phase has been obtained from the correlation proposed by Cussler<sup>[11]</sup>.

$$k_{g_i} = 10^3 \times 1.7 \text{Re}^{-0.42} \text{Sc}_i^{-0.67} u_g \quad (9)$$

Gas phase is multi component, therefore mass transfer diffusion coefficient for each component and binary mass diffusion coefficient in the mixture have been estimated by the following equations respectively<sup>[12]</sup>:

$$D_{im} = \left( \sum_{j=1}^n \frac{y_j}{D_{ij}} \right)^{-1} \quad (10)$$

$$D_{ij} = \frac{0.001 T^{1.75} M_{AB}^{1/2}}{P \left[ (\sum v)_A^{1/3} + (\sum v)_B^{1/3} \right]^2} \quad (11)$$

The overall heat transfer coefficient between solid and gas phase ( $h_r$ ) has been predicted from<sup>[13]</sup>:

$$\frac{h_r}{c_p \rho \mu} \left( \frac{c_p \mu}{K} \right)^2 = \frac{0.485}{\varepsilon_B} \left( \frac{\rho u d_p}{\mu} \right)^{-0.407} \quad (12)$$

The overall heat capacity depends on the temperature and composition<sup>[14]</sup>, and is calculated using Eqs. (13) and (14):

$$C_p(i) = a + bT + cT^2 + dT^3 \quad (13)$$

$$C_p = \sum y_i C_p(i) \quad (14)$$

The heat of reactions depend on temperature, and is calculated using Eqs. (15):

$$\Delta H = \Delta H_{ref} + \int_{T_{ref}}^T C_p dT \quad (15)$$

A modification of the Benedict-Webb-Rubin EOS with 11 parameters has been applied in this work.

$$\begin{aligned} P = \rho_m RT + \left( B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right) \\ \rho_m^2 + \left( bRT - a - \frac{d}{T} \right) \rho_m^3 + \alpha \left( a + \frac{d}{T} \right) \rho_m^6 \\ + \frac{c \rho_m^3}{T^2} (1 + \gamma \rho_m^2) \exp(-\gamma \rho_m^2) \end{aligned} \quad (16)$$

Where  $\rho_M$  is molar density and the 11 coefficient can be evaluated. The correlation of Carr et al. is used to estimate the mixture gas viscosity<sup>[15]</sup>.

The surface area of the particle per unit volume of the bed is described as<sup>[16]</sup>:

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$$as = \frac{A_c(1-\varepsilon)}{v} \quad (17)$$

The bed void fraction of the catalyst is calculated by the following equation. This equation has been developed for packed bed of spheres<sup>[16]</sup>:

$$\varepsilon = 0.38 + 0.073 \left[ 1 + \frac{\left( \left( \frac{D_R}{d_s} \right) - 2 \right)^2}{\left( \frac{D_R}{d_s} \right)^2} \right] \quad (18)$$

For cylindrical particles, the equivalent spherical is given by the following equation<sup>[16]</sup>:

$$d_s = \left[ d_c L_c + \left( \frac{d_c^2}{2} \right) \right]^{1/2} \quad (19)$$

### Activity function

A major problem in hydrotreating of heavy feedstocks is deactivation of the catalyst by coke formation. The properties of the carbon deposit is a function of the feed composition, the type of catalyst and reaction conditions. The coking reaction is a consequence of dehydrogenation-polycondensation reactions which generate coke structures capable of blocking the access of the reagents to the active catalytic sites and progressively closing off the porous structure of the catalyst<sup>[16]</sup>. In this study, the following equation that proposed by fatemi et al, is used for intrinsic activity as a function of time<sup>[6]</sup>:

$$\gamma = (t^{-0.045}) \quad (20)$$

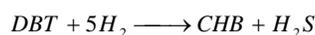
Where t is time in hr., at initial condition, the relative activity of the fresh catalyst is considered unity.

### Hydrodesulfurization kinetics

In this work, the dibenzothiophene (DBT) is used to represent the sulfur compounds since it is one of the less reactive sulfur organic compounds present in the light gas oil. In addition, its concentration is significant. It is generally accepted that the DBT reacts via two parallel pathways, the hydrogenolysis:



And the hydrogenation



where BiPh is the biphenyl and CHB the

cyclohexylbenzene. In this work, the kinetics proposed by Broderick and Gates, a Langmuir-Hinshelwood equation, is used. The reaction rates are<sup>[17]</sup>:

$$r_{hs} = \frac{kK_{DBT}K_{H_2}C_{DBT}C_{H_2}}{(1 + K_{DBT}C_{DBT} + K_{H_2S}C_{H_2S})^2(1 + K_{H_2}C_{H_2})} \quad (21)$$

$$r_{hn} = \frac{k'K'_{DBT}K'_{H_2}C_{DBT}C_{H_2}}{(1 + K'_{DBT}C_{DBT})} \quad (22)$$

where  $r_{hs}$  is the hydrogenolysis reaction rate,  $r_{hn}$  the hydrogenation reaction rate.

$$K_{DBT} = k_{a2} e^{\left( \frac{k_{a1}}{RGT} \right)} \quad (23)$$

$$K_{H_2} = k_{a4} e^{\left( \frac{k_{a3}}{RGT} \right)} \quad (24)$$

$$K_{H_2S} = k_{a6} e^{\left( \frac{ka5}{RGT} \right)} \quad (25)$$

$$k' = k_{b2} e^{\left( \frac{k_{b1}}{RGT} \right)} \quad (26)$$

$$K'_{DBT} = k_{b4} e^{\left( \frac{k_{b3}}{RGT} \right)} \quad (27)$$

TABLE 1 : Kinetic coefficients

$k_{a1}$ (mol/Ecats)	78000
$k_{a2}$ (cal/mol)	-30115
$k_{a3}$ (l/mol)	0/18
$k_{a4}$ (cal/mol)	4541
$k_{a5}$ (l/mol)	4000
$k_{a6}$ (cal/mol)	-8365
$k_{a7}$ (l/mol)	0/7
$k_{a8}$ (cal/mol)	5258
$k_{b1}$ (l/mol)	42194
$k_{b2}$ (cal/mol)	-27728
$k_{b3}$ (l/mol)	1/999
$k_{b4}$ (cal/mol)	142338

TABLE 2 : Characteristics of the catalyst, feed and reactor

specific gravity	0/75
concentration of sulfur(ppm)	1500
Inlet temperature (K)	670
Inlet pressure (bar)	28/27
Molar rate of feed (mole/m <sup>3</sup> )	223/3
Catalyst diameter (mm)	1/3
Density of catalyst(Kg/m3)	1200
Length of reactor (m)	3/8
Reactor diameter (m)	1/525

## Catalyst and feed

A commercial hydrotreating catalyst, containing Ni and Mo oxides supported on  $\gamma$ -alumina was used for this research. The feed used in the hydrodesulfurization reaction was a medium diesel oil, without any metal compounds. Characteristics of the catalyst and feed are presented in TABLE 2.

## Numerical solution

To solve the set of nonlinear partial differential equations (PDE) obtained from dynamic modeling, length and radius of the reactor are divided into equal discrete intervals, and by implicit finite difference method that coupled with simple iteration method, the set of equations are solved. Before carrying out dynamic simulation, the stationary condition of the system should be obtained through solving the governing steady-state equations. The aim of performing steady simulation of the HDS reactor is to determine the concentration and temperature profiles and used as the initial conditions of the unsteady state PDEs. After rearranging the modeling equations for the steady state one dimensional condition, a set of ordinary equations was solved by the method of 4th order Rung-Kutta<sup>[18]</sup>.

## RESULTS AND DISCUSSION

In this section, steady state simulation results of DME reactor have been presented. Assuming an adiabatic tubular reactor with plug flow pattern, the reactor has been simulated based on a two-dimensional heterogeneous nonisothermal model.

### Steady state simulation

Modeling validation is done through comparing the

**TABLE 3 : Comparison of the steady state simulation results of the reactor with plant data**

	Industrial data	Simulation results for thiophen	Simulation results for DBT
Inlet concentration	ppm1500	ppm1500	ppm1500
Out let concentration	ppm3	ppm7 /5	ppm67
Inlet temperature	K670	K670	K670
Out let temperature	K680	K671/1	K676/5
Inlet pressure	Bar28/27	Bar28/27	Bar28/27
Outlet pressure	Bar26/51	Bar27/56	Bar27/56

simulation results with the industrial reactor data from Shiraz refinery. TABLE 3 indicates the simulation results in comparison to available data of the industrial reactor. This table shows that the proposed model has been able to predict the exit concentrations and temperature very well for thiophene but The differences between simulation results and industrial data for DBT are due to that we considered all of 1500ppm sulfur

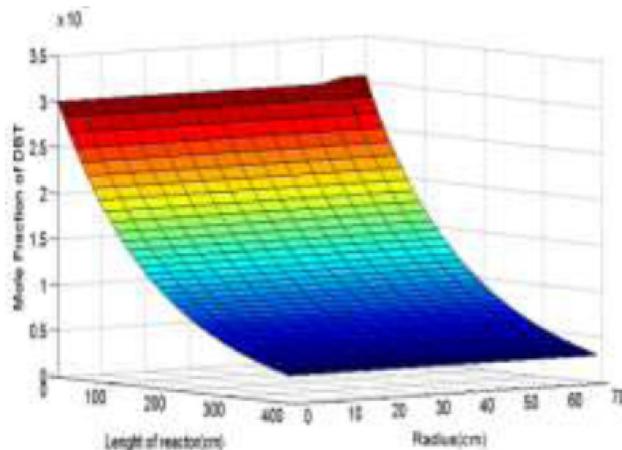


Figure 1 : Mole fraction of DBT

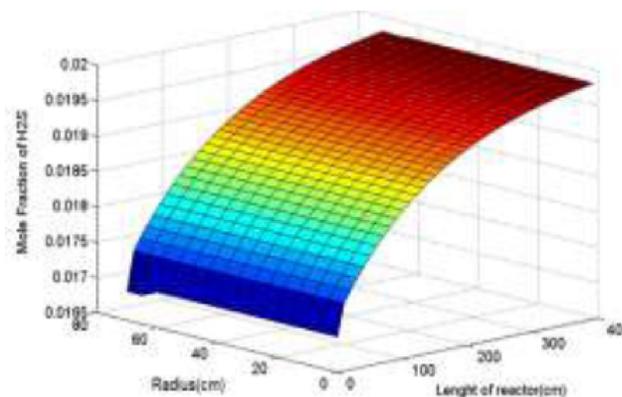


Figure 2 : Mole fraction of H2S

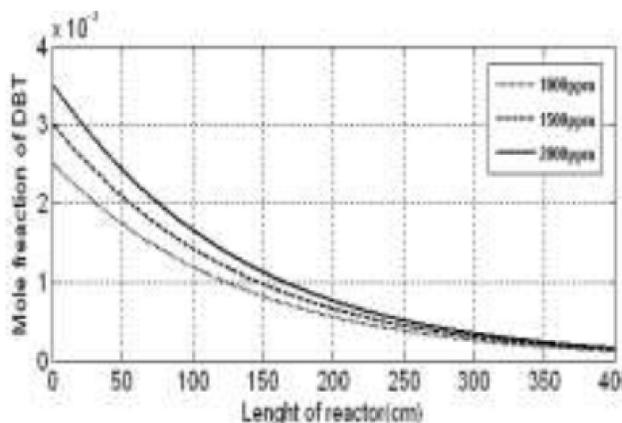


Figure 3 : Mole fraction of DBT along the reactor length in three concentration of DBT

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are DBT, but the feed of the industrial reactor contains few concentration of DBT and consist of other sulfur components that are very reactive related to DBT.

### Two dimensional simulation

Two dimensional profiles of the predicted mole fraction of DBT and  $H_2S$  are shown in Figures 1 and 2. These figures indicate that we can neglect from changes in radial direction in comparison with changes in axial direction. Therefore, we can consider industrial reactor one dimensional.

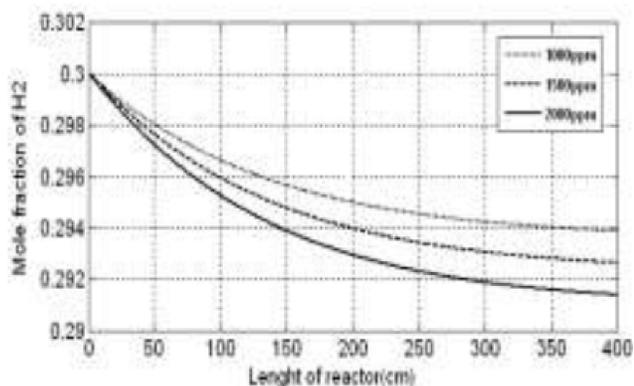


Figure 4 : Mole fraction of  $H_2$  along the reactor length in three concentration of DBT

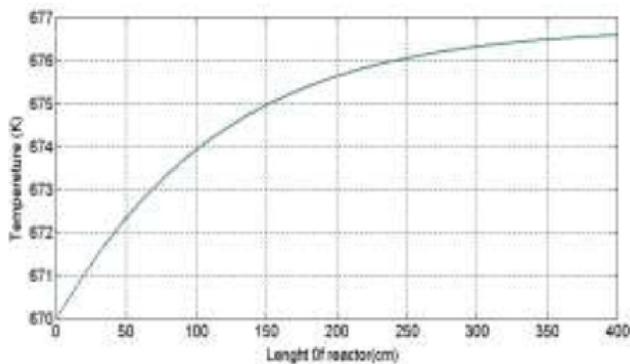


Figure 5 : Temperature along the reactor length

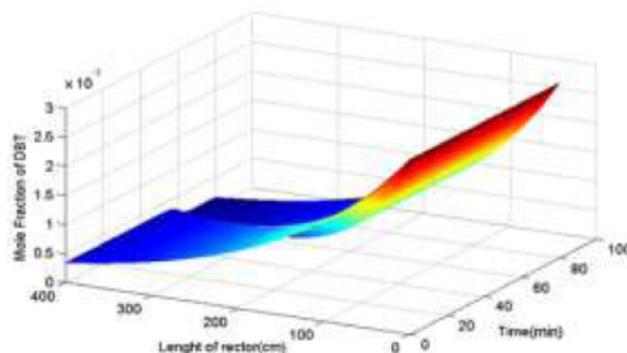


Figure 6 : Dynamic DBT profile along the reactor for  $10^\circ C$  step change in the inlet temperature

### One dimensional simulation

In this section, one dimensional steady state simulation results of DME reactor have been presented. Figures 3 and 4 illustrate the mole fraction of DBT and  $H_2$  along the reactor length in three concentration of DBT.

Also Figure 5 shows the temperature profile. temperature increases along the reactor due to heat generation by reaction.

### Dynamic simulation

To investigate the influence of disturbances on the dynamic behavior of HDS reactor, the feed temperature and composition have been considered as the main probable effective loads of the system.

Figure 6 indicates the step response of the system to  $10^\circ C$  increase in the feed temperature. In Figure 6,

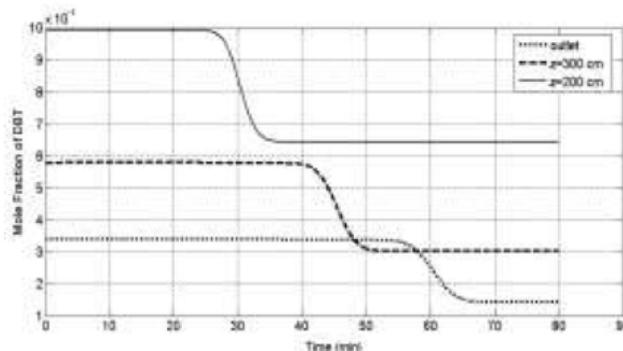


Figure 7 : The mole fraction of DBT at three height of reactor for  $10^\circ C$  step change in the inlet temperature

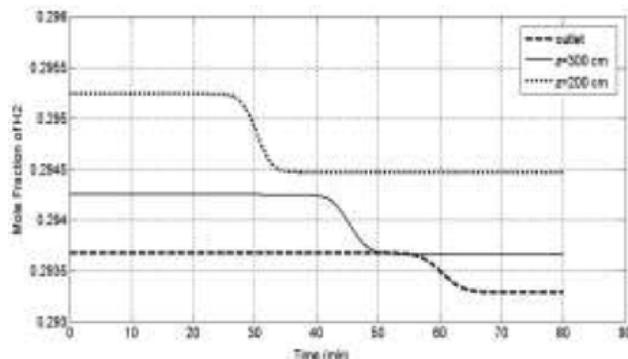


Figure 8 : The mole fraction of  $H_2$  at three height of reactor for  $10^\circ C$  step change in the inlet temperature

dynamic variation of the mole fraction of DBT along the reactor length has been illustrated in a three-dimensional diagram. As shown in Figures 7 and 8 the response of the outlet mole fraction of DBT and  $H_2$  for this disturbance has a time delay about 58s, and they

reach to the new steady state point in 68 s.

The feed composition effect was studied by applying 0.05 step change in mole fraction of DBT. Figures 9 and 10 represent dynamic responses of the  $H_2$  mole fraction and reactor temperature profiles along the reactor, respectively.

The response of the reactor temperature to the step change in composition at three height of reactor is shown in Figure 11.

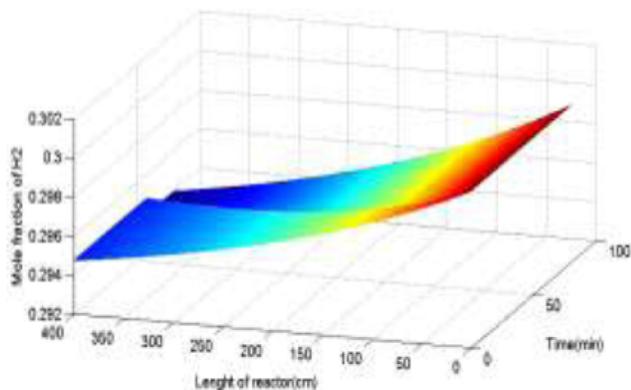


Figure 9 : Dynamic mole fraction profile for 0.05 step change in the DBT mole fraction of inlet stream

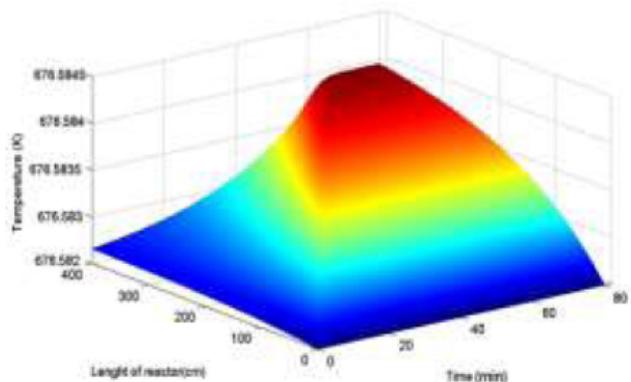


Figure 10 : Dynamic temperature profile for 0.05 step change in the DBT mole fraction of inlet stream

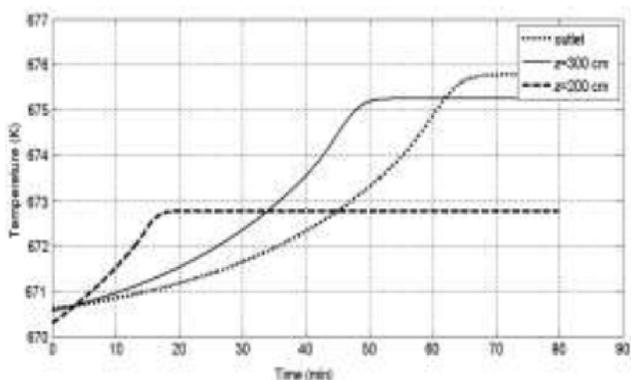


Figure 11 : The temperature profile for 0.05 step change in the DBT mole fraction of inlet stream at three high of reactor

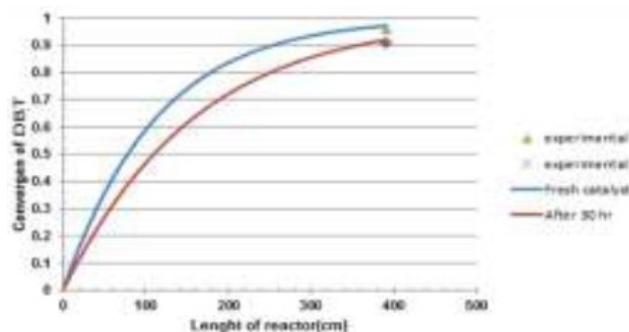


Figure 12 : Conversion of DBT along the reactor for fresh catalyst and after 30 hr

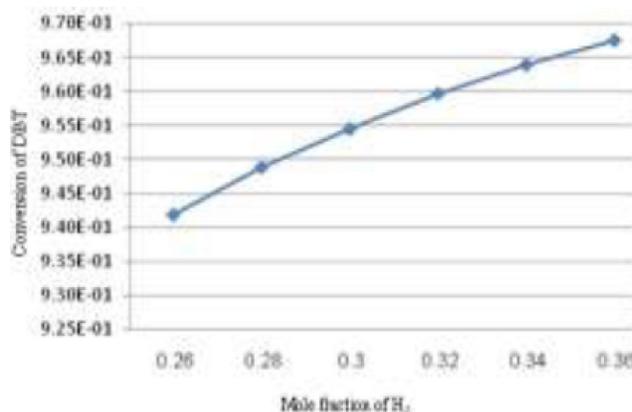


Figure 13 : Effect of inlet mole fraction of  $H_2$  on conversion of DBT

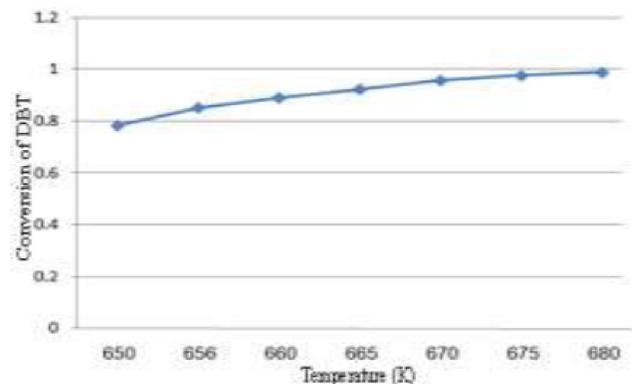


Figure 14 : Effect of inlet temperature on conversion of DBT

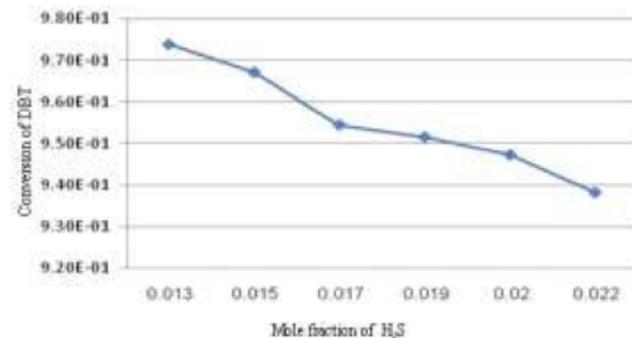


Figure 15 : Effect of inlet mole fraction of  $H_2S$  on conversion of DBT

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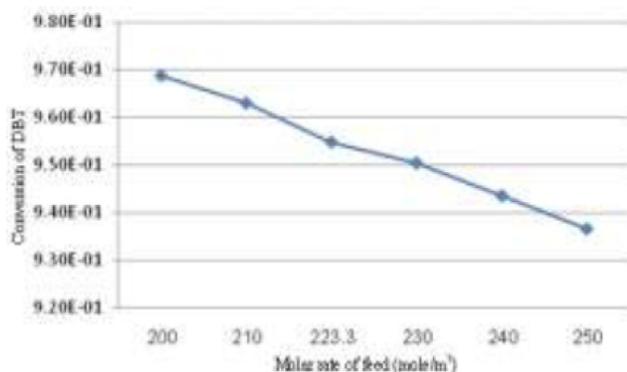


Figure 16 : Effect of inlet molar rate on conversion of DBT

### Effect of catalyst deactivation

As mentioned in the modeling section, the catalyst deactivation is included in the model because of coke formation on catalyst surface in high temperature. Figure 12 shows the effect of deactivation of catalyst (experimental data from<sup>[6]</sup>).

### Sensitivity analysis

A sensitivity analysis has been carried out to evaluate the influence of several parameters on the process. Figures 13 and 14 show the effect of mole fraction of  $H_2$  and temperature. As it is evident from these figures, with increment in temperature and mole fraction of  $H_2$ , conversion of DBT increase.

Also figures 15 and 16 show that with increase of mole fraction of  $H_2S$  and rate of feed, conversion of DBT decrease.

The impact of the main operational variables on the reactor performance can be summarized as follows: to improve DBT conversion several procedures can be chosen: increase temperature, increase mole fraction of  $H_2$ , decrease rate of feed and decrease mole fraction of  $H_2S$ .

## CONCLUSION

In this study, an industrial HDS reactor has been simulated in steady and unsteady state conditions. The reactor mathematical formulation is based on a two-dimensional heterogeneous model. The comparison of the simulation results and the industrial data show that the proposed model can predict the reactor outlet temperature and concentration of sulfur component with relative errors less than 4%. Some important distur-

bance such as inlet reactor temperature and feed composition have been applied to the process for investigating its dynamic behavior. Results of simulation showed that conversion decreased from 0.9548 to 0.923 with increase in concentration of sulfur in the feed of reactor from 1500 ppm to 2000 ppm. In this study, the equation that proposed by Fatemi et al, is used for intrinsic activity as a function of time and at high temperature conversion decreased from 0.9548 to 0.91 because of coke formation on catalyst. A sensitivity analysis showed that increase temperature, mole fraction of  $H_2$  increase, decreases the rate of feed and lowers the mole fraction of  $H_2S$ , improve conversion of sulfur component.

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