Fixed-Bed Reactor Modeling and Simulation with e-Learning Tools

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Abstract - **Fixed-bed reactors (FBR) are largely used in industrial catalytic processes requiring a careful understanding at the undergraduate level of Chemical Engineering. Several mathematical models are available to represent the behavior of such heterogeneous systems with various degrees of complexity, including different transfer mechanisms at the fluid level or inside the catalyst particles. This will permit the application of the fundamental concepts of the transport mechanisms previously learned by the students in the first years of the course. One-dimension and two dimension models with or without dispersion effects in the axial and radial directions may lead to transient and steady state models, while the heterogeneity of the system can be simplified by assuming a pseudo-homogeneous behavior, which neglects inter and intraparticle resistances. Regarding the most complete heterogeneous models accounting for external and internal mass and thermal gradients, the behavior of the catalyst particles is fundamental to follow the multiscale characteristics of such systems. This, is in agreement with the "New Frontiers in Chemical Engineering Education" that claim systems teaching embracing the understanding of the physical and chemical phenomena in a broad scale. In this context, several intraparticle models including diffusional and convective transports can be developed and integrated in the global model of the fixed bed reactor. The different mathematical models are represented by partial or ordinary differential equations associated to algebraic expressions, requiring numerical solutions through various computational codes. Therefore, the great interest associated to the teaching of these industrial systems is frequently inhibited by their complexity, so that modern tools based on e-learning methodologies will be much welcome. In this context, the global objective of the present work addresses the construction of a platform for visualizing the general behavior of fixed-beds involving reactants and products profiles and thermal gradients as well.**

Index Terms - Chemical Processes, E-learning, Fixed-bed reactors, Modeling.

INTRODUCTION

The industrial chemical processes convert raw materials in products, and the reactor is often considered as the "heart" of the plant. The selection and design of the reaction units are essential for the economic success of a chemical industry, imposing final yields and conversions. The Chemical Reaction Engineering is then an area of Chemical Engineering with a significant role, and our main goal focus on the development of e-learning tools in the domain of heterogeneous processes, specifically fixed-bed reactors (FBR). This work addresses catalytic reactional systems with particular emphasis in fixed-bed reactors that are largely used in industry. These processes may be studied through diverse mathematical models: pseudo-homogeneous and heterogeneous models in steady state or transient regimes [1-3]. For real systems, in general, no analytical solutions are available, and different numerical techniques are required for computational simulation. The ordinary differential equations, ODEs, and/or partial differential equations, PDES, may be solved by using various commercial Fortran codes: GEAR, PDECOL, FORSIM, DDASAC, DASSL.

The analysis of the behavior of FBR is proposed in the e-learning platform in two levels:

- general analysis through different mathematic models, including the catalyst particle and the film resistances;

- two case studies involving the synthesis of phthalic anhydride and formaldehyde through partial oxidation of ortho-xylene and methanol, respectively.

In particular, the operation of these systems highlights the thermal instabilities that are possible to occur in such exothermic processes, namely temperature runaway and wrong way behavior, relevant for safety. The virtual platform allows the students to understand the effect of different operating conditions on the FBR behavior. Also, some complex theoretical concepts can be easily understood since the time consuming for mathematical calculations are almost instantaneous. The e-learning philosophy has then important advantages when compared with classical teaching, since is embedded into a web page permitting a broad dissemination of the behavior of industrial systems, often impossible to teach in conventional classes.

MATHEMATICAL MODELS

The behavior of fixed-bed reactors (FBR) may be studied by using several mathematical models, depending on the complexity that is taken into account for, and Figure 1 resumes the different possibilities. For example, PH1D model correspond to a pseudo-homogeneous approach in one dimension, and in this case the film and the particle are implicitly considered. In the case of heterogeneous models, the gradients in the film and in the catalyst may be taken into account ($HT1D_d$, $HT1D_{dc}$, $HT2D_d$, $HT2D_{dc}$). The model $HT2D_d$ in transient conditions includes equations (1) to (12), indicated in Table 1, and corresponds to a complex approach for simulating the dynamic behavior of FBR.

TABLE 1

TWO DIMENSION DYNAMIC HETEROGENEOUS MODEL WITH DIFFUSIONAL TRANSPORT IN THE CATALYST (HT2Dd)

Fluid phase in the reactor

Mass balance to specie i :

$$\varepsilon \frac{\partial C_{i,b}}{\partial t} = -\varepsilon u_i \frac{\partial C_{i,b}}{\partial z} + \varepsilon D_{ea} \frac{\partial^2 C_{i,b}}{\partial z^2} + \varepsilon D_{er} \left(\frac{\partial^2 C_{i,b}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{i,b}}{\partial r} \right) + \overline{\eta}_i \, r_{i,b} \tag{1}$$

Energy balance:

$$\varepsilon \rho_f Cp_f \frac{\partial T_b}{\partial t} = -\varepsilon u_i \rho_f Cp_f \frac{\partial T_b}{\partial z} + \varepsilon \lambda_{ea} \frac{\partial^2 T_b}{\partial z^2} + \varepsilon \lambda_{er} \left(\frac{\partial^2 T_b}{\partial r^2} + \frac{1}{r} \frac{\partial T_b}{\partial r} \right) + \sum_j (-\Delta H_j) \overline{\eta}_j \, r_{j,b} \tag{2}$$

Initial Conditions: $\quad \forall z, \forall r; \, t = 0 \quad C_{i,b} = C_{i,b}^0; \quad T_b = T_b^0 \tag{3}$

Boundary Conditions:

$$\forall t, \forall r; \quad z = 0 \qquad \varepsilon u_i (C_{i,0} - C_{i,b}) = -\varepsilon D_{ea} \frac{\partial C_{i,b}}{\partial z}\bigg|_{z=0} ; \qquad \varepsilon u_i \rho_f Cp_f (T_0 - T_b) = -\varepsilon \lambda_{ea} \frac{\partial T_b}{\partial z}\bigg|_{z=0} \tag{4}$$

$$\forall t, \forall r; \quad z = L \qquad \frac{\partial C_{i,b}}{\partial z}\bigg|_{z=L} = 0 ; \quad \frac{\partial T_b}{\partial z}\bigg|_{z=L} = 0$$

$$\forall t, \forall z; \quad r = 0 \qquad \frac{\partial C_{i,b}}{\partial r}\bigg|_{r=0} = 0 ; \quad \frac{\partial T_b}{\partial r}\bigg|_{r=0} = 0$$

$$\forall t, \forall z; \quad R_0 = 0 \qquad \frac{\partial C_{i,b}}{\partial r}\bigg|_{r=R_0} = 0 ; \quad -\lambda_{er} \frac{\partial T_b}{\partial r}\bigg|_{r=R_0} = h_w (T_b - T_w) \tag{5}$$

Fluid/solid interface

Mass balance to specie i: $\qquad k_{f,i} \, a_p \, (C_{i,s} - C_{i,b}) = r_{i,obs} \tag{6}$

Energy balance: $\qquad h_f \, a_p \, (T_s - T_b) = \sum_j (-\Delta H_j) \, r_{j,obs} \tag{7}$

Catalyst particle

Mass balance to specie i: $\qquad \varepsilon_p \frac{\partial C_{i,p}}{\partial t} = D_{e,i} \left(\frac{\partial^2 C_{i,p}}{\partial r_p^2} + \frac{s}{r_p} \frac{\partial C_{i,p}}{\partial r_p} \right) + \sum_j \alpha_{i,j} \, r_{j,p} \tag{8}$

Energy balance: $\qquad (\rho Cp)_p \frac{\partial T_p}{\partial t} = \lambda_e \left(\frac{\partial^2 T_p}{\partial r_p^2} + \frac{s}{r_p} \frac{\partial T_p}{\partial r_p} \right) + \sum_j (-\Delta H_j) \, r_{j,p} \tag{9}$

Initial Conditions: $\qquad \forall r_p; \forall z; \, t = 0 \qquad C_{i,p} = C_{i,p}^0; \quad T_p = T_p^0 \tag{10}$

Boundary conditions: $\qquad \forall t, \forall z; \, r_p = R_p \qquad C_{i,p} = C_{i,s} ; \quad T_p = T_s$

$$\forall t, \forall z; \, r_p = 0 \qquad \frac{\partial C_{i,p}}{\partial r_p}\bigg|_{r_p=0} = 0 ; \quad \frac{\partial T_p}{\partial r_p}\bigg|_{r_p=0} = 0 \tag{11}$$

Effectiveness factor referred to bulk conditions

$$\overline{\eta} = \frac{r_{obs}}{r(C_b, T_b)} = \frac{\frac{1}{V_p} \iiint_{V_p} r(C_p, T_p) \, dV_p}{r(C_b, T_b)} \tag{12}$$

	One-dimension model		Two-dimensions model	
	PH1D	HT1D$_d$/ HT1D$_{dc}$	PH2D	HT2D$_d$/ HT2D$_{dc}$
- with/without axial dispersion	✓	✓	✓	✓
- with/without film gradients	not applicable	✓	not applicable	✓
- with/without particle gradients	not applicable	✓	not applicable	✓

FIGURE 1
STEADY-STATE MODELS FOR FIXED BED REACTOR.

This general model is presented to students in classroom, and the meaning of each term is fully explained. Starting from this model (HT2D) the simplest ones are easily obtained. The meaning of the different symbols is indicated in the notation section, at the end of the paper.

The subscripts coupled to HT1D and HT2D are referred to the mass mechanism inside the catalyst (Figure 1). Therefore, when only the diffusion flow is considered the reference is HT1D$_d$ or HT2D$_d$. In the case of both intraparticle convection and diffusion flows are considered, the models are referred HT1D$_{dc}$ or HT2D$_{dc}$. The axial dispersion can be included in any case (PH1D, HT1D$_d$/ HT1D$_{dc}$, PH2D and HT2D$_d$/ HT2D$_{dc}$).

SIMULATION METHODS

The e-learning platform for teaching FBR will be included in a most global one referred "Virtual Laboratories of Chemical Processes", and in particular, in a sub-level "Chemical Reaction". The virtual platform will be supported by interactive simulation modules, and the web interface allows the students entering data for simulations. The outputs are mainly graphics or numerical results.

The Matlab and Fortran are used as computational platforms for all simulation concerning FBR. Depending on the type of differential equations referred above the models may be solved using commercial Fortran codes such as GEAR, PDCOL, FORSIM, DDASAC, or routines from the Matlab.

As referred in the introduction, the students may try simulations in the e-learning platform by two main approaches: a general analysis through different mathematic models, including the catalyst particle and the film resistances and based on two case studies of industrial interest.

CASE STUDIES

Two case studies are available for students, aiming the understanding of real industrial processes: partial oxidation of ortho-xylene to phthalic anhydride [4-7] and partial oxidation of methanol to formaldehyde [8-11].

I. Case Study 1 – Synthesis of Phthalic Anhydride

This case study refers to the partial oxidation of *o*-xylene to phthalic anhydride in a fixed-bed reactor packed with a V$_2$O$_5$-TiO$_2$ catalyst supported on large-pore particles. The following scheme of consecutive/parallel pathways is used to describe this chemical process, where A stands for *o*-xylene, B for phthalic anhydride and C for the final oxidation products (CO and CO$_2$) [12]:

Due to the large excess of oxygen, the rate equation for each step *j* (*j*=1,2,3) is considered to be of pseudo-first-order: $r_j = K_j\, p_i\, p_{O_2}$, where *i* is the corresponding reactant (*i*=A,B).

Two one-dimensional heterogeneous models are used for the description of the system, one that accounts for both intraparticle mechanisms of convection and diffusion (HT1D$_{dc}$) inside the catalyst pellets and the other considering only the diffusive flow (HT1D$_d$). Axial dispersion of mass and heat was neglected and a constant wall temperature (equal to the inlet fluid temperature) was assumed in the fixed-bed. An isothermal catalyst with slab geometry was also considered. The steady-state equations and the reactor and kinetic parameters may be found elsewhere [7]. The resulting system of differential-algebraic equations is integrated by using the commercial software code DDASAC - *Double Precision Differential Algebraic Sensitivity Code* [13].

From the resolution of the equations, several results may be simulated, for the analysis of different perspectives of the reactor steady-state behavior. For example, Figure 2(a)

FIGURE 2
EVOLUTION OF FLUID TEMPERATURE AND CONCENTRATION OF O-XYLENE (A) AND PHTHALIC ANHYDRIDE (B) ALONG THE REACTOR AXIAL COORDINATE.

shows the bulk temperature profiles and Figure 2(b) the o-xylene and phthalic anhydride dimensionless concentration profiles along the reactor axial coordinate for different values of the intraparticle mass Peclet number, λ_m, at the inlet conditions $T_0 = 625K$ and $P_0 = 0,01$ atm. The intraparticle and interfacial profiles of the dimensionless concentration of o-xylene and phthalic anhydride calculated at the reactor inlet ($z^* = 0$) are also depicted in Figures 3.
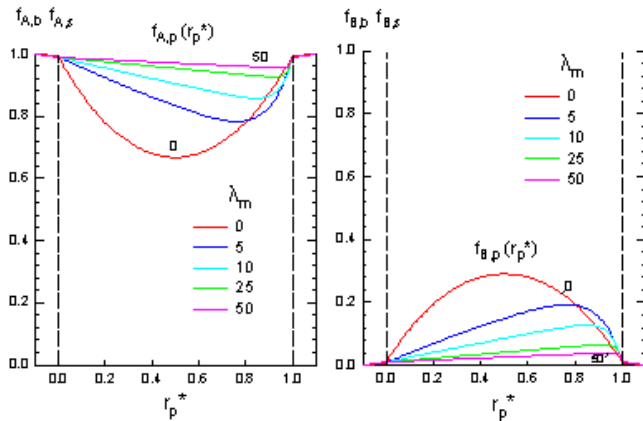

FIGURE 3
INTRAPARTICULAR AND INTERFACIAL DIMENSIONLESS CONCENTRATION PROFILES OF O-XYLENE (A) AND PHTHALIC ANHYDRIDE (B) AT THE REACTOR ENTRANCE ($Z^* = 0$) FOR DIFFERENT VALUES OF λ_M ($T_0 = T_W = 625K$ AND $P_0 = 0,01$ ATM).

For chemical processes involving competitive reactions, yield and selectivity are very important parameters for the evaluation of the reactor efficiency. Figures 4 (a)-(b) show
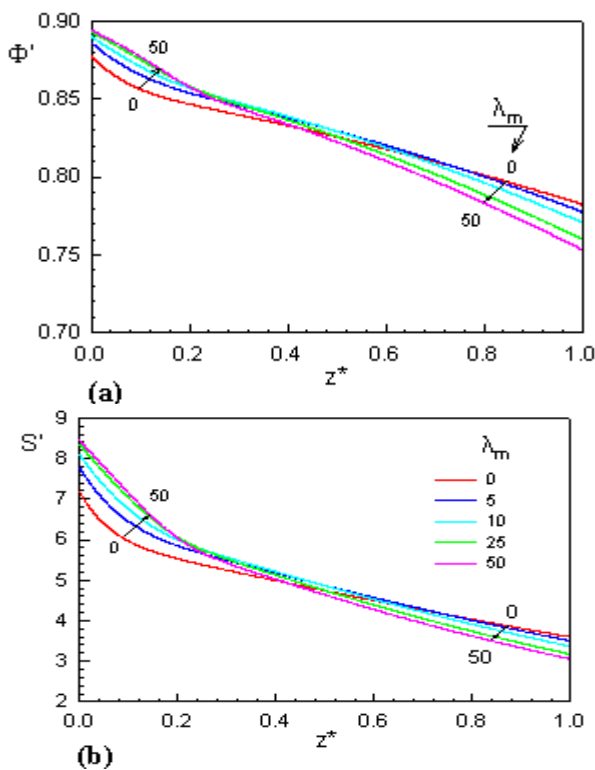
FIGURE 4
DIFFERENTIAL YIELD, Φ', AND THE DIFFERENTIAL SELECTIVITY OF PHTHALIC ANHYDRIDE, S', ALONG THE REACTOR AXIAL COORDINATE.

the evolution of the differential yield, Φ', and the differential selectivity of phthalic anhydride, S', along the reactor axial coordinate, calculated at the same conditions of Figure 2.
The results indicated in Figures 2 to 4 are examples, which students may simulate interactively, being possible to change the operating conditions of the system. The effect of those changes is observable in graphical representations.

II. Case Study 2 – Synthesis of Formaldehyde

The system analyzed under this case study was the partial oxidation of the methanol to formaldehyde over iron/molybdenum oxides catalyst. The kinetic model involves two reactions: the partial oxidation of methanol to formaldehyde, which may be followed by a side reaction involving the partial oxidation of the formaldehyde to CO and H_2O. The kinetic model may be found in [10] and the operating conditions used by default correspond to the industrial ones (1.4 atm; 257ºC; 7.5% for feed methanol mole fraction). Although the industrial production of formaldehyde involve FBR with thousands of tubes, in the simulations only a single tube is considered with a length of 0.75 m and divided into two zones: 0.2 m of diluted catalyst with 50% inert in the first region (less active bed) and 0.55 m of pure catalyst. This distribution of the catalyst allows mild heat generation, and then lower hot spots are obtained. The e-learning platform allows the observation of:
- steady state profiles for concentrations and temperature, according to different mathematical models (PH1D, HT1D and HT2D). For heterogeneous models, the mass flux inside the particle may account for only diffusion ($HT1D_d$; $HT2D_d$) or both diffusion and convection ($HT1D_{dc}$; $HT2D_{dc}$).
- transient behavior of the reactor according PH1D, $HT1D_d$ and $HT1D_{dc}$.

Figure 5 and 6 show as example, some axial profiles of temperature in the case of steady state conditions and for dynamic conditions, respectively.
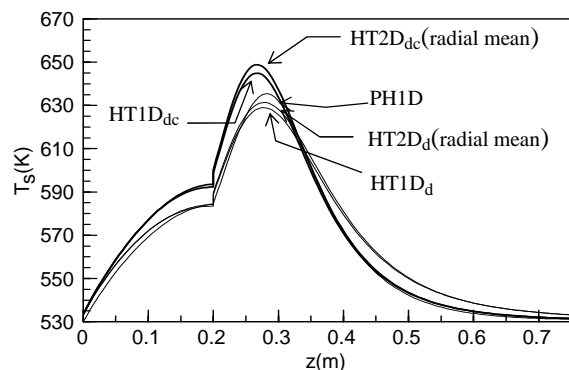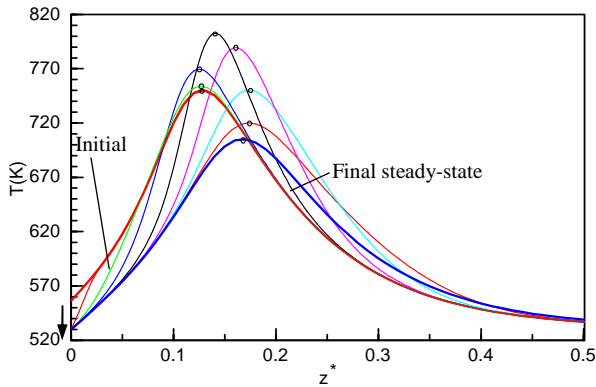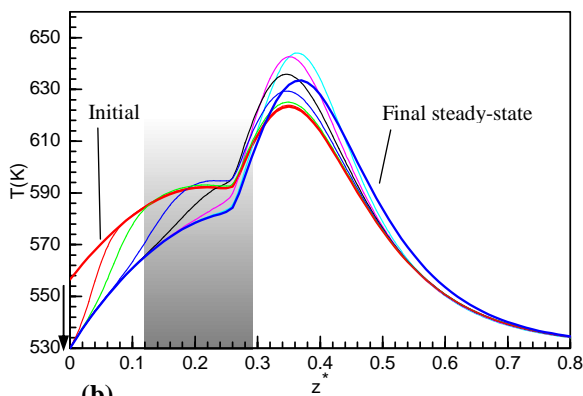

FIGURE 5
AXIAL SOLID TEMPERATURE PROFILES PREDICTED WITH DIFFERENT MATHEMATICAL MODELS: PH1D, HT1D$_D$, HT1D$_{DC}$, HT2D$_D$, HT2D$_{DC}$

FIGURE 6
TRANSIENT AXIAL TEMPERATURE PROFILES OBTAINED
WITH PH1DT MODEL FOR A FIXED BED PACKED WITH (a)
PURE CATALYST, (b) – DILUTED CATALYST, BY DECREASING
THE FEED TEMPERATURE -5% ($T_O=557\rightarrow530$ K).

These mathematical models are based on common assumptions: constant pressure in the reactor, constant values for physical and transport properties, constant wall temperature, constant bed porosity, flat radial velocity profiles (plug flow) and constant catalyst activity in each catalytic zone. The simulated mathematical equations may be found in [8] for the case of steady state and in [10] for transient conditions. The commercial code DDASAC package was used for solving the steady state [13-14], which is an extension of DASSL code, developed by Petzold [15]. The transient model was solved with the PDECOL [16]. The numerical solutions involve complex strategies which were discussed in detail elsewhere [11].

It is important to note that the dilution of the catalyst bed in the first part of the tubes has advantages concerning the parametric sensitivity and runaway behavior [9].

In this case study students may test the influence of several variables such as the operating conditions (concentration, temperature), the wall temperature, the inlet pressure, etc. In transient conditions, different changes may be virtually experimented (steps, ramps, etc.). Moreover, the influence of the dilution of the catalyst can be easily understood, mainly in thermal profiles, by simulating this important industrial process.

CONCLUSIONS

E-learning tools may be the key for the success of students to understand the behavior of FBR. In fact, due to the high complexity of the mathematical equations involved in the description of these systems, the classical approach for teaching this engineering subject sometimes fails, since only very simplified case studies may be solved in the classroom. Through simple computational simulations, made in a friendly web-based interface, the performance of a FBR is easily obtained for a given set of operation conditions. Moreover, the effect of changes in the operating conditions may also be straightforwardly understood, based on simple graphical representations of the system behavior.

To conclude, it is important to note that e-learning tools may lead to a reduction of the number of classical lectures, being students more independent, which is in accordance with the methodologies stated by the Bologna Process.

ACKNOWLEDGMENT

NOTATION

a_p - specific particle area (m^{-1})
C_i - concentration of species i (mol/ m^3)
C_0 - o-xylene feed concentration, (mol/m^3)
Cp - heat capacity (J/kg K)
D_e - effective diffusivity (m^2/s)
d_p - particle diameter (m)
f_i - dimensionless concentration of species i , C_i/C_0
h_f - film heat transfer coefficient (J/ m^2 s K)
h_w - wall heat transfer coefficient (J/ m^2 s K)
k_{fi} - film mass transfer coefficient of species i (m/s)
L - reactor length (m)
r - reactor coordinate (m)
r_j - rate of reaction j (mol/ s kg_{cat})
$r_{obs,i}$ - observed reaction rate inside the catalyst (mol/s kg_{cat})
r_p - particle coordinate (m)
R_p - half thickness of the catalyst particle (m)
R_0 - tube radius of the reactor (m)
s - catalyst shape factor (slab: s=0; cylinder: s=1; sphere:s=2)
t^*- dimensioless time (t/τ)
t - time (s)
T- absolute temperature (K)
T_0 - feed temperature (K)
u_i - interticial velocity (m/s)
v_0 - intraparticle fluid velocity (m/s)
z - reactor axial coordinate (m)
z^*- dimensioless reactor axial coordinate (z/L)

Greek symbols

$\alpha_{i,j}$ - stoichiometric coefficient of specie i, in the reaction j
ΔH_j - enthalpy of reaction j (J/mol)
ε - bed porosity
λ_e - effective thermal conductivity (J/m s K)

η_j - effectiveness factor of reaction j

ρ - density (kg/m^3)

τ – space time for the fluid (L/u$_i$)

Subscripts

a- axial

b - bulk

f - fluid

i- chemical specie

j - reaction

p - particle

r - radial

s - particle surface

w - wall

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