

Influence of intraparticle reaction–diffusion in a catalytic reactor

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Abstract

A mathematical model was developed for a catalytic, batch-wise operating basket reactor used for liquid-phase systems. This kind of reactor is frequently used to study the reaction kinetics and diffusion effects in porous catalyst particles. The model comprises dynamic mass balances for the catalyst particles and the turbulent liquid phase surrounding the particles. Simultaneous reaction and diffusion in particles is handled by the model, which was successfully applied to describe the kinetic and mass transfer effects in a complex organic reaction system, which is relevant for catalytic recovery of anthraquinones. The model predicted the reactor performance for different catalyst particle diameters, which is relevant for a successful process scale up.

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1. Introduction

Catalytic reactors are usually described with pseudo-homogeneous models that do not account for the diffusion resistance in the catalyst particles. With a heterogeneous reactor model that accounts for simultaneous reaction and diffusion in the catalyst particles, it is possible to simulate the real reaction rate over different catalyst particle sizes.

As a result of our study, the method to determine the governing kinetics was developed. A part of the kinetic experiments were carried out with crushed catalyst particles and a part with granulates. The reaction rate with the crushed catalyst usually defines the intrinsic kinetics (no diffusion resistance assumed). The difference between the experiments shows how much the pore diffusion decreases the reaction rate depending on the catalyst particle size.

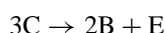
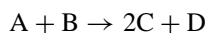
2. The role of intraparticle diffusion

Intraparticle diffusion is the governing transfer mechanism inside the pores of catalyst particles. Molecular diffusion can be described with various models, starting from the simple Fick's law with effective diffusion coefficients and ending with the complete set of Stefan–Maxwell equations [1,2]. Since the current case reflects the situation that few reactant and product molecules co-exist in an environment of solvent molecules, the simplest approach can

be considered as sufficient for the description of diffusion effects.

3. Experimental

A reaction, which is relevant in the recovery of anthraquinones in the H₂O₂ production process was considered in our study:



Experiments were carried out in a slurry reactor as well as in a catalytic spinning basket reactor. Crushed catalyst particles were studied in the slurry reactor and uncrushed were tested in a spinning basket reactor. The size of the slurry and spinning basket reactors was 0.5 l and the catalyst amount was 150 g. The crushed catalyst particles were sieved into two fractions of particles with the diameters 0.4 and 0.7 mm, respectively. The size of the uncrushed particles was 1.4 mm in diameter.

The laboratory tests were performed in such conditions that liquid–solid mass transfer effects could be neglected. This was achieved in the slurry reactor by a high agitation speed. For the spinning basket reactor, the liquid–solid mass transfer rates were calculated with the use of a CFD model [3] and the CFD calculations indicated that the liquid–solid mass transfer rates in the spinning basket reactor did not affect the reaction rates. However, the liquid–solid mass transfer resistance cannot be eliminated in the large-scale reactors.

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Nomenclature

<i>A</i>	mass transfer area/volume
<i>c</i>	concentration
<i>D</i>	diffusion coefficient
<i>k</i>	mass transfer rate
<i>M</i>	molecular weight
<i>n</i>	amount of substance
<i>N</i>	flux from/to catalyst
<i>r</i>	reaction rate
<i>R</i>	catalyst particle dimension
<i>s</i>	shape factor of catalyst
<i>t</i>	time
<i>T</i>	temperature
<i>V</i>	volume
<i>x</i>	co-ordinate in catalyst

Greek letters

ε	catalyst porosity
ρ	density
τ	catalyst tortuosity
ϕ	association factor
φ	mass of catalyst/reactor volume

Subscripts

B	bulk phase
<i>i</i>	component index
L	liquid
p	catalyst particle

4. Diffusion in a catalyst particle

The simplest textural model for a porous particle is based on the average porosity and tortuosity of the material. The effective diffusion coefficient is obtained from the molecular diffusion coefficient (D_i), the catalyst particle porosity (ε_p) and tortuosity (τ_p):

$$D_{e,i} = \frac{\varepsilon_p}{\tau_p} D_i \quad (1)$$

The particle tortuosity describes the deviation of the pores from an ideal linear structure.

The molecular diffusion coefficient (D_i) of a single component is basically obtained from the binary diffusion coefficients of the molecular pairs in the solution (D_{ik}). The approximate formula of Wilke and Chang [4] for a component dissolved in a solvent is:

$$D_i = \frac{a\sqrt{\phi MT}}{\eta V_i^{0.6}} \quad (2)$$

The viscosity of the liquid (η) was determined experimentally and the molar volumes of the components (V_i) were estimated from the atomic contributions of LeBas [4]. According to Fick's law, the component flux (N_i) is directly proportional to the diffusion coefficient and the concentra-

tion gradient (dc'_i/dt):

$$N_i = -D_{e,i} \left(\frac{dc'_i}{dt} \right) \quad (3)$$

where c'_i is the volume-based concentration ($c'_i = c_i \rho_L$).

5. Mass balance for a catalyst particle

For a catalyst particle with an arbitrary geometry, the component mass balance is written as follows:

$$(N_i A)_{in} + r_i \rho_p \Delta V_p = (N_i A)_{out} + \frac{dn_i}{dt} \quad (4)$$

where A is the particle surface in the reference volume, ρ_p the density of the particle, ΔV_p the volume element of the particle and $n_i = c_i \rho_L \varepsilon_p \Delta V_L$ the amount of substance in the reference volume.

Arbitrary geometries of catalyst particles can be considered by using the shape factor (s):

$$s + 1 = \frac{A_p}{V_p} R \quad (5)$$

The shape factor (s) obtains the values 0, 1 and 2 for a slab, an infinitely long cylinder and a sphere, respectively. When the model of the diffusion flux (Eq. (3)), is inserted in the balance equation and a dimensionless co-ordinate ($x = r/R$) is introduced, we obtain the final form of the model equation:

$$\frac{d(c_i \rho_L)}{dt} = \varepsilon_p^{-1} \left[r_i \rho_p + \frac{D_{e,i}}{R^2} \left(\frac{d^2(c_i \rho_L)}{dx^2} + s \frac{d(c_i \rho_L)}{dx^2} \right) \right] \quad (6)$$

provided that the effective diffusion coefficient can be considered to be constant inside the particle.

The initial conditions of the mass balance equations are trivial. Flat concentration profiles corresponding to the bulk phase conditions were assumed in the beginning of the reaction ($t = 0$). The boundary conditions at the centre of the catalyst particle ($r = 0$) are $dc_i/dr = 0$ and $dc_i/dr = k_{LS} a(c_L - c_S)$ at the outer surface of the catalyst particle.

6. Mass balance for a batch reactor

For a batch reactor with immersed catalyst particles, the component mass balance can be written as follows:

$$N_i A_p = \frac{dn_i}{dt} \quad (7)$$

where N_i denotes the flux at the outer surface of the catalyst particle ($r = R$). The total catalyst particle area is $A_p = n_p A'_p$, where n_p and A'_p denote the total number of particles and the outer surface area of an individual particle. The flux (N_i) in Eq. (7) is calculated from

$$N_i = -D_{e,i} \left(\frac{dc'_i}{dr} \right)_{r=R} \quad (8)$$

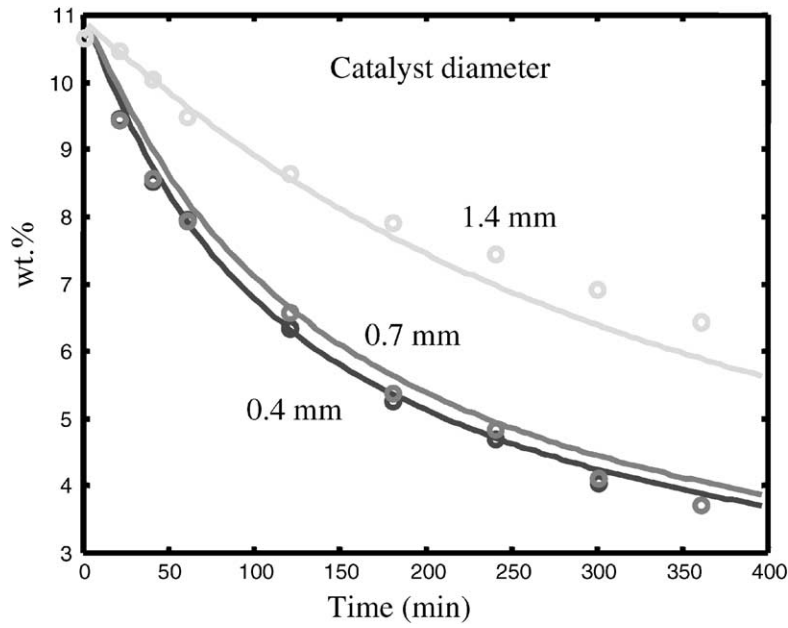


Fig. 1. Concentration of component B (wt.%) as a function of time and with different catalyst particle sizes. Experimental dots and simulated lines.

However, a numerically more robust way is to utilise the integrated form of the steady state (Wärnå, 1994). After a formal integration of the balance Eq. (6), we get under pseudo-steady state conditions:

$$\int_0^{N_i R^s} d(N_i r^s) = \rho_p \int_0^R r_i r^s dr \quad (9)$$

After introducing the dimensionless co-ordinate $x = r/R$ and performing the integration of the left hand side the flux is obtained:

$$N_i = \rho_p R \int_0^1 r_i x^s dx \quad (10)$$

The amount of substance (n_i) is expressed with the mass-based concentration (c_i) and the liquid volume (V_L): $n_i = c_i \rho_B V_L$. Elementary geometric considerations and inserting the flux expression into the mass balance give the operational form of the mass balance:

$$\frac{dc_i}{dt} = \varphi \int_0^1 (s+1)x^s r_i dx \quad (11)$$

The generation rates (r_i) are obtained for each x -value by utilising the concentration profiles which are solved numerically from the reaction–diffusion Eq. (6).

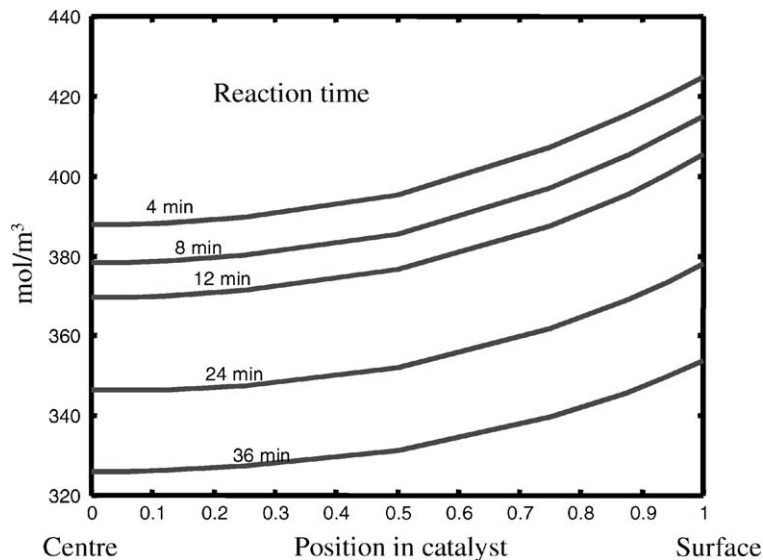


Fig. 2. Concentration profiles of component B inside the catalyst particles at different reaction times.

7. Numerical method

The model equations were solved numerically by discretizing the partial differential equations (PDEs) (Eq. (6)) with respect to the spatial co-ordinate (x). Central finite difference formulae were used to approximate the first and second derivatives (dc_i/dx). Thus, the PDEs were transformed to ordinary differential equations (ODEs) with respect to the reaction time and the powerful finite difference method was used in the numerical solution. The recently developed software of the Italian group [5] was used, since it turned out to be more rapid than the classical LSODE code of [6].

8. Results

Fig. 1 shows the concentration of the component B (wt.%) as a function of reaction time in the reactor for different catalyst particle sizes. It can be seen that the simulated lines agree rather well with the experimental points. Fig. 2 shows the concentration profiles of the component B inside the catalyst particles at different reaction times when the largest catalyst particle size is used. The diffusion resistance inside the particles is evident.

9. Conclusions

Experiments with catalyst particles of different size were performed in slurry and spinning basket reactors. A mathematical model that accounts for simultaneous reaction and

diffusion was used to simulate the performance of the systems. It was shown that the simulated results agreed well with the experimental data. With this model it is possible to investigate the reactor performance with different catalyst particle sizes or forms as the intrinsic kinetics of the reaction is known.

Acknowledgements

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