HETEROGENEOUS MODELING OF AN ADIABATIC PACKED BED REACTOR WITH CATALYST DECAY. INTRAPARTICLE DIFFUSION EFFECTS

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INTRODUCTION

Reactor models for catalytic reactions overlaid with transport restrictions and with catalyst deactivation are still not completely developed. The interrelation between internal diffusion and deactivation in a catalytic pellet was previously examined [1,2].

In the present work, an algorithm for simulation of an adiabatic fixed bed reactor subjected to catalyst deactivation by poisoning is developed applying the heterogeneous model. An irreversible first order reaction is considered for modeling purposes. The integral packed bed reactor is nodalized by N state equations corresponding to the N differential continuous stirred tank reactors into which the whole reactor is divided. For each differential reactor the energy and mass balances are solved and the concentration value at the center of the catalyst pellet is found using the shooting technique.

MATHEMATICAL MODEL

For an adiabatic fixed bed reactor and considering the one dimensional heterogeneous model nodalized as a series of differential CSTR's, the dimensionless mass balances for the main reactant and poison at the jth reactor are:

$$(C_{ij} - C_{oj}) = N_j \, av \frac{V_j}{Q} \tag{1}$$

$$(Cp_{ij} - Cp_{oj}) = Np_j \, av \frac{V_j}{Q} \tag{2}$$

and the dimensionless energy balance is:

$$T_{oj} = T_{ij} + \beta \, (C_{ij} - C_{oj}) \tag{3}$$

In equation (3) it was assumed that the only contribution to the temperature rise is given by the main reaction, since the poison is highly diluted in the feed.

On the other hand, for an isothermal, cylindrical catalyst pellet with constant properties and ignoring the external diffusional effects, the mass conservation equations for the reactant and poison are:

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\xi}{dr}\right) = \phi^2 a_P(r,t) \exp\left[\gamma_1 \frac{(T-1)}{T}\right] \xi \tag{4}$$

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\xi_P}{dr}\right) = \phi_P^2 a_P(r,t) \exp\left[\gamma_{P2} \frac{(T-1)}{T}\right] \xi_P \tag{5}$$

An irreversible first order reaction is assumed for the main reaction, like :

$$r_m = k_0 \exp\left[-\frac{\gamma_1}{T}\right] \xi \, a_P(r,t) = k \, \xi(r,t) \, a_p(r,t) \tag{6}$$

while a kinetic expression such as:

$$r_p = k_{20} \exp\left[-\frac{\gamma_{P2}}{T}\right] \xi_P\, a_P(r,t) = k_2\ \xi_p(r,t)\, a_p(r,t) \tag{7}$$

is considered for the poison.

The boundary conditions for equations (4) and (5) are:

$$\text{at } r=0,\ d\xi / dr = 0 \qquad \text{and} \qquad d\xi p / dr = 0 \tag{8}$$

at r=1 :

$$(C_{ij} - C_{oj}) = \frac{\text{Deff av } V_j}{\text{Rp Q}} \left(\frac{\partial \xi}{\partial r}\right) \tag{9}$$

$$(Cp_{ij} - Cp_{oj}) = \frac{\text{Dpeff av } V_j}{\text{Rp Q}} \left(\frac{\partial \xi_P}{\partial r}\right) \tag{10}$$

where:

$$N_j = \frac{\text{Deff}}{\text{Rp}} \left(\frac{\partial \xi}{\partial r}\right) \tag{11}$$

$$Np_j = \frac{\text{Dpeff}}{\text{Rp}} \left(\frac{\partial \xi_P}{\partial r}\right) \tag{12}$$

The deactivation rate into the pellet is given by:

$$\frac{da_P(r,t)}{dt} = -k_{10} \exp\left[-\frac{\gamma_{P1}}{T}\right] \xi_P\ a_P(r,t) = -k_1\, \xi_P\, a_P(r,t) \tag{13}$$

The system of equations (1)-(13) is solved assuming a quasi-steady state for the reactant and poison profiles into the pellet because the deactivation rate is relatively slow.
Beginning from t=0 and j=1 (the first CSTR), the reactant and poison profiles into the pellet are found using the shooting technique. The pellet is deactivated a given period of time and the procedure is repeated until the final operating time of the reactor is achieved. The same method is applied to the other differential reactors.

RESULTS

The plots shown in Figures 1 to 6 were obtained for the following reactor inlet conditions: T^0 = 503 K, C^0 = 8.5 mol / m^3, $C^0{}_p$ = 8.3 10^{-9} mol / m^3. Feed rate, reactor volume and specific area of the bed are Q = 1.13 m^3 / sec, V = 14 m^3 and av = 950 m^2 / m^3 respectively. The reaction enthalpy is ΔH = -41190 J / mol. The specific heat and density of the feed mixture are, Cpg = 2576 J / Kg °C and ρ_g = 8.46 Kg / m^3.
The parameters of the pellet are: R_p = 0.0022 m ; Deff = 4.3 10^{-7} m^2 / sec; Dpeff = 6 10^{-6} m^2 / sec.

In figures 1 to 3 the evolution of the profiles of reactant, poison and activity into the pellet is presented for poison and reactant Thiele modulus values such that strong diffusional effects exist. It can be seen that, at t = 0 , the reactant and poison profiles are pronounced and became flatter along the time. Consequently, at short operating time the activity is almost nulle in the pellet surface and remain high toward the center.
The evolution of the poison and activity profiles along the fixed bed reactor is shown in figures 4 and 5. It is observed that, in agreement with the highly diffusional effects achieved into the pellet, the reactor is deactivated as a plug flow. This effect is frequently observed in industrial reactors; for instance in the case of CO converters [4].
Finally, reactant profiles along the reactor for two different poison Thiele modulus are presented in figure 6. It can be appreciated that as higher the poison Thiele modulus, higher is the fixed bed life.

CONCLUSIONS

The simulation of a fixed bed undergoing catalyst deactivation by poisoning was presented by means of the heterogeneous one-dimensional model. The parameter values of the model and the operating conditions were chosen such that relatively high diffusional effects appeared into the pellet for the poison as well as for the main reactant.
Activity and concentration profiles into the pellet and along the reactor and their evolution with the operating time are presented. The effect of the reaction rate of the poison is examined. It is proved that the performance of the reactor and the life of the catalyst improve when diffusional resistance for the poison increases.

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NOTATION

a_P : activity by poison.
av : specific area of the catalytic bed
C : dimensionless reactant concentration (bed)
C_P : dimensionless poison concentration (bed)
Cpg : specific heat of the mixture
Deff : effective diffusion of the reactant.
Dpeff : effective diffusion of the poison
k : kinetic coeff. of the main reaction
k_1 : kinetic coeff. of the deactivation rate
k_2 : kinetic coeff. of the poison reaction
N : reactive flux toward the pellet
Np : poison flux toward the pellet
Q : volumetric flow rate
r_m : main reaction velocity
r : dimensionless radial position into the pellet
r_P : poison reaction velocity
R_p : Pellet radius
T : dimensionless temperature
t : time
V : reactor volume
z : dimensionless axial position

Greek Symbols

ϕ_P^2 : $R^2\, r_P^S$ / Dpeff ξ_P^S
ϕ^2 : $R^2\, r_m^S$ / Deff ξ^S
γ_{P1} : dimensionless activation energy, eq.(13)
γ_1 : dimensionless activation energy, eq. (6)
γ_{p2} : dimensionless activation energy, eq. (7)
ξ : dimensionless reactant concentration into the pellet
ξ_P : dimensionless poison concentration into the pellet
ΔH : enthalpy of reaction
ρ_g : feed density
β : $(-\Delta H)\, C^0 / \rho_g$ Cpg T^0

Superscripts

S : pellet surface value
0 : conditions at the bed entrance

Subscripts

i : differential reactor inlet value
j : differential reactor number
o : differential reactor outlet value

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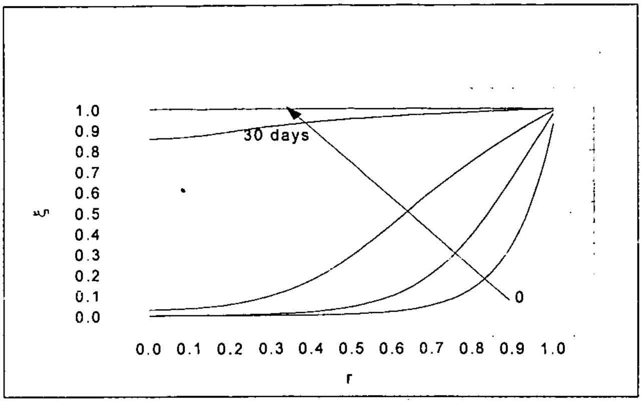

Figure 1 : Main reactant profile into the catalyst. First CSTR, $\phi = 10$, $\phi_P = 6$, $k_1 = 0.2$ 1 / h

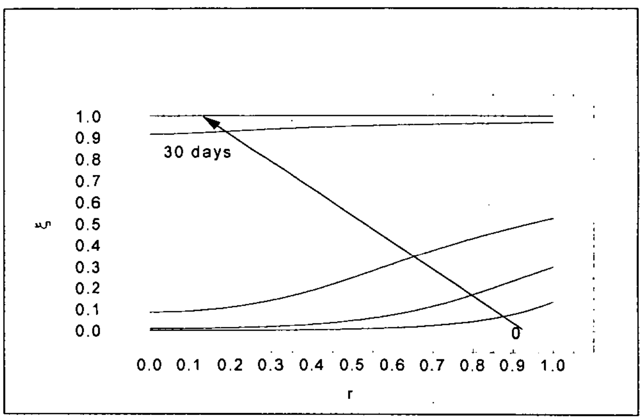

Figure 2: Poison profile into the catalyst. First CSTR, $\phi = 10$, $\phi_P = 6$, $k_1 = 0.2$ 1 / h

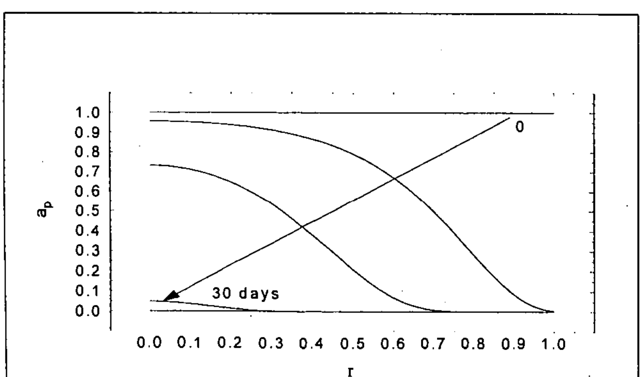

Figure 3 : Activity by poison into the catalyst. First CSRT, $\phi = 10$, $\phi_P = 6$, $k_1 = 0.2$ 1 / h

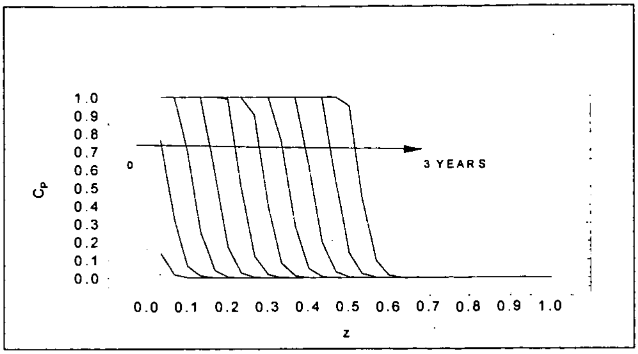

Figure 4: Dimensionless poison concentration vs. axial position. $\phi_P = 6$, $k_I = 0.2$ 1 / h

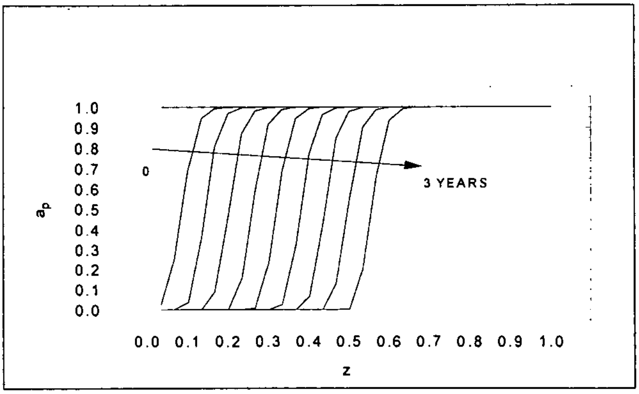

Figure 5: Activity by poison vs. axial position. $\phi_P = 6$, $k_I = 0.2$ 1 / h

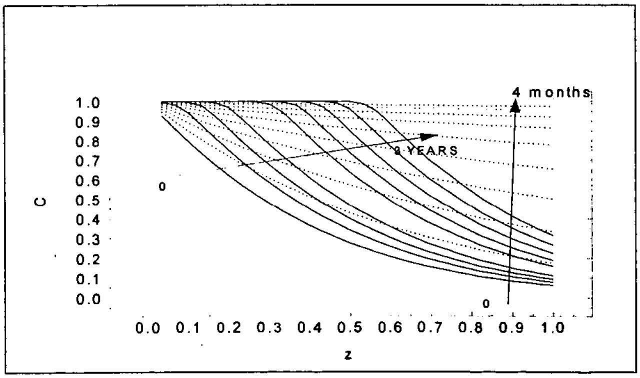

Figure 6: Main reactant profile vs. axial position. Solid line: $\phi = 10$, $\phi_P = 6$; Dots line: $\phi = 10$, $\phi_P = 3\ 10^{-2}$.