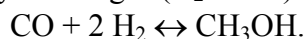


Day 29: The fixed bed catalytic reactor

The fixed bed catalytic reactor is one of the most widely used reactor types in the refining and petrochemicals industry. In its simplest form, it is just a tube filled with solid catalyst, through which gaseous (or, less frequently, liquid) reactants flow and are converted into products. When a new process is to be developed, this is often the first type of reactor to be considered. Froment and Bischoff (p. 392) present a list of large-scale refining and petrochemical processes that are carried out in fixed bed reactors. On the pages following that list, they list key factors that have led to improvements in these processes. Note that many of these are not due to the kind of reactor engineering that we learn in this course, but on 'common sense' or infrastructure improvements. An example of such an advance is the use of larger multitube reactors, which was made possible by improved welding techniques for making them and by increased shipping clearance for moving them to the plant site. Nevertheless, we will focus on the kinetics and reactor modeling in such systems. Advances in these areas have also made important contributions. Froment and Bischoff's chapter on fixed bed reactors is quite good, and we will follow their book more closely than usual in this section.

One of the first questions that we must address in designing a fixed bed reactor is if and how we will add or remove heat to and from the reactor. The simplest choice is to use an adiabatic reactor. Because heat transfer is not an issue in this case, the reactor can be a single vessel of relatively large diameter that will require no utilities during steady state operation, and only a single catalyst bed will be required. Unfortunately, many reactions of interest cannot be successfully carried out in a single adiabatic reactor. If the reaction is sufficiently endothermic, then the temperature in the reactor will drop as the reaction proceeds, and the reaction may become unacceptably slow before the desired amount of reaction has occurred. For the case of exothermic reactions, the adiabatic reaction temperature may be higher than economically acceptable reactor materials can withstand, or high temperatures may lead to unfavorable equilibria or production of unwanted byproducts. The next-simplest choice is to use a series of adiabatic reactors with interstage heating or cooling. Examples of such reactors are given on pages 395 and 396 of Froment and Bischoff. This allows us to add heat to an endothermic reaction or remove it from an exothermic reaction while still having separate heat exchangers and reactors, or separate heat exchange and reaction sections within the same reactor. Finally, we could have continuous heat addition or removal through the wall of the fixed bed reactor. This will require that the reactor have fairly small diameter so that heat transfer in or out of it is fast enough to avoid unacceptable temperature gradients in the radial direction.

A useful way to consider and compare these design alternatives is on a contour plot of reaction rate as a function of conversion and temperature. This is similar to what is done on page 397 of Froment and Bischoff (figure 11.3-4). As another example, consider methanol production from synthesis gas ($\text{H}_2 + \text{CO}$) according to the reaction



The enthalpy and entropy change of reaction for this process are $\Delta H_{rxn} = -90.1 \text{ kJ mol}^{-1}$ and $\Delta S_{rxn} = -219.2 \text{ kJ mol}^{-1} \text{ K}^{-1}$. For a given inlet composition, total pressure, and temperature, this information allows us to compute the equilibrium composition. Note that the reaction is exothermic and reversible, so we expect that there may be an optimal temperature or temperature

profile for the reactor. Suppose that for a particular catalyst, the forward rate of this reaction was given by

$$r_f \left(\frac{\text{kgmol of CH}_4\text{OH}}{\text{kg catalyst} \cdot \text{s}} \right) = 1.0 \times 10^6 \exp\left(\frac{-10000}{T}\right) p_{CO} p_{H_2}^2$$

where p_{CO} and p_{H_2} are the partial pressures of the reactants in bar. Note that the rate is expressed per catalyst mass rather than per reactor volume. This is a common practice for catalytic reactions. The net rate (even though this is not an elementary reaction) must therefore be given by

$$r \left(\frac{\text{kgmol of CH}_4\text{OH}}{\text{kg catalyst} \cdot \text{s}} \right) = 1.0 \times 10^6 \exp\left(\frac{-10000}{T}\right) \left(p_{CO} p_{H_2}^2 - \frac{1}{K_{eq}} p_{CH_4} \right)$$

where K_{eq} is the pressure equilibrium constant, given by

$$K_{eq} = \frac{p_{CH_4,eq}}{p_{CO,eq} (p_{H_2,eq})^2} = \left(\frac{1}{p_{ref}} \right)^2 \exp\left(\frac{\Delta S_{rxn}}{R}\right) \exp\left(\frac{-\Delta H}{RT}\right)$$

where p_{ref} is the reference pressure for the standard state enthalpy and entropy of reaction, which is 1 atmosphere. Therefore, we have

$$\frac{1}{K_{eq}} = \exp\left(\frac{-\Delta S}{R}\right) \exp\left(\frac{\Delta H}{RT}\right) = 2.82 \times 10^{11} \exp\left(\frac{-10840}{T}\right)$$

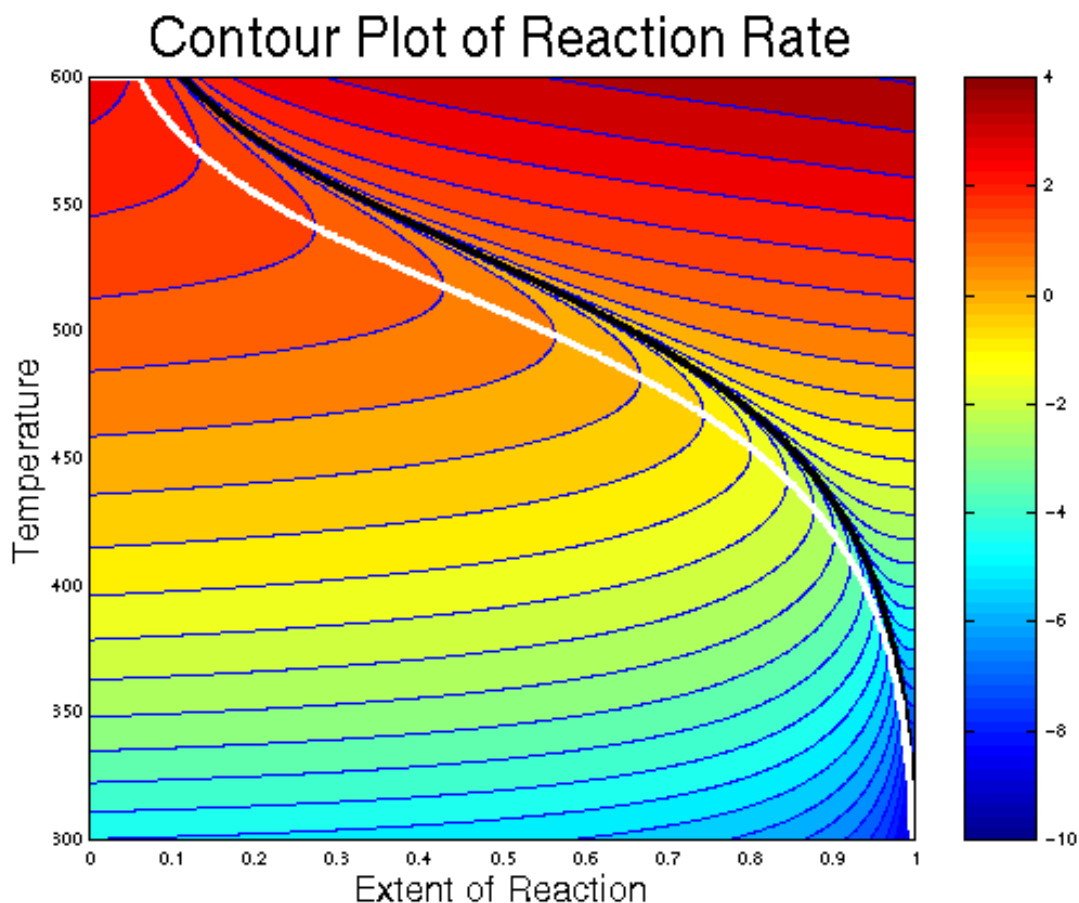
The reactant and product compositions are related by stoichiometry. For constant-pressure operation, we can characterize the reaction by a single extent of reaction, x . If we have a stoichiometric feed (2 moles of H_2 for each mole of CO), the number of moles of each species is given by $N_{CO} = N_o(1-x)$, $N_{H_2} = 2N_o(1-x)$, $N_{CH_3OH} = N_o x$, and $N_{tot} = N_o(3-2x)$, where N_o is the initial number of moles of CO . The partial pressures are given by

$$p_{CO} = p_{tot} \frac{1-x}{3-2x}, \quad p_{H_2} = p_{tot} \frac{2(1-x)}{3-2x}, \quad p_{CH_3OH} = p_{tot} \frac{x}{3-2x}$$

So, the net reaction rate is

$$r = 1.0 \times 10^6 \exp\left(\frac{-10000}{T}\right) \left(2 \left(\frac{p_{tot}(1-x)}{3-2x} \right)^3 - 2.82 \times 10^{11} \exp\left(\frac{-10840}{T}\right) \frac{p_{tot} x}{3-2x} \right)$$

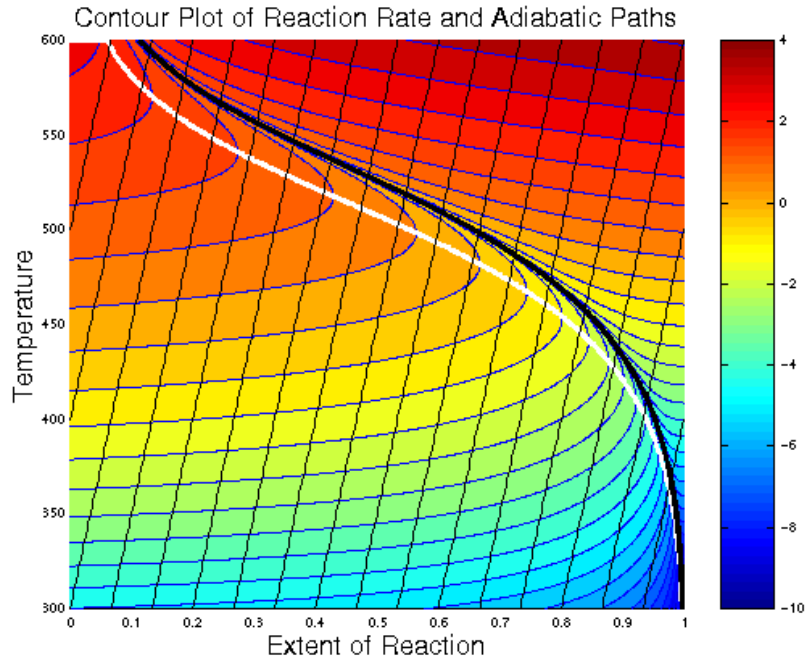
This allows us (for a given total pressure) to construct a contour map of reaction rate vs. temperature and extent of reaction. This is shown below for a total pressure of 50 bar, where the color indicates the logarithm (base 10) of the reaction rate in kgmol per kg catalyst per second. The dark curve is the equilibrium line. Below that curve, we have net reaction in the forward direction, and above that line, we have net reaction in the reverse direction. The white curve shows the locus of temperatures that give the maximum rate for a given extent of reaction. This curve follows the equilibrium curve quite closely. Following this path of maximum reaction rate would give the minimum total residence time (minimum catalyst) for the reactor.



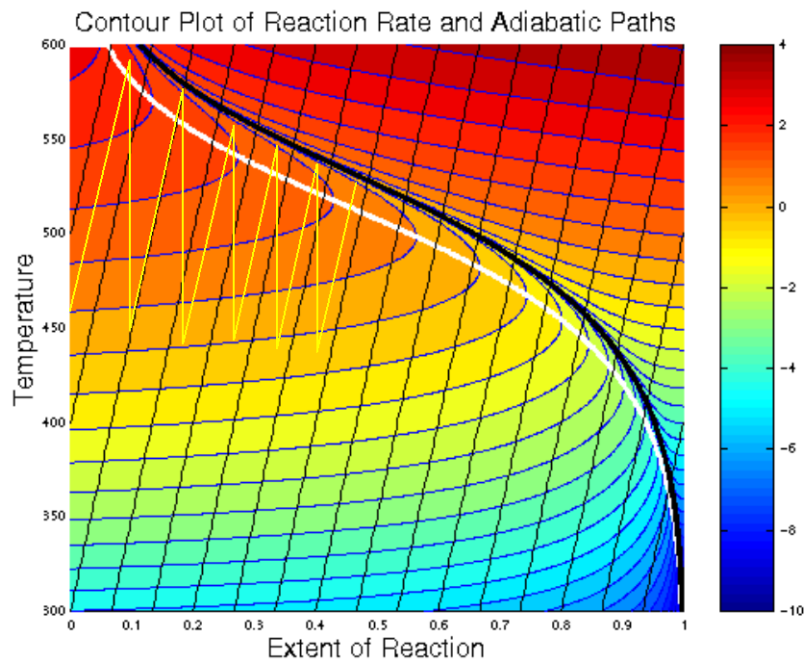
If the reactor is run adiabatically, then the temperature and extent of reaction are related by the energy balance. When we assume constant heat of reaction and total specific heat (not such a great assumption in this case, but the results will be qualitatively correct) then this relationship is

$$T = T_o + \frac{-\Delta H}{C_p} x$$

where C_p is the specific heat of the mixture, *per mole of methanol* (assumed constant). On the above plot, this is a straight line, with slope $(-\Delta H/C_p)$. For an exothermic reaction (like the one considered here) that slope will be positive. H_2 and CO both have a molar heat capacity of about $7/2 R = 29 \text{ J mol}^{-1} \text{ K}^{-1}$, while the molar heat capacity of methanol is about $44 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298 K, increasing at higher temperatures. So, at $x = 0$, the mixture specific heat per mole methanol is about $3 \times 29 = 87 \text{ J mol}^{-1} \text{ K}^{-1}$. At $x = 1$, the mixture specific heat is $44 \text{ J mol}^{-1} \text{ K}^{-1}$ (at 298 K). So, the heat capacity per mole methanol (which is proportional to the heat capacity per unit mass) drops by almost a factor of 2 over the course of the reaction. Nevertheless, we will assume it is constant, with a value of $60 \text{ J mol}^{-1} \text{ K}^{-1}$. Then, the adiabatic reaction paths on the above plot will have a slope of $90000 \text{ J mol}^{-1} / 60 \text{ J mol}^{-1} \text{ K}^{-1} = 1500 \text{ K}$. These adiabatic reaction paths are superimposed on the reaction rate contour plot presented below.



In an adiabatic reactor, we necessarily follow one of these straight lines. As you can see, we cannot follow any of them over a very large range of conversion without running into the equilibrium line. However, we can move from line to line by using multiple reactors with cooling in between. Thus, we might follow a zig-zag pattern on the above chart, as illustrated below.



As you can see from the above picture, for a very exothermic reaction like this one a large number of stages will be required to get to high extent of reaction. It may, therefore be more economical to design a reactor with continuous cooling through the reactor wall. This could be engineered to more closely follow the curve that gives the maximum reaction rate. Alternatively,

we could change the slope of the adiabatic paths by adding an inert diluent (e.g. nitrogen) that increases the heat capacity, per mole of reactant. We could also use a large excess of one of the reactants, which would have a similar effect on the heat capacity, but would cause less of a decrease in reaction rate.

Once we have decided on the basic layout of the reactor (adiabatic, multiple adiabatic reactors with interstage cooling, multitube continuously cooled, or some combination thereof), we must model the reactor more quantitatively for doing actual reactor design. At the micro- and meso-scale, we need to model the reaction kinetics and any transport limitations within or at the surface of the catalyst particle. We learned how to do that in the first half of the course. However, we must now couple those micro-and meso-scale models to a macro-scale reactor model. The simplest way to do that is to separate the two. We assume that we can write the overall reaction rate as a function only of the gas phase concentrations and temperature, and we only model the gas phase. This is called a pseudohomogeneous model. We can further subclassify the pseudohomogeneous models based on the types of transport that are included. If we have only convection (no mixing in the radial direction, no diffusion or dispersion in the axial direction) then we have the ideal plug flow reactor model. If we also consider transport by diffusion or dispersion in the axial direction, then we have the plug flow model with axial dispersion. If we explicitly consider mixing by diffusion or dispersion in both the radial and axial directions then we have a 2-dimensional reactor model. We can write the same 3 analogous models as heterogeneous models, where we explicitly consider differences between the bulk fluid phase composition and the composition at the catalyst surface.

For the ideal PFTR model with no axial mixing, the governing equations are (in Froment and Bischoff's notation)

$$\frac{d(u_s C_A)}{dz} = -r_A \rho_B$$

$$u_s \rho_g c_p \frac{dT}{dz} = (-\Delta H) r_A \rho_B - 4 \frac{U}{d_t} (T - T_r)$$

$$\frac{dp}{dz} = f \frac{\rho_g u_s^2}{d_p}$$

where u_s is the superficial velocity (volume of gas per reactor cross-sectional area per time), C_A is the concentration of reactant (A) in the gas phase, r_A is the rate of production of A per unit time per unit mass of catalyst, ρ_B is the overall bed density (mass of catalyst per volume of reactor), c_p is the specific heat (per unit mass) of the gas phase, T is the gas phase temperature, ΔH is the heat of reaction, U is an overall heat transfer coefficient for heat transfer through the reactor wall, d_t is the tube diameter, T_r is the temperature of the heating or cooling fluid outside the tube, p is the pressure, f is a friction factor (dimensionless), and d_p is the equivalent particle diameter (defined as the diameter of a sphere with the same external surface area per unit volume as the catalyst particle). The first two of these equations are the plug flow reactor model that we have considered extensively already. The third equation gives the pressure drop across the packed bed. Usually, we want the pressure drop across the bed to be small, because we don't want to spend money buying and running compressors. Various correlations are available for the friction factor. The most popular correlation for the pressure drop is the Ergun equation. For the

low Reynolds number conditions typical of flow through beds of catalyst pellets, the friction factor is calculated from

$$f = \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{150}{d_p \rho_g u_s / \mu}, \text{ with } d_p = \frac{6(1-\varepsilon)}{a_v}$$

where ε is the void fraction of the bed, G is the superficial mass flow velocity (mass per reactor area per second = ρu_s), μ is the dynamic viscosity, and a_v is the external particle surface area per unit reactor volume. Extensions of this equation and other correlations are given in Froment and Bischoff and references therein.

Given these equations and some feed conditions (temperature, pressure, and composition), it is straightforward to integrate the initial value problem given by the above three equations. For exothermic reactions, a critical determination to be made from the model is whether any ‘hot-spots’ will develop in the reactor, and whether ‘runaway’ or ‘extreme parametric sensitivity’ is possible. For an irreversible exothermic reaction (for example, most complete or partial oxidation reactions), the reaction rate will increase very sharply with conversion, due to the temperature rise caused by the heat release from the reaction and the strong temperature dependence of the rate parameters. This can lead to localized hot spots in the reactor, and in the worst case can lead to reactor runaway – generation of heat sufficient to damage the reactor. If the adiabatic reaction temperature for the reaction under consideration, *plus any others that would be initiated at high temperatures*, is above the maximum allowable operating temperature for the reactor, then it is essential that the development of hot-spots be avoided. Froment and Bischoff discuss analytical criteria that have been developed for determining whether hot-spots will be a problem. A more straightforward approach is to simply solve the one-dimensional model presented above for a range of initial conditions and see whether and for what conditions unacceptable temperatures are attained.

The application of this model to multiple catalyst beds in series, with heating or cooling between them is straightforward. We simply apply this model to each reactor bed, following the flow through the system. However, deciding how many beds to use and how to size them (given the fact that we can model the system) is a more difficult problem. This is discussed fairly extensively in Froment and Bischoff.

A technique that is used to recover heat released by exothermic reactions in a fixed bed reactor is to use the hot product to heat the cold feed. If this can be done without any additional heat input, it is called *autothermal operation*. It is usually economically favorable to recover the heat of reaction, and this offers a way of doing so without using an intermediate heat transfer fluid (i.e. steam). It complicates the reactor modeling task, because it couples the inlet reactor temperature to the outlet temperature. It also increases the difficulty of reactor start-up, because the heat produced by reaction is used to initiate the reaction. Analysis of this reactor configuration is an important topic, and is discussed by Froment and Bischoff, but since we will not have time to cover it in class, I will not reproduce that discussion here.

The next level of sophistication in modeling of fixed bed reactors is to consider mass transport by dispersion in addition to mass transport by the overall flow. We are still assuming a

uniform velocity, and uniform properties across the bed cross-section. As discussed previously, the importance of axial dispersion can be assessed based on the Peclet number, defined as $Pe = \frac{u_s L}{D_{ea}}$, where u_s is the superficial velocity, L is the length of the reactor, and D_{ea} is the effective dispersion coefficient in the axial direction. The model equations, with this axial dispersion term included are

$$\frac{d(u_s C_A)}{dz} = -r_A \rho_B + D_{ea} \frac{d^2 C_A}{dz^2}$$

$$u_s \rho_g c_p \frac{dT}{dz} = (-\Delta H) r_A \rho_B - 4 \frac{U}{d_t} (T - T_r) + \lambda_{ea} \frac{d^2 T}{dz^2}$$

$$\frac{dp}{dz} = f \frac{\rho_g u_s^2}{d_p}$$

where λ_{ea} is the effective thermal conductivity in the axial direction. It depends on the catalyst properties and the catalyst packing as well as the flow, since much of the heat conduction will be through the solid catalyst. The effective transport coefficients, in principle, capture mixing and heat conduction in the axial direction from all sources, including non-uniformities in the flow field. Mathematically, we now have a boundary-value problem rather than an initial value problem. In principle, this leads to the possibility of multiple steady states in the reactor. However, it is unlikely that for any realistic conditions that would be present in a fixed-bed catalytic reactor, these multiple steady states could be achieved. In the previous lecture we saw how to solve such boundary value problems numerically. Unless the bed is unusually shallow or axial mixing is unusually strong, this model usually only results in slight changes from the ideal plug flow model.

For reactors with heat addition or removal at the wall, it may be necessary to consider gradients of temperature and composition in the radial direction. As was the case for axial dispersion, effective transport parameters that capture mixing due to an assortment of physical mechanisms are used. With these terms, the equations become

$$\frac{\partial(u_s C_A)}{\partial z} = -r_A \rho_B + D_{ea} \frac{\partial^2 C_A}{\partial z^2} + \frac{D_{er}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right)$$

$$u_s \rho_g c_p \frac{\partial T}{\partial z} = (-\Delta H) r_A \rho_B + \lambda_{ea} \frac{\partial^2 T}{\partial z^2} + \frac{\lambda_{er}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right)$$

$$\frac{\partial p}{\partial z} = f \frac{\rho_g u_s^2}{d_p}$$

Mathematically, these are now partial differential equations, in two dimensions (the cylindrical coordinates r and z). As written, they are a boundary value problem in two dimensions – that is, the PDEs are 2nd order in both the r and z coordinates. Sometimes, it will be possible to neglect the axial mixing term in this formulation, in which case the equations become

$$\frac{\partial(u_s C_A)}{\partial z} = -r_A \rho_B + \frac{D_{er}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right)$$

$$u_s \rho_g c_p \frac{\partial T}{\partial z} = (-\Delta H) r_A \rho_B + \frac{\lambda_{er}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right)$$

$$\frac{\partial p}{\partial z} = f \frac{\rho_g u_s^2}{d_p}$$

These are now an initial-boundary value problem – equivalent to a time-dependent one-dimensional boundary value problem. Mathematically, they can be handled much more easily than the full 2-dimensional boundary value problem. Since we are now explicitly considering transport in the radial direction, the term corresponding to overall heat transfer from the heating or cooling medium to the reactor has disappeared from the equations. Heat transfer within the bed is now being treated explicitly in the equations, and heat transfer across the wall is included in the boundary condition at the wall. At the wall, we have the boundary conditions

$$\frac{\partial C_A}{\partial r} = 0$$

$$-\lambda_{er} \frac{\partial T}{\partial r} = \alpha_w (T - T_w)$$

where T_w is the temperature of the (inner surface of) the wall and α_w is a heat transfer coefficient from the wall to the bed. This assumes that the wall temperature is known. Of course, one might replace the wall temperature with the temperature of a heating or cooling fluid and replace the heat transfer coefficient with one that represents heat transfer from that fluid to the bed. Various correlations for the effective conductivity and for the heat transfer coefficient are given by Froment and Bischoff. If we wish to accurately predict radial temperature gradients, it is essential that we use an accurate value for the effective conductivity. For given heat generation, it determines the temperature rise within the reactor. Froment and Bischoff (beginning on p. 457) give a fairly detailed presentation of the application of this model to catalytic oxidation of o-xylene to phthalic anhydride on a vanadia catalyst. They show that there is strong parametric sensitivity to the feed temperature, and how dilution of the catalyst bed with inert material can reduce this sensitivity. They also compare this to an equivalent one-dimensional model, and find that the predicted temperature for runaway differs by 5°C from the prediction of the 2-D model.

The next level of sophistication in modeling a fixed bed reactor is to explicitly account for non-uniform axial velocity. Up to this point, we have assumed plug flow in all of the fixed bed reactor models, even when we were considering radial variations in other quantities. This is a good approximation across most of the bed, but near the wall there are variations in velocity due to variations in the void fraction near the wall. This can be included in the model by modifying the equations as shown in Froment and Bischoff on p. 463-464. This is still not a complete hydrodynamic model, in the sense that there is no attempt made to accurately simulate the flow patterns in the reactor. Rather it simply takes into account the effect of the wall and of the changes in void fraction near it on the velocity in the reactor.

All of the above models were categorized as *pseudohomogeneous* models. Only equations describing the fluid phase were considered, and it was assumed that the reaction rate could be written as a simple function of the gas phase concentrations. This is not necessarily the case. For all of the above model types, we could also explicitly model the solid phase and any heat and mass transfer processes within it and in the boundary layer adjacent to it. As we saw earlier when we were considering intraparticle and interfacial gradients alone (without an overall reactor model), we can write for a single (spherical) catalyst particle

$$\frac{D_e}{\xi'^2} \frac{d}{d\xi'} \left(\xi'^2 \frac{dC_s}{d\xi'} \right) = \rho_s r_A(C_s, T_s)$$

$$\frac{\lambda_e}{\xi'^2} \frac{d}{d\xi'} \left(\xi'^2 \frac{dT_s}{d\xi'} \right) = \rho_s (\Delta H) r_A(C_s, T_s)$$

with boundary conditions

$$\text{at } \xi' = 0 \quad \frac{dC_s}{d\xi'} = \frac{dT_s}{d\xi'} = 0$$

$$\text{at } \xi' = \frac{d_p}{2} \quad k_g(C_s^s - C) = -D_e \frac{dC_s}{d\xi'} \quad h_f(T_s^s - T) = -\lambda_e \frac{dT_s}{d\xi'}$$

where C_s is the local concentration within the particle (a function of position), T_s is the local temperature within the particle, ξ' is the radial position within the particle, $r_A(C_s, T_s)$ is the local reaction rate within the particle, per unit particle volume, D_e is the effective diffusion coefficient within the particle, λ_e is the effective thermal conductivity within the particle, k_g is the mass transfer coefficient for mass transfer between the external surface of the particle and the bulk fluid, h_f is the heat transfer coefficient for heat transfer between the external surface of the particle and the bulk fluid, C_s^s is the local concentration at the surface of the particle, T_s^s is the temperature at the surface of the particle, C is the concentration in the bulk gas flow, and T is the temperature in the bulk gas flow. This is a boundary value problem that we can solve for particular values of the bulk concentration and temperature. It is coupled to the reactor model by replacing the pseudohomogeneous reaction rate terms with terms that give the mass and heat transfer to or from the particles. For the ideal plug flow model of the gas phase, the model equations then become

$$\frac{d(u_s C_A)}{dz} = -k_g a_v (C - C_s^s)$$

$$u_s \rho_g c_p \frac{dT}{dz} = h_f a_v (T_s^s - T) - 4 \frac{U}{d_t} (T - T_r)$$

$$\frac{dp}{dz} = f \frac{\rho_g u_s^2}{d_p}$$

The extensions of this to include axial and/or radial dispersion are exactly as in the pseudohomogeneous model. There are two possibilities for treating this coupled model. The most straightforward approach is to simply solve the boundary value problem for the particle at each temperature and concentration predicted by the overall reactor model. It may be more efficient to solve the equations for the individual particle for a grid of temperature-concentration

pairs and then parameterize these results or interpolate between the points in this table for use in the overall reactor model. For each set of conditions, we would calculate the whole concentration profile within the pellet, but all we need to keep for use in the reactor model is the global effectiveness factor.

As we saw earlier in the semester, when the reaction is exothermic there can be multiple possible steady states for the catalyst particle. Therefore, even for the ideal plug flow overall reactor model, there can be multiple steady states for the whole reactor due to the possibility of multiple steady states within the individual particles. Usually, due to heat transfer between the particles, all of them will be in the same (either the upper, high conversion, high temperature or the lower, low conversion, lower temperature steady state) steady state. Therefore, the whole reactor is effectively either in a high conversion or low conversion steady state. If multiple steady states are possible, then transient computations have to be performed to determine which will be achieved. This is conceptually identical to what we did in constructing a phase plane for a stirred tank reactor. Obviously, implementation of the transient modeling will be substantially more difficult here than for the CSTR, since we have ordinary or partial differential equations for the steady state conditions rather than algebraic equations. Application of heterogeneous modeling for a PFTR is illustrated with two nice examples in Froment and Bischoff.

After completing your study of these lecture notes and the associated homework, you should be able to:

- (1) Construct a contour plot of reaction rate vs. conversion and temperature and use it to aid in the design of the heat addition/removal system for a fixed bed catalytic reactor
- (2) Write the governing equations for a fixed bed catalytic reactor at various levels of approximation and explain the approximations that are being made in each set of equations
- (3) Use the Ergun equation and related correlations to find the pressure drop through a packed bed
- (4) Correctly couple the pseudohomogeneous reactor modeling equations to the governing equations for reaction and diffusion within a catalyst pellet