

# Chapter 6. Experimental determination of kinetic model

## 6.1 Kinetic models from catalyst development studies

In the petrochemical industry, catalyst development studies are normally conducted in small, tubular fixed bed reactors, often in an electric furnace or in a cooling bath. The catalysts being screened are usually powdered or small grain agglomerates. Unless care has been taken to operate the reactor in an isothermal, differential (i.e. low conversion) manner, it is very difficult to develop a model from this kind of reactor. Heating or cooling almost certainly violates the isothermal criterion.

If a model were developed using the powdered catalyst, then the effective diffusivity in the pores of the commercial catalyst has to be predicted. In addition, some catalyst manufacturing methods result in unevenly distributed active sites. Finally, any model that requires solution of the intraparticle diffusion/reaction equations at each point in the reactor will be computationally intensive.

## 6.2 Modeling the Commercial Catalyst

A preferred approach [e.g. Rase (1977, vol 1), Rose (1981)], is to develop the kinetic model using the catalyst to be used in the commercial reactor (i.e. size, shape, and method of manufacture). This approach eliminates the need to predict effective diffusivity and the activity profile in the catalyst. Reaction rate expressions are developed using the concentrations in the bulk fluid outside the catalyst. Effectiveness factors or the solution of intraparticle diffusion/reaction equations are not needed with this approach.

The reader may question the wisdom of this approach since most reactor design books include a large section devoted to detailed kinetic mechanisms, tortuosity, porosity, and effectiveness factors. In the author's opinion, the kinetic mechanism investigations are more useful to the catalyst developer than to the reactor designer. Historically, a big breakthrough occurred in reactor design when the current methodology of conservation equations was first used to model a reactor. Prior methods used (probably without much success) either scaling rules or polynomial models of the data. The major accomplishment of the conservation balance method was the separation of the material and energy effects. The use of the Arrhenius form for the temperature dependency of the reaction rate was another major improvement because it modeled the highly nonlinear temperature effect on the reaction rate with a single parameter. Due to the success in this method, which came to be called the "fundamental" method, research continued to develop more detailed models.

Has that continued development of rate limiting steps, steady-state intermediates, effectiveness factors for multiple reactions or complicated rate expressions added significant improvement to the design process? In most cases, it probably has not. Due to the highly nonlinear effect of temperature on the reaction rate, the most important part of a reactor model is the prediction of the local temperature. The sensitivity of reaction rate to composition is small compared to the temperature sensitivity. As a consequence, the mathematical form of the concentration effect is not critical. Thus, power law rate expressions may work equally well as Hougen-Watson (HW) expressions with adsorption terms.

Another factor that the development engineer must consider is the time needed to develop the kinetic model. Examples of extremely detailed models of reactions that appear in the literature can be misleading. For example, the production of ammonia is a very important process that has existed for many

decades. Because of its importance, numerous studies of the reactions and catalysts have been reported, resulting in complicated models. These studies have been done well after the first plant design. When designing the first reactor for a new chemical process, the development team does not have decades of time available. Thus, power law models and a set of experiments designed for efficiency are the preferred route to a reactor model.

### **Catalyst temperature**

The catalyst temperature is usually nearly isothermal, regardless of the reaction distribution in the catalyst. In some cases, the film of fluid around the catalyst may result in a significant temperature difference between the catalyst and the flowing fluid. With a measured rate of reaction for the laboratory experiment, this temperature difference may be calculated. It is best to use the calculated catalyst temperature when building the kinetic model.

### **Intraparticle diffusion and effectiveness factors**

Conducting the kinetic experiments on commercial size catalyst will result in significant radial variation within the catalyst in the rates of each reaction. However, for a given external composition, and a given catalyst temperature, the catalyst particle will usually have a unique rate of production or consumption of each component. By modeling the net production rate at the catalyst surface as a function of the fluid composition and catalyst temperature, "intrinsic" or "fundamental" intraparticle rates are not required. Effectiveness factors or particle diffusion equations are also not required.

There is a small range of conditions that can lead to multiple steady states in a catalyst particle which would invalidate the "whole particle" approach described in the previous paragraph. Finlayson (1980) studied the effect of five dimensionless variables on the effectiveness factor for a first order, irreversible reaction. The five variables are the dimensionless heat of reaction, activation energy, two Biot numbers for heat and mass transfer to the fluid, and the Thiele modulus. The first four parameters determine whether or not multiple steady states exist (see Fig 4 and Fig 5 in Finlayson). What is more important is that multiple steady states exist over a narrow range of Thiele modulus. The existence of multiple steady states should be observed as strange or unstable results during catalyst development. By designing the catalyst with a lower activity (i.e. lower Thiele modulus), the multiple solutions and instabilities can be avoided.

### **A case for a Hougen-Watson model**

In some cases, the adsorption effects may cause the reaction rate to exhibit unusual behavior with respect to temperature. Normally, adsorption is exothermic, so the adsorption term decreases with increasing temperature. With adsorption terms in the denominator of the reaction rate, the reaction rate increases with temperature as usual. However, with an endothermic adsorption, adsorption increases and the reaction rate decreases with an increase in temperature. The overall result may cause the rate to have a local maximum value, a valley, and then return to an increasing rate as the temperature is increased. In such cases, the HW model may be the appropriate choice. In order to model this unusual behavior, the HW model must have temperature dependent adsorption coefficients. As stated earlier, the temperature effects are the most important aspect of reactor modeling. The kinetic model must have the correct temperature response, and the reactor model must provide accurate temperature profiles.

### 6.3 Reactors for kinetic studies

The Bertly Reactor, or similar, can be used for gas or liquid systems with a solid catalyst. This reactor is a CSTR so the reaction rates are determined by analyzing the effluent and subtracting the feed rates for each component.

This reactor will not adequately circulate gas through the catalyst bed if the pressure is too low. The pressure can be increased and the composition diluted back to the desired partial pressures with the addition of nitrogen, argon, or other inert gas.

The Bertly reactor should be sufficient for the single fluid phase reactors modeled in this book. As an alternative, a fixed bed with a recycle stream may be used. This system requires either a pump or a compressor, and for some systems, care must be taken to prevent condensation in the recycle stream.

### 6.4 The experimental program using a CSTR

The experimental program consists of two phases: (1) determining the powers of the concentrations or partial pressures of the species in the power law model and (2) determining the activation energy of the rate constant.

1. The first phase is conducted at one temperature. An experimental design is created that varies the feed rates of each of the reactants and products. In addition, total pressure is added as another variable. The different feed compositions in each experiment result in a different composition in the reactor and in the effluent. The reaction rates are determined by measuring the feed and effluent compositions and flow rates. The effluent composition also provides the composition used in the parameter estimation step. A minimization routine estimates the powers and the rate constant.
2. The second phase is to make runs at a constant feed composition (usually the centerpoint case in the experimental design) but at different temperatures. The rate constant,  $k$ , for each run is easily determined by algebra as shown in Example 4. The slope of a least squares line,  $\ln(k) = -E/RT$  provides the activation energy,  $E$ .

The procedure is demonstrated with two changes in **Example 4**. The first change is that the CSTR itself was not modeled to obtain the reactor and effluent compositions. Instead, the design compositions were assumed to be those of the reactor contents and effluent. The second change is that the reaction rates were determined by integration of the assumed complex reaction rates in the catalyst particle and using the slope of a reactant at the catalyst surface. This example demonstrated that a complex reaction rate could be easily reduced to a simple power law model. Provided the experimental design included the expected concentration ranges, the resulting model can be used for plant scaleup and plant design. The actual procedure has been used for design of commercial reactors and process plants.