The Dynamics of a Nonisothermal Catalyst Particle in a Surrounding Fluid

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The dynamics of a first-order exothermic chemical reaction in an idealized (lumped) catalyst particle are considered. The particle exchanges heat and mass with its surroundings. When the concentration and temperature of the surroundings are constant the system is governed by a set of two ordinary differential equations and either steady state or oscillatory behavior can occur. (Uppal et al., 1976, present a discussion of the nonisothermal continuous stirred-tank reactor, which is also governed by the same equations.)

The behavior of such systems can be greatly influenced by exchange of heat or mass with nonconstant surroundings. Such an increase in complexity has been demonstrated, for example, in both the steady state stability (Tsotsis, 1983) and the dynamic behavior (Mankin and Hudson, 1985) of coupled catalyst particles, in the dynamics of a nonisothermal CSTR with a wall of finite heat capacity (Planeaux and Jensen, 1985), and in the dynamics of a biological cell which exchanges mass with its surroundings (Othmer, 1985).

For this note we consider an exothermic reaction that exchanges both heat and mass with a surrounding fluid such as that found in the interstices of a packed-bed reactor. The reactant flows into the interstitial fluid from some external source. The surrounding fluid is passive, i.e., no chemical reaction occurs in it. Furthermore, we assume that there is sufficient heat transfer to the reactor cooling system such that the surrounding fluid is isothermal. However, the concentration in the fluid is allowed to vary autonomously. Under these conditions the system is governed by three ordinary differential equations, namely, the material and energy balances for the particle, and the material balance for the fluid:

$$\frac{dC}{dt} = -C + Da(1 - C)\exp(T) + C_x \tag{1}$$

$$\frac{dT}{dt} = -\beta T + BDa(1 - C)\exp(T) \tag{2}$$

$$\frac{dC_x}{dt} = -C_x/\tau_x - \eta(C_x - C) \tag{3}$$

The large activation energy limit has been assumed in the temperature dependence of the reaction rate.

The behavior of the particle equations, Eqs. 1 and 2, with constant fluid conversion C_x, was first considered. Figure 1 shows a bifurcation diagram as a function of C_x for $Da = 0.085$, $B = 20$, and $\beta = 2.55$. At low values of the external conversion (high concentrations of reactant) the particle goes to a hot steady state. As the external conversion is increased, a limit cycle appears briefly before the system drops to a cold steady state.

We consider now the case where C_x is allowed to vary. For appropriate values of the system parameters C_x will oscillate slowly back and forth over the range where the limit cycle comes into existence, grows in amplitude, and disappears. A slow variation of the fluid relative to the oscillations of the particle is obtained by choosing large values of τ_x. In this manner a relaxation oscillator can be produced in which reactant in the external fluid builds up until it reaches a level where the particle ignites. When the particle ignites, the reactant from the surrounding fluid is depleted until the particle can no longer remain ignited and the process starts over again, producing complex periodic oscillations or chaos. Hudson and Rössler (1984) have obtained chaos in model isothermal chemical reactions by adding a third variable in a similar way. The oscillations being discussed here are autonomous; chaos can also be obtained in a forced second-order set of equations such as those governing a nonisothermal CSTR (Mankin and Hudson, 1984).

We consider the behavior of the system as a function of η, all other parameters being held constant. A time series of the temperature for a periodic oscillation obtained at $\eta = 0.1$ is presented in Figure 2. For decreasing η there is a series of period-doubling bifurcations, the first at $\eta = 0.098007$ and the second at $\eta = 0.0980015$, leading to chaos at 0.098001. The chaotic region is small; for $\eta < 0.098$ the system goes to a small-amplitude limit cycle, after a chaotic-appearing transient.

The chaos obtained at $\eta = 0.098$ is shown in Figure 3. The sigmoid-shaped curve through the center of the figure is the steady state obtained for constant C_x; the dotted portion of the curve denotes the unstable region. It can be seen from both Fig-

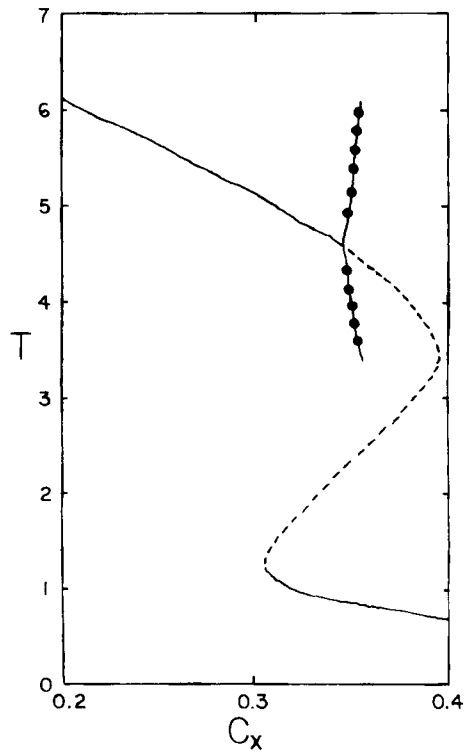

Figure 1. Bifurcation diagram of the particle (Eqs. 1 and 2) as a function of C_x.

$Da = 0.085, B = 22, \beta = 2.55$

——Stable steady state

– – –Unstable steady state

●–●–●Stable limit cycle

ure 2 (periodic) and Figure 3 (chaotic) that for some time the conversion and temperature of the particle remain close to the steady state (constant C_x) values, while C_x is increasing. When the steady state becomes unstable the particle starts oscillating and spiraling away from the steady state. When the conversion has increased to the point where the limit cycle no longer exists, the particle rapidly drops in temperature toward the cold steady state. When this happens, the reaction rate drops and reactant begins building up in the external fluid. When the fluid conversion has dropped sufficiently, the particle reignites in a large

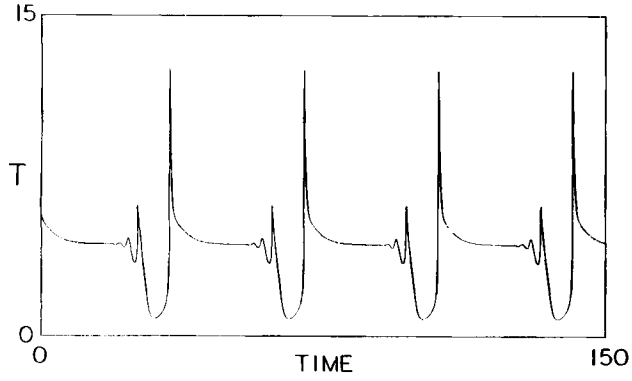

Figure 2. Time series of temperature in complex periodic behavior.

$Da = 0.085, B = 22, \beta = 2.55, \tau_x = 6.5786, \eta = 0.1$

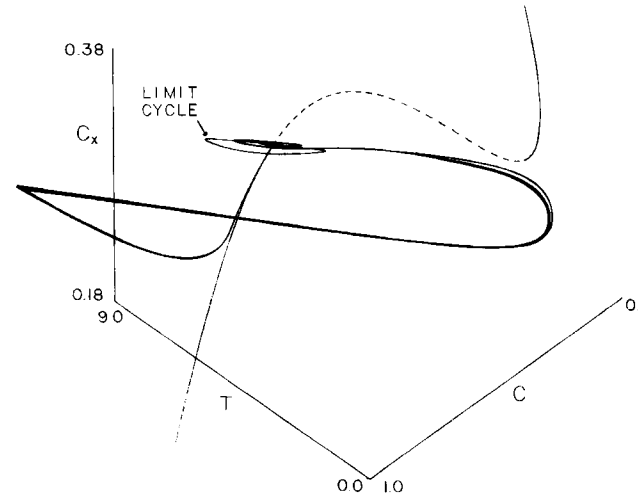

Figure 3. Three-dimensional state-space plot of the chaotic attractor.

$Da = 0.085, B = 22, \beta = 2.55, \tau_x = 6.5789, \eta = 0.098$

Also shown: stable limit cycle existing under the same conditions, and location of particle steady state at constant C_x.

temperature spike before pseudosteady state in the particle is reestablished.

Like many systems that exhibit chaos, this system also exhibits multiple oscillatory states. An unusual feature of this system, however, is a stable limit cycle that is topologically intertwined with the chaotic attractor. The chaotic attractor goes through the center of the limit cycle, as is seen in Figure 3. This limit cycle occurs approximately where the particle oscillates at constant fluid conversion, and is characterized by only a small variation in the fluid conversion along the limit cycle.

We have constructed a return map from a Poincaré section of the trajectories in Figure 3. This return map (not shown) is approximately parabolic, a shape that yields period-doubling bifurcations to chaos.

The general shape of the chaotic attractor, Figure 3, is similar to that of a class of chaotic attractors due originally to Shil'nikov (1965), and later studied by Arneodo et al. (1982). Chaos appears nearby in parameter space when there exists a homoclinic orbit involving a saddle focus. A saddle focus of the proper type was found in our problem, but it has not been verified that a homoclinic orbit exists.

As noted earlier, two catalyst particles that are coupled directly can have dynamics that are more complicated than those of a single particle. In particular, when the direct coupling is by means of mass transfer, nonuniform states and symmetry breaking can occur; however, the amount of direct mass transfer, relative to the amount of heat transfer, necessary to produce symmetry breaking is not attainable in a packed-bed reactor. In a packed-bed reactor, however, there is also indirect mass transfer between particles via the interstitial fluid. In order to determine if this indirect mass transfer can yield symmetry breaking or other phenomena not obtained with a single particle, we carried out a preliminary study of two particles in a single mixed fluid and of two particles in two separate fluid compartments connected by mass transfer. Two identical particles in the same fluid always gave uniform oscillations in which the conditions in the both particles were identical. This result is not surprising since a linear stability analysis shows that the coupling induced

by the fluid will not cause destabilization of a uniform steady state (Mankin 1985). Nonuniform oscillations and symmetry breaking were found with two identical particles when each particle was in a separate fluid and the fluids were coupled by mass transfer. No complex oscillations were found, however.

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Notation

B = dimensionless adiabatic temperature rise, $-\Delta H c_{xf} E/\rho C_p R(T_x)^2$
C = conversion of reactant inside particle
C_x = conversion of reactant in external fluid
Da = Damkohler number $k_0 \exp(E/RT_x)\tau$
E = activation energy
t = time made dimensionless with τ
T = dimensionless particle temperature $(T_p - T_x)E/R(T_x)^2$

Greek letters

β = ratio of dimensionless heat and mass transfer coefficients between particle and fluid
η = ratio of reactant capacity of the fluid to that of the particle
τ = characteristic time for mass transfer into particle, V/kA
τ_x = residence time of fluid made dimensionless with τ

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