Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

Homogeneous reactor

Chapter 3: Material balances in ideal reactors

Chapter 1: General

- Stoichiometry: Concept of conversion rate; Concept of advancement; Case of a single reaction; Case of several reactions.

Chapter 2: Classification of chemical reactors

- Perfectly stirred batch reactor;
- Perfectly stirred stationary continuous reactor;
- Stationary tubular continuous plug flow reactor.

Chapter 3: Material balances in ideal reactors

-Single reaction:
-Perfectly agitated closed reactor;
-Continuous perfectly stirred reactor in steady state;
-Piston reactor in steady state.

Chapter4: Study of homogeneous isothermal chemical reactors with one reaction

-R.D.P.A;   R.C.P.A; R.C.P;
-Chemical Reactor Association:
   => Association of stationary continuous reactors in plug flow (series/parallel);
   => Association of perfectly stirred stationary continuous reactors (series/parallel);
-Comparative performances of ideal reactors.

Chapter 5: Study of homogeneous isothermal chemical reactors with several reactions

- Consecutive irreversible reactions;
-Competitive reactions;
-Selectivity and yield;

Chapter 6: Ideal non-isothermal reactors

-Notions of thermal balances in ideal non-isothermal reactors.

Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

Chapter 3: Material balances in ideal reactors

- Single reaction:
- Perfectly agitated closed reactor;
- Continuous perfectly stirred reactor in steady state;
- Piston reactor in steady state.

....

III.1. Introduction

This chapter illustrates how to predict the behavior of chemical reactors and determine the volume of a reactor for a given operation. These calculations are mainly based on material balances, using the principles of stoichiometry and kinetics developed in chapter 1.

A material balance is a tool used in chemical engineering to analyze and quantify the flow of material through a system. This is essentially an application of the principle of conservation of mass.

To carry out a material balance, we examine the different inputs and outputs of a system, as well as the chemical or physical reactions that occur inside. By comparing the quantities of material entering and leaving, one can determine the rates of production or consumption of different substances, as well as the rates of conversion of reactants into products.

Material balances are essential in many areas of engineering, including the design and optimization of industrial processes, natural resource management, and environmental protection. They provide an understanding of how raw materials are used, how products are manufactured, and how waste is produced and disposed of, which is crucial to ensuring the efficiency and sustainability of industrial operations.

At the end of this chapter, the student should be able to:

• Explain the difference between a closed reactor (RDPA), a perfectly stirred continuous reactor (RCPA) or plug flow (RCEP),

• Explain how the concentrations of reactants and products vary in the three types of ideal reactors (RDPA, RCPA, RCEP),

• Establish the sizing equations for the three types of reactors by carrying out material balances,

• Calculate the reaction kinetics using the sizing equations for a perfectly stirred continuous reactor (RCPA).

III.2. Material Balance

A material balance (BM) reflects the conservation of matter during a physical or chemical process. In the case of a chemical reactor, the material balance is established in relation to a constituent, either a reactant or a product. It is written in terms of molar flux change (moles/time). The general equation for a material balance is:

INPUT FLOW + FLOW PRODUCED BY REACTION = OUTPUT FLOW + FLOW CONSUMED BY REACTION + ACCUMULATION

Or simply

INCOMING FLOW + APPEARANCE = OUTGOING FLOW + DISAPPEARANCE + ACCUMULATION

Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

III. 3. Perfectly stirred discontinuous reactor (batch)

■ A closed reactor corresponds to a system which does not exchange material with the external environment (E (in) = E (out) = 0).

■ In this type of reactor, we introduce an initial charge of reagents n_0 at the instant t=0, the reaction will then take place for a duration 't'. The number of moles n_i (at t) is a quantity which depends on time, n_i (t).

■ The ideality of the system is obtained thanks to the perfect agitation which results in total homogenization throughout the system. This homogenization implies a identical concentration (C_i) at all points of the reaction system (physical properties identical).
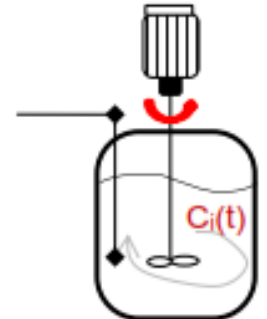
III.3.1. Sizing Equation of a Closed Reactor (discontinuous)

We consider the reaction: *ΣviAi = 0*

If A_i is a reagent, the MB (In + App = Out + Disp + Acc) in relation to the constituent A_i is written:

$$\text{Disp + Acc = 0} \qquad (1)$$

This because: **In = Out = 0** (Closed reactor) & **App = 0** (A_i is reagent)

Note: if A_i is a product; the MB is written like: **App = Acc**

■ The disappearance is linked to the chemical reaction and is given by: **(-r_i) x V**
■ The accumulation is expressed as: **dn_i/dt**.

So Equation (1) becomes:

$$(-r_i) \text{ x V} + dn_i/dt = 0 \qquad (2)$$

By expressing (-r_i)×V as a function of n_i, we obtain a differential equation whose integration gives the evolution of the number of moles n_i in the reactor as a function of time (n_i(t)).

We can also determine the residence time (t_r) if we express (−r_i)×V and n_i as a function of the quantities of the progress of the chemical reaction (ξ, χ, X_i), as follows:

$$- \quad n_i = n_{i0} + v_i \xi \Rightarrow dn_i = v_i d\xi \qquad (3)$$

$$- \quad n_i = n_{i0} + v_i n_0 \chi \Rightarrow dn_i = v_i n_0 d\chi \qquad (4)$$

$$- \quad n_i = n_{io} - \frac{v_i}{v_A} n_{A0} X_A \Rightarrow dn_i = -\frac{v_i}{v_A} n_{A0} dX_A \qquad (5)$$

We replace equations (3) to (5) in equation (2), we obtain:

Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

- $(-r_i)V + v_i \dfrac{d\xi}{dt} = 0$ (6)

- $(-r_i)V + v_i n_{io} \dfrac{d\chi}{dt} = 0$ (7)

- $(-r_i)V - \dfrac{v_i}{v_A} n_{Ao} \dfrac{dX_A}{dt} = 0$ (8)

From equation (8): [==Attention its tr not ts (ts is the notation in French==)]

$$\int_0^{ts} dt = \frac{v_i}{v_A} n_{Ao} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_i)V} \quad \Rightarrow \quad t_s = \frac{v_i}{v_A} n_{Ao} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_i)V} \quad (9)$$

Relation (9) expresses the residence time tr during which the reagents remain in the reactor to reach a conversion rate X_{Af}.

If the reactant A_i is A (the limiting reactant), equation (9) becomes: [==Attention its tr not ts==]

$$t_s = n_{Ao} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)V} \quad (10)$$

The integration of equation (10) can be carried out either **analytically** or **graphic**.

a) **Analytical Resolution:** In this case, it is necessary to express (-r$_A$) and V in terms of X_A. For an in-phase reaction gaseous of order 1 compared to reagent A:

$$(-r_A) = -v_A k C_A = k C_{A0} \frac{1 - X_A}{\beta(1 + \alpha' X_A)}$$

The reaction volume V is given by:

$$V = \beta V_0 (1 + \alpha' X_i)$$

Where :

$$(-r_A) \times V = k n_{A0}(1 - X_A)$$

The residence time tr is given by: [==Attention its tr not ts==]

$$t_s = \frac{1}{k} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{1 - X_A} = \frac{1}{k} \ln\left(\frac{1 - X_{Ai}}{1 - X_{Af}}\right)$$

Exemple:

> The following reaction is in gas phase A --> B, it is a reaction of order 1 with respect to reagent A.
> Calculate the residence time t_r if you know that the conversion rate are: 0.8, 0.9, 0.99 (k=0.1min^{-1})
> Answers: t_r=16min; 23min; 46min.

Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

b) Graphic resolution : **In this case, the integral of equation (10) is represented by the geometric surface delimited by the function** $\dfrac{1}{(-r_A)V}$ **and the X_{Ai} terminals and X_{Af}**
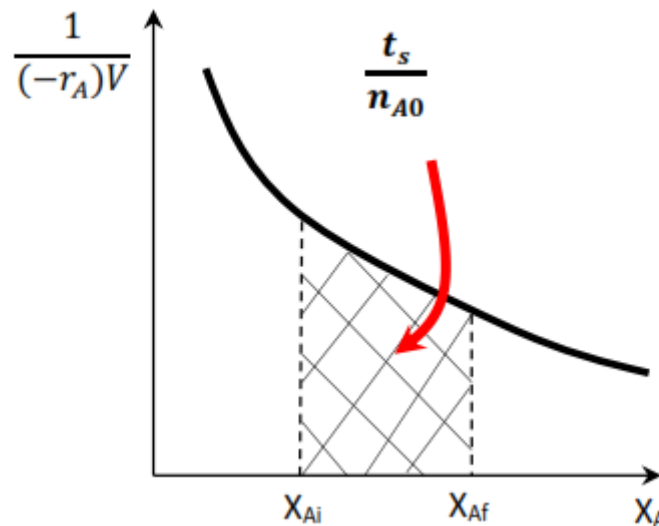

Fig. 1 graphical determination of residence time (t_r)
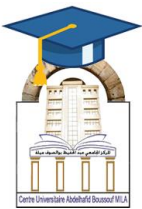
III. 4. Perfectly stirred continuous reactor

- **It is a reactor which characterized by an input current (power supply) and a output current.**
- **The system is agitated in a appropriate way to ensure identical physicochemical properties in all points inside the reactor.**
- **The concentration in the reactor is equal to the exit concentration (all molecules entering in the reactor have a concentration equal to Cis once mixed with the reaction volume).**
- **All the molecules which enter at time t exit at time t + τ (τ: time of passage). This implies that all molecules have the same passage time τ.**
- **The ideality of this reactor is obtained if all the molecules have the same passage time τ, and the concentration at the exit point of reactor is equal to Cis.**
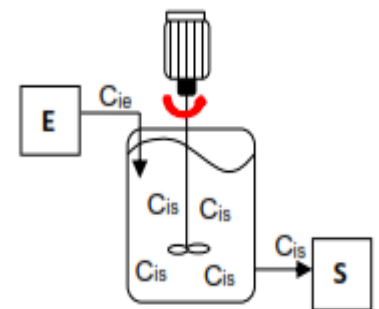
⇨ **Remarks :**

The non-ideality of the reactor comes from the fact that the molecules do not have the same passage time, mainly due to two phenomena that cause volume heterogeneity reaction:

a) The existence of dead zones (Figure 2a): the molecules found there will be trapped and will then have a very high passage time (Solution: Use of low-speed reactors concavity to reduce the formation of dead zones).

Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

b) The existence of a short circuit (Figure 2b): the reactant molecules escape directly from the reactor to the exit, resulting in a very low residence time (Solution: Use of appropriate agitation to promote homogeneous distribution of reactive and reduce short circuits).
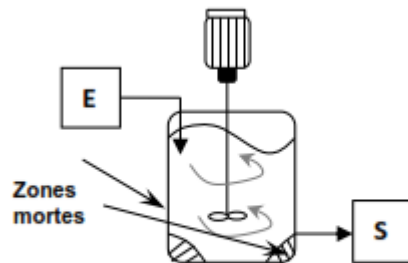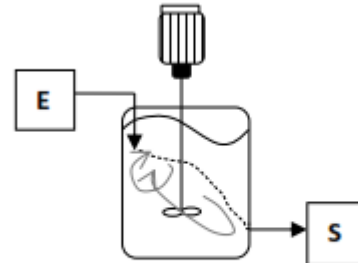

FIGURE 2A : Zones mortes   **FIGURE 2B** : Court-circuit

III.4.1. Sizing Equation of an Open Reactor (continuous)

Material balance (MB) in relation to the constituent A_i:

> **INCOMING FLOW + APPEARANCE = OUTGOING FLOW + DISAPPEARANCE + ACCUMULATION**

In + App = Out + Disp + Acc

A_i: is a reactant so App=0

Steady state: Ci = Cis = constant so Acc=0

The material balance become: In = Out + Disp (if A_i is a product, le MB is written: **In + App = Out**)

$$E = F_{ie}, \qquad S = F_{is}, \qquad Disp = (-r_i)V = (-r_i)_s V \quad \text{(V est le volume réactionnel)}$$

$$F_{ie} + (-r_i)V = F_{is} \quad (10)$$

$$\text{Or} : F_{is} = F_{ie}(1-X_{is}), \text{ ce qui donne} : \quad F_{ie} + (-r_i)_s V = F_{ie}(1-X_{is})$$

$$finalement : \qquad \boxed{\frac{V}{F_{ie}} = \frac{X_{is}}{(-r_i)_s}} \quad (11)$$

The relation (11) expresses the evolution of the conversion rate at the exit of the reactor (X_{ie}) in relation to the molar flux at the entrance (F_{ie}) and to the kinetics of the reaction, evaluated in relation to the output quantities (grandeurs de sortie) (C_{is}, T_s).

Noticed

It often happens that the conversion rate is evaluated not in relation to the flow entering into the reactor (F_{ie}), but in relation to a reference molar flow (F_{i0}) placed at the flow rate of the system (Figure 3).

In this case, the conversion rate at a given point in the system is defined in relation to the reference flow F_{i0}, as follows:

Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

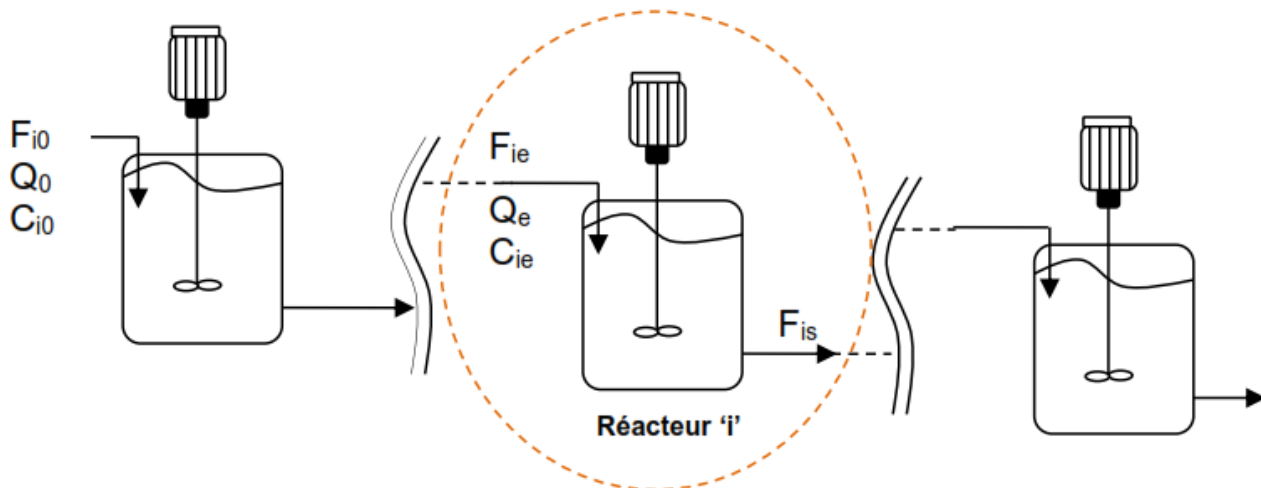$$X_i = \frac{F_{i0} - F_i}{F_{i0}} \qquad (12)$$

FIGURE 3: Open reactor cascade (system)

The flows at the entrance (F_{ie}) and at the exit (F_{iex}) of the reactor are then expressed by:

$$F_{ie} = F_{i0}(1-X_{ie})$$

$$F_{is} = F_{i0}(1-X_{is})$$

Returning to the balance equation:

$$F_{ie} + (-r_i)V = F_{is}$$
$$F_{i0}(1-X_{ie}) + (-r_i)_s V = F_{is} = F_{i0}(1-X_{is})$$

$$\frac{V}{F_{i0}} = \frac{X_{is} - X_{ie}}{(-r_i)_s} \qquad (13)$$

III.4.2. Concept of passage time (τ)

- **The passage time (τ) is an important characteristic of an open reactor in continuous mode.**
- **The mathematical definition is given by dividing the reactor volume (V) by the volume flow rate passing through the reactor under reference conditions (Q_0) (System input, Figure 3).**

$$\tau = \frac{V}{Q_0} \qquad (14)$$

Note: In this form, the passage time still corresponds to the filling time of the reactor.

7

Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

III.4.3. Relationship between τ and Xi

We have:

$$\frac{V}{F_{i0}} = \frac{X_{is} - X_{ie}}{(-r_i)_s} \quad (13)$$

Knowing that: $C_{i0} = F_{i0}/Q_0 \rightarrow F_{i0} = C_{i0}Q_0$

We replace F_{i0} by its expression in equation (13), we obtain:

$$\frac{V}{F_{i0}} = \frac{V}{C_{i0}Q_0} = \frac{\tau}{C_{i0}} = \frac{X_{is} - X_{ie}}{(-r_i)_s}$$

III.4.4. Graphic Representation
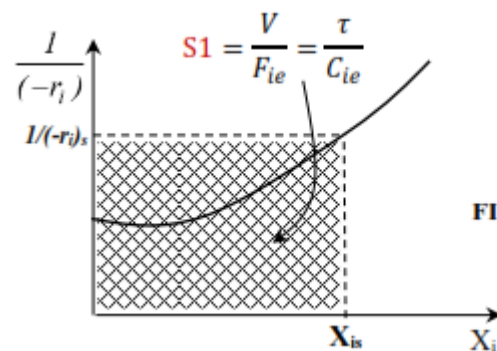
Case of a single reactor:

FIGURE 4

$$\frac{V}{F_{ie}} = \frac{\tau}{C_{ie}} = \frac{1}{(-r_i)_s} \times X_{is} = Surface\ S1$$
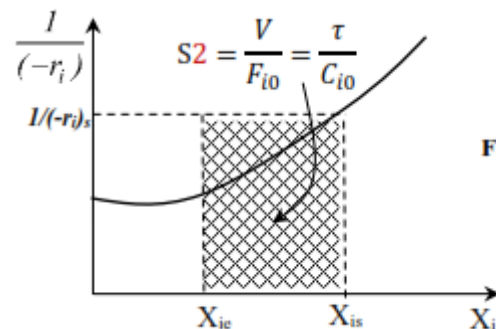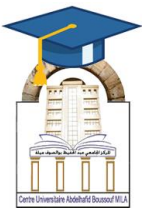
Case of a reactor in a system (cascade):

FIGURE 5

$$\frac{V}{F_{i0}} = \frac{\tau}{C_{i0}} = \frac{1}{(-r_i)_s} \times (X_{is} - X_{ie})\ Surface\ S2$$

Thus, the graphs make it possible to calculate the transit time τ = V/Q → knowledge of Q_0 (or Q_e) allows you to calculate the volume of the reactor (V).

8

Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

III.5. Piston (plug flow) reactor in steady state

- A reactor in the shape of a tube whose length is very large compared to its diameter (L >> D), in which all the molecules which pass through it have the same passage time τ,
- The flow inside the reactor is made in the form of slices parallel to each other and perpendicular to the direction of flow,
- The concentration relative to constituent i (C_i) will evolve along the reactor. From this done, the material balance is established in an element of volume dV delimited by two straight sections located at points z and z+dz (Figure 7),
- The flow is considered piston only when the flow of fluid inside of the reactor is turbulent (Re > 2000). In the case of laminar flow, the reactor is not considered a piston reactor.
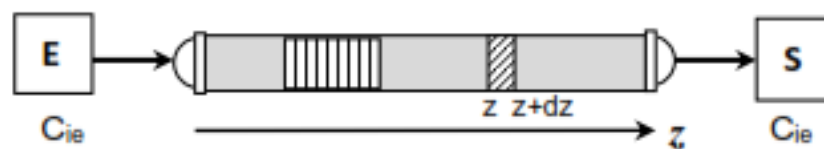

FIGURE 7 : Réacteur tubulaire

III.5.1. Sizing Equation in Piston reactor

Material balance (BM) relative to the constituent A_i in the volume element **dV**:

$$E + App = S + Disp + Acc$$

Ai is a reactant so: **App = 0**
Steady state: **Acc=0**, (for a given z, or given plane, the concentration C_i is constant whatever the time)

The material balance will be: E = S + Disp

$$E = F_i, \ S = F_i + dF_i, \ Disp = (-r_i)dV$$

$$F_i = F_i + dF_i + (-r_i)dV$$

$$- dF_i = (-r_i)dV$$

$$\text{Or}: F_i = F_{ie}(1-X_i) \quad \rightarrow \quad dF_i = - F_{ie}dX_i$$

$$d'\text{où}: \frac{V}{F_{ie}} = \frac{\tau}{C_{ie}} = \int_{X_{ie}}^{X_{is}} \frac{dX_i}{(-r_i)} \qquad (16)$$

The resolution of equation (16) can be done analytically if the integral is simple, or by numerical or graphical methods, as illustrated for the cases of closed and open reactors.
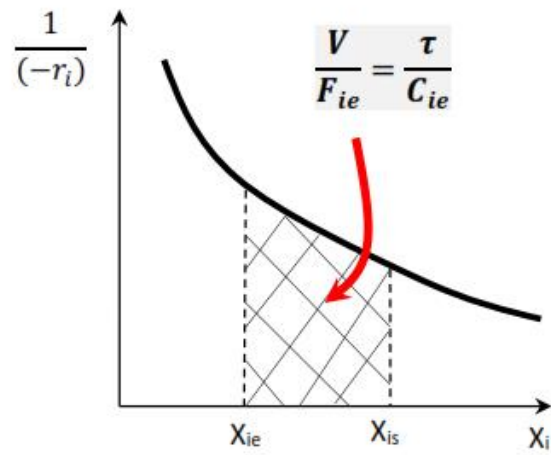
Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
3rd year L.M.D – Homogeneous reactor
Dr. Imane MAYOUF

FIGURE 8 : Détermination graphique du volume (temps de passage) de RP.