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A MATHEMATICAL MODEL FOR CALCULATION OF EFFECTIVENESS FACTOR IN CATALYST PELLETS OF HYDROTREATING PROCESS

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Abstract

Sulfur compounds are one of the most important impurities in various petroleum fractions that cause some problems. For example, in the case of fuels they cause environmental pollution, and in the refining and petrochemical industries they poison catalysts. One of the recent challenges in the petroleum refineries is the reduction of sulfur content of gas oil to the new lower limits. The specification for the sulfur content of gas oil has been reduced from 500 ppm to 50 ppm in 2005.

This purpose can be achieved by hydrodesulfurization process (HDS) in trickle bed reactors as specific multiphase reactors.

In the most of trickle bed reactors, reactions are carried out on the surface and within the pores of cobalt molybdom over alumina support ($CoMo/Al_2O_3$).

Catalyst.[1]

In this work a mathematical model for the effectiveness factor of HDS catalyst has been developed, based on the mass balance equations inside the catalyst pellet to gather with a kinetic model for dibenzothiophene as representative of sulfur component of gas oil.

Also, for solution non-linear algebraic equations in catalyst pellets has been used orthogonal collocation method and modified Powel dogleg numeric methods.

Key words: mathematical model; multiphase reactors; kinetics; gas oil; hydrotreating; orthogonal collocation

Introduction

Hydrodesulfurization process is carried out in a trickle bed reactor. The sulfur containing components are converted to H_2S and hydrocarbons in presence of hydrogen on solid catalyst.

Sulfur exists in gas oil in different forms such as: mercaptan (R-SH), disulfide(R-S-S-R´) , polysulfide($R-S_n-R'$), thiophen , benzothiofene(BT), dibenzothiophen(DBT) and it's alkyl derivatives.

With pay attentions to in deep desulfurization from gas oil, sulfur content in thiophen ring must be separated; therefore in this project kinetic modeling and calculation of effectiveness factor in gas oil has been carried out for dibenzothiophen (DBT) compound.

There have been reported many works on hydrodesulfurization. Song[2] reviewed both catalyst and process of desulfurization of fuels. Korsten and Hoffman[5] made a model for desulfurization of vacuum gas oil in a trickle bed reactor .The simulation results showed good agreement with experimental data over a wide range of temperature, pressure, space velocity and gas /oil ratio. They used Langmuir –Hinshelwood kinetics for rate equations.

In hydrodesulfurization process is used from catalysts such as: Co, Ni, Fe, Mo and W over alumina supports.

If main purpose be decrease of nitrogen uses from nickel molybdom over alumina support ($NiMo/Al_2O_3$), and if main purpose be decreases of sulfur compounds that's more effective uses from cobalt molybdom over alumina support ($CoMo/Al_2O_3$).

Mathematical modeling:

Hydrodesulfurization of oil fractions is carried out in a multiphase reactor. There is three phase in reactor: Fixed bed of porous catalyst particles, a gas phase and a liquid phase; both streams are cocurrent down flow.

In this paper we assume gas phase be hydrogen (H_2) compound and hydrogen sulfide (H_2S) *and* liquid phase be gasoil,contain sulfuric compounds of dibenzothiophene (*DBT)* and solution gases of hydrogen and hydrogen sulfide and solid phase be catalyst of cobalt molybdenum over alumina support (*CoMo/* Al_2O_3).Gas phase is continuous phase and liquid phase is dispersed ,where its stream on the particles is to laminar form .

Our model is a heterogeneous with two phases, where the liquid phase stream on the surface of catalyst[3].

The component that take part in catalytic reactions are enumerated as follows:

1) H_2 (*hydrogen)*
2) H_2S (*hydrogen sulfide*)
3) $C_{12}H_8S$ (*Dibenzothiophene,DBT*)
4) $C_{12}H_{10}$ (*Biphenyl*, *BPH*)
5) $C_{12}H_{16}$ (*Cyclohexyl benzene*, *CHB)*
6) $C_{12}H_{22}$ (*Bicyclohexyl*, *BCH)*

The corresponding chemical reactions are as follows:

1) $DBT + H_2 \longrightarrow BPH + H_2S \ (\sigma\text{ - Site})$ (1)
2) $DBT + 4\,H_2 \longrightarrow CHB + H_2S \ (\tau\text{ – Site})$ (2)
3) $BPH + 3\,H_2 \longrightarrow CHB \ (\tau\text{ – Site})$ (3)
4) $CHB + 3\,H_2 \longrightarrow BCH \ (\tau\text{ – Site})$ (4)

The above reactions constitutes a network that its schematics representation is shown below

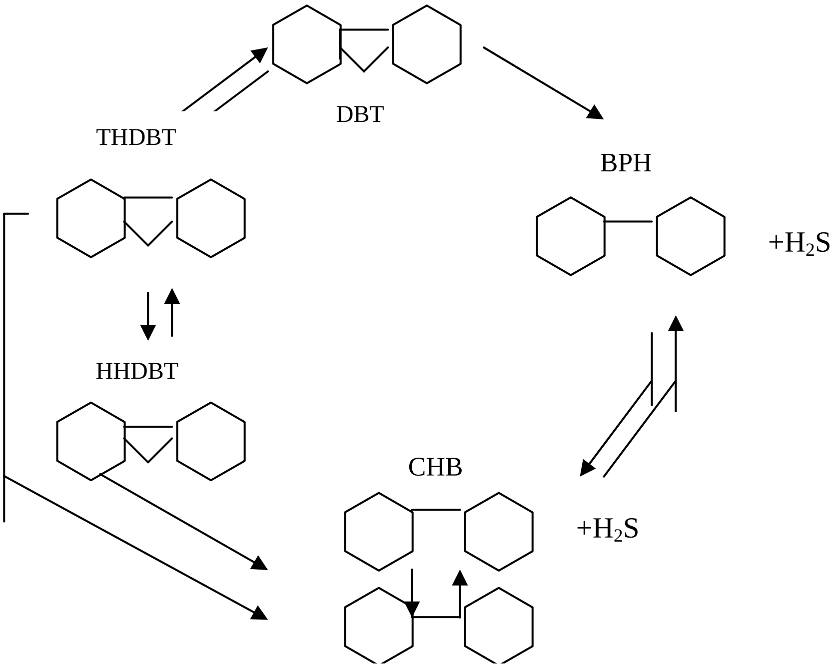

Fig 1. Reactions network for HDS of DBT

Based on recent studies of G.F.Froment et.all.[4], DBT reactions network divide to two sections: Hydrogenation and Hydrogenolysis; this ractions are accomplished on two active site of catalyst: σ - site for hydrogenolysis and τ - site for Hydrogenation.

Rate equations for DBT on the σ , τ sites and for BPH, CHB on the τ - site is written as follows:

$$r_{DBT,\sigma}=\frac{k_{DBT,\sigma}K_{H,\sigma}K_{DBT,\sigma}C_{DBT}C_{H_2}}{(1+K_{DBT,\sigma}C_{DBT}+\sqrt{K_{H,\sigma}C_{H_2}}+K_{BPH,\sigma}C_{BPH}+K_{H_2S,\sigma}C_{H_2S})^3} \qquad (5)$$

$$r_{DBT,\tau}=\frac{k_{DBT,\tau}K_{H,\tau}K_{DBT,\tau}C_{DBT}C_{H_2}}{(1+K_{DBT,\tau}C_{DBT}+\sqrt{K_{H,\tau}C_{H_2}}+K_{BPH,\tau}C_{BPH})^3} \qquad (6)$$

$$r_{BPH,\tau}=\frac{K_{BPH,\tau}K_{H,\tau}K_{BPH,\tau}C_{BPH}C_{H_2}}{(1+K_{DBT,\tau}C_{DBT}+\sqrt{K_{H,\tau}C_{H_2}}+K_{BPH,\tau}C_{BPH})^3} \qquad (7)$$

$$r_{CHB,\tau}=\frac{k_{BPH,\tau}K_{H,\tau}K_{CHB,\tau}C_{CHB}C_{H_2}}{(1+K_{DBT,\tau}C_{DBT}+\sqrt{K_{H,\tau}C_{H_2}}+K_{BPH,\tau}C_{BPH})^3} \qquad (8)$$

Mass -balance equations inside catalyst:

In the formulating the mass-conservation equations, the following assumptions have:

1. The catalyst is operating in steady state.
2. Chemical reactions only take place at the catalyst, and not in the gas or in the liquid phase.
3. Wetting efficiency of 100 percent is assumed.
4. Temperature differences have not existed inter the pores of catalyst.
5. Catalyst activity does not change with time

$$\frac{D_e}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{C_i^s}{\partial r}\right)=-\rho_c\sum_{m=1}^{NR}\upsilon_{im}r_m(C_i^s,\ldots,C_5^s,T_L) \qquad i=1,2,\ldots,6 \qquad (9)$$

B.C: $r=R$ $C_i^s=C_i^l$ *i = components number* (10)

$r=0$ $\frac{\partial c_i^s}{\partial r}=0$ *m = Reaction number*

C_i^l =component i concentrationon the catalyst surface

Effectiveness factor calculation:

With specification of concentration profiles we could calculate effectiveness factor for every reaction by the following equation:

$$\eta_m=\frac{3\int_0^{RC} r^2 r_m(C_1^s,\ldots C_5^s\ ,T_L)dr}{R_c^3 r_m(C_1^s,\ldots,C_5^s,\ T_L)} \qquad (11)$$

Where in its R_c is radius of catalysts.

Method used for physical property estimation:[5]

1. Molecular diffusivity

The diffusivity can be estimated by a Tyn-Calus correlation [6].

$$D_i^L=8.93.10^{-8}.\frac{\upsilon_L^{0.267}}{\upsilon_i^{0.433}}.\frac{T}{\mu_L} \qquad (12)$$

Where T is the temperature in °K and μ_l represents the viscosity of the solvent in mPa.s . By using Eq.10 we obtain the diffusivity in cm^2/s.

The molar volume of solute, or liquid solvent at its normal boiling temperature can be estimated by:

$$\upsilon_L\ ,\upsilon_i\ =\ 0285.V_C^{1.048} \qquad ,\ \upsilon_c\ (cm^3/gmol)$$

2. Viscosity:

The gas oil viscosity can be calculated by following equations:

$$\mu=3.141.\ 10^{10}.(T-460)^{-3.444}.[\log_{10}(API)]^{a} \tag{13}$$

$$\alpha=10.313.\ [\log_{10}(T-460)]-36.447 \tag{14}$$

With temperature T in °R and calculate API from following reaction represents viscosity in mPa.s.

$$API=\frac{141.5}{SP.Gr\frac{60}{60}}-131.5 \tag{15}$$

Solution algorithm for model equations:

The integration of differential equations in catalyst radius (*0<r<R*) has been used from approximate method that is called orthogonal collocation method. In orthogonal collocation method the solution is approximated with polynomial with an arbitrary degree.

The choice of degree is very important in achieving a particular accuracy. Choosing large polynomial degree leads to more accurate solution. We choose polynomial coefficient so that mass balance equations satisfied in choose interior point of catalyst radius domain. Usually, this n interior point is chosen as roots of the orthogonal polynomial (collocation point).

Of curse, increase of n leads to: large matrix dimensions, increase of calculation error from floating point arithmetic and increase s of time.

Therefore, the (n+1) interpolation points are chosen with the first n points being interior collocation points in the catalyst particle and the

(n+1)th interpolation point being the boundary point .

More details can be found in references [7,8]. Here, we choose 7-collocation points (n=7), which based on previous experience and our information for similar problems.

Satisfying conditions of equations in collocation points:

We make dimensionless the eq.(10) by introducing the dimensionless length as (*r*= r/R*)

$$\frac{1}{r*^2}\frac{\partial}{\partial r^*}(r^{*2}\frac{\partial C_i^s}{\partial r^*})=-y\sum_{m=1}^{NR}\upsilon_{im}r_m(C_1^s,...C_5^s,T_L) \tag{16}$$

Where ;

$$y=\frac{R^2\rho_C}{D_e} \qquad ,\ D_e=\frac{D_i\varepsilon}{\tau} \qquad ,\ 0<r^*<1$$

ε = Internal catalyst pore τ = 1.4 turtosity factor **[9]**

Using orthogonal collocation method, the first and second derivatives of C_i^s can be expandes as a linear combination of concentration in collocation points.

$$\sum_{K=1}^{NP+1} B_{jk} C_i(r_k^*) = -y \sum_{m=1}^{NR} \upsilon_{im} r_m (C_1^s, ..., C_5^s, T_L) \tag{17}$$

$$\sum_{K=1}^{NP} B_{jk} C_i(r_k^*) + B_{jNP+1} C_i(r_{NP+1}^*) = -y \sum_{m=1}^{NR} \upsilon_{im} r_m (C_1^s, ..., C_5^s, T_L) \tag{18}$$

Using the boundary conditions (10) we will have:

$$\sum_{K=1}^{NP} B_{jk} C_i(r_k *) + B_{j,NP+1} C_{iL} = -y \sum_{m=1}^{NR} \upsilon_{im} r_m (\overline{C}(rj), T_L) \tag{19}$$

$j = 1,2,..., NP$ *Collocation point numbers*

$i = 1,2,..., NC$ *Component numbers*

Above equations (18) show one set of non-linear algebraic equations. (non-linear phrases arise from nonlinear velocity of HDS reactions.)

Using Neqlu subroutine in Fortran language, we solve these nonlinear equations. (This program has been prepared based on Powel-Dogleg method).

For this purpose $C_i(r_k)$ which are unknown, are settled to in a one dimensional variable vector ; that this is showed with following equation:

$$C_i(r_k) \equiv X(I + NC(K-1)) \tag{20}$$

$i = 1,2,...,6$ *Component numbers*

$k = 2,3,..., NP - 1$ *Collocation point numbers*

NC = compound number

Also, above equations are showed with a one dimensional vector function as following form:

$$F(I + NC(K-1)) = \sum_{k=1}^{NP} B_{jk} X\left(I + NC(K-1) \right) + B_{j,NP+1} C_{iL} + y \sum_{m=1}^{NR} \upsilon_{im} r_m \left(\overline{C}(rj), T_L \right) = 0 \tag{21}$$

After solution of this equation and specification of concentrations inter catalyst point, we can calculate effectiveness factor, with used of Quadrature method[8].

$$\eta_m = \frac{3}{r_m(\overline{c}_s)} \sum_{j=1}^{NP+1} W_j r_m \left(\overline{C}_s(r_j) \right)$$

Results

This model prepared in Fortran 77 languages and has different abilities. there are:

1- Calculation of effectiveness factor in catalyst pellets.

2-Calculation of concentration profile for each of components and reaction compounds in catalyst radius.

3- Investigation of effects different catalysts on hydrodesulfurization process in a trickle bed reactor.

4- Effects of catalyst shape and its physical properties on hydrodesulfurization . Fig (1)-(7) show parts of foresights mathematical model and table (1) show that parts of catalyst physical property.

In Fig (1) is showed concentration profile of H_2 (hydrogen) in catalyst radius from catalyst surface to inside it's.

We observed that hydrogen concentration reduced from catalyst surface to inside it. Also it's observed that H_2S concentration increases by moving to inside catalyst and DBT concentration is reduced. Concentration profiles of BPH, CHB, BCH from catalyst surface to inside it, have been showed in figures (3), (4), (5). It is seen that BCH Concentration profile increases and so BPH and CHB Concentration profile decreases from catalyst surface to inside it.

In Fig(6) temperature effects upon effectiveness factor has been showed; . As it can be seen effect of reactor temperature on effectiveness factor was studied at the temperature range of 350-400°C. It can be seen that the effectiveness factor decreases with increasing temperature. Effects of radius catalyst on effectiveness factor are presented in Fig (7) and it's observed with increases of radius catalyst effectiveness factor is reduced.

In industry, the decline in the effectiveness factor with time is often compensated by an increase in the reaction temperature. Also the optimum reactor performance could be obtained by selecting a catalyst size, which will give the best average effectiveness factor for the sulfur removal reaction over the period of operation.

This work shows that effectiveness factor is an important tool for modeling of catalytic reactions kinetics.

Table(1) . Catalyst geometrical properties

Catalyst diameter	Bed void fraction	Catalyst void fraction	Catalyst density
0.13(m)	0.5(m_f^3/m_r^3)	0.6($m^3{}_f/m_p^3$)	1420(kg/m^3)

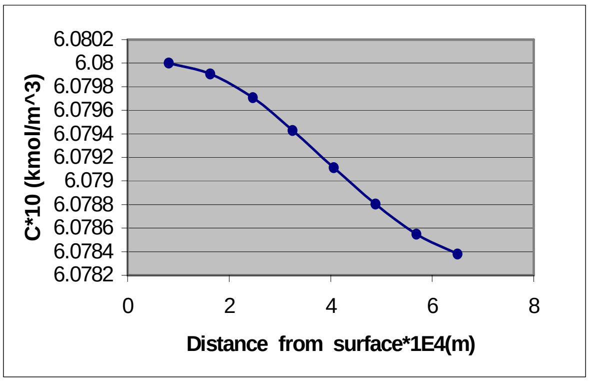

Fig 1. H_2 Concentration profiles inter catalyst pore

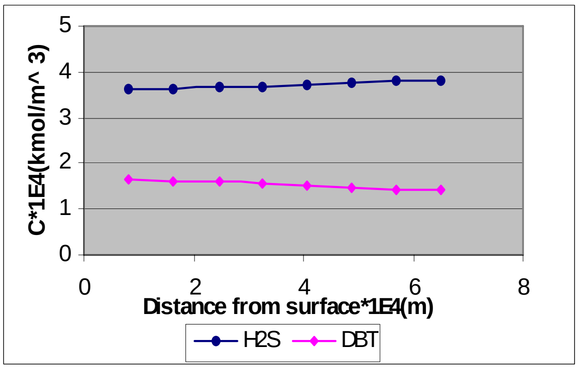

Fig 2. H_2S,DBT Concentration profiles inter catalyst pore

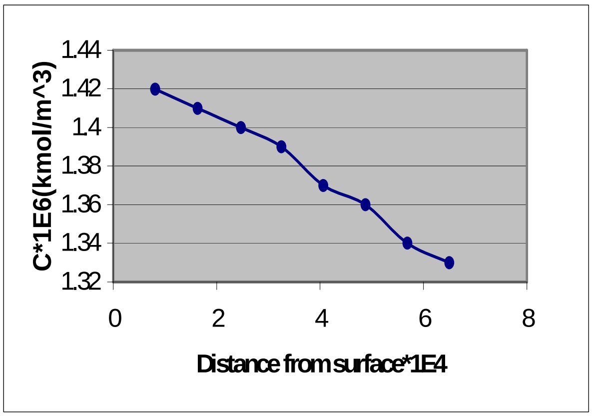

Fig 3. BPH Concentration profiles inter catalyst pore

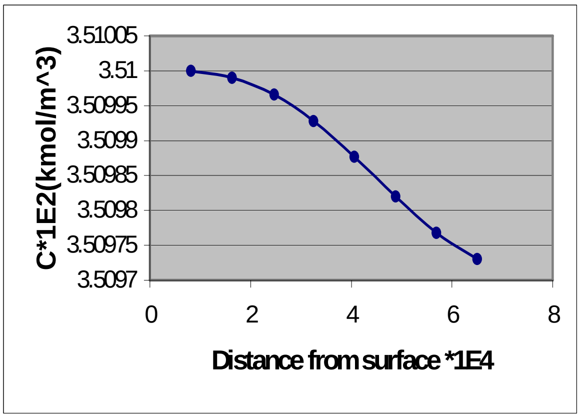

Fig 4. CHB Concentration profiles inter catalyst pore

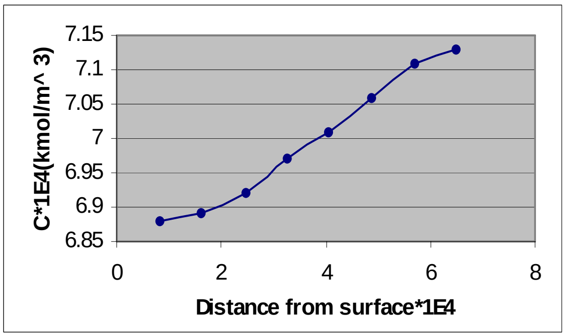	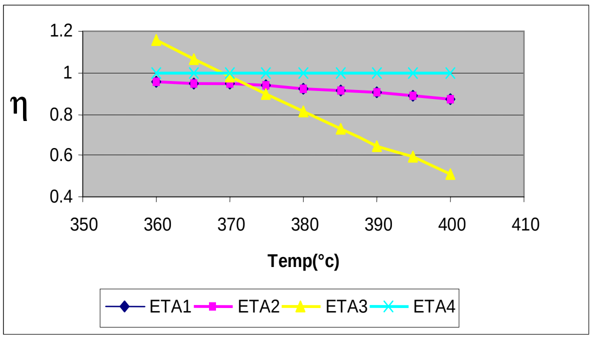
Fig 5. BCH Concentration profiles inter catalyst pore	Fig 6. Temperature profile effect on the effectiveness factor

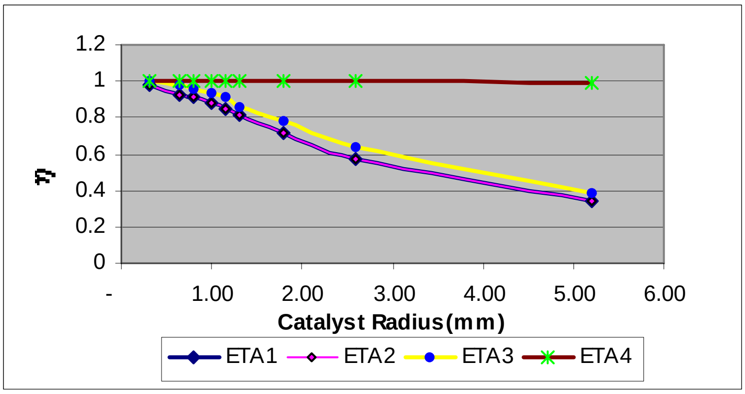

Fig 7. Radius differences effect on the effectiveness factor

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