

A First Course on Kinetics and Reaction Engineering

Unit 38. Heterogeneous Catalytic Reactions

Overview

Unit 38 presents an abbreviated and simplified discussion of the modeling of packed bed reactors where significant concentration and/or temperature gradients exist. Such gradients may be present in the boundary layer between the bulk fluid and the external surface of the catalyst particles, or they may exist within the porous catalyst particles themselves. Unit 38 defines the Thiele modulus for first order reactions in spherical catalyst particles and demonstrates its relationship to the catalyst effectiveness factor, which is also defined in the unit. The unit shows how the ideal PFR model can be modified to account for such gradients by incorporation of an effectiveness factor. It also illustrates how an independent set of design equations for the catalyst phase can be formulated and used in conjunction with a set of design equations for the fluid phase in situations where the effectiveness factor changes along the length of the reactor.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:

- Thiele modulus
- Effectiveness factor

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- Describe the limiting behavior of the effectiveness factor as the Thiele modulus varies and identify the preferred range of values for the Thiele modulus.
- Use the effectiveness factor to modify ideal reactor design equations so that they account for concentration gradients associated with heterogeneous catalytic reactions.
- Formulate design equations for the catalyst phase in a packed bed reactor and solve them simultaneously with design equations for the fluid phase like those in Unit 37.

Information

When a porous solid is used to catalyze a gas phase reaction, there is a possibility that there will be concentration and temperature gradients between the bulk fluid and the external surface of the catalyst particles as well as concentration and temperature gradients within the pores of the catalyst. These phenomena were discussed in Unit 12 with respect to their effect upon the measurement of reaction rates. In that situation, every effort should be taken to operate the reactor in a way that minimizes such gradients so that the concentration and temperature everywhere within the catalyst particle are essentially equal to the bulk fluid concentration and temperature. Doing so when using a laboratory reactor may require some effort, but it is necessary if one seeks to generate accurate kinetics data. As noted in Unit 37, in a commercial reactor it may not be easy, necessary or even desirable to operate a reactor so that concentration and temperature gradients are negligible. In those situations, in order to model the reactor

accurately, one cannot use the ideal reactor design equations, but instead must use design equations that account for the presence and effects of the gradients.

Several approaches are possible to account for concentration and temperature gradients associated with heterogeneous catalysts. This unit does not present a comprehensive discussion of the topic, but instead considers one of the simplest of situations, illustrating one approach to accounting for concentration gradients. In particular, this unit will only consider concentration gradients (an analogous approach can be used to account for temperature gradients), it only considers a system where Fick's law describes diffusion and where there is equal and opposite counter-diffusion, and it utilizes a pseudo-continuum model for the porous solid catalyst (there are other ways to model porous catalysts). In short, the unit is intended to provide an introductory basis for those who wish to learn more through independent study or a second course on reaction engineering.

Accounting for concentration gradients associated with heterogeneous catalysts requires some sort of model for the pore structure of the catalyst. Each catalyst particle is likely to have its own unique pore structure. As a result, it is not practical to attempt to construct an exact physical model for the pore structure. Instead, common approaches are to construct a network of pores that are interconnected at nodes where a specified number of pores meet or to assume straight pores with circular cross sections and a distribution of pore diameters. A simpler approach, that will be used here, is to adopt a pseudo-homogeneous or pseudo-continuum pore model.

The pseudo-continuum pore model completely ignores the pore structure of the solid. Instead, it treats the catalyst particle as if it is a single homogeneous phase. It further assumes that the reactants diffuse in a straight line in the radial direction, as shown in Figure 38.1. Here, the diffusion process is assumed to obey Fick's law, but an effective diffusivity is used in place of the true diffusion coefficient. With that, a steady state mole balance on reactant A within a spherical catalyst particle takes the form given in equation (38.1) where r_A is the rate of generation of A per unit catalyst volume, D_{eA} is the effective diffusivity of A and C_A is the concentration of A which varies as a function of radial position, r , measured from the center of the particle. It should be noted, in particular, that the appropriate diffusion coefficient to use when modeling a porous solid depends upon the chemical species present, the nominal diameter of the catalyst pores and the mode of diffusion. Possible modes of diffusion include ordinary molecular diffusion, Knudsen diffusion, configurational diffusion and surface diffusion.

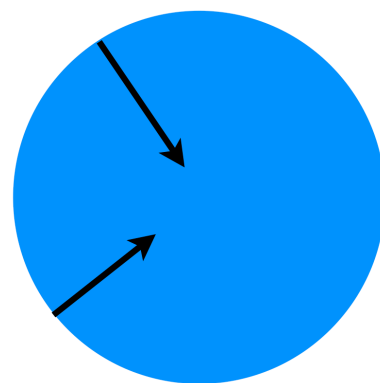


Figure 38.1. In the pseudo-continuum pore model, the species are assumed to diffuse in the radial direction. The arrows indicate diffusion paths for reactants.

$$-D_{eA} \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right) = r_A \quad (38.1)$$

In reality, of course, if you looked at any spherical shell within the catalyst particle, only a fraction of the surface of that shell would be available for diffusion because the reactant could not really diffuse through the solid, only the pores. It is commonly assumed that the fraction of the surface of any spherical shell that is available for diffusion is equal to the void fraction, ϵ , of the catalyst particle (not the void fraction of the packed bed of particles). Similarly, the actual path followed by a diffusing reactant in reality will twist and turn so that the distance the reactant travels to reach the center of the particle is greater than the radius of the particle. A quantity known as the tortuosity, τ , is used to account for the difference between the straight line distance and the actual path length. With these two correction factors, the effective diffusivity can be related to the appropriate true diffusion coefficient for species A according to equation (38.2).

$$D_{eA} = \frac{\epsilon D_A}{\tau} \quad (38.2)$$

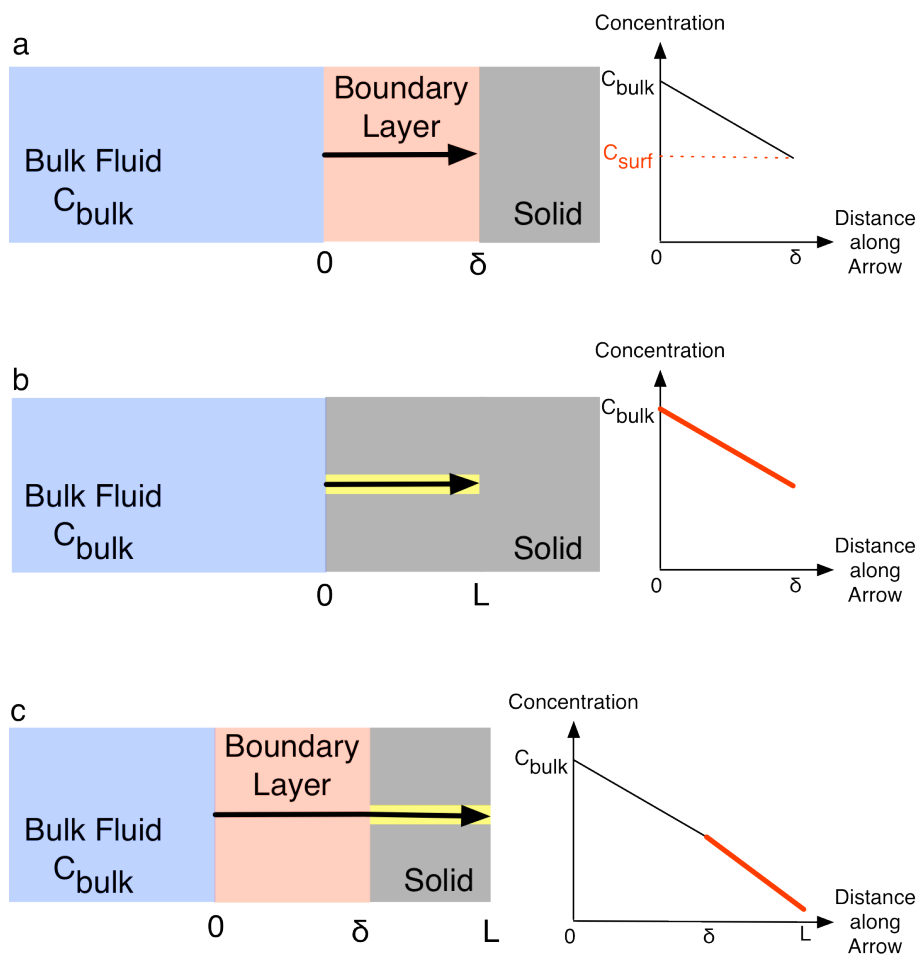


Figure 38.2. When fluid flows around a solid particle there can be appreciable concentration gradients (a) between the bulk fluid and the external surface of the solid, (b) within the pores of the solid or (c) both.

As noted in the introduction, and in Unit 12, concentration gradients can exist between the bulk flowing fluid and the external surface of the solid catalyst particles. When fluid flows around a solid, there is a thin layer of stagnant fluid near the surface of the solid known as the boundary layer. Within this boundary layer there isn't any forced convection, only diffusion. This is represented schematically in Figure 38.2. In Figure 38.2 (a), the boundary layer is represented by pink, and the concentration of a reactant would decrease steadily from its bulk value as a function of distance into the boundary layer, as indicated by the arrow. Thus, at the external surface of the catalyst, a lower, external surface concentration would prevail.

The flux of a reactant, A, through the boundary layer is usually described in terms of a mass transfer coefficient, k_c , where the subscript "c" denotes that the mass transfer coefficient is for use with concentrations as expressed in equation (38.3). The mass transfer coefficient will depend upon the geometry of the system under consideration, the fluid flow rate and fluid properties. As a consequence, values for mass transfer coefficients are often found from dimensionless correlations. Equation (38.4) is an example of such a correlation for the dimensionless quantity, j_D , in terms of the Reynolds number¹. Equations (38.5) and (38.6) show how j_D and the Reynolds number are defined in terms of the tube diameter, D_{tube} ; volumetric flow rate, \dot{V} ; fluid viscosity, μ ; fluid density, ρ ; diffusion coefficient, D_A ; bed porosity, ε ; and catalyst particle diameter, d_{part} . Equations (38.4) through (38.6) apply specifically to flow through a packed bed of spherical particles with Reynolds numbers greater than 50. A number of correlations of this type are available; a good mass transfer textbook or chemical engineering handbook should be consulted to find an appropriate correlation. Both j_D and N_{Re} may be defined differently, depending on the specific correlation being used.

$$N_A = k_c (C_{A,bulk} - C_{A,surf}) \quad (38.3)$$

$$j_D = 0.61 N_{Re}^{-0.41} \quad (38.4)$$

$$j_D = \frac{\pi D_{tube}^2 k_c}{4 \dot{V}} \left(\frac{\mu}{\rho D_A} \right)^{2/3} \quad (38.5)$$

$$N_{Re} = \frac{2 \dot{V} \rho}{3 \pi D_{tube}^2 \mu (1 - \varepsilon) d_{part}} \quad (38.6)$$

In general, the concentration of the reactant at the external surface of the catalyst particle is not known. Suppose, however, that the catalyst was not porous as in Figure 38.2 (a), and that the system had reached steady state. At steady state, the flux given by equation (38.3) must just equal the rate of reaction on the surface of the catalyst particle. If this weren't true, reactant would accumulate at the surface, and accumulation does not occur at steady state. Note that the rate expression should be

¹ "Mass Transfer, Fundamentals and Applications," by A. L. Hines and R. N. Maddox, Prentice-Hall, Engelwood Cliffs, NJ, 1985.

evaluated at $C_{A,surf}$, not $C_{A,bulk}$. Then, for a steady state system, the flux according to equation (38.3) can be set equal to the rate predicted by the rate expression at $C_{A,surf}$ (assuming the rate expression has been normalized per unit external catalyst surface area). The resulting expression can be solved to find the concentration of A at the surface. For example, if the reaction rate is first order in A, this leads to equation (38.7) for the surface concentration of A. Substitution of equation (38.7) back into the first order rate expression leads to a rate expression in terms of the bulk fluid concentration of A, equation (38.8). The rate expression in terms of the bulk fluid concentration still has the appearance of a first order rate expression, equation (38.9), but the apparent rate coefficient, k' , is no longer a simple rate coefficient, equation (38.10). Thus, if only external concentration gradients were present and the catalyst was non-porous, the rate expression in equation (38.8) could be used in an ideal reactor model, and the model would correctly account for the external concentration gradient.

$$C_{A,surf} = \frac{k_c}{k + k_c} C_{A,bulk} \quad (38.7)$$

$$-r_A = \frac{kk_c}{k + k_c} C_{A,bulk} = \left(\frac{1}{k} + \frac{1}{k_c} \right)^{-1} C_{A,bulk} \quad (38.8)$$

$$-r_A = k' C_{A,bulk} \quad (38.9)$$

$$\frac{1}{k'} = \frac{1}{k} + \frac{1}{k_c} \quad (38.10)$$

The preceding analysis only applies if the reaction is first order and the catalyst is non-porous. More commonly, the catalyst is a porous solid as depicted in Figure 38.2 (b) and (c). Assuming the total number of moles is not changed by reaction, a mole balance can be written for reactant A on a differentially thin spherical shell within the spherical catalyst particle. Assuming that the rate is again first order, but it is normalized per unit mass of catalyst, and letting ρ_s represent the apparent density of a catalyst particle, equation (38.11) results by taking the limit as the shell thickness goes to zero. Equation (38.11) is a second order differential equation that can be integrated analytically to obtain an expression for the concentration of A as a function of radial position within the catalyst particle. Doing so leads to two constants of integration. The values of these constants of integration are found by applying the boundary conditions specified in equations (38.12) and (38.13), where R_{part} is the radius of the spherical catalyst particle. The first boundary condition simply requires that the concentration of A at the entrance to the porous solid is equal to the external surface concentration of A. The second boundary condition requires that the concentration gradient go to zero at the center of the particle. This has to be true because otherwise as one continued through the center of the particle the gradient would be pointing toward the surface instead of toward the center of the particle.

$$D_{eA} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) = \rho_s k C_A \quad (38.11)$$

$$C_A|_{r=R_{part}} = C_{A,surf} \quad (38.12)$$

$$\left. \frac{dC_A}{dr} \right|_{r=0} = 0 \quad (38.13)$$

Integrating equation (38.11), finding the constants of integration and substituting them back into the result leads to equation (38.14) for the concentration of A as a function of radial position within the catalyst particle. Equation (38.14) only applies for a spherical catalyst particle with a first order reaction taking place. E. W. Thiele was among the first to derive models of this kind, and consequently the name Thiele modulus is given to the dimensionless quantity ϕ which represents the ratio of reaction rate to diffusion rate. It should be noted that in general, the definition of the Thiele modulus depends upon the geometry of the catalyst particle and the form of the rate expression.

$$C_A(r) = C_{A,surf} \frac{\sinh\left(\phi \frac{r}{R_{part}}\right)}{\left(\frac{r}{R_{part}}\right) \sinh\phi}; \text{ where } \phi = R_{part} \sqrt{\frac{k\rho_s}{D_{eA}}} \quad (38.14)$$

The flux of reactant A into the catalyst through its surface (i. e. in the $-r$ direction) is related to the gradient in the concentration of A at the surface according to equation (38.15). Substitution of the derivative of equation (38.14) into equation (38.15) gives an expression for the flux of A into the catalyst particle, equation (38.16). Multiplication of this flux by the external surface area of the catalyst particle gives the rate at which reactant A enters the particle.

$$-N_A = D_{eA} \left(\frac{dC_A}{dr} \right) \Big|_{r=R_{part}} \quad (38.15)$$

$$-N_A = \frac{\phi D_{eA} C_{A,surf}}{R_{part}} \left(\frac{1}{\tanh\phi} - \frac{1}{\phi} \right) \quad (38.16)$$

As before, at steady state, the rate at which A enters the catalyst particle must just equal the rate of reaction of A within the particle, because otherwise A would accumulate within the particle. It is interesting to compare the rate of reaction given above to the what the rate would equal if there were no concentration gradients. Letting η represent the ratio of the actual rate of reaction (where concentration gradients exist) to the rate that would be observed if there were no concentration gradients (and $C_A = C_{A,surf}$ everywhere within the catalyst particle) leads to equation (38.17). This quantity is known as the effectiveness factor; its value is given by equation (38.17) only when the reaction is first order and the catalyst particles are spherical.

$$\eta = \frac{3}{\phi} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \quad (38.17)$$

The utility of the effectiveness factor can be understood by first considering a situation where the external concentration gradients are negligible, such as that depicted in Figure 38.2 (b). That is, consider the case where the concentration gradient across the boundary layer is negligible. In this case, $C_{A,surf} = C_{A,bulk}$ and the actual rate of reaction, including the effect of the concentration gradients within the pores, is simply equal to the rate of reaction given by the rate expression for the bulk fluid concentration multiplied by the effectiveness factor. Put differently, in the absence of concentration gradients in the boundary layer, all that is needed in order to correct one of the ideal reactor models so that it accounts for the concentration gradients within the spherical catalyst particles is to multiply the rate expression by the effectiveness factor, as in equation (38.18), where the rate would be normalized per unit catalyst volume.

$$-r_A = \eta \rho_s k C_{A,bulk} \quad (38.18)$$

Figure 38.3 plots the effectiveness factor for a first order reaction taking place in a spherical catalyst particle as a function of the Thiele modulus. The figure shows that as the Thiele modulus goes to zero, the effectiveness factor approaches one. The effectiveness factor remains close to one for values of the Thiele modulus up to ca. 1, so generally one would prefer to operate a reactor at a Thiele modulus around 1 or less. At values of the Thiele modulus greater than 1, the effectiveness factor decreases rapidly, eventually approaching an asymptotic slope equal to $3/\phi$ (for a first-order reaction in a spherical particle).

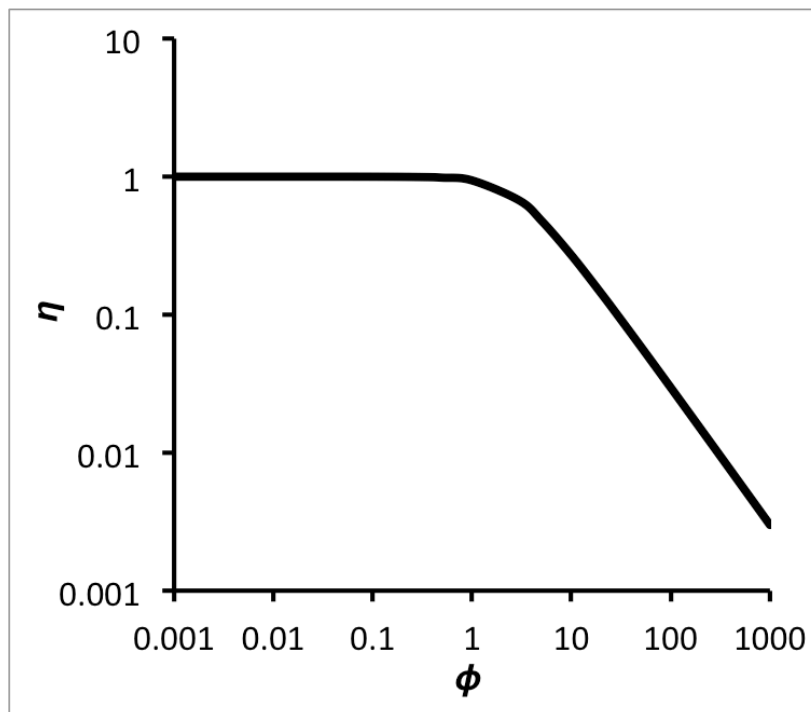


Figure 38.3. Effectiveness factor for a first order reaction in a spherical catalyst particle.

A word of caution is in order. When the reaction is first order, as in the analysis presented above, the Thiele modulus does not depend upon the concentration of A at the catalyst surface. This is rarely the case; for other reaction orders, the corresponding Thiele modulus, and consequently the effectiveness factor, depends upon the concentration of A at the catalyst surface. This means that as the reaction proceeds, the effectiveness factor will change. In addition, for a spherical catalyst particle and most reaction orders other than one, it has not proven possible to obtain an analytical expression for the effectiveness factor like equation (38.17), which is for a first order reaction. Instead, the effectiveness factor must be calculated numerically. Thus, it is possible to construct a plot of the effectiveness factor as a function of the Thiele modulus, similar to Figure 38.3. The problem, however, is that when that effectiveness factor is substituted into the PFR design equation, as in equation (38.18), it is no longer a constant. A rigorous solution of equation (38.18) requires that the variation in the effectiveness factor be accounted for.

Returning to the first order case, if the concentration gradient across the boundary layer is significant, as in Figure 38.2 (c), equation (38.16) is still valid. The only problem is that $C_{A,surf}$ is no longer equal to $C_{A,bulk}$. However, for a steady state process, the flux into the catalyst must just equal the flux through the boundary layer. This is expressed in equation (38.19). Equation (38.19) can be solved for $C_{A,surf}$ giving equation (38.20) and the result can be substituted back into equation (38.16) to get an expression for the flux of reactant A into the catalyst in terms of the bulk fluid concentration of A, equation (38.21). From that, an expression for the global effectiveness factor, η_G , can be derived, equation (38.22). The global effectiveness factor in equation (38.22) is the actual rate of reaction (i. e. in the presence of concentration gradients in both the boundary layer and the pores) divided by the rate of reaction in the absence of concentration gradients (i. e. if $C_A = C_{A,bulk}$ everywhere). Equation (38.22) only applies for a first order reaction taking place isothermally in a spherical catalyst particle.

$$\frac{\phi D_{eA} C_{A,surf}}{R_{part}} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) = k_c (C_{A,bulk} - C_{A,surf}) \quad (38.19)$$

$$C_{A,surf} = \frac{\gamma C_{A,bulk} \tanh \phi}{\phi + (\gamma - 1) \tanh \phi}; \quad \gamma = \frac{k_c R_{part}}{D_{eA}} \quad (38.20)$$

$$-N_A = \frac{\gamma C_{A,bulk} D_{eA}}{R_{part}} \frac{\phi - \tanh \phi}{\phi + (\gamma - 1) \tanh \phi} \quad (38.21)$$

$$\eta_G = \frac{3}{\phi} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \frac{\gamma \tanh \phi}{\phi + (\gamma - 1) \tanh \phi} \quad (38.22)$$

In situations where the effectiveness factor is not a constant, concentration gradients can be accounted for if one separately writes mole balances on A for the fluid phase and for the catalyst phase, as described in Unit 37. Since no reaction occurs in the fluid phase, due to the absence of catalyst, the fluid phase mole balance will not contain a term including the reaction rate. It will, however include a term

representing the net flux of A from the fluid phase to the catalyst phase. If the gradients in the boundary layer are significant, equation (38.3) can be used to describe that flux. The catalyst phase mole balance on A is then given by equation (38.11), together with the boundary conditions expressed in equations (38.12) and (38.13). The mole balance for the fluid phase and the catalyst phase mole balance are coupled by the unknown surface concentration of A, $C_{A,surf}$. Consequently, the two mole balances must be solved simultaneously. In essence, in this approach is equivalent to calculating the effectiveness factor on the fly. The advantage in doing this is that the variation of the effectiveness factor with the surface concentration is automatically accounted for.

To review, this unit has presented an analysis for a first order heterogeneous catalytic reaction taking place isothermally (a) on the external surface of non-porous heterogeneous catalysts (Figure 38.2a) (b) in porous spherical catalyst particles under conditions where concentration gradients exist only within the catalyst pores, but not across the external boundary layer (Figure 38.2b) and (c) in porous spherical catalyst particles under conditions where concentration gradients exist both across the external boundary layer and within the pores (Figure 38.2c). The unit has illustrated how the ideal reactor models can be corrected to account for concentration gradients by adding the effectiveness factor, and, alternatively, it has described how to account for concentration gradients by writing separate mole balances on the fluid phase and on the catalyst phase.

Once again, the approach presented in this unit is but one of many means of accounting for concentration gradients during heterogeneous catalysis. A similar approach can be applied to additionally account for temperature gradients. The approach used here uses the pseudo-continuum model for the porous solid; models can also be developed using other pore models. This approach can be adapted to catalyst geometries other than spherical and to situations where the total number of moles changes upon reaction. These topics are typically treated in much greater detail in advanced courses on kinetics and reaction engineering.