

## CATALYTIC REACTORS: A REVIEW

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### Summary

Catalytic reactions and reactors have widespread applications in the production of chemicals in bulk, petroleum and petrochemicals, pharmaceuticals, specialty chemicals etc. This chapter aims at highlighting various aspects of catalytic reactors. Considering the wide spread application of the fixed bed reactors, they are discussed first with emphasis on both steady and unsteady state operations, fluid dynamics and heat transfer. This is followed by discussion on the reactors with moving catalyst like fluidized bed reactors. Effects of heat and mass transfer and high-pressure operation in multiphase fluidized bed reactors have been summarized. Applications of the biocatalytic reactions

in various fields, methods of immobilization and advantages of using immobilized reactors have been discussed. Further, unconventional reactors like membrane reactor, Photocatalytic reactor, moving bed and chromatographic reactors, monolith reactors, reactive distillation cum catalytic reactors and microstructured catalytic reactors are discussed.

## 1. Introduction

The simultaneous developments in catalysis and reaction engineering in 1930s and 1940s acted as a driving force for the onset of rational design of catalytic reactors. These rigorous design efforts, firmly based on sound mathematical principles, in turn triggered the development of several profitable catalytic processes. In the late 1930s, it was established that for very rapid reactions, increase in the size of porous catalyst particle size resulted in decrease in the activity of a catalyst per unit volume due to insufficient intraparticle diffusion. Various authors had studied the engineering aspects of diffusional mass transport and reaction rate interaction. In particular, Thiele explained the fractional reduction in catalyst particle activity due to intraparticle mass transfer limitations and the concept of the effectiveness factor reflecting the extent of utilization of the catalyst pellet was proposed. The diffusional disguise of the activity of a catalyst pellet is now routinely gauged by a dimensional parameter known as the Thiele modulus. In the mid 1940s, Chemical Reaction Engineering (CRE) developed into a separate branch of chemical engineering. Rapid expansion of petroleum and petrochemical based industries in the 1950s and the 1960s fueled the growth of catalytic reactors. Denbigh proposed the concept of ideal reactors and explained the importance of reaction kinetics on reactor performance. Scholarly contributions from several eminent researchers like Denbigh, Danckwerts, Levenspiel, Houghen and Watson laid the foundation of catalytic reactor modeling. Several alternative reactor configurations were examined for conducting industrially important catalytic reactions.

Simplified homogeneous models were mainly used in the beginning to measure the performance of catalytic reactors. Rigorous mathematical models developed in the 1950s and the 1960s showed that importance of intra- and inter-particle diffusion for a variety of complex situations. At the same time, non-isothermal studies of catalyst particle and reactors were also investigated. With the advent of computers, solution of complex mathematical models became relatively easy. Further, with more powerful numerical analysis and faster computers, sophisticated heterogeneous reactor models were proposed and solved. One well-known example of application of such a model in an industrial process is KINPtR, developed by Mobil for its reformer operations.

Parallel to the development of rigorous mathematical analysis of reactors, research in catalysis grew rapidly with an aim for identifying and preparing highly active, selective, and stable catalysts. With advancements in new instrumentation and analytical techniques, it is now possible to study catalysis at the atomic level, determine the structure and composition of the catalyst and precisely carry out quantitative estimation of the interaction of reactant and product at the surface of the catalyst. This information is highly useful in determining the effect of surface chemistry on the overall performance of the catalyst.

The decade of the 1970s saw widespread use of catalytic reactors in several industrial processes. Catalyst manufacturers along with automobile manufacturers were engaged in active research in search for low emission vehicles. The exciting phenomena of multiplicity and stability of steady states of catalytic reactors became an active area of research in several reputed schools. Research in optimal placement of the active catalyst (i.e. Pt, Pd, and Rh) components on the support and the optimal configuration of the support (e.g., beads versus monoliths) were also vigorously investigated.

During the 1980s catalytic reaction engineering principles were applied successfully to biochemical systems. In immobilized reactors, the reactions are catalyzed by either enzyme or whole cells immobilized by various methods. Stirred tanks, bubble columns and hollow fibers were also frequently employed for bioprocesses.

From the beginning of the 1990s to till date the research focus is on the exploration of design of novel catalytic reactors. micro-reaction engineering is an emerging field, which is rapidly developing. Several alternative micro channel catalytic reactors have been recently introduced. The high surface to volume ratio, efficient heat and mass transfer characteristics and vastly improved fluid mixing allow efficient control of process parameters with improved conversions, selectivity and yields of desired products. A broad variety of other reactor configurations have also been employed with considerable success. Of particular interest are membrane reactors, distillation and crystallization reactor configurations, which enable us to conduct reaction and separation simultaneously. Rigorous implementation of optimal policies for maximizing conversion and integration of control strategies has also been given importance in this decade. Performance enhancement employing CFD enabled flow modeling has received serious attention of industry as well as academia. The availability of super fast computing facilities has prompted incorporation of such detailed fluid dynamical and kinetic descriptions. But increased level of phenomenological description requires accurate evaluation of larger number of system parameters; this becomes rather cumbersome and difficult. To circumvent these difficulties, researchers have started looking at advancement in machine learning and artificial intelligence involving data driven models. Neural Networks and Genetic algorithms are increasingly employed along with conventional first principle models for rational design of catalysts, kinetic models and reactors. Specifically, use of Artificial Neural Modeling (ANM) has been extensively exploited to describe chemical processes. This is mainly due to their inherent ability to approximate arbitrary complex functional relationships. Artificial Neural Networks (ANN) have been used to formulate approximate kinetic models for biological as well as conventional chemical reactors. A simple neural network assisted by genetic algorithms was employed successfully to optimize the temperature profiles of a temperature gradient reactor for the catalytic synthesis of dimethyl ether.

Owing to their industrial importance, state-of-the-art reviews on catalytic reactors have appeared periodically in the literature. Currently work on preparation of an encyclopedic account of different reactors and a user-friendly interactive database is in progress at the National Chemical Laboratory, India. This work is one such effort to briefly review the development of catalytic reactors right from the days of early development to its current status. Section 2 discusses the fixed bed reactor, its types, importance of fluid dynamics, and catalyst on the reactor performance. Section 3 and

Section 4 summarize the modeling aspects of fluidized bed catalytic reactors and biocatalytic reactors respectively. Section 5 highlights the developments in unconventional reactors.

## 2. Fixed Bed Reactor

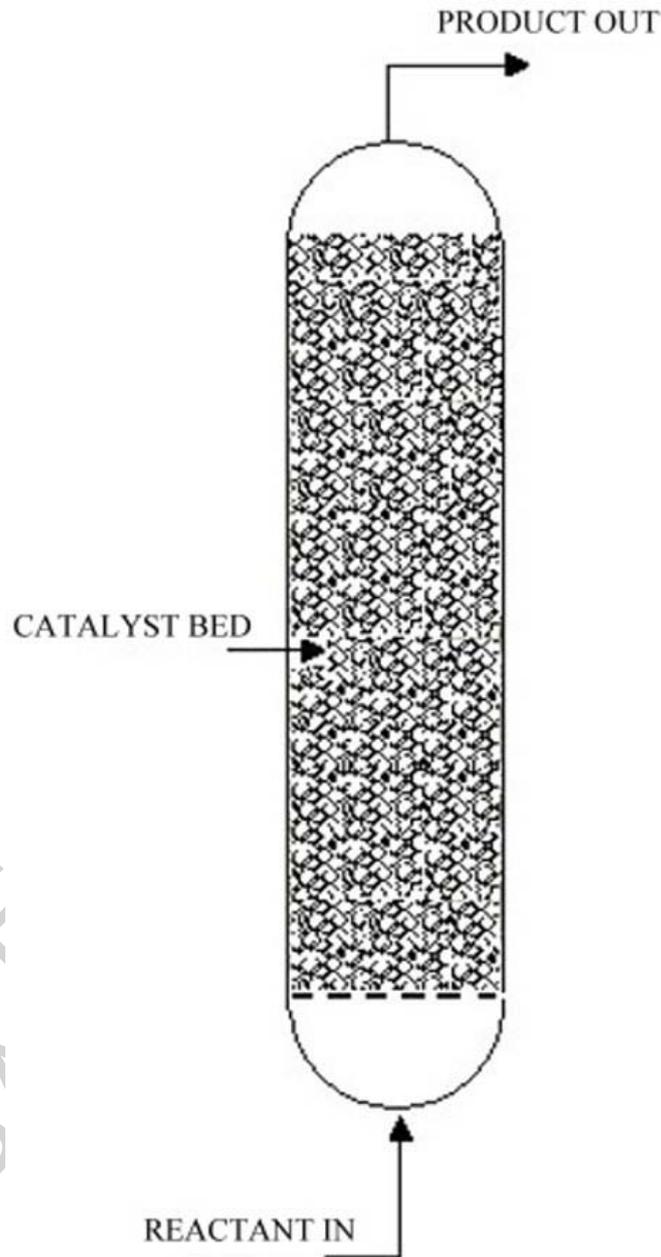


Figure 1: Packed Bed Reactor

A fixed or packed bed is an assembly of randomly arranged particles that are bathed by the reactant fluid, which flows in random manner around the pellets. A schematic representation of fixed bed reactor is shown in Figure 1. Catalytic fixed bed reactors find wide spread use in chemical industries. Several highly exothermic processes like oxidation of ethylene, naphthalene, vinyl acetate synthesis and hydrogenation reactions

are routinely conducted in fixed bed reactors. Depending on the requirements, three main types of reactor configurations, namely, adiabatic tubular reactor, nonisothermal non-adiabatic tubular reactor and heat exchanger fixed bed reactors are normally employed. A combination of tubular heat exchanger type reactor and an adiabatically operated stage is often employed to increase the capacity of production with enhanced yields. Key issues like flow patterns, heat transfer, mass transfer are studied by various groups and vast literature are available on these topics.

## 2.1. Adiabatic Reactors

Because of no heat exchange with the surroundings in adiabatic reactors, radial heat transport is absent. Many industrial reactions like, dehydrogenation of n-butenes to butadiene, hydrogenation of nitrobenzene to aniline, amination of methanol to methylamines, dehydrogenation of ethylbenzene to styrene etc., are carried out in adiabatic reactors. Normally, the diameter to length ratio is close to unity and the reactor to particle ratio is 50 or more.

Combined effects of the interactions between chemical kinetics and transport processes are simpler in adiabatic reactors than in the non-adiabatic arrangements. Mathematically, the fixed bed reactor consisting of a bed of catalyst particles can be described by two fields, viz., macro and micro fields. Due to the complex random flow pattern, large spatial variations of concentration and temperature can exist on the macro level and heat and mass dispersion effects can considerably alter the performance characteristics of the reactor. On the microscopic level, within the particle intraparticle mass and heat transfer limitations can exist. Apart from this a resistance to heat and mass transfer between the catalyst surface and macroscopic field can exist.

The earliest available models consider the fixed bed consisting of catalyst particles as an anisotropic continuum and treat the temperature and concentration fields as smooth functions of the axial distance. In the cell model, each catalyst pellet along with the neighboring empty volume was treated as a small reactor and the sequence of these cells are connected in the direction of fluid flow. Radial dispersion could be accounted for by lateral connection of cells. A set of models, known as channel models, incorporate local variations in the void volume.

Non-uniform distribution of local void volume was integrated in a group of models called channel models. Void volume reaches the maximum value near the wall; with increasing distance from the wall, it decreases to minimum. Consequently, in the region of high values of local void volume, linear velocity of the gaseous reactant mixture will be higher.

Several quasi-continuum models consisting of both single phase and two phase descriptions with differing levels of rigorousness are available in the literature for fixed bed reactor modeling. Numerically, these problems require solutions of simple initial value problems to more complicated boundary value problems. The simplest model, which considers convection of heat and mass transfer, is popularly known as piston flow model. This model predicts the performance characteristics of long packed beds with high linear velocity, smaller catalyst particles, and reactions associated with low heat

effects. Dispersion model, which takes convection along with dispersion effects into consideration, is more appropriate for the short packed beds. Both these models can be categorized as one-phase models, as they do not describe the concentration and temperature profile at the particle level.

Experimental observations by several investigators have indicated that in most industrial situations temperature gradients are small within the pellet and isothermal conditions prevail. Thus, the most relevant description of the adiabatic packed bed is provided by the two-phase model that considers axial heat conduction, mass dispersion, gas to pellet transfer, and intraparticle mass diffusion. More detailed descriptions have also been taken into account for solving more complex ignition and extinction phenomena occurring in fixed bed reactors.

Various mixing cell models (also known as *finite stage models*) have been proposed which differ in the number of stages and interaction among stages. These models include one-dimensional array of stirred pots, cell model with axial backflow, one-dimensional array of stirred pots with gas-to-solid heat and mass transfer, cell model with axial backflow, and gas-to-solid heat and mass transfer and two one-dimensional arrays of interconnected mixers.

Computation of the internal heat transfer coefficient with the desired accuracy in tubular packed bed reactors with small reactor to particle diameter ratios deserves attention. Two solutions to this problem have been proposed. Catalyst packed in the narrow tube with recorded surface coordinates can be simulated. Then, with the help of the mesh-generating program, Navier-Stokes equation can be solved in the presence of a prescribed heat generation rate in the particles. Hence, heat transfer coefficient can be calculated. Another solution to the above problem is replacement of the random packing with structural packing of catalyst.

To obtain high heat and mass transfer with low-pressure drop in adiabatic reactor, gas flow modeling and optimal catalyst shape need better attention. As particle-by-particle modeling is difficult in the massive beds, use of structured packing can provide the answer. Fluid dynamics and hence transport coefficient can be calculated for structural packing. Also, structural packing will provide reproducible packing characteristics.

## **2.2. Nonisothermal-Nonadiabatic Tubular Reactor**

Tubular nonadiabatic fixed bed reactors are usually employed for conducting highly exothermic reactions occurring in porous catalysts. Hence design of these reactors must consider safety aspects very carefully. A schematic description of Nonisothermal-Nonadiabatic tubular reactor is shown in Figure 2. In these reactors considerable concentration and temperature gradients can exist in both axial and radial directions. A detailed quasi-continuum single-phase model considering these gradients in both directions requires solution of a set of elliptic partial differential equations. Models considering gas to pellet heat and mass transfer resistances have also been proposed in the literature. Various one-dimensional and two dimensional mixed cell models considering both axial and radial heat and mass transfer have also been proposed.

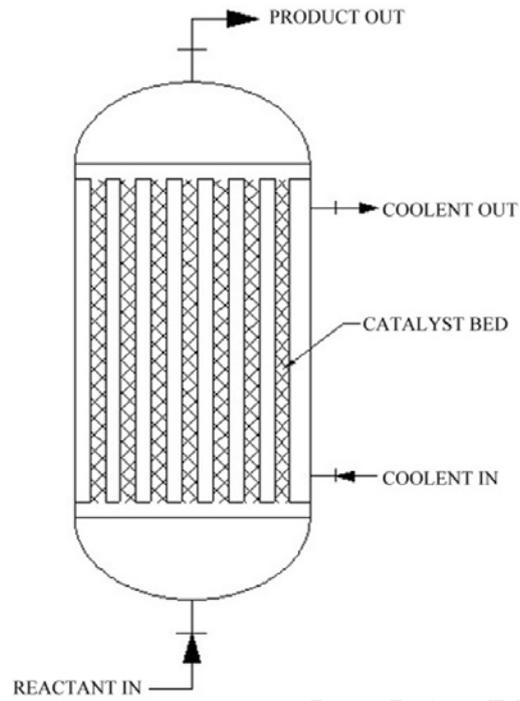


Figure 2: Non Isothermal Non Adiabatic Tubular Reactor

### 2.3. Fixed Bed Reactors with Heat Exchangers

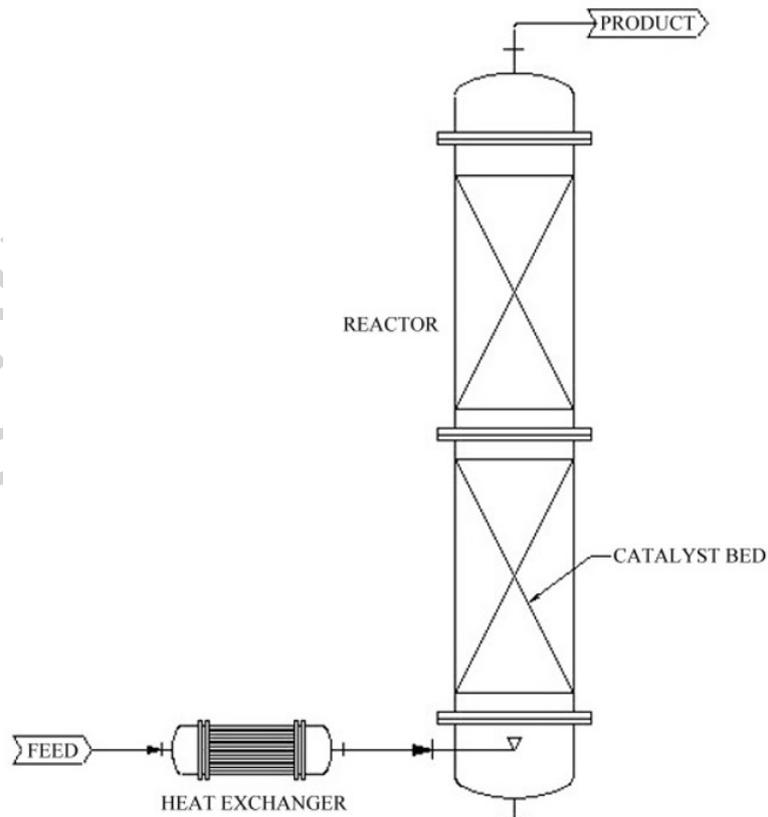


Figure 3: Packed Bed Reactor with Heat Exchanger

To carry out strongly exothermic reactions in tubular reactors, an external heat exchanger is often used to maintain the inlet temperature at the prescribed level. A diagram of packed bed reactor with external heat exchanger is shown in Figure 3. Ammonia synthesis, sulfuric acid manufacturing, and water-gas reactions are some of the commercial examples of such reactors. This configuration is also known as autothermic operation i.e. the process is capable of sustaining the appropriate reaction temperature at the reactor inlet by means of the heat liberated by the reaction itself. Various reactor configurations like reactors with external or internal heat exchangers, recycle reactors, and non-adiabatic cooled reactors are possible for carrying out such reactions. Different phenomenological models have been employed in literature for packed bed reactors accompanied by external or internal heat exchange equipment.

#### 2.4. Reverse Flow Tubular Reactor

The energy storing capacity of the packed bed is utilized by conducting unsteady state chemical reactions. Briefly, the feed gas enters the opposing ends of the adiabatic fixed bed periodically. The gas flow, controlled by valves, occurs either upward through the reactor during one half – cycle or downward during the other half cycle. Reverse flow reactors possess the main advantage of capturing the inverted U temperature profile. This is particularly beneficial in achieving high conversion with exothermic reactions. Also, maximum temperature can go beyond the adiabatic temperature rise of steady state operation.

Similarly, exothermic and endothermic reactions can be coupled effectively with reverse flow concept. Based on this theory, the Wisconsin process was developed for the thermal production of nitric oxide. Here, combustion reaction (exothermic) was coupled with the reaction between nitrogen and oxygen in air (endothermic) using reverse flow in the packed bed. The simple operation is as follows: during the odd half cycles, the feed of the exothermic reaction enters the bed. Due to the exothermic nature of reaction, the bed gets heated. In the even half cycles, the feed undergoes an endothermic reaction and it enters from the opposite end of the bed. It produces the desired product and cools down the bed.

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### **Biographical Sketches**

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