Research Assistants

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CATALYTIC REACTORS

1. INTRODUCTION

Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a catalyst. One of the features of catalysts is that they are not consumed by the chemical reaction, although it is possible that they suffer some deterioration. This deterioration is due to the fact they lose their catalytic features.

A catalyst can make a reaction go faster and in a more selective manner. Because of its ability to speed up some reactions and not others, a catalyst enables a chemical process to work more efficiently and often with less waste. Hence, catalysts are important in industrial chemistry. At present, research and development of catalysts is extremely important in the chemical industry. It is thought that approximately 90% of industry-made chemical products involve some catalytic process in their making. A common example of a catalytic reactor is the catalytic converter following an engine.

Although catalytic reactors are often implemented as plug flow reactors, their analysis requires more complicated treatment. The rate of a catalytic reaction is proportional to the amount of catalyst the reagents contact. With a solid phase catalyst and fluid phase reagents, this is proportional to the exposed area, efficiency of diffusion of reagents in and products out, and turbulent mixing. Perfect mixing cannot be assumed. Furthermore, a catalytic reaction pathway is often multi-step with intermediates that are chemically bound to the catalyst; and as the chemical binding to the catalyst is also a chemical reaction, it may affect the kinetics.

The behavior of the catalyst is also a consideration. Particularly in high-temperature petrochemical processes, catalysts are deactivated by sintering, coking, and similar processes.[1]

2. THEORY

2.1. Energy of Reactions

Actually, for occurrence of any process, an energy, which is called as **activation energy** is always required. For reactants of every reaction, it's a necessity to achieve this activation energy, to get converted into the final products. This energy barrier of a reaction is called as activation energy barrier. For reactants alone, it is very tedious to achieve this barrier. But when a catalyst is present in a particular reaction it decreases the activation energy barrier. So, reaction occurs at a rate faster than before. In brief, activation energy is the amount of energy needed to cause a reaction to occur.

A catalyst speeds up a reaction by changing the specific structures of the reactant molecules; this alteration causes reactant molecules to collide with each other in order to release energy or product. For example, under normal circumstances, hydrogen and oxygen don't react with each other, but in the presence of a specific catalyst, they react with each other to produce water. The relationship between activation energy (E_a) and enthalpy of formation (ΔH) with and without a catalyst is given in Fig. 1. The highest energy position (peak position) represents the transition state. With the catalyst, the energy required to enter transition state decreases, thereby decreasing the energy required to initiate the reaction.

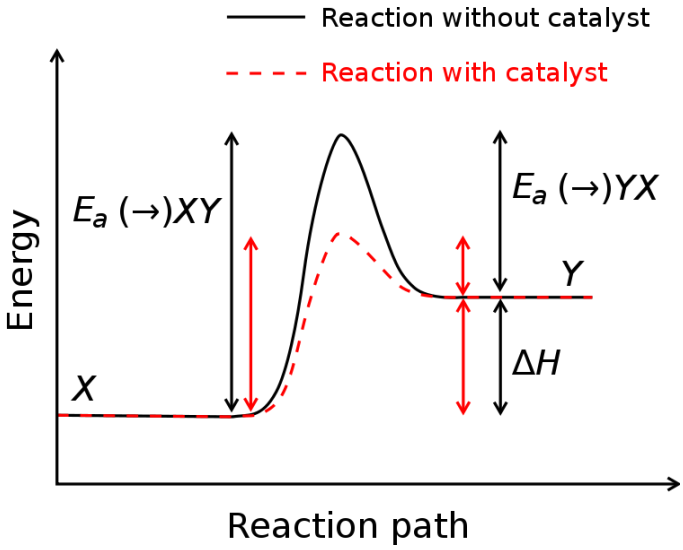


Figure 1. The effect of a catalyst on the activation energy of a reaction.

At a more advanced level, the Arrhenius activation energy term from the Arrhenius equation is best regarded as an experimentally determined parameter which indicates the sensitivity of

the reaction rate to temperature. The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds. From the Arrhenius equation, the activation energy can be expressed as[2]:

$$E_a = -RT \ln\left(\frac{k}{A}\right) \tag{1}$$

where A is the frequency factor for the reaction, R is the universal gas constant, T is the temperature (in Kelvins), and k is the reaction rate coefficient. While this equation suggests that the activation energy is dependent on temperature, in regimes in which the Arrhenius equation is valid this is cancelled by the temperature dependence of k. Thus E_a can be evaluated from the reaction rate coefficient at any temperature (within the validity of the Arrhenius equation).

Apart from requiring activation energy, a chemical reaction can be[3]:

a) Endothermic reaction: in which products absorb part of the reagents' energy. This is the case of our example, where part of the energy (ΔH) needed for the reaction to take place, is absorbed by the products.

b) Exothermic reaction: in which the energy level of the products is lower than that of the reagents and as a result of its performance, energy is released to the environment.

Reaction enthalpy and course of reaction relationship is shown in Fig. 2.

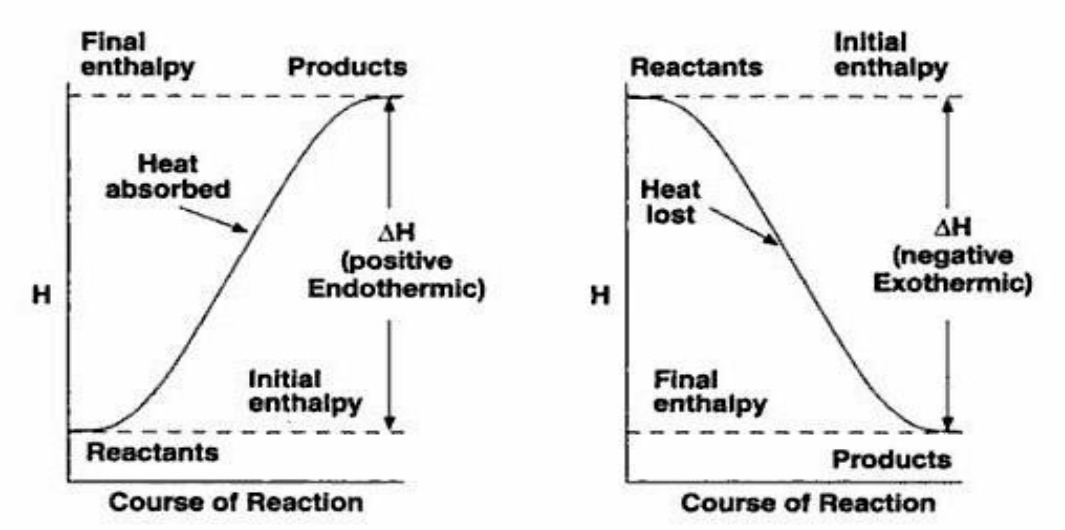


Figure 2. Endothermic and exothermic reactions.

2.2. Factors That Affect Reaction Rates

Five important factors control the rate of a chemical reaction. These are summarized below.[4]

The nature of the reactants: In chemical reactions, some bonds break and others form. Therefore, the rates of chemical reactions should be affected by the nature of the bonds in the reacting substances. For example, reactions between ions in an aqueous solution may take place in a fraction of a second. Thus, the reaction between silver nitrate and sodium chloride is very fast. In reactions where many covalent bonds must be broken, reaction usually takes place slowly at room temperatures.

The concentrations: The reaction rate is usually proportional to the concentrations of the reactants. The usual dependence of the reaction rate on the concentration of the reactants can simply be explained by theorizing that, if more molecules or ions of the reactant are in the reaction area and then there is a greater chance that more reactions will occur.

The temperature: A temperature increase 10°C above room temperature usually causes the reaction rate to double or triple. The basis for this generality is that, as the temperature increases, the average kinetic energy of the particles involved increases. As a result, the particles move faster and have a greater probability of hitting other reactant particles. Because the particles have more energy, they can cause an effective collision, resulting in the chemical reaction that forms the product substance.

The presence of a catalyst: The catalyst provides an alternative pathway by which the reaction can proceed and in which the activation energy is lower. It thus increases the rate at which the reaction comes to completion or equilibrium.

2.3. Catalyst

A catalyst can be defined as a substance that increases the rate of a chemical reaction. It can be synthetic, organic or simply a metal. The process through which a particular catalyst increases the rate of a particular reaction is called as catalysis.

During a catalyzed chemical reaction, catalysts don’t show any significant change in their structures and compositions. Catalysts are not able to bring any changes to the nature of final

product. Usually, a catalyst can be easily recovered after the reaction and can be reused for other reactions.[5]

Catalysts are classified according to their kinetics. Positive catalysts increase the speed of the chemical reaction in question and they are also called activators. Negative catalysts decrease the speed of a chemical reaction and they are called inhibitors. These negative catalysts have great uses in medical science. They help in slowing down of various detrimental biochemical reactions.

Catalysts are also very important in manufacturing industry as well as in laboratory. One very important type of catalyst is "catalytic converter"; this catalyst participates in preventing the automobile emissions, by doing so this catalyst reduces the consumption of fuel. In fact, various fertilizers are also catalysts, which speed up the growth of the plant.[5]

2.4. Enzymes

Enzymes are catalytic proteins that speed up chemical reactions. Without enzymes, these reactions would occur at a much slower rate or not at all. Like other proteins, enzymes consist of long chains of amino acids held together by peptide bonds.

Enzymes should not be confused with catalysts. Enzyme is also a class of catalysts, but they catalyze only biochemical reactions, so they are also termed as "biochemical enzymes". Enzymes are actually protein molecules which are present in living systems, but they don't lose their ability of catalysis, when extracted out from living systems. Because of this exclusive feature, they have great uses in fermentation industry. Enzymes are much more specific than catalysts and for proper working they depend upon strict optimum conditions.

In living systems, enzymes have crucial role to play. Life will be impossible without enzymes. For example, there is an enzyme (amylase), present in human saliva. This enzyme participates in digestion of the food, without the presence of this enzyme digestion process will take billions of years to digest a single meal. The food that you eat is exposed to enzymes from beginning to end. *Amylase* works in your mouth while you chew, breaking down starch (a big sugar) into smaller sugars. In your stomach, food is exposed to acidic gastric juices which contain the enzyme *pepsin*. Even in under highly acidic conditions, pepsin functions to split proteins.[6]

Each enzyme has a unique 3-D shape, including a surface groove called an active site, which fits its target substrate much like a key fits in a lock. Other substances that don't fit can't enter the active site and no reaction occurs.

The favored model for the enzyme-substrate interaction is the induced fit model which is shown in Fig. 3. This model proposes that the initial interaction between enzyme and substrate is relatively weak, but that these weak interactions rapidly induce conformational changes in the enzyme that strengthen binding.[7]

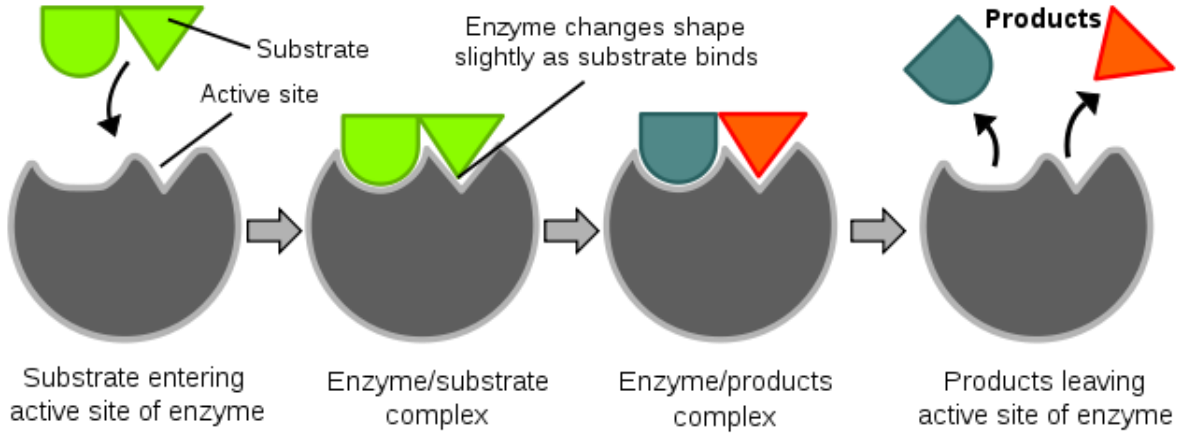


Figure 3. Diagrams to show the induced fit hypothesis of enzyme action.

2.5. Sucrose Hydrolysis

Sucrose (common name: table sugar, also called saccharose) is a disaccharide that is composed by the monosaccharides fructose and glucose with the molecular formula $C_{12}H_{22}O_{11}$. It is best known for its role in human nutrition and is formed by plants but not by higher organisms. The chemical structure of sucrose is shown in Fig. 4.

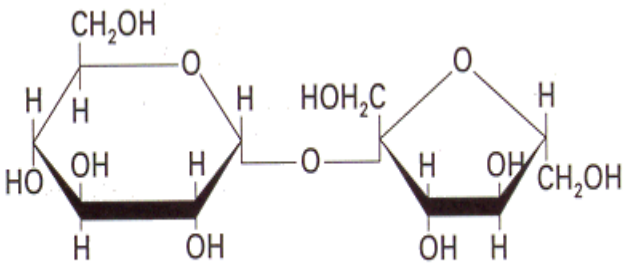


Figure 4. Chemical structure of sucrose.

Sucrose hydrolysis is an irreversible reaction that incorporates a water molecule breaking the link that joins the monosaccharides (glucose and fructose). Water breaks down sucrose by hydrolysis as indicated in Eq. 2, however the process is so gradual that it could sit in neutral solution for years with negligible change. If the sucrase enzyme (β-fructofuranidase) or a high concentration of strong acid is added as catalyst, however, the reaction will proceed rapidly:

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underbrace{\underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}}_{\text{invert sugar}} \qquad (2)$$

The importance of this process lies in the fact that sugar is obtained directly from the plant in the form of sucrose. This disaccharide sugar is not a directly digestible product; it is first dissolved by enzymes contained in our saliva and in our stomach.[8]

This process is also called “inversion”, and the product is called “invert sugar”. Commercial invert sugar is a liquid product that contains equal amounts of glucose and fructose. Because fructose is sweeter than either glucose or sucrose, invert sugar is sweeter than white sugar (sucrose). Invert sugar is used mainly by food manufacturers to retard the crystallization of sugar and to retain moisture in the packaged food.

The rate of inversion is given by

$$\text{Rate} = k\,[\text{Sucrose}]\,[H_2O] \qquad (3)$$

This reaction seems to be second order, i.e. first order with respect to each sucrose and H_2O. The $[H_2O]$ is also constant as it is used as solvent and present in large amount. Therefore, the reaction is only first order with respect to sucrose.[9]

Inverted sugar syrups are made by either of three hydrolytic methods: (1) acid hydrolysis with mineral acids (sulfuric or hydrochloric acid), (2) hydrolysis by cation ion-exchange resin or (3) inversion by enzymes. Acid hydrolysis by mineral acids has the disadvantage that the resulting syrups have high ash content because the solution is neutralized with sodium or potassium hydroxide. Enzymatic conversion has the disadvantage of being expensive and not

very efficient at the high temperature and densities of solutions being hydrolyzed due to the deactivation of enzyme. Cationic resin treatment offers the best alternative, resulting in almost ash-free invert syrup. The most popular invert syrup is a 50 percent mixture of sucrose and invert.[10]

Use of enzymes as catalysts especially for large-scale industrial processes is limited by their high cost of production and stabilization on storage. During use, their stability decreases due to changes in pH, temperature, conformational changes as a result of friction, osmotic pressure imposed by the environs of their use and a cumulative effect of all these factors as a function of duration of their use. Secondly, since they are soluble, their recovery from a mixture of substrate and product for reuse is not economically practical rendering the costly enzymatic process even more costly. However, the advent of immobilized enzyme technology has led to increasing efforts to replace conventional enzymatic process with immobilized preparations as immobilization [a] allows the enzymes to process large amounts of substrate since it can be separated easily from the mixture of substrate and product(s) thus enabling the enzyme to be reused [b] in general, imparts greater stability to the enzyme, so that it can be used for the development of continuous process [c] affords greater control of the catalytic process and [d] permits the economical utilization of an otherwise cost-prohibitive enzyme.

Invertase is a yeast derived enzyme. Invertase splits sucrose into glucose and fructose. The official name for invertase is beta-fructofuranosidase, which implies that the reaction catalyzed by this enzyme is the hydrolysis of the terminal nonreducing beta-fructofuranoside residues in beta-fructofuranosides.

Invertase is mainly used in the food industry where fructose is preferred over sucrose because it is sweeter and does not crystallize as easily. However, the use of invertase is rather limited because another enzyme, glucose isomerase, can be used to convert glucose to fructose more inexpensively. For health and taste reasons, its use in food industry requires that invertase be highly purified.

A wide range of microorganisms produce invertase and can, thus, utilize sucrose as a nutrient. Commercially, invertase is biosynthesized chiefly by yeast strains of *Saccharomyces cerevisiae* or *Saccharomyces carlsbergensis*. Even within the same yeast culture, invertase exists in more than one form. For example, the intracellular invertase has a molecular weight

of 135,000 Daltons, whereas the extracellular variety has a molecular weight of 270,000 Daltons.

In contrary to most other enzymes, invertase exhibits relatively high activity over a broad range of pH (3.5-5.5), with the optimum near pH = 4.5. The enzyme activity reaches a maximum at about 55ºC.[11]

The catalytic inversion of sucrose solutions by fixed beds of ion exchange resin has received attention in the past few years for two principal reasons. On one hand, the sucrose inversion reaction has been used as a convenient means for studying catalysis by ion exchange resins in general. In addition, there is commercial interest in sucrose inversion by such catalytic beds.

The rate of ion-exchange reactions is undoubtedly determined by the ratio of the reactant's molecular size to the size of "micropores" of the ion exchanger. It is therefore not surprising that the rate of sucrose inversion in the presence of a sulphonated phenolformaldehyde cation exchanger is smaller than in HCl solutions, and that it depends on the size of resin particles. At a small degree of cross-linking the "micropores" of ion exchangers permit free passage of reacting molecules, and the process therefore proceeds faster under heterogeneous than under homogeneous conditions. Finally, the rate of a reaction catalyzed by ion exchangers depends on the concentration of the catalytically active counter-ions in the unit volume of catalyst.[12]

The state of bonding of mobile hydrogen ions in active sites affects the catalytic activity of cation exchangers considerably. Thus, while all sulphonated cation exchangers with a limited degree of cross-linking are effective catalysts for inversion, the carboxylic resins either completely fail to accelerate this reaction, or, in the case of weakly cross-linked resins, fall far behind the strongly acidic cation exchangers in their activity. For this reason sulphonated cation exchangers are recommended for use in the industrial inversion of sucrose. Processes such as the purification of sucrose, on the other hand, in which inversion is harmful, should be carried out in the presence of carboxylic cation exchangers. Since the majority of reactions catalyzed by ion exchangers are affected in the interior of the catalyst's beads, the reaction rate is greatly affected by the lattice structure, and above all, by the degree of cross-linking of the resin. There is a linear relationship between minus the logarithm of the velocity constant and the degree of cross-linking of the cation exchanger. In the presence of the strongly cross-linked resin, at 50°C, the inversion proceeds very slowly, while at room temperature it altogether stops. Consequently, the increased structural density of the resin, due to cross-

linking, hinders internal diffusion, and may eventually lead to the localization of the reaction at the surface of the ion-exchanger beads, or even to a complete standstill.

2.6. Chemical Reactors

A reactor is a place designed for a chemical reaction to take place inside it. The reactor's purpose is to establish the right conditions to secure the contact between the reagents, offer enough time for the reaction to take place in controlled temperature and pressure conditions.

The design of an industrial chemical reactor must satisfy the following requirements:

1. The chemical factors: the kinetics of the reaction. The design must provide sufficient residence time for the desired reaction to proceed to the required degree of conversion.
2. The mass transfer factors: with heterogeneous reactions the reaction rate may be controlled by the rates of diffusion of the reacting species; rather than the chemical kinetics.
3. The heat transfer factors: the removal, or addition, of the heat of reaction.
4. The safety factors: the confinement of hazardous reactants and products, and the control of the reaction and the process conditions.

The need to satisfy these interrelated, and often contradictory factors, makes reactor design a complex and difficult task. However, in many instances one of the factors will predominate and will determine the choice of reactor type and the design method.[13]

2.6.1. Batch Reactors (Discontinuous Reactors)

Batch reactor is a type of reactor in which material does neither go in or out while the reaction takes place. In the beginning of the process reagents are introduced, the right temperature and pressure conditions are set and then it is all left to react for a certain amount of time. At the end of the process, the product of the reaction and the non-converted reactants are unloaded.

In a batch reactor the reactants and the catalyst are placed in the reactor which is then closed to transport of matter and the reaction is allowed to proceed for a given time whereupon the mixture of unreacted material together with the products is withdrawn.

A batch reactor is used for small-scale operation, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert to continuous operations. The batch reactor has the advantage of high conversions that can be obtained by leaving the reactant in the reactor for long periods of time, but it also has the disadvantages of high labor costs per batch, the variability of products from batch to batch, and the difficulty of large-scale production.[14]

2.6.2. Semi-Batch Reactors

A semi-batch reactor is a variation of a batch reactor in which one reactant may be added intermittently or continuously to another contained as a batch in a vessel, or a product may be removed intermittently or continuously from the vessel as reaction proceeds. The reaction may be single-phase or multiphase. As in a batch reactor, the operation is inherently unsteady-state and usually characterized by a cycle of operation, although in a more complex manner.

In a surprising contrast, the semi-batch reactor is the least covered in the chemical and biochemical industry. The major reason for this discrepancy is the difficulty in getting analytical solutions of the differential equations describing such a type of reactor. Additionally, in semi-batch reactors everything is usually varying, concentrations, temperature and volume.[15]

2.6.3. Continuous Reactors

While the chemical reaction takes place inside the reactor, the latter is constantly fed reactant material and the products are also removed from it uninterruptedly. Generally, it is any continuous-operation reactor, where one or all reagents perform a constant movement in a selected direction in space, and in which there is no intention to lead to their mixture.

Continuous reactors are almost always operated at steady state and they are considered three types: the continuous stirred tank reactor (CSTR), the plug flow reactor (PFR) and the packed bed reactor (PBR).

2.6.3.1. Continuous Stirred Tank Reactor

A continuous stirred tank reactor (CSTR) is normally used for liquid-phase reactions, both in a laboratory and on a large-scale. It is normally operated at steady state and is assumed to be perfectly mixed. Consequently, there is no time dependence or position dependence of the temperature, the concentration, or the reaction rate inside the CSTR. Therefore, every variable is the same at every point inside the reactor. Because the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the exit point as they are elsewhere in the tank. A schematic diagram of two-staged CSTR is given in Fig. 5.

There are some basic assumptions made in analyzing CSTR reactors. These are:

- The reactor runs at steady state i.e. all of the time derivatives go to zero.
- None of the variables (temperature, concentration, reaction rate, etc) are functions of position, i.e. all of the spatial derivatives go to zero.
- The conditions that exist at the exit are the same as those everywhere in the reactor.

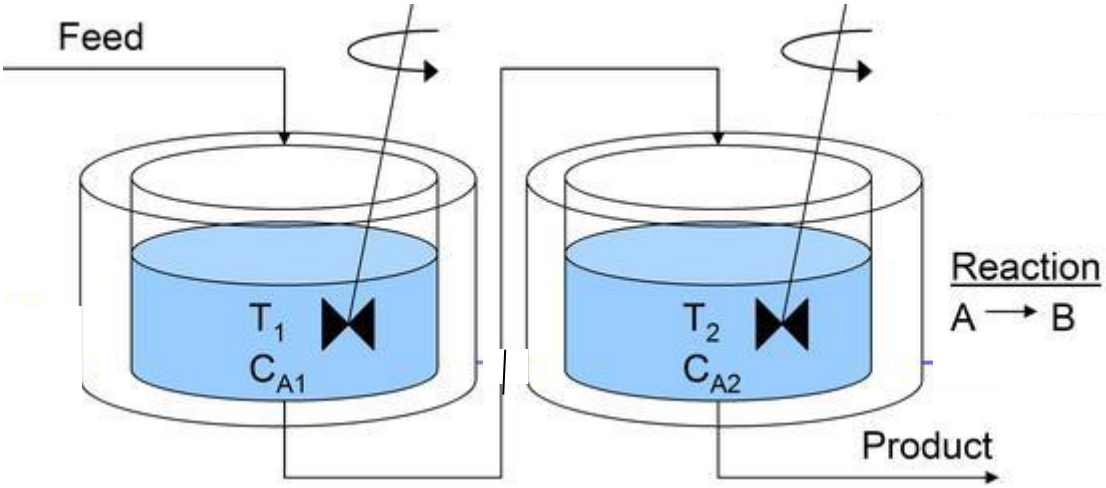


Figure 5. CSTRs in series.

Because the compositions of mixtures leaving a CSTR are those within the reactor, the reaction driving forces, usually the reactant concentrations, are necessarily low. Therefore, except for reaction orders zero- and negative, a CSTR requires the largest volume of the reactor types to obtain desired conversions. However, the low driving force makes possible better control of rapid exothermic and endothermic reactions. When high conversions of reactants are needed, several CSTRs in series can be used. Equally good results can be

obtained by dividing a single vessel into compartments while minimizing back-mixing and short-circuiting. The larger the number of CSTR stages, the closer the performance approaches that of a tubular plug-flow reactor.

2.6.3.2. Plug Flow Reactor (Tubular Reactor)

The plug flow reactor (PBR) may be used for both liquid-phase and gas-phase reactions, and for both laboratory-scale investigations of kinetics and large-scale production. They arranged as one long reactor or many short reactors in a tube bank; no radial variation in reaction rate (concentration); concentration changes only with length down the reactor.

This model is based on some assumptions:

- The reactor is operated at steady state.
- The fluid moves in a flat (piston-like or plug) velocity profile.
- There is no spatial variation in species concentrations or temperature at any cross section in the reactor.

Chemical reactions take place along the reactor and consequently species compositions and temperature vary from point to point along the reactor.

Characteristics of ideal plug flow reactor are: perfect mixing in the radial dimension (uniform cross section concentration) and no mixing in the axial direction, or no axial dispersion (segregated flow). [16]

2.6.3.3. Packed Bed Reactor

One of the most common reactors in the chemical industry, for use in heterogeneous catalytic processes, is the packed bed reactor. This type of reactor is used both in synthesis as well as in effluent treatment and catalytic combustion. The reactor consists in essence of a container filled with catalyst particles. These particles can be contained within a supporting structure, like tubes or channels, or they can be packed in one single compartment in the reactor.

The structure that is formed by the packed catalyst particles makes the modeling of mass and energy transport in the reactor a challenging task. The difficulty lies in the description of the

porous structure, which gives transport of different orders of magnitudes within the particles and between the particles. In most cases, the structure between the particles is described as macro porous and the pore radius can be of the order of magnitude of mm. When a pressure difference is applied across the bed, convection arises in the macro pores. The pores inside the catalyst particles form the microstructure of the bed.

Packed bed reactors (PBR) are tubular and are filled with solid catalyst particles, most often used to catalyze gas reactions. The chemical reaction takes place on the surface of the catalyst. The advantage of using a packed bed reactor is the higher conversion per weight of catalyst than other catalytic reactors. The reaction rate is based on the amount of the solid catalyst rather than the volume of the reactor.

Fixed Bed Reactor:

In a fixed-bed reactor the catalyst pellets are held in place and do not move with respect to a fixed reference frame. Essentially all reaction occurs within the catalyst particles.

Catalytic fixed-bed reactors are the most important type of reactor for the synthesis of large scale basic chemicals and intermediates. In these reactors, the reaction takes place in the form of a heterogeneously catalyzed gas reaction on the surface of catalysts that are arranged as a so called fixed bed in the reactor. In addition to the synthesis of valuable chemicals, fixed-bed reactors have been increasingly used in recent years to treat harmful and toxic substances. For example, the reaction chambers used to remove nitrogen oxides from power station flue gases constitute the largest type of fixed-bed reactors as regards reactor volume and throughput, while automobile exhaust purification represents by far the most widely employed application of fixed-bed reactors. Basic types of catalytic fixed bed reactors are shown in Fig. 6. These consist of one or more tubes packed with catalyst particles that perform vertically. Catalytic particles can vary in size and shape: granular, cylindrical, spherical, etc.[17]

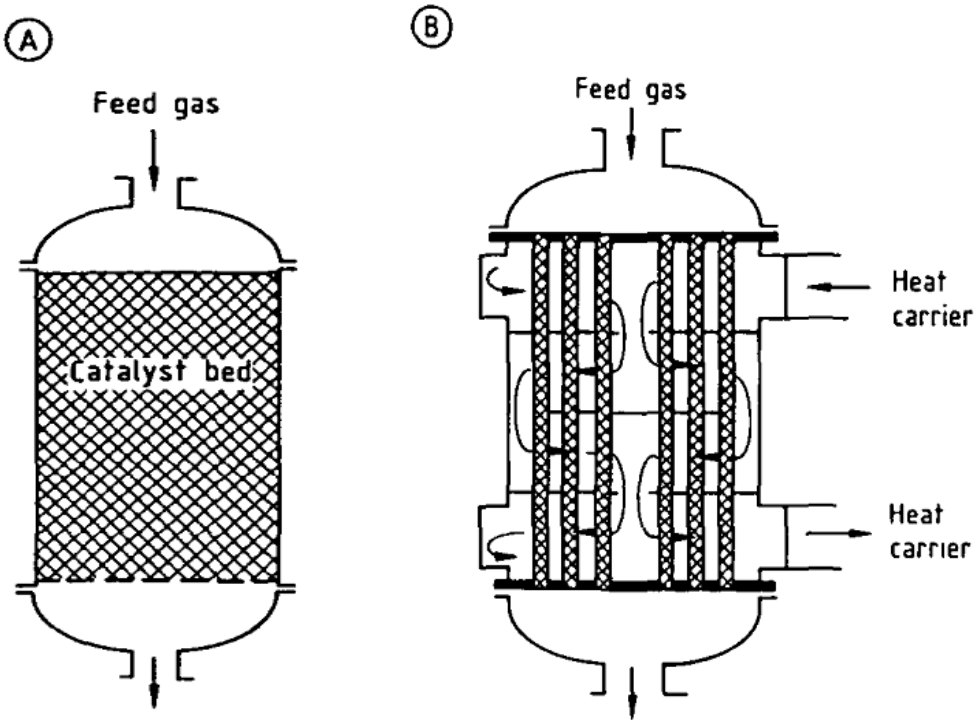


Figure 6. Basic types of catalytic fixed bed reactors A) Adiabatic fixed bed reactor; B) Multi-tubular fixed-bed reactor.

For ion exchange based fixed bed reactors, the simplest approach is to describe it as an ideal plug flow reactor, and therefore the conversion can be derived for a first order reaction as:

$$\ln(1-X) = -k\tau \tag{4}$$

X=fractional conversion

k= reaction rate constant for a first order reaction, s^{-1}

τ = space time, s

It is assumed that the active sites are homogeneously distributed in the packed bed.

Fluidized Bed Reactor:

A fluidized bed is a packed bed through which fluid flows at such a high velocity that the bed is loosened and the particle-fluid mixture behaves as though it is a fluid. Thus, when a bed of particles is fluidized, the entire bed can be transported like a fluid, if desired. Both gas and liquid flows can be used to fluidize a bed of particles. The most common reason for fluidizing a bed is to obtain vigorous agitation of the solids in contact with the fluid, leading to excellent

contact of the solid and the fluid and the solid and the wall. This means that nearly uniform temperatures can be maintained even in highly exothermic reaction situations where the particles are used to catalyze a reaction in the species contained in the fluid.

In fact, fluidized beds were used in catalytic cracking in the petroleum industry in the past. The catalyst is suspended in the fluid by fluidizing a bed of catalytic particles so that intimate contact can be achieved between the particles and the fluid. Nowadays, fluidized beds are used in catalyst regeneration, solid-gas reactors, combustion of coal, roasting of ores, drying, and gas adsorption operations.[18]

Fluidization occurs when small solid particles are suspended in an upward-flowing stream of fluid, as shown in Fig. 7. The fluid velocity is sufficient to suspend the particles, but not large enough to carry them out of the vessel. The solid particles swirl around the bed rapidly, creating excellent mixing among them. The material *fluidized* is almost always a solid and the *fluidizing medium* is either a liquid or a gas. The characteristics and behavior of a fluidized bed are strongly dependent on both the solid and liquid or gas properties. Nearly all of the significant commercial applications of fluidized-bed technology concern gas-solid systems.[19]

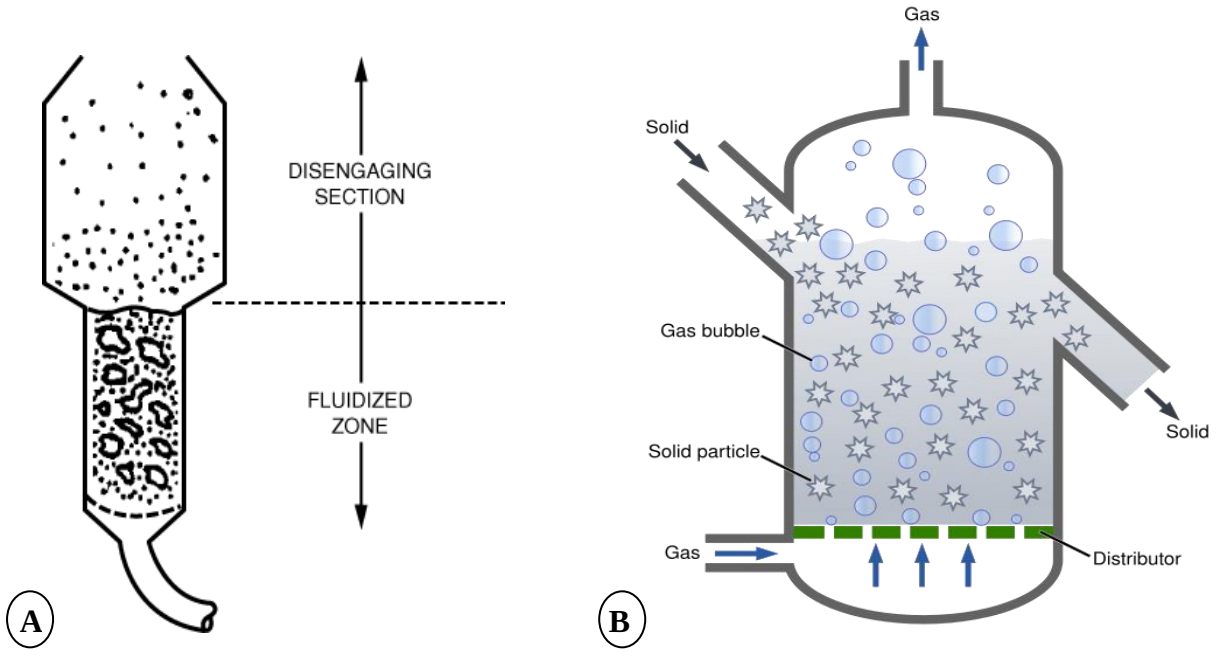


Figure 7. Basic types of fluidized bed reactors A) Simple fluidized bed reactor; B) Circulating fluidized bed reactors.

2.7. Steps in a Catalytic Reaction

A schematic diagram of a tubular reactor packed with catalytic pellets is shown in Fig. 8. The overall process by which heterogeneous catalytic reactions proceed can be broken down into the sequence of individual steps shown in Table 1.

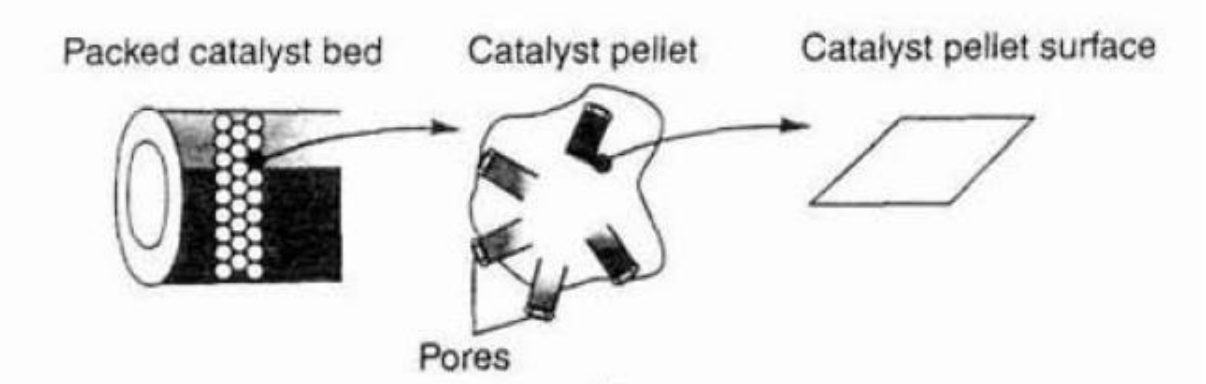


Figure 8. Catalytic packed-bed reactor.

Each step in Table 1 is also shown schematically in Fig. 9.

Table 1. Steps in a catalytic reaction.

1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet.
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalyst surface.
3. Adsorption of reactant A onto the catalyst surface.
4. Reaction on the surface of the catalyst (e.g., A →B).
5. Desorption of the products (e.g., B) from the surface.
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface.
7. Mass transfer of the products from the external pellet surface to the bulk fluid.

Usually one or at most two of those seven steps are rate limiting and act to influence the overall rate of reaction in the pellet. The other steps are inherently faster than the slow step(s) and can accommodate any change in the rate of the slow step. The system is *intraparticle transport controlled* if step 3 is the slow process (sometimes referred to as diffusion limited). For *kinetic or reaction control*, step 4 is the slowest process. Finally, if step 1 is the slowest process, the reaction is said to be *externally transport controlled*.

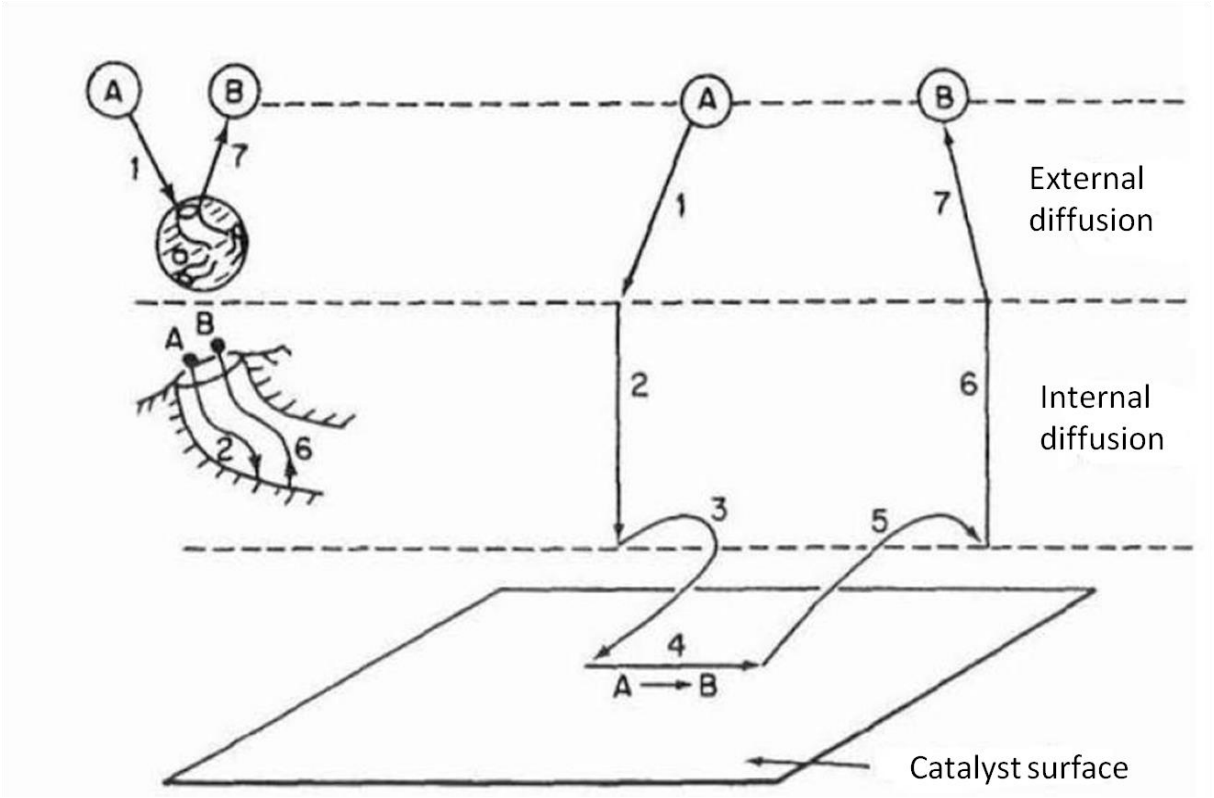


Figure 9. Steps in a heterogeneous catalytic reaction.

The overall rate of reaction is equal to the rate of the slowest step in the mechanism. When the diffusion steps (1, 2, 6, and 7 in Table 1) are very fast compared with the reaction steps (3, 4. and 5), the concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk fluid. In this situation, the transport or diffusion steps do not affect the overall rate of the reaction. In other situations, if the reaction steps are very fast compared with the diffusion steps, mass transport does affect the reaction rate. In systems where diffusion from the bulk gas or liquid to the catalyst surface or to the mouths of catalyst pores affects the rate, changing the flow conditions past the catalyst should change the overall reaction rate. In porous catalyst, on the other hand, diffusion within the catalyst pores may limit the rate of reaction. Under these circumstances, the overall rate will be unaffected by external flow conditions even though diffusion affects the overall reaction rate.[3]

2.8. Definition and Formulation of Effectiveness Factor

Fig. 10 shows the concentration profile within the catalyst pellet, $C_A(r)$, in schematic form. As reactants diffuse towards the center of the pellet they are gradually consumed and their

concentration decrease. The reaction rate within the pellet is, therefore, not uniform: it is a function of position.

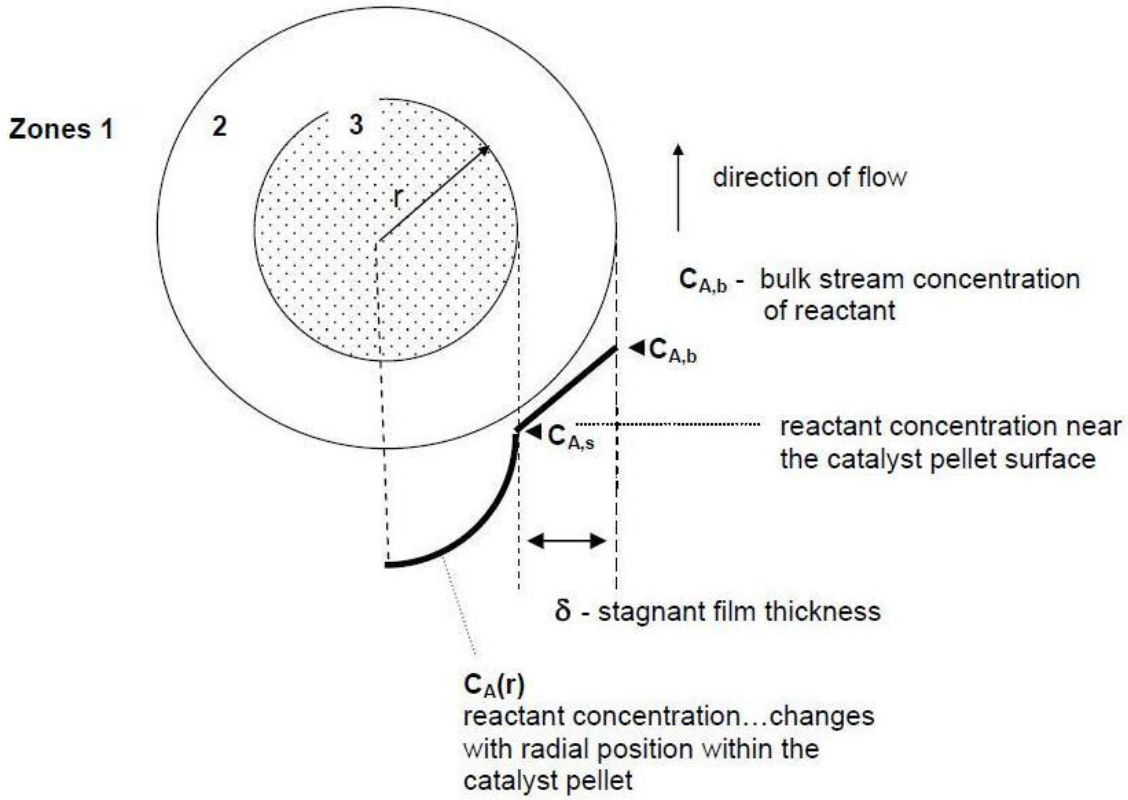


Figure 10. Three zones are defined to help reaction rate expressions in catalyst beds: (1) bulk fluid phase, (2) stagnant film surrounding the catalyst pellet and (3) the catalyst pellet.

In heterogeneous catalytic studies it is important to establish the mechanism that is limiting the overall rate of transformation within the catalytic particle, that is, to know whether the diffusive effects are controlling the process rate, or whether the chemical reaction at the particles surface controls.

To have an idea of the relative importance of diffusion and chemical reaction phenomenon, an effectiveness factor for catalytic particles is defined, for a steady state flow condition, as

$$\eta = \frac{Actual\ amount\ of\ substance\ reacting\ in\ the\ whole\ particle}{Amount\ that\ would\ react\ if\ the\ whole\ particle\ were\ at\ the\ external\ surface\ temperature\ and\ concentration}$$

Effectiveness factor is defined as;

$$\eta = r_A / r_s \quad (5)$$

where r_A (mol/s.kg catalyst) is defined as the actual overall rate of reaction and r_s (mol/s.kg catalyst) is the reaction rate evaluated at the conditions present at the external surface of the pellet.

More formally, the effectiveness factor is defined in the form of an integral over the particle volume of the ratio of the real reaction rate over the rate of reaction at surface conditions.

$$\eta = \frac{1}{V_p} \int \frac{r_A(C_i, C_j, ..., T) dV_p}{r_A(C_{is}, ..., T_s)} \quad (6)$$

where V_p is particle volume (m^3).

An effectiveness factor less than unit shows that the diffusive effects are important in the control of global velocity of transformation: the smaller the effectiveness factor is, the larger importance of the physical processes of mass transfer is.

The case of an effectiveness factor greater than unit can also appear, which indicates that heat transfer effects are important, and even though in appearance this would be an ideal situation, in practice this is not recommendable due to catalytic deactivation originated by high temperatures within the particle.[20]

2.9. Mathematical Expression of the Isothermal Effectiveness Factor for Spherical Catalyst Pellet

Consider the irreversible first order chemical reaction A → B taking place within a spherical catalyst pellet with intrinsic reaction rate, $r_A = k.C_A$. The mass balance for the reactant A leads to

$$\frac{D_e}{r^2} \frac{d}{dr} \left\{ r^2 \frac{dC_A}{dr} \right\} - k\, C_A = 0 \quad (7)$$

where D_e is the effective diffusivity of reactant A through the porous matrix (m^2/s), C_A is the concentration of molecule A (mol A/m^3) and r is the radius of particle (m).

The symmetry boundary conditions is

$$\frac{dC_A}{dr} = 0 \quad at \;\; r = 0 \tag{8}$$

and the surface concentration boundary condition is:

$$C_A = C_S \qquad at \quad r = R_S \tag{9}$$

where C_s is concentration of molecule A at the surface of catalyst (mol/m^3).

By solving Eq.7 in the frame of boundary conditions given in Eq. 8 and Eq.9, the following expression for the effectiveness factor of a spherical catalyst pellet can be derived.

$$\eta = \frac{3}{\Phi}\left\{\frac{1}{\tanh\Phi} - \frac{1}{\Phi}\right\} \tag{10}$$

Where the Thiele modulus, is given by

$$\Phi = \sqrt{\frac{k\,R_s^{\,2}}{D_e}} = \frac{\text{Re}\,action\;\; rate}{Diffusion\;\; rate} \tag{11}$$

where R_s is radius of the particle at the surface (m).

For non-zero order reactions in isothermal pellets, examination of the forms of η in Table 2 shows that the value of the effectiveness factor changes between zero and unity.

$$0 \le \eta \le 1$$

Table 2. Effectiveness factors for three catalyst pellet geometries.

Sphere	$\eta = \frac{3}{\Phi}\left\{\frac{1}{\tanh\Phi} - \frac{1}{\Phi}\right\}$
Cylinder	$\eta = \frac{1}{\Phi}\frac{I_1(2\Phi)}{I_0(2\Phi)}$
Flat plate	$\eta = \frac{\tanh\Phi}{\Phi}$

Thiele modulus is proportional to $[k/D_e]^{1/2}$. When $D_e >> k$, diffusive process is far faster than the rate at which reactant is being consumed by the reaction. When reaction process is much slower than diffusive processes, the process is said to be "kinetically controlled". For an isothermal pellet, this is the case where ϕ is small and η tends to unity ($\eta \sim 1$). In this case, it is expected to observe reactant concentrations and reaction rates to be relatively uniform over the pellet radius and close to values observed at external particle surfaces.

Conversely, when $k >> D_e$, ϕ tends to large values and η becomes much smaller than unity ($\eta << 1$). When reaction processes are much faster than diffusive processes, the process is said to be "diffusion controlled". This is the case when reactive processes are far faster than rates at which diffusive processes can replenish the supply of reactant. In this case, much of the reactant is consumed, immediately it contacts the catalyst pellet. Most reaction takes place, therefore, near the periphery of the catalyst pellet. Concentration gradients within the pellet are sharp and most reactant molecules are consumed near the periphery of the pellet.[20]

When the temperature of an (isothermal) catalyst pellet rises, it is expected the intrinsic reaction rate at external surface temperatures ($r_s = k.C_s$) to increase. Since k rises exponentially with the temperature but D_e increases more slowly, an increase in temperature signals an increase in Thiele modulus (irrespective of catalyst geometry) and a corresponding decrease in the effectiveness factor (Fig. 11). The actual rate of reaction r_A, would also be expected to increase with the rising temperature but less rapidly than r_s, since $r_A = (\eta\downarrow)x(r_s\uparrow)$ with increasing temperature.[20]

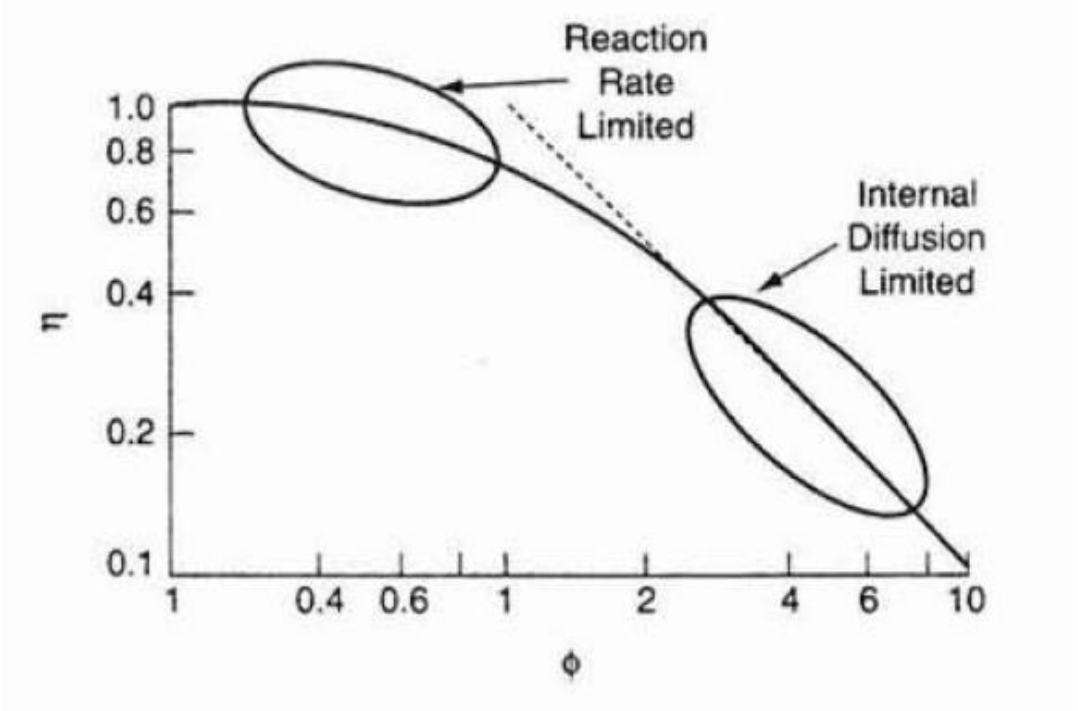


Figure 11. The effectiveness factor as a function of Thiele modulus for *n*th-order kinetics spherical catalyst particles.

3. EXPERIMENTAL SET-UP

3.1. Elements

The experiment mechanism consists of the following elements:

- Thermostatic bath

Figure 12. The picture of thermostatic bath.

- Heating-water pumps

Figure 13. Water pump.

- Three continuous reactors for converting sucrose into glucose

Figure 14. Installed reactors (2 catalytic reactors with different grain size and 1 enzymatic reactor).

- Collectors with two-way valves to regulate the circulation of water depending on the process:

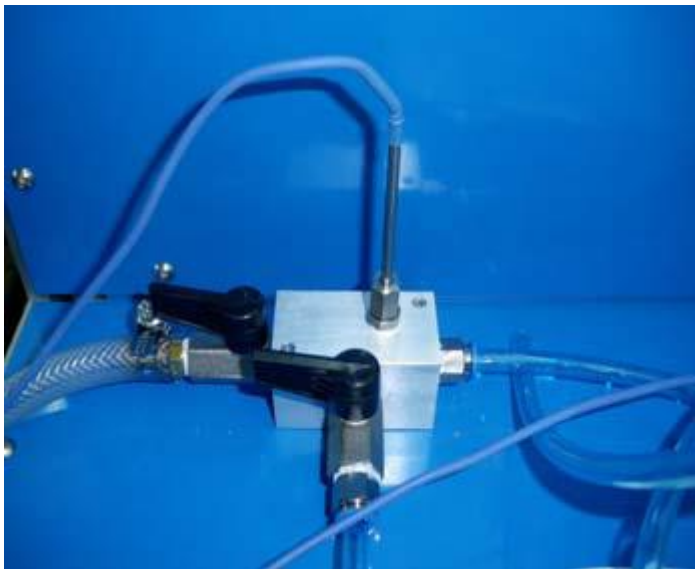


Figure 15. Two-way valves.

- Peristaltic pump for feeding product to the reactors.

- Diagram showing the connections between the basic device and the reactor, located on the upper-right corner on the front of the basic module. It helps identifying the different connections.

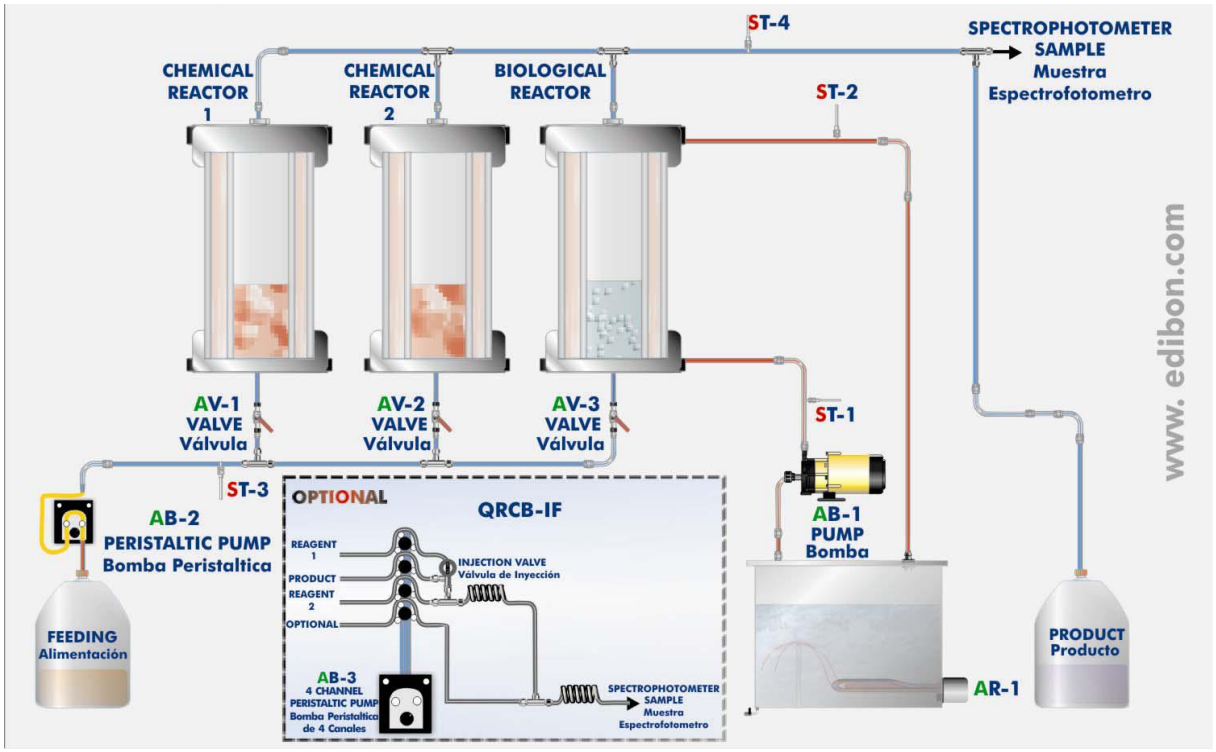


Figure 16. Diagram that represents the performance of the Catalytic Reactor Unit.

- Blood glucose meter for measuring the glucose concentration at the outlet stream in mg/dL.

Figure 17. Blood Glucose Meter.

4. EXPERIMENTAL PROCEDURES

The experiment system contains two fixed-bed chemical reactors. The same chemical catalyst product, known as ionic exchange resins, composes each reactor but each one of them presents different grain size.

Temperatures between 50 and 70ºC favour sucrose hydrolysis. This is the reason for which reactors are jacketed, and we will make hot water circulate though them. The temperature of this water is regulated by the potentiometer of the thermostatic bath in the unit, together with T3 and T4 temperature sensors.

Sucrose is fed to the reactors through a peristaltic pump which allows the speed regulation by using the interface's potentiometer. The final product or result is sent to the final-product flask. A sample of the obtained product (fructose + glucose) is analyzed with the included blood glucose meter, analyzing the conversion degree of our chemical reaction.

4.1. Study of the principles of fixed-bed reactors

In this practice we will take a first look at the way a Fixed-Bed reactor works. We are going to see how the different variables (feed flow, reaction temperature, reagents' concentration) can vary the final result.

4.1.1. Objective

The purpose of this practice is to see the advantages of continuous reactors and become familiar with its use by understanding the reason of the variation parameters.

4.1.2. Necessary elements

The elements you will need in this practice are:

- QRCB unit
- Pure sucrose
- Colorant reagent: Fehling's solution
- Flask for reaction
- Water supply for the thermostatic bath
- Lighter

4.1.3. Theoretical basics of the practice

As it was explained in the introduction, fixed-bed reactors consist of one or more tubes packed with catalyst particles that work vertically. Catalytic particles can vary in size and shape: granular, cylindrical, and spherical. Outside it there is a concentric bath of water with controlled temperature that adjusts the temperature of the chemical reaction.

4.1.4. Procedure

Step 1: Prepare a 150 g/L sucrose solution with water in the initial tank.

Step 2: Before beginning, make sure the collectors' valves are open correctly feeding the reactor we want to study. We have to fill the thermostatic bath and start it, selecting the required temperature. Check the collectors' valves to make sure you are bathing the studied reactor.

Step 3: Once QCRB unit is ready and its valves are set correctly, turn on the Electronic Console by using the "Power" button on the right. Turn on the thermostatic bath using its lateral switch. To feed the bath that heats the reactor in question, we are only short of activating AB-1 pump. We leave it run for two minutes to achieve the right temperature in the bed.

Step 4: Start the peristaltic pump at a certain flow by using AB-2 potentiometer. The pump's flow is shown in its corresponding Digital Indicator.

Step 5: Once the system is stabilized the final tank will start getting filled with product.

When we have enough of the resulting product (Glucose + Fructose) we can stop the experiment.

Step 6: To analyze the result, extract a sample of the resulting solution.

a) Perform Benedict's test

Introduce 5 mL of the sample in a flask.

Add 1.5 mL of Fehling's A solution and 1.5 mL of Fehling's B solution.

Then, heat it with a lighter:

- If it remains blue it is sucrose.

- If it turns a reddish color we will have turned sucrose in part of glucose.

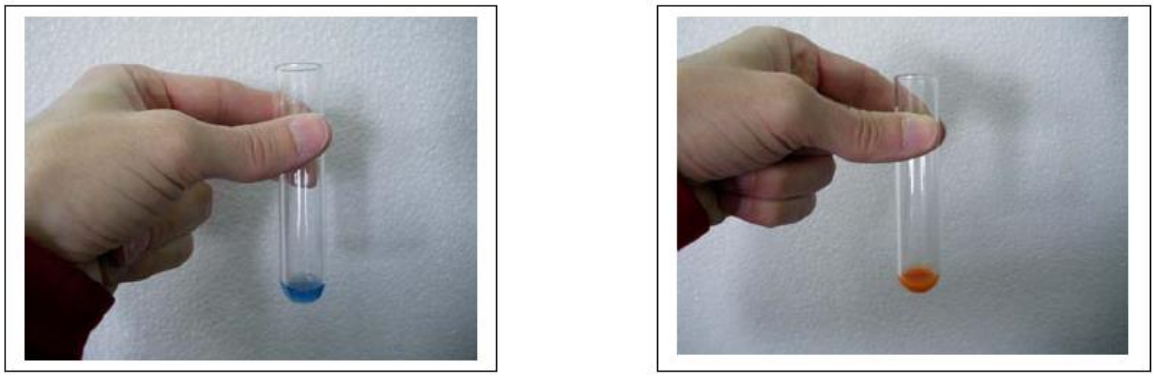


Figure 18. Benedict's Test.

b) Analyze the sample by using blood glucose meter.

The test would be taken again varying the temperature of the reactor's bath.

The test would be taken again varying the sucrose feed flow in the fixed bed reactor.

4.2. Effect of the variation in the particle's size in the effectiveness of a fixed-bed reactor

4.2.1. Objective

The aim is to compare the differences between fixed-bed reactors with different grain size.

4.2.2. Necessary elements

Those included with the piece of equipment:

- QRCB unit
- Sucrose
- Water supply for the thermostatic bath
- Blood glucose meter.

4.2.3. Theoretical basics of the practice

In order to proceed to compare two reactors with a chemical catalyst with the same composition (ion-exchange resins) and different grain size, we are going to make tests in the same conditions to see the differences between the reactors. At first sight we can see that the reactor on the left is the one with the finest grain, and the one in the centre is the one with the thickest grain.

4.2.4. Procedure

Step 1: Prepare a solution with a sucrose concentration of 150 g/L in the initial tank.

Step 2: Before starting make sure the collectors' valves are opened correctly feeding the reactor you want to study.

First analyze the ion-exchange reactor with the fine grain. It will be the one located **at the left.**

Fill the thermostatic bath and start it, selecting the required temperature. Check the collector's valves to make sure you are bathing the studied reactor.

Step 3: Once QRCB unit is ready and its valves are set correctly turn on the Electronic Console by pressing the "Power" button on the right.

To feed the bath that heats the reactor in question, we are only short of activating AB-1 pump. We leave it run for two minutes to achieve the right temperature in the bed.

Step 4: Start the peristaltic pump at a certain flow by using AB-2 potentiometer.

The pump flow is proportional to the given selection.

Step 5: Once the system is stabilized the final flask will start getting filled with product.

When we have enough of the resulting product (Glucose + Fructose) we can stop the experiment.

Step 6: To analyze the result, extract a sample. This sample should be analyzed with the spectrophotometer.

- Repeat the experiment in the same conditions but changing the studied reagent.

5. CALCULATIONS

- Plot a calibration curve for peristaltic pump and blood glucose meter. From the curve find the actual values of flow rates and glucose concentrations.

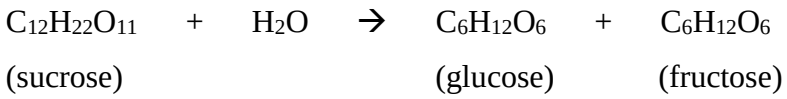
5.1. Calibration data for peristaltic pump

Value Read on QRCB Unit	Actual Value (mL/min)
2.5	20
5	25
10	30

5.2. Calibration data for blood glucose meter

Value Read on Blood Glucose Meter (mg/dL)	Actual Value (mg/dL)
Low	30
55	50
142	100
234	150
303	200
422	250
497	300
High	400

- Calculate the molar conversion of sucrose for each reaction from measured glucose concentrations depending on the sucrose inversion reaction given as,



- Calculate space times (τ, min) of each reaction.

  $\tau = V_r / \upsilon_0$

  where V_r is the volume of reactor and is the flow rate of sucrose solution fed to the reactor. ($ID_{reactor}$ = 1.7 cm, $L_{reactor}$= 10 cm)
- From experiments 1 and 2 find reaction rate constant for 50°C.
- From experiments 3, 4 and 5 find reaction rate constant for 70°C.
- Calculate the activation energy from Arrhenius equation.
- Calculate the Thiele modulus and effectiveness factor values for each reaction.

6. NOMENCLATURE

A	Frequency factor
E_a	Activation energy (J/mol)
H	Enthalpy (J)
R	Universal gas constant (J/mol.K)
T	Temperature (K)
k	Reaction rate constant (for n order reaction unit is $mol^{1-n}.m^{n-1}.s^{-1}$)
CSTR	Continuous stirred tank reactor
PFR	Plug flow reactor
PBR	Packed bed reactor
X	Conversion (dimensionless)
τ	Space time (s)
C_A	Concentration of A (mol A/m^3)
C_{As}	Concentration of A at the external surface of the pellet (mol A/m^3)
η	Effectiveness factor (dimensionless)
r_A	Reaction rate (mol/s.m^3 or mol/s.$kg_{catalyst}$)
V_p	Particle volume (m^3)
V_r	Reactor volume (m^3)
υ_0	Entering volumetric flow rate (m^3/s)
F_{A0}	Entering molar flow rate of species A (mol/s)
D_e	Effective diffusivity (m^2/s)
ϕ	Thiele modulus (dimensionless)
R_s	Radius of a spherical catalyst particle (m)

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8. DATA SHEET

Name, Surname: ***Date:***

Group No:

Assistant:

8.1. Experiment #: 1

Reactor 1

T = 50°C

Feed= 150 g/L sucrose

Feed flow rate (read) = 5 mL/min

Period of reaction = 30 minutes

T (°C)	C_{A0} (g/L)	F_{A0} (mL/min)	Calibrated F_{A0} (mL/min)	Period of reaction (min)	Glucose concentration (mg/dL)

8.2. Experiment #: 2

Reactor 1

T = 50°C

Feed= 150 g/L sucrose

Feed flow rate (read) = 10 mL/min

Period of reaction = 30 minutes

T (°C)	C_{A0} (g/L)	F_{A0} (mL/min)	Calibrated F_{A0} (mL/min)	Period of reaction (min)	Glucose concentration (mg/dL)

8.3. Experiment #: 3

Reactor 1

T = 70°C

Feed= 150 g/L sucrose

Feed flow rate (read) = 2.5 mL/min

Period of reaction = 30 minutes

T (°C)	C_{A0} (g/L)	F_{A0} (mL/min)	Calibrated F_{A0} (mL/min)	Period of reaction (min)	Glucose concentration (mg/dL)

8.4. Experiment #: 4

Reactor 1

T = 70°C

Feed= 150 g/L sucrose

Feed flow rate (read) = 5 mL/min

Period of reaction = 30 minutes

T (°C)	C_{A0} (g/L)	F_{A0} (mL/min)	Calibrated F_{A0} (mL/min)	Period of reaction (min)	Glucose concentration (mg/dL)

8.5. Experiment #: 5

Reactor 1

T = 70°C

Feed= 150 g/L sucrose

Feed flow rate (read) = 10 mL/min

Period of reaction = 30 minutes

T (°C)	C_{A0} (g/L)	F_{A0} (mL/min)	Calibrated F_{A0} (mL/min)	Period of reaction (min)	Glucose concentration (mg/dL)

8.6. Experiment #: 6

Reactor 2

T = 70°C

Feed= 150 g/L sucrose

Feed flow rate (read) = 2.5 mL/min

Period of reaction = 30 minutes

T (°C)	C_{A0} (g/L)	F_{A0} (mL/min)	Calibrated F_{A0} (mL/min)	Period of reaction (min)	Glucose concentration (mg/dL)

GUIDE FOR "RESULTS and DISCUSSION" SECTION

- Plot a calibration curve for blood glucose meter. Data were given in "Calculations" part.

Figure 3.1. Calibration graph for glucose concentration.

Table 3.1. Read and calibrated values for each experiment.

Experiment #	T (°C)	Read F_{A0} (mL/min)	Calibrated F_{A0} (mL/min)	Glucose concentration (mg/dL)	Calibrated glucose concentration (mg/dL)
1					
2					
3					
4					
5					
6					

Table 3.2. Basic properties for each experiment.

Experiment #	T (°C)	C_{A0} (g/L)	Calibrated F_{A0} (mL/min)	Reaction period (min)	Calibrated glucose concentration (mg/dL)	Space time, τ (min)	Conversion, X	ln (1-X)
1								
2								
3								
4								
5								
6								

- Plot volumetric flow rate, F_{A0} (mL/min) versus conversion, X graph for Experiments 1 and 2.

Figure 3.2. F_{A0} (mL/min) versus X graph for 50°C.

- Plot volumetric flow rate, F_{A0} (mL/min) versus conversion, X graph for Experiments 3, 4 and 5.

Figure 3.3. F_{A0} (mL/min) versus X graph for 70°C.

Table 3.3. Molar conversion values for Reactor 1 and Reactor 2 at 70°C.

Experiment #	Reactor #	T (°C)	C_{A0} (g/L)	Calibrated F_{A0} (mL/min)	Reaction period (min)	Calibrated glucose concentration (mg/dL)	Space time, τ (min)	Conversion, X
3	1							
6	2							

- Compare conversion values for Experiments 3 and 6.

- Plot ln (1-X) versus τ graph for Experiments 1 and 2.

Figure 3.4. Ln (1-X) versus τ graph for Experiments 1 and 2.

- Plot ln (1-X) versus τ graph for Experiments 3, 4 and 5.

Figure 3.5. Ln (1-X) versus τ graph for Experiments 3, 4 and 5.

Table 3.4. Reaction rate constants for 50°C and 70°C.

Experiment #	T (°C)	k (1/min)
1&2		
3&4&5		

- Plot ln k versus 1/T graph.

Figure 3.6. Ln k versus 1/T graph.

- Compare the experimental activation energy with the theoretical activation energy of reaction.

$$Error\,\% = \frac{|Theoretical\ activation\ energy - Experimental\ activation\ energy|}{Theoretical\ activation\ energy}$$

Table 3.5. Thiele modulus and effectiveness factor values for 50°C and 70°C.

Temperature (°C)	Thiele Modulus ϕ	Effectiveness Factor η
50		
70		

- Plot η versus ϕ graph.

Figure 3.7. Effectiveness factor (η) versus Thiele modulus (ϕ) graph.

For reactor 1, particle radius = 0.2 mm

For reactor 2, particle radius = 0.4 mm

Effective diffusivity of sucrose at 50°C= 24 x 10^{-8} cm^2/s

Effective diffusivity of sucrose at 70°C= 52.5 x 10^{-8} cm^2/s