Monte Carlo Simulation of Diffusion and Chemical Reaction in Catalyst Pores

Diffusion and chemical reaction in a catalyst pore is simulated as a Monte Carlo process. In this analysis the average diffusion distance, calculated for a large number of wall collisions, and the reaction probability are computed as two independent statistical events. This formulation yields results that compare very well with the theoretical values, yet uses minimal computer time. Results reported include typical concentration profiles and effectiveness factors for first- and second-order isothermal reactions using the method described. These results show promise of extension to more complex systems where analytical solutions are not available.

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Introduction

Over the past 35 years, the subject of simultaneous diffusion and chemical reaction in porous catalysts has received considerable attention from catalytic chemists and chemical engineers. Many analytical, asymptotic, and numerical solutions to the governing equations have appeared in the literature. Included among the numerous solutions are systems involving complex order kinetics, nonisothermal catalyst particles, and deactivating systems. More recently, a complex and important industrial problem has begun to receive attention, that relating to the desulfurization of crude oil that have high vanadium and nickel contents. When the cobalt-molybdenum catalyst generally used in this process is exposed to these crudes, the vanadium, in particular, tends to plug the pore mouths of the catalyst. Conventional numerical solutions to this type of system are cumbersome and expensive in terms of computer time.

The purpose of this paper is to explore the Monte Carlo method as an alternative to the more usual numerical methods for solving the governing equations of diffusion. We apply the Monte Carlo method to the simplest of systems for the purpose of developing the method and appraising its use in practical problems.

If one applies the Monte Carlo method in a conventional fashion to problems of simultaneous diffusion and reaction, one quickly learns that the number of diffusion jumps required before a single reaction takes place is extremely large. This is because the reaction probability in the time interval of one collision is small in catalysts of normal activity. The ethylene dehydrogenation reaction over a platinum catalyst at 273 K and 10,000 Pa for example, has a reaction probability of 6.3×10^{-7} (Somorjai, 1981). This means that one would have to follow 10^7 collisions of the reactant with the wall to obtain, on the average, one reaction. Such a numerical algorithm would use excessive computer time. In this work, we utilize a method that effectively increases the number of molecular collisions with the pore wall in a defined interval. This value, coupled with the reaction probability per collision, yields the reaction probability in an interval and may be set to an arbitrary value. The ideal value of the reaction probability minimizes the number of inventoried events necessary to yield accurate results.

As we have applied it to this problem, the Monte Carlo method inherently gives the concentration profiles; however, what we want is the effectiveness factor, or a quantity related to the rate of reaction of the catalyst. In this paper we offer an accurate and relatively convenient method to make this calculation from the concentration profiles.

Modeling

A simple mass balance on a single pore, as seen in Figure 1 leads to

$$D\frac{d^2C}{dz^2} - \rho SkC^n = 0 \qquad (1)$$

The boundary conditions are at $z = 0$, $C = C_o$, and at $z = L$, $dC/dz = 0$. Here, k is the reaction rate constant, D is the diffusivity, C is the reactant concentration, z is the distance into the pore, and ρS is the surface area per unit volume of catalyst. This

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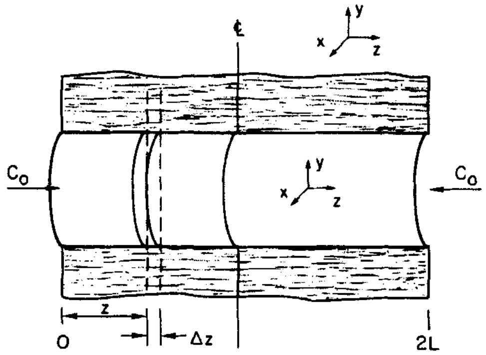

Figure 1. A single idealized cylindrical pore in a catalyst particle.

product corresponds to $2/r$ for a uniformly cylindrical pore. For convenience in further analysis we nondimensionalize Eq. 1 by defining

$$\psi \equiv \frac{C}{C_o}; \quad \xi \equiv \frac{z}{L}; \quad \Phi \equiv L\left(\frac{2kC_o^{n-1}}{rD}\right)^{1/2} \tag{2}$$

Substituting in Eq. 1 yields

$$\frac{d^2\psi}{d\xi^2} = \Phi^2\psi^n \tag{3}$$

which is subject to the conditions at $\xi = 0$, $\psi = 1$, and at $\xi = 1$, $d\psi/d\xi = 0$. The parameter Φ is often referred to as the Thiele parameter, or modulus, and represents the ratio of the surface reaction rate to the diffusion rate throughout the catalyst pellet. The magnitude of the concentration gradient within the catalyst pore depends upon the magnitude of the Thiele parameter.

Although the concentration profile is of interest, of more practical concern is the rate of reaction. The effectiveness factor, η, is defined as the ratio of the actual reaction rate for the entire catalyst particle to the rate of the same particle evaluated at conditions at the exterior surface (Thiele, 1939). This quantity also serves as the measure by which the reaction rate is changed due to the resistance of diffusion in the pores. A form of the effectiveness factor is given by Petersen (1965) as

$$\eta = \int_0^1 \psi^n \, d\xi \tag{4}$$

and may be determined by integrating the concentration profile.

The immediate objective of this work is to solve Eq. 3 for the concentration profile by a Monte Carlo method and use Eq. 4 to obtain the effectiveness factor. This exercise enables us to appraise the utility of the Monte Carlo method in solving problems involving complex catalytic systems.

Monte Carlo Simulation

Consider the first-order isothermal reaction represented by

$$\frac{d^2\psi}{d\xi^2} - \Phi^2\psi = 0 \tag{5}$$

where at $\xi = 0$, $\psi = 1$, and at $\xi = 1$, $d\psi/d\xi = 0$. The behavior of this system depends uniquely on the numerical value of the Thiele parameter. In molecular terms, when a molecule strikes a pore wall it has two alternatives, to bounce off or to react. If the probability of reaction and distance traveled in the pores can be expressed in terms of the Thiele parameter, then a Monte Carlo simulation can be performed. In order to accomplish this k is redefined in terms of αX, which represents the reaction probability per collision. In simple form

$$k = \frac{\alpha X \bar{u}}{4} \tag{6}$$

α = reaction probability on striking an active surface
X = fraction of surface that is active
$\bar{u}$ = mean molecular velocity

Diffusion is assumed to be in the Knudsen flow regime, characterized by a bulk phase mean free path greater than the pore diameter, thereby eliminating the influence of intermolecular collisions. Upon substituting Eq. 6 and the Knudsen form of the diffusion coefficient (Knudsen, 1909; also Appendix, Eq. A1) into our previous expression for the Thiele parameter, we find that

$$\Phi^2 = \frac{3L^2\alpha X}{(2r)^2} \tag{7}$$

which is quite similar to the form proposed by Wheeler (1951). A closer examination of Eq. 7 leads to the understanding that the square of the length-to-diameter ratio is proportional to (a) the number of collisions with the pore wall, or (b) the number of random walks required for a molecule to penetrate the pellet or the length L (Merrill, 1977; also Appendix).

To determine a concentration profile, and keep the reaction probability within a meaningful range, we divide the pore into N equal intervals and define a distance Y such that

$$Y = \frac{L}{N} \tag{8}$$

In the Appendix we show that the number of random walks, or wall collisions, necessary to traverse a distance $\sqrt{\overline{Y^2}}$ in the z direction is

$$n_Y = \frac{3\overline{Y^2}}{2(2r)^2} \tag{9}$$

Hence

$$\frac{1}{2}\left(\frac{\Phi}{N}\right)^2 = \frac{3\overline{Y^2}\alpha X}{2(2r)^2} \tag{10}$$

is the reaction probability for n_Y collisions. This readily lends itself to a Monte Carlo calculation by observing that $(1/2)(\Phi/N)^2$ is the reaction probability after a molecule has traversed a distance $\sqrt{\overline{Y^2}}$. Hence, random numbers between 0 and $(1/2)(\Phi/N)^2$ indicate reaction, while the remainder between $1 - (1/2)(\Phi/N)^2$ and 1 indicate no reaction.

The second and more difficult part of this Monte Carlo simulation requires that we know the location of the molecule in the pore. To do this we ask how far and in what direction, on the average, will a molecule go in n_Y collisions with the wall? More precisely stated, if a molecule makes n_Y collisions with the pore wall in a time t, what is the probability that it will travel a distance z? Let us call this probability $P(z, t)\,dz$.

The probability distribution $P(z, t)$ comes directly from the solution to the unsteady state diffusion in an infinite solid having a source at $z = 0$ when $t = 0$. The mathematical problem is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \tag{11}$$

where $C = 0$ at $t = 0$ for all $z \neq 0$ and C has a finite value at $t = 0$ at $z = 0$.

The general solution to Eq. 11 is

$$C(z, t) = \beta t^{1/2} e^{-z^2/4Dt} \tag{12}$$

where $C(z, t)$ is a function of position and time and β is an integration constant (Carslaw and Jaeger 1959).

We know that n_o, the amount of substance per unit area initially present at $z = 0$ and $t = 0$, remains the same at all times; hence,

$$n_o = \int_{-\infty}^{\infty} C(z, t)\,dz \tag{13}$$

Consequently, we arrive at the form of the equation in which we are interested:

$$C(z, t) = \frac{n_o e^{-z^2/4Dt}}{2(\pi Dt)^{1/2}} \tag{14}$$

for $t \geq 0$. The probability, $P(z, t)\,dz$, that a molecule has diffused a distance between z and $z + \Delta z$, is the concentration of molecules found in that volume element dividend by the total number of molecules in the original source; that is,

$$P(z, t)\,dz = \frac{C(z, t)\,dz}{n_o} = \frac{e^{-z^2/4Dt}\,dz}{2(\pi Dt)^{1/2}} \tag{15}$$

Consequently, the integral of Eq. 15 with limits on z from zero to z must represent the probability that a molecule has diffused a distance between zero and z.

$$I = \int_0^z P(z, t)\,dz = \int_0^z \frac{e^{-z^2/4Dt}\,dz}{2(\pi Dt)^{1/2}} \tag{16}$$

If we let $\zeta^2 = z^2/4Dt$, then we find that

$$I = \frac{\operatorname{erf}(\zeta)}{2} \tag{17}$$

Equation 17 shows that the probability that ζ lies between 0 and ∞ is equal to 0.5. Since $\operatorname{erf}(-\zeta) = -\operatorname{erf}(\zeta)$, the probability that ζ lies between $-\infty$ and 0 is also 0.5. This leads to a curve defined by the ordinate value equal to $0.5 + [\operatorname{erf}(\zeta)/2]$ for $\zeta \geq 0$ and $0.5 - [\operatorname{erf}(\zeta)/2]$ for $\zeta < 0$. This is equivalent to ordinate = $[\operatorname{erf}c\,(-\zeta)/2]$. To obtain a value of ζ for the Monte Carlo calculation then, Figure 2 provides the necessary weighting function to correctly translate uniformly distributed random numbers into nonuniformly distributed values of ζ. Note that, as $P(z, t)$ indicates, the most probable value of ζ is zero. Finally, ζ is translated into a distance using the equation (Einstein, 1906; also Eq. A2)

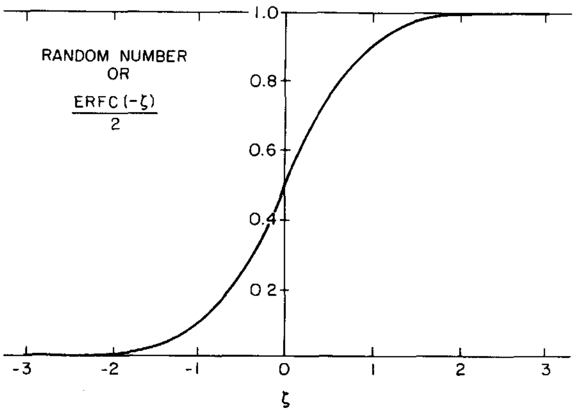

Figure 2. Diffusion distance probability relation.

$$\overline{Y^2} = 2Dt \tag{18}$$

and our previous definitions $\zeta^2 = z^2/4Dt$ or $z^2 = 4Dt\zeta^2$ and $Y = L/N$. We now introduce $\xi = z/L$ into our analysis and obtain our final result given in

$$\xi = \frac{\sqrt{2}\zeta}{N} \tag{19}$$

where ξ is the dimensionless distance traveled between subsequent n_Y collisions with the wall. Utilizing a random number, Figure 2, and Eq. 19, one may obtain a value of ξ for each set of n_Y collisions. Since N is used to determine the distance traveled, the time is indirectly set by Eq. 18. Hence, we need not introduce additional time dependence into the model.

To acquire reasonable accuracy, we choose N so that the probability of reaction within the distance Y is small. Experience is required to estimate the optimum value of $(1/2)(\Phi/N)^2$. If it is too high, inaccurate concentration profiles result because N is small. If this reaction probability is too low, an exorbitant amount of computer time is required to obtain meaningful results. For the tests run in this work a value of $N = 10$ was generally satisfactory. For large Thiele parameters, however, a greater value of N was chosen to maintain a low reaction probability. Smooth profiles were obtained within 20,000 pore wall collisions.

The Monte Carlo simulation to obtain the concentration profile in a pore follows a molecule in its journey through the pore. From the starting point its position is determined after each n_Y collisions by a random number, and whether it reacts is determined by another random number. If the molecule is determined to react, the event is recorded in its appropriate pore interval, and a new molecule is followed starting somewhere randomly determined within a mean distance $Y = -L/N$ in front of the pore mouth. [*It became apparent in using the method that starting all the molecules at the pore mouth was incorrect. They must be started within a region before the pore mouth equal to the mean distance traveled,* $Y = \sqrt{\overline{Y^2}}$ *(Zielinski, 1986). This is comparable to starting a molecule at a random* *point at the base of the cylindrical pore (Evans et al., 1980).*] If, however, the molecule is determined not to react, then, as before, the event is recorded in its appropriate pore interval and the molecule again diffuses for an additional n_Y collisions with the pore surface and the reaction/nonreaction criterion is tested again.

In calculating a new position upon diffusion we must consider two important cases: the molecule diffuses back out of the pore (i.e., $z < 0$) and the molecule diffuses past the end of the pore (i.e., $z > L$). In this simulation we argue that if a molecule reemerges from the pore mouth ($z < 0$), it is no longer monitored, and a new molecule is followed. If, however, $z > L$ a symmetry argument leads to regarding the centerline as a mirror, thus the distance z exceeding L is reflected back.

Having the concentration profiles enables us to calculate the area under the curve and the corresponding value of the effectiveness factor for various Thiele parameters. Although derivative forms are available for the effectiveness factor, the form presented in Eq. 4 is far more accurate for computer simulations since graphical differentiations are very sensitive to slight numerical inaccuracies whereas graphical integrations tend to average numerical inaccuracies.

Results and Conclusions

Monte Carlo simulation recorded the number of reactive and unreactive collisions with the pore wall inside a specified number of intervals with a statistical averaging of molecular trajectories. The pore mouth concentration, C_o, had to be determined in order to compare our Monte Carlo results to the normalized analytical solutions. To obtain C_o we developed an effective method of numerical extrapolation (Zielinski, 1986). By integrating Eq. 3 once, one notes that the slope of the concentration profile curve at a position $\xi = a$ is proportional to the area under the curve between $\xi = a$ and $\xi = 1$. A Taylor series expansion for C_o about a point near the pore mouth, used in conjunction with this area/slope relationship, yields an accurate normalization factor.

In a first-order reaction, the number of bounces within a given region is directly proportional to the local concentration and to the number of reactions in that same region. Since the number of bounces is significantly greater than the number of reactions, smoother concentration profiles are obtained using the bounce results; however, both are identical in principle. We used the number of nonreactive bounces to obtain the concentration profiles.

The general trends of the concentration profiles corresponded well with *a priori* expectations, and the simulation results provided a very satisfactory comparison to the analytical solution. A sampling of our results is depicted in Figure 3.

Effectiveness factors may now be determined from Eq. 4. These results are shown in Figure 4 and exhibit an excellent match to the analytical result. The accuracy of the predicted effectiveness factors is not surprising since they are based on the integrals of the concentration curves. Thus, the Monte Carlo method is capable of rendering accurate solutions of both concentration profiles and effectiveness factors for various Thiele parameters in first-order reactions.

The modeling of a second-order isothermal reaction in a long cylindrical pore by a Monte Carlo simulation can be performed in much the same way as that of the first-order reaction. For the second-order case, the concentration profile is a direct function of the local concentration, and to generate a final concentration profile an interative calculation must be performed with revisions of the profile subsequently made. The effectiveness factor is evaluated from the area under the square of the concentration profile curve. Results for various Thiele parameters are also provided in Figure 4. Concentration profiles and a discussion of curve-fitting techniques required to model these systems may be found in Zielinski (1986).

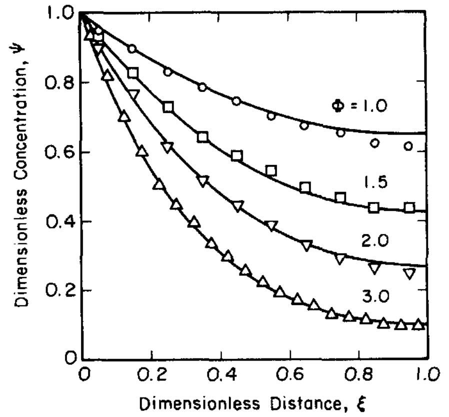

Figure 3. Concentration profiles representing analytical and normalized simulation results for various Thiele parameters.

The problems studied and modeled in this work have been examined and solved by investigators before, and accordingly the numerical results are not of major interest. The focus of this work is, rather, to adapt the Monte Carlo method to solve this type of problem and to evaluate various techniques by comparing the results to known analytical solutions. The detailed techniques presented herein are simple to program and give accurate results with relatively small amounts of computer time. In fact, the programs are short and the calculations are easily obtained on a personal computer.

It is typical of Monte Carlo methods that the difficulty in obtaining solutions does not increase rapidly with geometric or kinetic complexities, as is characteristic of analytical or more traditional numerical methods. Future work will adapt the Monte Carlo method to solve complex problems using small

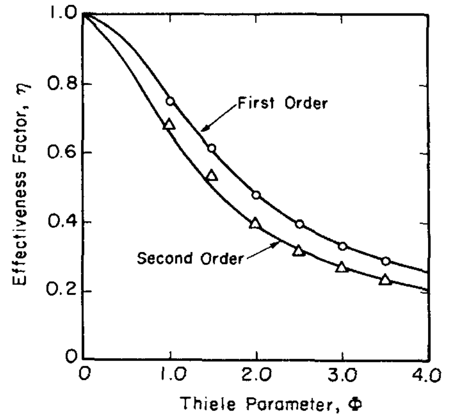

Figure 4. Effectiveness factor vs. Thiele parameter representing analytical and simulation results for first- and second-order reactions.

computers. For example, problems involving deactivation and pore size changes with reaction might be handled more easily with this method. Clearly, the Monte Carlo simulation presented in this work yields accurate results for concentration profiles and effectiveness factors, and should be considered as a method for exploring complex new applications.

Notation

A = area, cm^2
C = reactant concentration, mol/cm^3pellet
$C(z, t)$ = reactant concentration at position z and time t, mol/cm^3pellet
C_o = reactant pore mouth concentration, mol/cm^3pellet
D = diffusivity, cm^2/s
dn = differential amount of solute, mol
I = probability that a molecule has diffused a distance between 0 and z
J = flux, mol/s
k = reaction rate constant, reaction-order dependent
L = length of catalyst pore, cm
n = kinetic order of reaction
n_o = amount of diffusing species present at $z = 0$ and $t = 0$, mol/cm^2
n_Y = number of random walks required to travel distance $\sqrt{\overline{Y^2}}$
N = number of pore intervals and simulation points
$P(z, t)$ = diffusion probability per distance, cm^{-1}
r = pore radius, cm
S = surface area per gram of catalyst, cm^2/g
t = time, s
t^* = time between collisions in the pore
$\overline{u}$ = mean molecular velocity, cm/s
X = active fraction of catalyst surface
$\overline{Y}$ = mean distance, cm
$\overline{Y^2}$ = mean square distance, cm^2
z = Cartesian distance coordinate, cm

Greek letters

α = reaction probability upon striking an active surface
β = integration constant
ζ = dimensionless exponent
η = effectiveness factor
λ = mean free path, cm
ξ = dimensionless distance
ρ = catalyst pellet density, g/cm^3
Φ = Thiele parameter
ψ = dimensionless distance

Appendix

The Knudsen diffusion coefficient (Knudsen, 1909) is given as

$$D = \frac{2r\overline{u}}{3} \tag{A1}$$

for a uniformly cylindrical pore where $\overline{u}$ represents the average molecular velocity and $2r$ is the molecular mean free path. This is the same diffusion coefficient that is presented in the Einstein expression

$$D = \frac{\overline{Y^2}}{2t} \tag{A2}$$

where $\overline{Y^2}$ is the mean square distance a molecule travels in the z direction in a time t.

The average molecular velocity may also be viewed as the mean free path over the time required to travel that distance. Thus for our cylindrical pore we have

$$\overline{u} = \frac{2r}{t^*} \tag{A3}$$

By making the appropriate substitutions and equating the diffusion coefficients of Eqs. A1 and A2 we obtain

$$\frac{(2r)^2}{3t^*} = \frac{\overline{Y^2}}{2t} \tag{A4}$$

which when rearranged yields

$$\frac{t}{t^*} = \frac{3\overline{Y^2}}{2(2r)^2} \tag{A5}$$

The ratio t/t^* represents the number of collisions a molecule experiences in traveling a distance $\sqrt{\overline{Y^2}}$. Let us call this ratio n_Y.

If αX represents the reaction probability per collision, then the product of n_Y and αX expresses the reaction probability for a molecule traversing a mean distance of $\sqrt{\overline{Y^2}}$.

$$\text{Reaction probability} = \frac{3\overline{Y^2}\alpha X}{2(2r)^2} \tag{A6}$$

By identifying Y of Eq. 8 with $\sqrt{\overline{Y^2}}$, and substituting Eq. 7 into Eq. A6, one obtains

$$\text{Reaction probability} = \frac{1}{2}\left(\frac{\Phi}{N}\right)^2 \tag{A7}$$

Thus, we define the reaction probability within an interval Y by setting a number of pore intervals N.

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