

# **BIODEGRADATION OF ORGANIC COMPOUNDS USING FLUIDIZED BED REACTOR**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF

**Bachelor of Technology  
in  
Chemical Engineering**

Under the guidance of

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### CERTIFICATE

This is to certify that the thesis entitled, “BIODEGRADATION OF AN ORGANIC COMPOUNDS USING FLUIDIZED BED REACTOR” submitted by Mr. Gaurav Singh in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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# ABSTRACT

Fluidized beds reactors are used for different purposes; they are still used to produce gasoline and other fuels, along with many other chemicals. Many industrially produced polymers are made using FBR technology, such as rubber, vinyl chloride, polyethylene, and styrene's. Various utilities also use Fluidized bed reactor for coal gasification, nuclear power plants, and water and waste treatment settings. Used in these applications, fluidized bed reactors allow for a cleaner, more efficient process than previous standard reactor technologies. In this paper a theoretical study about fluidized bed reactors are carried out and also a fluidized bed reactor for three different reaction schemes (oxidation of benzene to form maleic anhydride, oxidation of naphthalene to form phthalic anhydride and oxidation of ethylene to form ethylene oxide) is designed. Cost optimization for multiple fluidized bed reactors with continuous transport of an immobilized enzyme is also studied and calculated.

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# CHAPTER 1

## INTRODUCTION

## 1 INTRODUCTION

Increasing discharge and improper management of liquid and solid industrial wastes have created a great concern among industrialists and the scientific community over their economic treatment and safe disposal. The final disposal or destination of residues specially the wastewater generated by industrial processes (such as the milk industry, slaughter houses, tanneries, breweries, food-processing industries, etc.) and that from domestic sewage, has become a serious problem to be tackled.

The wide variety and large quantity of chemical compounds found in these wastewaters are responsible for most of the environmental pollution of aquatic bodies. In view of the extensive contamination of the environment by persistent and toxic chemical pollutants originating from industrial wastewaters, it is imperative to develop cost effective and efficient methods. Biodegradation is a popular and attractive technology that utilizes the metabolic potential of microorganisms to clean up the environment.

Application of biological methods such as fluidized bed reactors has generated a lot of interest in the recent past. The major advantage of fluidized bed reactor over other biodegradation systems is a higher biomass concentration, and a higher mass transfer, resulting in a higher rate of biodegradation. The application of the fluidized bed reactor makes it possible to achieve phase homogeneity and larger solid-liquid contact area. These characteristics of a fluidized bed reactor enable an operation at a high volumetric loading, a fact that makes a fluidized bed an appropriate choice for treatment of toxic effluents.

Biological treatment of wastewater, using either aerobic or anaerobic microorganisms, has been used to degrade organic loads. An Aerobic process uses oxygen as the main electrons acceptor, there by causing the oxidation of organic compounds. It transforms complex molecules into simpler and more stable ones. This respiratory metabolism



liberates the necessary energy for maintenance and growth of bacterial cells. While total oxidation of organic compounds can be achieved in the aerobic process, oxidation in the anaerobic process is only partial and occurs in the absence of oxygen. In the latter process microorganisms interact in order to cause a stable and self-regulating fermentation of organic compounds producing  $\text{CH}_4$  and  $\text{CO}_2$ .

# CHAPTER 2

## LITERATURE REVIEW

## 2.1 WASTEWATER POLLUTENTS

The extent of pollutants present in the wastewater varies according to both the source of the effluent and the precautions taken within the manufacturing plant before are discharged.

1. The industries involved in metal cleaning, plating, tanning, textiles, battery making, pickling and refining produce chemical pollutants such as As, Cr, Cd, Cu, Hg, Pb and Zn.
2. The discharge of acids and alkaline materials from the textile, coal-fuelled and chemical industries disrupts the pH buffer system of the natural water, reducing potential to kill harmful micro-organisms.
3. The presence of  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^-$  in wastewater from the metallurgical, cement and ceramic industries changes the nature of the water into which they are discharged, affecting its staining characteristics, hardness and salinity.
4. Various oxidizing and reducing agents, such as the ammonia, nitrite, nitrate and sulphate discharged from the fertilizer, textile and dyeing industries, alter the chemical balance of the wastewater and cause problems with rapid oxygen depletion, etc. This not only decreases the nutritional value of the water but also causes foul odours and microbial growth.
5. The large amount of soluble carbohydrates from sugar refining and discharges from distilleries, tanneries, milk processing, pulping, paper making and textile mills contain quantities of bio-oxidizables which increase the BOD level.
6. The wastewater discharges from poultry processing, wood processing and tanning contain large amounts of pathogenic organisms.

7. Huge volumes of raw sewage are discharged into the main streams. These sewage wastes and industrial effluents undoubtedly contribute to water pollution.

## **2.2 HARMFUL EFFECTS OF INDUSTRIAL WASTEWATER**

Both industries and household wastewater contain chemicals and biological matter that impose high demands on the oxygen present in water. Polluted water thus contains low levels of dissolved oxygen as a result of the heavy biological oxygen demand (BOD) and chemical oxygen demand (COD) placed by industrial and household waste materials discharged into water bodies and water systems, both above and below the earth's surface. In addition to low levels of dissolved oxygen in water, industrial wastes (effluents) also contain chemicals and metals that are directly harmful to human health and the ecosystem.

The supply of water through river valley projects and ground water extraction thus has repercussions for the health and safety of people. Apart from health effects, which indirectly affect human productivity, polluted water also affects land productivity. Crop production suffers from using contaminated irrigation water from both surface sources and from groundwater aquifers. The definition of pollution in economics is based not only on the physical effect on the environment but crucially on the human response to the physical effect. The physical effect can be biological (e.g. change in biodiversity, or ill- health) or chemical (e.g. effect of harmful chemicals from industrial waste on aquatic life in a river).

## **2.3 FLUIDIZATION**

When a gas flow is introduced through the bottom of a bed of solid particles, it will move upwards through the bed via the empty spaces between the particles. At low gas velocities, aerodynamic drag on each particle is also low, and thus the bed remains in a fixed state. Increasing the velocity, the aerodynamic drag forces will begin to counteract the gravitational forces, causing the bed to expand in volume as the particles move away from each other. Further increasing the velocity, it will reach a critical value at which the

upward drag forces will exactly equal the downward gravitational forces, causing the particles to become suspended within the fluid. At this critical value, the bed is said to be fluidized and will exhibit fluidic behavior. By further increasing gas velocity, the bulk density of the bed will continue to decrease, and its fluidization becomes more violent, until the particles no longer form a bed and are “conveyed” upwards by the gas flow. When fluidized, a bed of solid particles will behave as a fluid, like a liquid or gas.

### **2.3.1 A FLUIDIZED BED REACTOR**

A fluidized bed reactor (FBR) is a type of reactor device that can be used to carry out a variety of multiphase chemical reactions. In this type of reactor, a fluid (gas or liquid) is passed through a granular solid material (usually a catalyst possibly shaped as tiny spheres) at high enough velocities to suspend the solid and cause it to behave as though it were a fluid.

The solid substrate (the catalytic material upon which chemical species react) material in the fluidized bed reactor is typically supported by a porous plate, known as a distributor. The fluid is then forced through the distributor up through the solid material. At lower fluid velocities, the solids remain in place as the fluid passes through the voids in the material. This is known as a packed reactor. As the fluid velocity is increased, the reactor will reach a stage where the force of the fluid on the solids is enough to balance the weight of the solid material. This stage is known as incipient fluidization and occurs at this minimum fluidization velocity. Once this minimum velocity is surpassed, the contents of the reactor bed begin to expand and swirl around much like an agitated tank or boiling pot of water. The reactor is now a fluidized bed. Depending on the operating conditions and properties of solid phase various flow regimes can be observed in this reactor.

In the 30's the fluidized bed reactor (FBR) appeared as a new alternative for biological treatment of wastewaters. In this type of reactor a high concentration of biomass is maintained inside because, microorganisms are attached to support particles. In order to achieve aerobic degradation in this reactor, support particles are fluidized by the flowing

wastewater, which must have been previously oxygenated or flow co currently together with an air stream. Applications of FBRs to treat wastewater appeared only towards the end of the 70's and the beginning of the 80's with several advantages over the conventional treatment used up to that time. The main advantages are the lower hydraulic retention time (HRT) and the small size of equipment required.

In FBRs it is possible to achieve a high concentration of biomass depending on the operational conditions used in the process and the type of support used to immobilize the microorganisms, which are found within a complex structure of cells and their extra cellular products, referred to as a biofilm. The cell volume inside the biofilm is only a small part of its total volume. Dense particles were traditionally used in FBRs as a support for the biofilm. Entrainment of support particles from the reactor was problem that appeared as the biofilm grew, decreasing particle density.

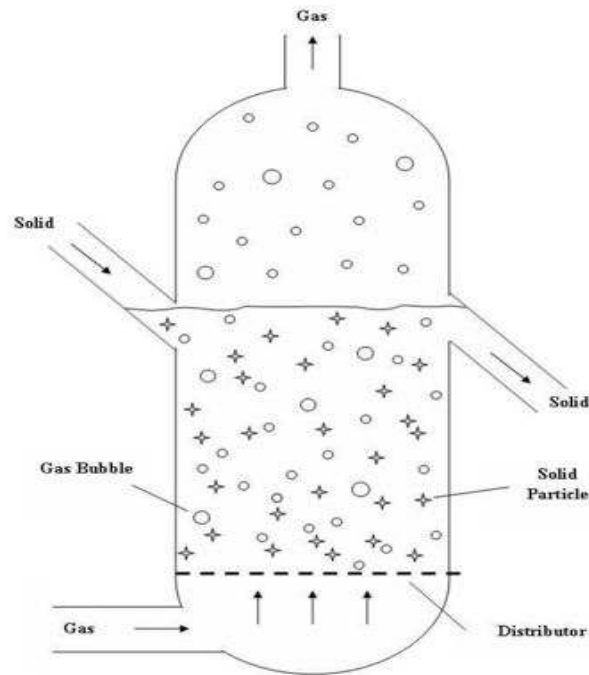


Fig 1: Basic diagram of a fluidized bed reactor.

### **2.3.2 APPLICATION OF A FLUIDIZED BED REACTOR**

Today fluidized bed reactors are still used to produce gasoline and other fuels, along with many other chemicals. Many industrially produced polymers are made using FBR technology, such as rubber, vinyl chloride, polyethylene, and styrene's. Various utilities also use FBR's for coal gasification, nuclear power plants, and water and waste treatment settings. Used in these applications, fluidized bed reactors allow for a cleaner, more efficient process than previous standard reactor technologies.

### **2.3.3 ADVANTAGES OF A FLUIDIZED BED OVER OTHER PROCESSES**

- (1) High specific area is available to micro organisms.
- (2) Minimum problems related to channeling, plugging and gas hold up.
- (3) Biofilm thickness is controlled by particle motion and liquid upflow velocities minimizing the diffusion problems through biofilms.
- (4) Uniform liquid flow distribution.
- (5) Small installation is required

### **2.3.4 VARIABLES AFFECTING THE QUALITY OF FLUIDIZATION**

Some of the variables affecting the quality of fluidization are

o Fluid inlet: It must be designed in such a way that the fluid entering the bed is well distributed.

o Fluid flow rate: It should be high enough to keep the solids in suspension but it should not be so high that the fluid channeling occurs.

o Bed height: With other variables remaining constant, the greater the bed height, the more difficult it is to obtain good fluidization.

o Particle size: It is easier to maintain fluidization quality with particles having wide range than with particles of uniform size.

o Gas, Liquid and solid densities: The closer the relative density of the gas, liquid and the solid, the easier it is to maintain smooth fluidization.

o Bed internals: In commercial fluidizers internals are provided to perform the following functions.

1. To prevent the growth of bubble sizes
2. To prevent lateral movement of fluid and solids.
3. To prevent slug formation.
4. To prevent elutriation of fine particles

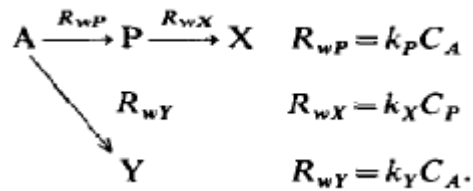


# CHAPTER 3

## DESIGN OF A REACTOR

### 3.1 DERIVING DIMENSIONLESS GROUPS FOR KINETIC SYSTEMS

We choose three different reaction schemes—two parallel, two consecutive, and a combination of both—and we combine them in a model for a reaction network that consists of three reactions, according to the following reaction scheme and reaction rate equations:



All reactions are first-order and the reaction rate constants are of the Arrhenius type, so  $k_i = A_i \exp[-E_i/(RT)]$ .

The reaction rates are expressed in moles of species  $i$  converted per unit of catalyst mass and per unit of time. The major reaction system parameters that determine how we should operate our reactor are the ratios of activation energies,  $p = E_Y/E_p$  and  $q = E_X/E_p$ .

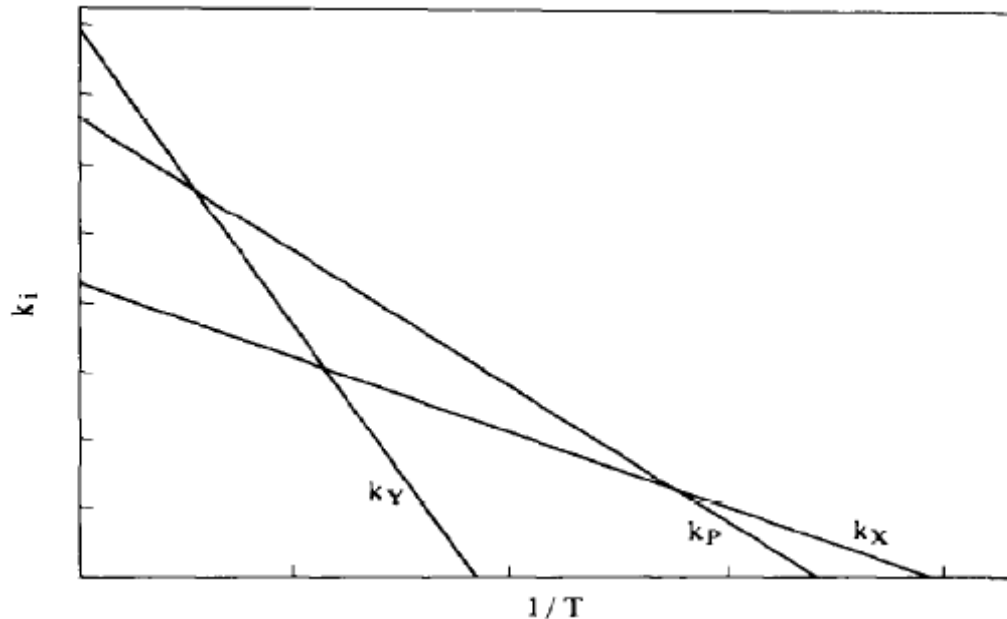


Fig. 2. Arrhenius plot for a system of three reactions, where  $p > 1$  and  $q < 1$

In Fig. 2 we plotted the reaction rate constants as a function of the reciprocal temperature  $1/T$  for  $p > 1$  and  $q < 1$ . We know that for high conversions we should operate at the left-hand side of the plot, where the temperatures, and consequently the reaction rates, are high. From Fig. 2 we can see that at this point the reaction rate of the undesired parallel reaction  $A \rightarrow Y$  is higher than the reaction rate of the desired reaction  $A \rightarrow P$ , so at high temperatures we will produce mainly undesired product  $Y$ . From Fig. 2 we also can see that at low temperatures the reaction rate of the reaction  $P \rightarrow X$  is higher than that of the desired reaction  $A \rightarrow P$ , which means that the product  $P$  which is produced will be mainly consumed to produce the undesired product  $X$ . So for a high yield or selectivity we should operate at an optimal temperature.

We will now rearrange the kinetics of the reaction system to obtain a set of dimensionless variables that fully describes the reaction system. To this end we define a reference temperature  $T_R$  and a reaction rate  $k_R$ , at which the reaction rate of the desired reaction  $k_P$ , equals that of the undesired reaction  $k_Y$ . From this definition it follows that

$$T_R = \frac{E_Y - E_P}{R \ln(A_Y/A_P)} \quad \text{And } k_R = k(T_R) = k_Y(T_R).$$

With them we define a dimensionless group  $Y_p$ , representing the activation temperature of the desired reaction, as

$$Y_p = E_P / RT_R.$$

Now the reaction rate constants can be made dimensionless by dividing each rate constant by the reference rate constant  $k_R$ . To this end we define a dimensionless rate constant  $K$  for the desired reaction, which leads to

$$K_F/K_R = K = \exp[Y_p(1 - 1/\theta)] \quad \text{with a dimensionless temperature } \theta = T/T_K.$$

$$K_Y/K_R = K^p \quad \text{with } p = E_Y/E_P$$

$$K_X/K_R = \beta K^q \text{ with } q = E_X/E_P$$

$$\text{and } \beta = A_X/A_P \exp[Y_F(1-q)]$$

Concentrations are made dimensionless by defining conversions. From the overall mass balance over the reactor we obtain

$$C_{A0} - C_A/C_{A0} = C_P/C_{A0} + C_X/C_{A0} + C_Y/C_{A0} = X_A = X_P + X_X + X_Y$$

We assume that the density of the gas is constant throughout the reactor. The various heat effects are made dimensionless by dividing the heats of reaction  $\Delta H_X$ , and  $\Delta H_Y$ , by the heat of reaction of the desired reaction,  $\Delta H_P$ . This leads to

$$H_X = \Delta H_X/\Delta H_P \text{ and } H_Y = \Delta H_Y/\Delta H_P$$

With these dimensionless rate constants, conversions and reaction heats we are able to describe any reaction system without using any design or operating parameters.

Here the model consists of a gas phase, through which the gas is transported in the direction of flow, and a dense phase in which the reaction takes place. In this model it is assumed that the gas flow-passing through the dense phase with velocity  $u_{mf}$  is negligible, or  $u_g \gg u_{mf}$ .

Owing to this assumption the results of the model is not valid for gas loads close to the minimum fluidization velocity. In the radial direction both phases are perfectly mixed, so no radial concentration gradient exists.

These two phases are separated by a film and the reactants have to be transported through the film in order to react in the dense phase, while the products are transported from the dense phase to the gas phase. This transport takes place by diffusion and the reaction already occurs in the film.

So it has been described the difference between the concentrations in the gas and the dense phase by diffusion through a separating film.

### 3.2 The dimensionless model equations

In the models mass is transported from the gas phase to the dense phase via a film between them. Even in this film reaction can take place, so the mass transport may be chemically enhanced. For the derivation of the model equations the assumptions taken are:

(1) The diffusion coefficient is constant and equal for all species.

(2) Secondly, there is no axial mixing in the dense phase.

(3) The gas flows in plug flow with a velocity  $u_g - u_{mf}$  through the gas bubble phase.

(4) The bed is also considered to be isothermal.

With these assumptions the following mass balances for the two phases and the film are obtained:

for the gas phase:

$$(u_g - u_{mf}) \frac{dC_{bJ}}{dz} - D_{eff} a \frac{\partial C_{fJ}}{\partial y} \Big|_{y=0}$$

For the film:

$$-D_{eff} \frac{\partial^2 C_{fJ}}{\partial y^2} = \rho_b R_{wJ}$$

For the dense phase:

$$D_{\text{eff}} a \frac{\partial C_{fj}}{\partial y} \Big|_{y=\delta} = (1 - \varepsilon_b - a\delta) R_{wdj}.$$

Here  $R_{wfj}$  and  $R_{wdj}$  are the conversion rates of species J in the film and the dense phase, respectively, and the length coordinates are in the axial direction  $z$  and the film  $y$ . To obtain a set of dimensionless equations we introduce dimensionless group's representative of the reactor operating and design variables, which are defined as

$$z = Z/L_r, \quad s = y/\delta, \quad V = \frac{1 - \varepsilon_b - a\delta}{a\delta}$$

$$M = \frac{L_{mf} D_{\text{eff}} a}{(u_g - u_{mf})(1 - \varepsilon_b)\delta}.$$

Furthermore  $\Omega$ ,  $\Psi$ , and  $\chi$  are called Hatta numbers, defined as

$$\chi^2 = \beta \kappa^q \frac{\rho_b k_R \delta^2}{D_{\text{eff}}}$$

$$\psi^2 = (\kappa + \kappa^p) \frac{\rho_b k_R \delta^2}{D_{\text{eff}}}$$

$$\Omega^2 = \kappa \frac{\rho_b k_R \delta^2}{D_{\text{eff}}}.$$

The film thickness  $\delta$  can be obtained from  $\alpha_m = D_{\text{eff}}/h$ . Introducing these groups in the mass balances and solving the differential equation for the film we obtain:

For reactant A:

$$C_{fA}(s) = A_1 \exp(s\psi) + A_2 \exp(-s\psi)$$

For product p:

$$C_{fP}(s) = B_1 \exp(s\chi) + B_2 \exp(-s\chi) - \frac{\kappa}{\kappa + \kappa^p - \beta\kappa^q} C_{fA}$$

where  $A_i$  and  $B_i$  are integration constants, which can be obtained from the boundary conditions:

$$C_{fa}(0) = C_{ba} \text{ and } C_{fa}(1) = C_{da}$$

$$C_{fp}(0) = C_{bp} \text{ and } C_{fp}(1) = C_{dp}$$

After setting up the equations for the derivatives at the film boundaries and eliminating them in the equations for the dense and the gas phase we obtain for the gas phase:

$$\frac{dC_{bA}}{dz} - M\psi(A_1 - A_2) = 0$$

$$\frac{dC_{bP}}{dz} - M\chi(B_1 - B_2) + \frac{\kappa}{\kappa + \kappa^p - \beta\kappa^q} (A_1 - A_2) = 0$$

And for the dense phase:

$$\psi [A_1 \exp(\psi) - A_2 \exp(-\psi)] = V\psi^2 C_{dA}$$

$$\chi [B_1 \exp(\chi) - B_2 \exp(-\chi)] - \frac{\kappa}{\kappa + \kappa^p - \beta\kappa^q} [A_1 \exp(\psi) - A_2 \exp(-\psi)] = V\Omega^2 C_{dA} - V\chi^2 C_{dP}$$

After introduction of the boundary conditions for the film to obtain relations for the constants  $A$  and  $B$  equations only in  $C_{ba}$ ,  $C_{da}$ ,  $C_{bp}$ , and  $C_{dp}$ , remain. After elimination of the dense phase concentrations  $C_{da}$  and  $C_{dp}$ , ordinary differential equations for  $C_{ba}$  and  $C_{bp}$  are obtained. Solving these equations leads to for the reactant A:

$$C_{bA}(z) = C_{bA0} \exp(-N_A Mz)$$

For the product P:

$$C_{bP}(z) = C_{bA0} \frac{\kappa}{\kappa + \kappa^P - \beta \kappa^q} [\exp(-N_P Mz) - \exp(-N_A Mz)]$$

where  $N_A$  and  $N_P$  are dimensionless groups defined as

$$N_A = \frac{V\psi^2 + \psi \tanh(\psi)}{1 + \psi V \tanh(\psi)}$$

$$N_P = \frac{V\chi^2 + \chi \tanh(\chi)}{1 + \chi V \tanh(\chi)}$$

After application of the definitions for the conversion  $X_A = (C_{bA0} - C_{bA})/C_{bA0}$  and  $X_P = C_{bP}/C_{bA0}$  we obtain

$$X_A(z) = 1 - \exp(-N_A Mz)$$

$$X_P(z) = \frac{\kappa}{\kappa + \kappa^P - \beta \kappa^q} [\exp(-N_P Mz) - \exp(-N_A Mz)].$$

After evaluation of the reaction rate equation for the undesired product Y in a similar way we obtain  $X_Y = K^P/(K + K^P)[1 - \exp(-N_A Mz)]$  and finally  $X_X$  from the overall mass balance:  $X_X = X_A - X_P - X_Y$

The relation for the heat balance is :

$$\theta - \theta_o = \Delta\theta_{ad} [X_P + (1 + H_X)X_X + H_Y X_Y] - Da U^*(\theta - \theta_c).$$



Three unknown parameters have to be determined from empirical correlations: the bubble hold-up  $\epsilon_b$ , the mass transfer coefficient  $\alpha_m$  and the specific bubble area  $a$ . From  $\alpha_m$ , and  $D_{eff}$  the film thickness  $\delta$  can be obtained. For  $\epsilon_b$  we use the relation

$$\epsilon_b = 2.47 \frac{u_g - u_{mf}}{[1 + 27.2(u_g - u_{mf})]^{1/6}} \frac{J(L, L^*)}{\Phi(D_t)}$$

The relation for  $\alpha_m$  is

$$\alpha_m = 6.26 \times 10^{-3} \sqrt{1 + 27.2(u_g - u_{mf})} \text{ m/s}$$

and the specific bubble area can be obtained from

$$a = 2910 \frac{u_g - u_{mf}}{\sqrt{1 + 27.2(u_g - u_{mf})}} (\Phi F)^{-1} \text{ m}^2/\text{m}^3.$$

Here  $F$  is a similar function to the relation for  $J(L, L^*)$  used for the bubble hold-up  $\epsilon_b$ . It can be obtained from

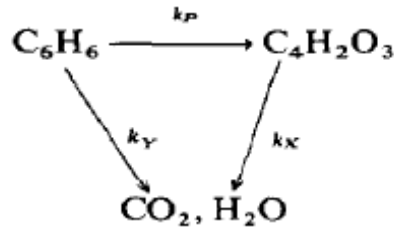
$$F(L, L^*) = \frac{L}{0.18[1 - (1 + 6.84L)^{-0.8}]} \quad \text{if } L \leq L^*$$

$$F(L, L^*) = \frac{L}{0.18[1 - (1 + 6.84L^*)^{-0.8}] + (L - L^*)(1 + 6.84L^*)} \quad \text{if } L > L^*.$$

Using these equations we are able to calculate  $\epsilon_b$ ,  $\alpha_m$  and  $a$ .

### 3.2.1 OPERATING AREA FOR THE PRODUCTION OF MALEIC ANHYDRIDE

Here we will discuss the production of maleic anhydride in a plant of industrial scale. For the production of maleic anhydride from benzene following reaction scheme is suggested.



With the following recommended reaction rate constants and reaction enthalpies:

$$K_p = 4280 \exp(-12,660/T) \text{ m}^3/(\text{kg catalysts})$$

$$k_y = 70,100 \exp(-15,030/T) \text{ m}^3/(\text{kg catalysts})$$

$$k_x = 26 \exp(-10,790/T) \text{ m}^3/(\text{kg catalysts})$$

$$\Delta H_p = 1.85 \times 10^6 \text{ J/mol}$$

$$\Delta H_y = 3.27 \times 10^6 \text{ J/mol}$$

$$\Delta H_x = 1.42 \times 10^6 \text{ J/mol.}$$

With  $T_R = 848 \text{ K}$  and  $K_R = 1.4 \times 10^{-3} \text{ m}^3/(\text{kg catalysts})$

This leads to the following dimensionless kinetic parameters:

$$p = 1.18, q = 0.85, \beta = 0.055, H_y = 1.77, H_x = 0.77, \gamma_p = 14.9$$

Furthermore the following physical data are available:

$$\rho_b = 800 \text{ kg/m}^3, D_{\text{eff}}=80 \times 10^{-6} \text{ m/s}^2, \rho_g = 1.01 \text{ kg/m}^3, C_{\text{pg}} = 1090 \text{ J/(kg K)}$$
$$\eta_g = 15 \times 10^{-6} \text{ Pas}, \rho_p = 1800 \text{ kg/m}^3, D_p = 150 \times 10^{-6} \text{ m}.$$

At the minimum fluidization velocity the bulk density of the catalyst bed is  $\rho_b = 800 \text{ kg/m}^3$ . Moreover as a starting value we take  $C_{A0} = 0.30 \text{ mol/m}^3$ . For our design we take an industrial scale reactor with a bed height at minimum fluidization of  $L_{\text{mf}} = 4.0 \text{ m}$  and a reactor diameter of  $D_t = 6.0 \text{ m}$ .

The reactants cannot be recovered from the reaction mixture leaving the reactor, so a maximum yield should be aimed.

Fluidized beds cannot be operated at any arbitrary gas load or reactor temperature. On the contrary the regime of possible combinations of the operating conditions is controlled by several constraints.

These constraints on the design can be divided into those due to physical and mechanical limitations of the reactor and those due to operational aspects. The first set of constraints are the possible gas velocities, the amount of cooling area that can be installed, and the minimum and maximum temperatures for the selected coolant. The second set is concerned with reactor stability and unique operating conditions.

### **3.2.2 Constraints to the residence time**

The residence time cannot be chosen at will, because it strongly depends on the physical properties of the catalyst particles. At low gas loads the particles do not fluidize and behave as in a packed bed. At a certain minimum gas velocity-the minimum fluidization velocity  $u_{\text{mf}}$  the particles start to fluidize. With increasing gas loads the bed will expand till at maximum velocity  $u_t$  the particles start to be blown out of the reactor. Between these gas loads,  $u_{\text{mf}}$  and  $u_t$  operation under fluidized conditions is possible.

For the minimum velocity

$$u_{mf} = \frac{0.0093 D_p^{1.82} (\rho_b - \rho_g)^{0.94}}{\rho_g^{0.06} \eta_g^{0.88}}$$

resulting in the maximum residence time

$$Da_{max} = k_R \rho_b L_{mf} / u_{mf}.$$

For the maximum velocity

$$u_t = \sqrt{\frac{4gd_p(\rho_b - \rho_g)}{3\rho_g C_D}}$$

where the drag factor  $C_d$  is calculated by

$$C_D = 24/Re \text{ if } Re < 5$$

$$C_D = 10/Re^{0.66} \text{ if } 5 < Re < 500$$

$$C_D = 0.43 \text{ if } 500 < Re < 10^5$$

Where

$$Re = \frac{D_p \phi_m}{\frac{1}{4} \pi D_t^2 \eta_g}$$

Hence, the minimum residence time is given by  $Da_{\min} = k_R \rho_b L_{mf} / u_t$

### 3.2.3 Constraints on the cooling area

When no cooling area is installed  $U^*$  is zero. The other constraint is the maximum cooling area that can be installed in a unit of reactor volume, and results in a maximum value of  $UA_w/V_R$  or  $U^*_{\max}$ . It depends on the method of construction reactor and the largest number of cooling pipes that can be installed.

The good heat transfer characteristics in a fluidized bed are caused by the circulation of the solids. Therefore the total heat transfer coefficient  $U$  strongly depends on the gas flow rate, below a certain gas flow rate the solids circulation becomes poor and the total heat transfer coefficient  $U$  rapidly decreases, eventually approaching the value of  $U$  for a packed bed.

we assumed a constant minimum value of  $U$ , and to be have a good heat transfer the gas flow rate should be about 3 times the minimum fluidization velocity. At this fluidization velocity the heat transfer coefficient will reach about 70% of its final value, to become truly constant at about 10 times the fluidization velocity.

### 3.2.4 Constraints on the cooling temperature

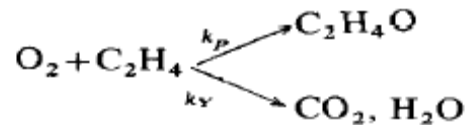
Normally the feed is not pre-heated and enters the reactor at the temperature  $T_0$ , at which it is available in the plant. The range of possible coolant temperatures,  $T_{0\min}-T_{0\max}$  depends on the choice of coolant. In the case of boiling water the range is about 180 to 320<sup>0</sup>C, for heating oils 200 to 400<sup>0</sup>C, and for molten salts 150 to 500<sup>0</sup>C.

### 3.2.5 Stability requirement for the operating point

In the steady state the operation of a fluidized bed should be such that a small disturbance of one of the operating parameters will not lead to completely different operating conditions.

## 3.3 THE PRODUCTION OF ETHYLENE OXIDE IN A SMALL PILOT PLANT

Ethylene oxide is produced by oxidation of ethylene over a silver catalyst. The reaction system can be considered as a set of two parallel reactions according to



Here all reactions are first-order in oxygen and the reaction rate constants are of the Arrhenius type. The following kinetic data are presented

$$k_p = 70.4 \exp(-7200/T) \text{ m}^3/(\text{kg catalysts})$$

$$k_y = 70,100 \exp(-10,800/T) \text{ m}^3/(\text{kg catalysts})$$

$$\Delta H_p = 2.10 \times 10^5 \text{ J/mol}$$

$$\Delta H_y = 4.73 \times 10^5 \text{ J/mol}$$

With  $T_R = 549 \text{ K}$  and  $k_R = 1.42 \times 10^{-4} \text{ m}^3/(\text{kg catalysts})$  this leads to the following dimensionless kinetic parameters:

$$p = 1.5, H_y = 2.25, y_p = 13.1$$

For the design the following data are available or have been chosen:

$$C_{A0} = 22.0 \text{ mol/m}^3, \rho_b = 800 \text{ kg/m}^3$$

$$\rho_g = 6.06 \text{ kg/m}^3, C_{pg} = 1140 \text{ J/(kg K)}$$

$$\rho_p = 1800 \text{ kg/m}^3, D = 150 \times 10^{-6} \text{ m}$$

$$T_0 = 320 \text{ K}, D_{\text{eff}} = 80 \times 10^{-6} \text{ m}^2$$

$$\eta_g = 15 \times 10^{-6} \text{ Pas}, T_{\text{cmin}} = 400 \text{ K}$$

$$T_{\text{Cmax}} = 600 \text{ K}.$$

The cooling is done with the generation of steam. The economic production of ethylene oxide is impossible without a recycling of non-converted reactant.

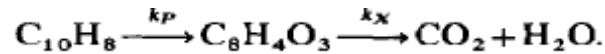
For equal-order parallel reactions irrespective of the model used the relation for the differential selectivity is always

$$S_P = \frac{\kappa}{\kappa + \kappa^P}.$$

For the small-scale pilot plant reactor we take for the bed diameter  $D_t = 0.3 \text{ m}$  and for the bed height at minimum fluidization velocity  $L_{mf} = 0.5 \text{ m}$ . The maximum cooling area is installed with  $U_{\text{max}} A_w / V_R = 8000 \text{ W/m}^3 \text{ K}$ .

### 3.4 THE PRODUCTION OF PHTHALIC ANHYDRIDE

As an example of a system of consecutive reactions the production of phthalic anhydride by oxidation of naphthalene is taken.. The reaction system is given by a set of two consecutive reactions:



$$k_p = 14,050 \exp(-10,390/T) \text{ m}^3/(\text{kg catalysts})$$

$$k_x = 133 \times 10^9 \exp(-22,770/T) \text{ m}^3/(\text{kg catalysts})$$

$$\Delta H_p = 1.88 \times 10^6 \text{ J/mol}$$

$$\Delta H_x = 3.29 \times 10^6 \text{ J/mol}$$

Here  $T_r = 770 \text{ K}$  and  $k_R = 1.94 \times 10^{-2} \text{ m}^3/(\text{kg catalysts})$ , where both are based on  $k_x$  and  $k_p$  so  $\beta = 1$ .

This leads to the following dimensionless reaction system parameters:

$$q = 2.19, H_x = 1.75, \gamma_p = 13.5$$

For the design the following physical data are chosen:

$$C_{A0} = 0.37 \text{ mol/m}^3, \rho_b = 675 \text{ kg/m}^3$$

$$\rho_g = 0.90 \text{ kg/m}^3, C_{pg} = 1040 \text{ J/(kg K)}$$



$$\rho_p = 1500 \text{ kg/m}^3, D_p = 150 \times 10^{-6} \text{ m}$$

$$T_0 = 360 \text{ K}, D_{\text{eff}} = 80 \times 10^{-6} \text{ m/s}^2$$

$$\eta_g = 15 \times 10^{-6} \text{ Pas}, T_{\text{cmin}} = 520 \text{ K}$$

$$T_{\text{Cmax}} = 620 \text{ K.}$$

Oil has been chosen as the coolant. The reactor diameter is  $D_t = 3.0 \text{ m}$  and the bed height at minimum fluidization is  $L_{\text{mf}} = 4.0 \text{ m}$ .

# CHAPTER 4

## BIODEGRADATION PROCESS

## **4.1 Biodegradation process: Pulp wastewater Treatment**

For the production of sugar and ethyl alcohol, which are basically the only products manufactured from sugarcane, enormous amounts of water and energy are required. More than one million cubic meters of water per day are used, and the main energy source is the combustion —usually inefficient— of bagasse and other low-quality fossil fuels with high sulphur content. In sugar production, the water used for processes such as cane washing, clarification of juice, cleaning of evaporators, heaters and purging of boilers and from cooling systems and sanitary services, is discarded. In ethyl alcohol production, the wastewater is a byproduct of the cooling waters for condensers and fermentation containers and vinasses or residues from the distillation towers. In most alcohol manufacturing plants, energy consumption is not optimal. Of all the wastewater produced by the sugar/alcohol manufacturing complexes, the most polluting, owing to its high content of biodegradable and nonbiodegradable organic matter, are the vinasses. These are produced in a proportion of 12 to 15 liters per liter of ethyl alcohol. Considering their volume, although the concentration of organic and inorganic matter is not so high, the wastewater from cane washing pollutes almost as much as the vinasses. There is also wastewater from condensers and other energy exchange systems which is not used and which contributes to dissipating heat, decreasing the overall energy efficiency of the system and polluting the environment.

To reduce these serious pollution problems, strategies have been established, mainly by using of biotechnological systems, to comply with current technical ecological standards for liquid effluents.

## **4.2 Analytical Methods**

Samples of the mixed liquors from all the reactors was used to measure total solids, suspended and dissolved. The samples were then centrifuged and the supernatant used to determine the chemical oxygen demand and biochemical oxygen demand, Samples of biofilm from the aerobic reactor discs were analyzed by gravimetry to determine dry

weight and ashes. In the case of anaerobic systems, sulphates and organic acids were determined.

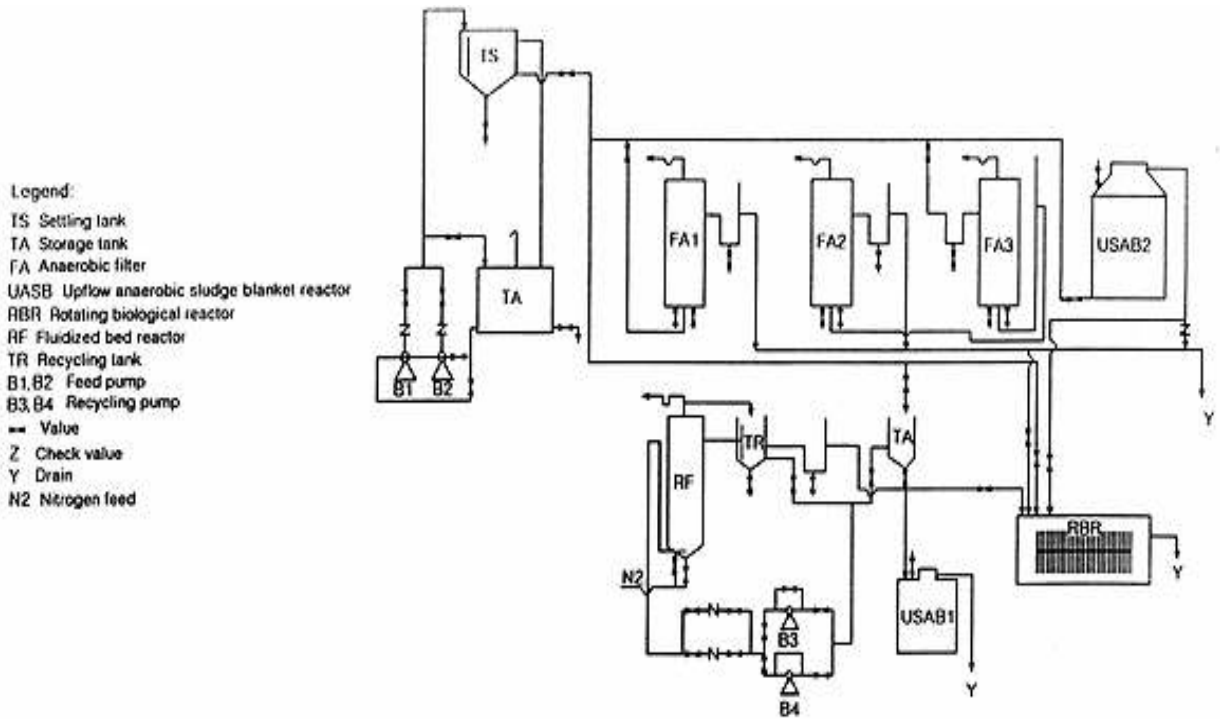


Fig: 3 Block diagram of the pilot plant for pulp waste treatment

# CHAPTER 5

## PROCESS OPTIMIZATION

## 5.1 Process optimization strategy

In order to optimize the reactor design, the total costs function can be minimized. A general costs function of a chemical process is as follows

$$C_{TOT}=C_{RM}+C_{DISP}+C_{VAR}+C_{FIX}$$

The total costs per unit of time consist of costs  $C_{RM}$ , for raw materials, costs  $C_{DISP}$  for disposal of waste materials, and variable costs  $C_{VAR}$  and fixed costs  $C_{FIX}$ .

Let the flow rate and compositions of the reactor influent and effluent are fixed, thus when minimizing the total costs of the process, only the variable and fixed costs need to be taken into account. The fixed costs, or overall reactor costs, can be subdivided into truly fixed costs (e.g. personnel) and investment-related fixed costs (e.g. insurance, maintenance and depreciation costs).

In a process using immobilized enzyme the variable costs are mainly determined by biocatalyst consumption and energy requirements. However, biocatalysts are only active and stable in a narrow temperature range; thus the energy requirements can be regarded as not affected by the optimal choice for the reactor temperature.

By doing so, the optimization problem can be separated into technological and economic problems. The technological aspect is the determination of the operating temperature at a given biocatalyst residence time, substrate flow and conversion, such that the hold-up of biocatalyst (i.e. the total amount of biocatalyst present in the reactor) is minimized. This simultaneously minimizes the biocatalyst consumption (variable costs) and the reactor dimensions (fixed costs), and thus also the total costs function.

The economic aspect is to make an optimum selection from the combinations of biocatalyst residence time and operating temperature that can be regarded as technological sub optima. The economic aspect is to make an optimum selection from the combinations of biocatalyst residence time and operating temperature that can be regarded as technological sub optima.

## 5.2 Application of the optimization strategy to the multistage fixed bed reactor using an immobilized biocatalyst

(1) Within a batch of immobilized biocatalyst particles, there always will be a certain spread in size. When particle mixing is incomplete, the smaller particles tend to accumulate in the top of a compartment and, since the biocatalyst is mainly transported from the bottom of a compartment, this causes an unequal residence time for small and large particles. Therefore for an efficient use of the biocatalyst it is essential that the particles are perfectly mixed. The conditions under which particles can be mixed are dependent on the properties of the particles and liquid, and the scale of the reactor. These conditions must be determined from full-scale experiments and can be related to the bed porosity, e.g.  $0.6 \leq \epsilon \leq 0.7$ . As a result, the required liquid velocity follows from the particle properties (diameter and density) and the demand for the bed porosity.

(2) The diameter of the reactor is determined by the allowable liquid velocity and the desired capacity.

(3) Approximately plug flow transport of the biocatalyst can be realized by increasing the number of reactor compartments, and only particles with a low activity are removed from the reactor. The reactor efficiency improves with increasing number of compartments but requires a larger investment for extra distributor plates. It is not expected that this is a major cost factor in the overall process economics, and we therefore assume, somewhat arbitrarily, that ten compartments are used in order to achieve a limited degree of back mixing of the biocatalyst. If desired, the number of plates can be optimized by comparing the optimization results for different numbers of compartments.

The resulting procedure for the optimal design of an MFBR is summarized in Fig. 4. For given values of the compartment temperatures, the biocatalyst residence time and the number of reactor compartments, the active biocatalyst fraction  $\omega_1$  and  $\omega_N$  in each reactor compartment can be calculated from the given equation.

$$\omega_n = \prod_{i=n}^N \left( 1 + \frac{\tau_b}{N} k_d(T_i) \right)^{-1}$$

$\tau_b$ =Total biocatalyst residence time

$n$ = number of compartments

$K_d$ =first-order enzyme deactivation constant.

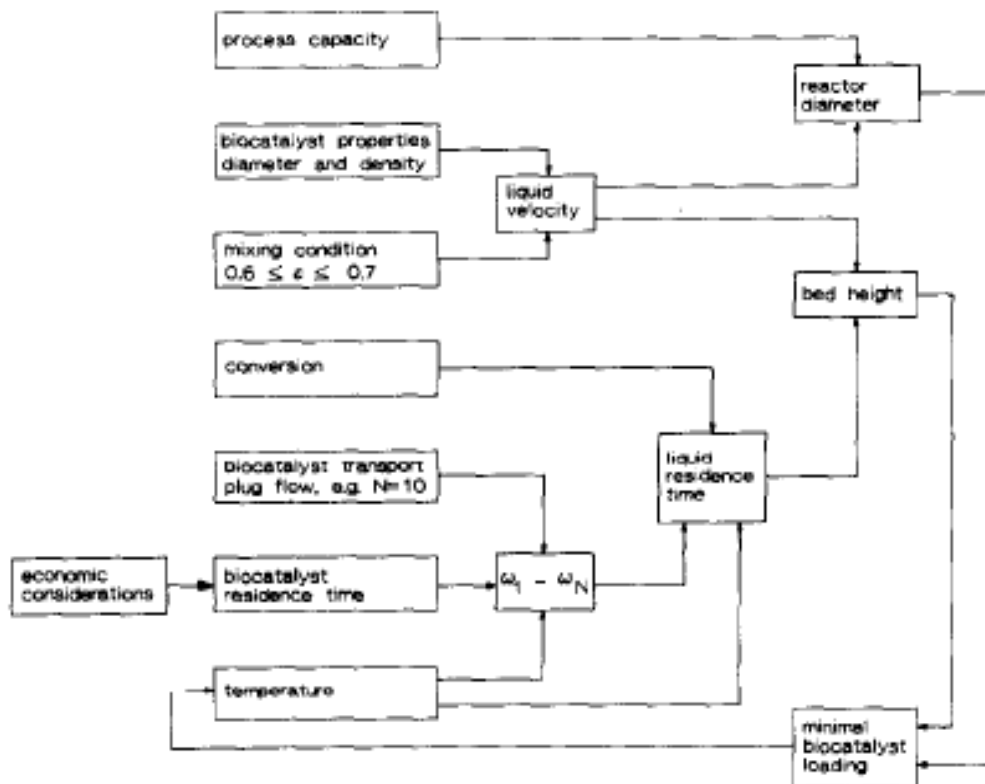


Fig: 4 Diagram for the optimal design of an MFBR.

From the temperature and the biocatalyst activity in the compartments, the liquid residence time is found iteratively, such that the desired degree of conversion is attained. The bed height, which is proportional to the biocatalyst loading, is calculated from the



liquid residence time and the liquid velocity. Because of a biocatalyst activity gradient and a possible temperature gradient, the effectiveness factor is different for every reactor compartment. Therefore the mass transfer resistances, related to heterogeneous catalysis do influence the optimal operating conditions of the MFBR. The technological aspect of the optimization problem is the determination of the temperatures in the reactor compartments at a given value of the biocatalyst residence time, such that the hold-up of biocatalyst is minimized. A non-linear parameter estimation routine must be used to find these temperatures. From the technologically optimal combinations of temperature and biocatalyst residence time which can be obtained by following this procedure, the economically optimal combination can be selected by minimization of a total costs function.

# CHAPTER 6

CONCLUSION

## CONCLUSION

Fluidized bed reactor for three different reaction schemes (oxidation of benzene to form maleic anhydride, oxidation of naphthalene to form phthalic anhydride and oxidation of ethylene to form ethylene oxide) is designed.

The models developed here is a simple and realistic one. Careful studies in laboratory and pilot-scale experiments for the determination of the threshold values can provide sufficient data to design a large-scale system and to predict its performance.

We considered 3 times the minimum fluidization velocity as an absolute minimum for the gas load.

Gas loads close to the minimum fluidization velocity are not realistic because there heat transfer and mass transfer are too poor.

For reaction systems with continuous refreshment of such a biocatalyst, the process optimization can be split into technical and economic parts. The technical aspect is the determination of the optimal temperature at a given biocatalyst residence time. At this temperature, the biocatalyst productivity is maximal, resulting in a minimization of both the biocatalyst consumption and the hold-up; thus the smallest possible reactor is obtained. Costs functions for biocatalyst and investment-related fixed costs can be used to determine the economic optimum from various possible suboptimal combinations of biocatalyst residence time and operating temperature.

# NOMENCLATURE

$a$	specific interfacial area between bubbles and the dense phase, $\text{m}^2/\text{m}^3$
$c_{\text{BJ}}$	concentration of species $i$ in the bubble phase, $\text{mol}/\text{m}^3$
$C_{\text{dJ}}$	concentration of species $J$ in the dense phase, $\text{mol}/\text{m}^3$
$C_{\text{fJ}}$	concentration of species $J$ in the film, $\text{mol}/\text{m}^3$
$D_{\text{eff}}$	effective diffusion coefficient in the film, $\text{m}^2/\text{s}$
$Da$	dimensionless residence time
$D_p$	particle diameter, $\text{m}$
$D_t$	diameter of the bed, $\text{m}$
$E_i$	activation energy for the reaction towards product $i$ , $\text{J}/\text{mol}$
$Hi$	ratio of reaction heats
$K_i$	reaction rate constant
$K$	number of transfer units

$k_R$	reference reaction rate constant, $m^3/(kg\ s)$
$L$	height of the expanded bed, m
$L^*$	height of the fluid bed in which the bubbles coalesce, m
$\alpha_m$	mass transfer coefficient, m/s
$\beta$	dimensionless pre-exponential constant
$\gamma_P$	dimensionless activation temperature
$\delta$	thickness of film, m
$\epsilon_b$	bubble hold-up in the reactor
$\Theta$	dimensionless temperature
$\rho_b$	bulk density of the catalyst at minimum fluidization, $kg/m^3$
$\rho_g$	density of the reaction mixture, $kg/m^3$
$\rho_p$	density of the catalyst particles, $kg/m^3$
$\mu$	fraction of the gas flowing through the dense phase

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