

## IDEAL REACTORS

One of the key goals of chemical reaction engineering is to quantify the relationship between production rate, reactor size, reaction kinetics and selected operating conditions. This requires a mathematical model of the system, which in turn rests on application of conservation laws to a well-defined control volume of the reaction system and on use of appropriate constitutive expressions for the reaction rates. The concepts of ideal reactors allow us to quantify reactor performance as a function of its size and selected operating conditions.

To illustrate this useful concept we deal here with a single, homogeneous phase, single reaction at constant temperature. We introduce then the ideal batch reactor, and two ideal continuous flow reactors. In each case we apply the conservation of species mass principle which states

$$(\text{Rate of Accumulation}) = (\text{Rate of Input}) - (\text{Rate of Output}) + (\text{Rate of Generation}) \quad (2-1)$$

Equation (2-1) is applied to an appropriately selected control volume, the largest arbitrarily selected volume of the system in which there are no gradients in composition.

### 2.1 Batch Reactor

The ideal batch reactor is assumed to be perfectly mixed. This implies that at a given moment in time the concentration is uniform throughout the vessel. The volume,  $V$  in the development below is assumed equal to the volume of the reaction mixture. This is then equal to the reactor volume  $V_R$  in case of gas phase reaction but not in case of liquids ( $V < V_R$ , then). The batch reactor can be an autoclave of  $V = \text{const}$  (Figure 2.1-a) and a constant pressure,  $P = \text{const}$  (Figure 2.1-b) vessel. The former is almost always encountered in practice.

Our goal is:

- a) To find a relationship between species concentration (reactant conversion) and time on stream.
- b) To relate reactor size and production rate.

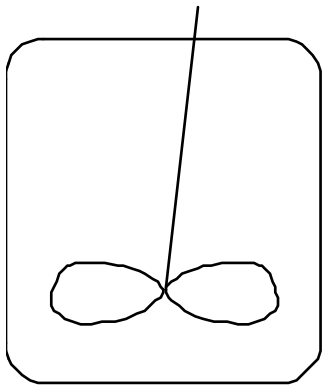
Let us consider a single irreversible reaction  $A \rightarrow P$  with an n-th order irreversible rate of reaction

$$-R_A = kC_A^n \quad (2-2)$$

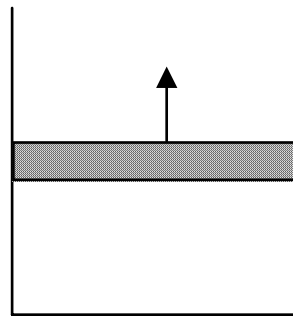
At  $t = 0$  a batch of volume  $V$  is filled with fluid of concentration  $C_{A0}$ . Reaction is started ( $n_{A0} = C_{A0}V_0$ ). Find how reactant conversion depends on reaction time? Also determine the production rate as a function of reaction time.

We apply (eq 2-1) to reactant A:

$$0 - 0 + (R_A V) = \frac{dn_A}{dt} = \frac{d(VC_A)}{dt} \quad (2-3)$$



a)  $V = \text{const}$



b)  $P = \text{const}$

**FIGURE 2-1: Schematic of Batch Reactors**

In our case due to the fact that  $\sum_{j=1}^2 \nu_j = 0$ ,  $V = \text{const}$  irrespective of the batch reactor type, so that

eq (2-3) becomes

$$\frac{dC_A}{dt} = R_A \quad (2-4)$$

$$-\frac{dC_A}{dt} = (-R_A) = kC_A^n; \quad t = 0 \quad C_A = C_{A0} \quad (2-5)$$

Separation of variables and integration yields:

$$\int_0^t dt = - \int_{C_{A0}}^{C_A} \frac{dC_A}{kC_A^n} = \frac{1}{k} \int_{C_A}^{C_{A0}} \frac{dC_A}{C_A^n} \quad (2-6)$$

$$d_o^t = \frac{1}{k} \frac{C_A^{1-n}}{1-n} \Big|_{C_A}^{C_{Ao}} \quad (2-7)$$

$$t-0 = \frac{1}{k(1-n)} [C_{Ao}^{1-n} - C_A^{1-n}]$$

$$t = \frac{C_{Ao}^{1-n}}{k(1-n)} [1 - (1-x_A)^{1-n}] \quad (2-8a)$$

or

$$t = \frac{1}{k(n-1)C_{Ao}^{n-1}} [(1-x_A)^{1-n} - 1] \quad (2-8b)$$

Once order of reaction, n, is specified (as shown below for n=0, 1, 2, 1.5), the relation between t and x<sub>A</sub> is readily found

$$n=0 \quad n=1 \quad n=2$$

$$t = \frac{C_{Ao}x_A}{k} \quad t = \frac{1}{k} \ln \frac{1}{1-x_A} \quad t = \frac{1}{kC_{Ao}} \left[ \frac{1}{1-x_A} - 1 \right] \quad (2-9)$$

$$n=1.5; \quad t = \frac{1}{0.5k\sqrt{C_{Ao}}} \left[ \frac{1}{(1-x_A)^{0.5}} - 1 \right]$$

Production Rate of Product P can be related by stoichiometry to the consumption rate of A as

$$F_P \left( \frac{\text{mol}}{S} \right) = \frac{F_{Ao}x_A}{1}$$

The production rate of P is given by:

$$F_P = \frac{\text{(moles of P processed per batch)}}{\text{(reaction time + shut down time per batch)}} \quad (2-10)$$

$$F_P = \frac{C_{Ao}V x_A}{t + t_s} = \frac{C_{Ao}V x_A}{\frac{1}{k(n-1)C_{Ao}^{n-1}} [(1-x_A)^{1-n}] + t_s} \quad (2-11)$$

**NOTA BENE:** Equation (2-11) is valid only for systems of constant density. Thus, it is valid for all systems, gas or liquid, conducted in an autoclave at V = const (see Figure 2-1a). It is also valid for gaseous systems with no change in the

number of moles ( $\sum \nu_j = 0$ ) conducted in P = const. system at T = const  
(Figure 2-1b).

The first equality in equation (2-11) gives the general result, the second equality presents the result for an n-th order irreversible reaction with respect to reactant A.

To use this equation the shut down time, i.e. the time needed between batches,  $t_s$ , must be known. Consider now the following second order reaction with stoichiometry A = P.

$$-R_A = 0.1 C_A^2 \left( \frac{\text{mol}}{\text{L min}} \right)$$

- a) Find the batch reactor volume needed to produce  $F_P = 38 \text{ kmol/min}$  if reactor shut down time is 60 minutes and the desired conversion is 0.95. Initial reactant concentration is  $C_{A0} = 1 \text{ (mol L)}$ .

Using the right form of equation (2-9) for  $n = 2$  we get the reaction time.

$$t = \frac{1}{0.1 * 1} \left[ \frac{1}{1-0.95} - 1 \right] = \frac{1}{1-0.95} = 190.0(\text{min})$$

Then, solving equation (2-11) for the volume we get

$$V = \frac{F_P(t + t_s)}{C_{A0} x_A} = \frac{1.38(190 + 60)}{1 * 0.95} = 10,000 \text{ L} = 10 \text{ m}^3$$

- b) What is the maximum production rate,  $F_P$ , achievable in the above batch reactor of volume  $V=10\text{m}^3$  if  $t_s$ , T,  $C_{A0}$  all are fixed at previous values.

Consider eq (2-11) for production rate as a function of conversion

$$F_P = \frac{C_{A0} V x_A}{\frac{1}{k C_{A0} \left[ \frac{x_A}{1-x_A} \right]} + t_s} = \frac{10^4 x_A}{10 \frac{x_A}{1-x_A} + 60} = \frac{10^3 x_A}{\frac{x_A}{1-x_A} + 6}$$

$$F_P = 10^3 \frac{x_A(1-x_A)}{x_A + 6(1-x_A)} = 10^3 \frac{x_A - x_A^2}{6 - 5x_A}$$

This expression has a maximum which we can locate by differentiation

$$\frac{dF_P}{dx_A} = 0 \Rightarrow (1 - 2x_A)(6 - 5x_A) + 5(x_A - x_A^2) = 0$$

$$6 - 5x_A - 12x_A + 10x_A^2 + 5x_A - 5x_A^2 = 0$$

$$6 - 12x_A + 5x_A^2 = 0$$

$$x_{A12} = \frac{6 \pm \sqrt{36 - 30}}{5} = \frac{6 - \sqrt{6}}{5} = 0.710$$

Clearly, the positive sign is not permissible as conversion cannot exceed unity. We need to check whether the answer is a maximum or a minimum.

$$\frac{dF_P}{dx_A} > 0 \text{ for } x_A < 0.710$$

$$\frac{dF_P}{dx_A} < 0 \text{ for } x_A > 0.710$$

Maximum at  $x_A = 0.710$ .

$$F_{P_{\max}} = 10^3 \frac{0.710 - 0.710^2}{6 - 5 \times 0.710} = 84.0 \frac{\text{mol}}{\text{min}}$$

An increase in productivity of  $\frac{84 - 38}{38} \times 100 = 121\%$  can be achieved at the expense of more unreacted A to be recycled.

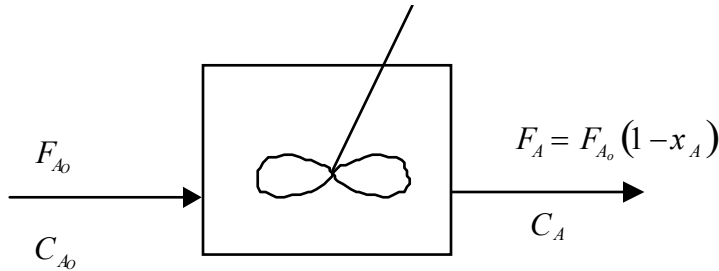
One must include the cost of separation into the real economic optimization.

## 2.2 Continuous Flow Reactors (Steady State)

### 2.2.1 Continuous Flow Stirred Tank Reactor (CFSTR or CSTR or STR)

The CSTR is assumed perfectly mixed, which implies that there are no spatial gradients of composition throughout the reactor. Since the reactor operates at steady state, this implies that a single value of species concentration is found in each point of the reactor at all times and this is

equal to the value in the outflow. The outflow stream is a true representative of the reaction mixture in the reactor.



**FIGURE 2-2: Schematic of a Continuous Flow Stirred Tank Reactor (CSTR)**

What does the above idealization of the mixing pattern in a CSTR imply? It postulates that the rate of mixing is “instantaneous” so that the feed loses its identity instantly and all the reaction mixture is at the composition of the outlet. Practically this implies that the rate of mixing from macroscopic level down to a molecular scale is orders of magnitude faster than the reaction rate and is so fast in every point of the vessel.

Then the mass balance of eq (2-1) can be applied to the whole volume of the reactor recognizing that at steady state the accumulation term is identically zero. Again, taking a simple example of an irreversible reaction  $A \rightarrow P$  application of eq (2-1) to reactant A yields:

$$F_{A_0} - F_A + (-R_A)V = 0 \quad (2-12)$$

Molar flow rate of unreacted A in the outflow by definition is given by  $F_A = F_{A_0}(1-x_A) = Q C_{A_0}(1-x_A)$ . The production rate of P is given by

$$F_P = (-R_A)V = (R_P)V \quad (2-13)$$

Reactor volume is given by eq (2-12)

$$V = \frac{F_{A_0}x_A}{(-R_A)} = \frac{Q C_{A_0}x_A}{(-R_A)} \quad (2-14)$$

Reactor space time is defined by

$$\tau = \frac{V}{Q_o} = \frac{C_{Ao} x_A}{(-R_A)} \quad (2-15)$$

Using stoichiometry we readily develop the relation between production rate,  $F_P$ , and reactor volume,  $V$ .

Let us consider again the example of our 2<sup>nd</sup> order reaction,  $A = P$ , with the rate below:

$$-R_A = kC_A^n = 0.1C_A^2 \left( \frac{\text{mol}}{\text{L min}} \right)$$

Find CSTR volume needed to process  $F_P = 38 \text{ mol/min}$ . Suppose we choose again  $x_A = 0.95$  for our exit conversion.

From eq (2-13) we get

$$F_P = 0.1 C_{Ao}^2 (1-x_A)^2 V$$

And solving for volume  $V$

$$V = \frac{F_P}{0.1C_{Ao}^2 (1-x_A)^2} = \frac{38}{0.1 \times 1 \times (1-0.95)^2} = 152,000 \text{ L} = 152 \text{ m}^3$$

If we consider eq (2-13) it is clear that now the maximum production rate is obtained when the reaction rate is the highest. That for n-th order reactions is at zero conversion. So the maximum  $F_P$  from  $V_{\text{CSTR}} = 12,000 \text{ L}$  is obtainable at  $x_A = 0$ .

$$F_{P_{\text{max}}} = 0.1 \times 1 \times 152,000 = 15,200 \text{ mol/min.}$$

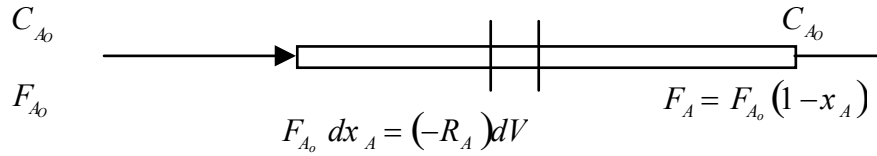
The penalty of this enormous production rate is that the product is at “zero” purity. Hence, the separation costs would be enormous. The average rate in a CSTR is equal to the rate at exit conditions.

$$(-\overline{R_A}) = (-R_A)_{\text{exit}} = 0.1C_{Ao}^2 (1-x_A)_{\text{exit}}^2 = 0.1 \times 1 \times (1-0.95)^2 = 2.5 \times 10^{-4} (\text{mol/L min})$$

### 2.2.2 Plug Flow Reactor (PFR)

The main assumptions of the plug flow reactor are: i) perfect instantaneous mixing perpendicular to flow, ii) no mixing in direction of flow

This implies piston like flow with the reaction rate and concentration that vary along reactor



**FIGURE 2-3: Schematic of a Plug Flow Reactor (PFR)**

Since there are now composition gradients in the direction of flow, the control volume is a differential volume  $\Delta V$  to which eq (2-1) is applied. Let us again use the mass balance on reactant A

$$F_A|_V - F_A|_{V+\Delta V} + R_A \Delta V = 0 \quad (2-16)$$

$$-\Delta F_A + R_A \Delta V = 0$$

$$-\lim_{\Delta V \rightarrow 0} \frac{\Delta F_A}{\Delta V} = (\lim_{\Delta V \rightarrow 0}) (-R_A)$$

$$-\frac{dF_A}{dV} = (-R_A) \quad (2-17)$$

Since  $F_A = F_{A0}(1 - x_A)$  then  $dF_A = -F_{A0} dx_A$

so that

$$F_{A0} \frac{dx_A}{dV} = (-R_A) \quad (2-18)$$

With initial conditions:

$$V = 0 \quad x_A = 0 \quad (2-19)$$



Upon separation of variables in (eq 2-18) and integration:

$$\int_0^V dV = F_{A_o} \int_0^{x_A} \frac{dx_A}{(-R_A)} \quad (2-20)$$

For an n-th order reaction (with  $\varepsilon_A = 0$ ) we get

$$V = \frac{F_{A_o}}{kC_{A_o}^n} \int_0^{x_A} \frac{dx_A}{(1-x_A)^n} = \frac{Q_o}{kC_{A_o}^{n-1}} \frac{[(1-x_A)^{1-n} - 1]}{(n-1)} \quad (2-21)$$

The expression for the PFR space time

$$\tau = \frac{V}{Q_o} = \frac{1}{kC_{A_o}^{n-1} (n-1)} [(1-x_A)^{1-n} - 1] \quad (2-22)$$

is now identical to the expression for reaction time  $t$  in the batch reactor.

For the example of the second order reaction used earlier we get

$$V = F_{A_o} \int_0^{x_A} \frac{dx_A}{kC_{A_o}^2 (1-x_A)^2} = \frac{F_{A_o}}{kC_{A_o}^2} \left[ \frac{1}{1-x_A} \right]_0^{x_A}$$

$$V = \frac{F_{A_o}}{kC_{A_o}^2} \left[ \frac{1}{1-x_A} - 1 \right] = \frac{F_{A_o}}{kC_{A_o}^2} \left[ \frac{x_A}{1-x_A} \right]$$

$$F_{A_o} = Q_o C_{A_o}$$

$$\tau = \frac{V}{Q_o} = \frac{1}{kC_{A_o}} \frac{x_A}{1-x_A} \quad (\text{Same as the expression for reaction time } t \text{ in the batch reactor})$$

Let us consider our example of the second order reaction and find the PFR volume needed to produce  $F_P = 38 \text{ mol/min}$

$$(-R_A) = 0.1 C_A^2 \left( \frac{\text{mol}}{\text{L min}} \right)$$

when  $C_{A_o} = 1 \left( \frac{\text{mol}}{\text{L}} \right)$  and desired conversion  $x_A = 0.95$ .

From stoichiometry it follows that

$$F_{A_o} x_A = F_P \quad F_{A_o} = \frac{F_P}{x_A}$$

Substitution in the expression for reactor volume (eq (2-21)) we get:

$$V = \frac{F_P}{kC_{A_0}^2 x_A} \left[ \frac{x_A}{1-x_A} \right] = \frac{F_P}{kC_{A_0}^2 (1-x_A)}$$

$$V = \frac{38}{0.1 \times 1 \times (1-0.95)} = 7,600L = 7.6m^3$$

The maximum production rate from that volume can be obtained at zero conversion

$$F_P = kC_{A_0}^2 (1-x_A)V$$

$$F_{P_{\max}} = 0.1 \times 1 \times 7600 = 760 \text{ mol/min}$$

$$\text{Average rate in PFR } -\overline{R}_A = \frac{F_{A_0} x_A}{V} = \frac{F_P}{V} = \frac{38}{7,600} = 5.0 \times 10^{-3} \frac{\text{mol}}{\text{min}}$$

$$(-R_A)_{\text{entrance}} = 0.1 C_{A_0}^2 = 0.1 = 10^{-1} \left( \frac{\text{mol}}{L \text{ min}} \right)$$

$$(-R_A)_{\text{exit}} = 0.1 C_{A_0}^2 (1-0.95)^2 = 2.5 \times 10^{-4} \left( \frac{\text{mol}}{L \text{ min}} \right)$$

Clearly there is a big variation in the reaction rate between the entrance and exit of the plug flow reactor (PFR).

## 2.3 STY – Space Time Yield

### Volumetric Reactor Productivity - RVP

Reactor volumetric productivity (RVP) is defined by:

$$\overline{R}_P = \frac{F_P}{V} \tag{2-23}$$

For our 2<sup>nd</sup> order reaction example of stoichiometry A=P, RVP for the two continuous flow reactors is:

$$\text{CSTR } \overline{R}_P = (R_P)_{\text{exit}} = (-R_A)_{\text{exit}} = kC_{A_0}^2 (1-x_A)^2 \tag{2-24a}$$

$$\text{PFR } \overline{R}_P = \frac{F_P}{V} = kC_{A_0}^2 (1-x_A) \tag{2-24b}$$

For the same exit conversion

$$\frac{\overline{(R_P)}_{PFR}}{\overline{(R_P)}_{CSTR}} = \frac{kC_{A0}^2(1-x_A)}{kC_{A0}^2} = \frac{1}{(1-x_A)}$$

At  $x_A = 0.95$

$$\frac{\overline{(R_P)}_{PFR}}{\overline{(R_P)}_{CSTR}} = 20$$

Indeed  $20 \times 7,600 \text{ L} = 152,000 \text{ L}$

This is why higher CSTR volume is needed.

$$\text{At } x_A = 0 \quad \overline{(R_P)}_{PFR} = \overline{(R_P)}_{CSTR}$$

There is no difference!

Let us consider another example to illustrate some important points.

Ex:  $2A + 3B = P + S$  – stoichiometry

$$r = 0.1C_A C_B^2 \left( \frac{\text{mol}}{\text{L min}} \right) \text{ - rate of reaction}$$

$C_{A0} = 2 \left( \frac{\text{mol}}{\text{L}} \right)$  and  $x_A = 0.95$  - are the feed reactant concentration and desired conversion

$F_P = 10 \text{ mol/min}$  is the desired production rate

Assume first that we will operate at stoichiometric ratio so that  $C_{B0} = 3 \text{ (mol/L)}$ . The reaction occurs in the liquid phase so that  $\varepsilon_A = 0$ . Find the needed reactor volume.

a) Batch ( $t_s = 60 \text{ min}$ )

$$-R_A = 0.2C_{A0}(1-x_A)\left(C_{B0} - \frac{b}{a}C_{A0}x_A\right)^2$$

$$-R_A = 0.2C_{A0}^3(1-x_A)\left(\frac{3}{2}\right)^2(1-x_A)^2$$

$$-R_A = 0.2C_{A0}^3(1-x_A)^3\left(\frac{3}{2}\right)^2$$

Reaction time is:

$$t = \frac{1}{0.2C_{A0}^2 \left(\frac{3}{2}\right)^2} \int_0^{x_A} \frac{dx_A}{(1-x_A)^3}$$

$$t = \frac{1}{0.2 \times 2^2 \times \frac{9}{4}} \int_0^{x_A} \frac{dx}{(1-x)^3} = \frac{1}{1.8} \frac{1}{2} \frac{1}{(1-x)^2} \Big|_0^{x_A}$$

$$t = \frac{1}{3.6} \left[ \frac{1}{(1-x_A)^2} - 1 \right] = \frac{1}{36} \left[ \frac{1}{(1-0.95)^2} - 1 \right]$$

$$t = 110.83 \text{ min}$$

$$F_P = \frac{\frac{1}{2} C_{A0} x_A V}{t + t_s} = \frac{0.95 x V}{110.83 + 60} = 10$$

$$V = \frac{170.83 \times 10}{0.95} = 1,798 \text{ L} = 1.8 \text{ m}^3$$

b) CSTR

$$\frac{F_{A0}}{2} = \frac{F_P}{1} \text{ - from stoichiometry}$$

$$\frac{V}{F_{A0}} = \frac{x_A}{-R_A} \text{ - basic design equation (2-14)}$$

$$V = \frac{F_{A0} x_A}{-R_A} = \frac{2F_P}{(-R_A)} = \frac{2F_P}{0.2C_A C_B^2}$$

$$V = \frac{F_P}{0.1C_{A0}^3 (1-x_A) \left( \frac{C_{B0}}{C_{A0}} - \frac{3}{2} x_A \right)^2} = \frac{F_P}{0.1C_{A0}^3 \left(\frac{3}{2}\right)^2 (1-x_A)^3}$$

$$V = \frac{10}{0.1 \times 2 \times 9 (1-0.95)^3} = \frac{10}{1.8} \frac{1}{0.05^3} = 4,444 \text{ (L)} = 44.4 \text{ m}^3$$

$$(-\bar{R}_A) = (-R_A)_{exit} = 0.2 x C_{A0}^3 \left(\frac{3}{2}\right)^2 (1-x_A)^3_{exit}$$

$$= 0.2 \times 2 \times 9 (1-0.95)^3 = 4.5 \times 10^{-4} \text{ (mol/L min)}$$

c) PFR

$$F_{A_0} = \frac{2F_P}{x_A} \quad \text{- from stoichiometry}$$

Basic design equation (2-21)

$$V = F_{A_0} \int_0^{x_A} \frac{dx}{-R_A} = F_{A_0} \int_0^{x_A} \frac{dx}{0.2C_{A_0}^3(1-x)\left(\frac{3}{2}\right)^2(1-x)^2}$$

$$V = \frac{2F_P}{0.2C_{A_0}^3\left(\frac{3}{2}\right)^2 x_A} \int_0^{x_A} \frac{dx}{(1-x)^3} = \frac{100}{18 \times 0.95} \int_0^{x_A} \frac{dx}{(1-x)^3}$$

$$V = \frac{100}{18 \times 0.95} \frac{1}{2} \left[ \frac{1}{(1-x_A)^2} - 1 \right]$$

$$= \frac{50}{10 \times 0.95} \left[ \frac{1}{(1-0.95)^2} - 1 \right] = 1,167(L) = 1.17 m^3$$

Now the rate, at stoichiometric feed ratio, along the PFR as a function of conversion is

$$-R_A = 0.2C_{A_0}^3\left(\frac{3}{2}\right)^2(1-x_A)^3 = 3.6(1-x_A)^3$$

PFR reactor volume as function of conversion at stoichiometric feed ratio is

$$V = \frac{2F_P}{3.6x_A} \int_0^{x_A} \frac{dx}{(1-x)^3} = \frac{F_P}{1.8x_A} \int_0^{x_A} \frac{dx}{(1-x)^3}$$

Hence, the production rate from a given PFR volume as a function of conversion (at stoichiometric feed rate) is

$$F_{P_{stoch}} = \frac{1.8x_A V}{\int_0^{x_A} \frac{dx}{(1-x)^3}} = \frac{3.6x_A V}{\frac{1}{(1-x_A)^2} - 1}$$

How much can we increase the production rate by doubling  $C_{B_0}$  to  $C_{B_0} = 6$  (mol/L), i.e. by using B in excess?

Now the rate as a function of conversion is:

$$-R_A = 0.2C_{A0}^3(1-x_A) \left( \left( \frac{C_{B0}}{C_{A0}} \right) - \frac{3}{2}x_A \right)^2 = 0.2x2^3x \left( \frac{3}{2} \right)^2 (1-x)(2-x_A)^2$$

$$-R_A = 3.6(1-x_A)(2-x_A)^2$$

a) Batch

$$t = C_{A0} \int_0^{x_A} \frac{dx_A}{(-R_A)} = \frac{2}{3.6} \int_0^{x_A} \frac{dx}{(1-x)(2-x)^2}$$

To integrate use partial fractions:

$$\frac{A}{1-x} + \frac{B+Cx}{(2-x)^2} = \frac{A(2-x)^2 + (B+Cx)(1-x)}{(1-x)(2-x)^2}$$

$$4A - 4Ax + Ax^2 + B - Bx + Cx - Cx^2 = 1$$

$$4A+B=1 \quad 4A-3A=1 \quad A=1$$

$$-4A-B+C=0 \quad -3A-B=0 \quad B=-3A \quad B=-3$$

$$A-C=0 \quad C=A=1$$

$$\int \frac{dx}{(1-x)(2-x)^2} = \int \frac{dx}{1-x} + \frac{x-3}{(2-x)^2} dx$$

$$= \int_0^{x_A} \left( \frac{dx}{1-x} - \frac{2-x}{(2-x)^2} dx - \frac{1}{(2-x)^2} dx \right)$$

$$= \left( -\ln(1-x) + \ln(2-x) - \frac{1}{2-x} \right)_0^{x_A}$$

$$= -\ln(1-x_A) + 0 + \ln(2-x_A) - \ln 2 - \frac{1}{2-x_A} + \frac{1}{2}$$

$$= \ln \frac{2-x_A}{2(1-x_A)} + \frac{1}{2} \left[ 1 - \frac{2}{2-x_A} \right] = \ln \left[ \frac{2-x_A}{2(1-x_A)} \right] - \frac{x_A}{2(2-x_A)}$$

$$t = \frac{1}{1.8} \left[ \ln \left( \frac{2-x_A}{2(1-x_A)} \right) - \frac{x_A}{2(2-x_A)} \right]_{x_A=0.95}$$

$$t = \frac{1}{1.8} \left[ \ln \frac{1.05}{2 \times 0.05} - \frac{0.95}{2 \times 1.05} \right] = \frac{1}{1.8} \left( \ln 10.5 - \frac{0.95}{2.1} \right)$$

$$t = 1.055 \text{ min}$$

Batch ill advised at these conditions since  $t_s \gg t!$

$$F_{P_{new}} = \frac{\frac{1}{2} C_{A0} x_A V}{t + t_s} = \frac{0.95 \times 1,798}{1.06 + 60} = 27.97 \frac{mol}{min}$$

$$\frac{\Delta F_P}{F_{P_{old}}} \times 100 = \frac{27.97 - 10}{10} \times 100 = 179.7\%$$

By operating at double the stoichiometric requirement of B we increase, at same  $x_A$ , the production rate of the batch reactor by 180%.

b) CSTR

$$-R_A = 3.6(1 - x_A)(2 - x_A)^2 - 3.6(1 - 0.95)(2 - 0.95)^2$$

$$-R_A = 3.6 \times 0.05 \times 1.05^2 = 0.19845 \left( \frac{mol}{L \cdot min} \right)$$

$$F_{P_{new}} = R_P V = \left( \frac{-R_A}{2} \right) V = \frac{0.19845}{2} \times 44,494 = 4,410 \frac{mol}{min}$$

$$\frac{\Delta F_P}{F_{P_{old}}} \times 100 = \frac{4,410 - 10}{10} \times 100 = 44,000\%$$

In a CSTR we increase the production rate by 44,000%!

c) PFR

$$V = F_{A0} \int_0^{x_A} \frac{dx}{3.6(1-x)(2-x)^2}$$

$$F_{P_{new}} \frac{V x_A}{3.6 \int_0^{x_A} \frac{dx}{(1-x)(-x)^3}} = \frac{1.8 x_A V}{\int_0^{x_A} \frac{dx}{(1-x)(2-x)^3}}$$

$$F_{P_{new}} = \frac{1.8 x_A V}{\left[ \ln \left( \frac{2 - x_A}{2(1 - x_A)} \right) - \frac{x_A}{2(2 - x_A)} \right]}$$

$$F_{P_{new}} = \frac{1.8 \times 0.95 \times 1,167}{\ln \frac{2 - 0.95}{2(1 - 0.95)} - \frac{0.95}{2(2 - 0.95)}} = \frac{1.8 \times 0.95 \times 1,167}{\ln \frac{1.05}{0.1} - \frac{0.95}{2.10}}$$

$$F_{P_{new}} = 1,051 \text{ mol/min}$$

$$\frac{\Delta F_P}{F_{P_{old}}} \times 100 = \frac{1,051 - 10}{10} \times 100 = 10,419\%$$

In a PFR over 10,000% increase in  $F_P$  is obtained.

We present below these ratios of production rate obtainable at nonstoichiometric ratio of  $C_{B_0}/C_{A_0} = 2(C_{B_0}/C_{A_0})_{stoich}$  and at stoichiometric ratio of  $C_{B_0}/C_{A_0} = 3/2$  for our example reaction.

This ratio is:

For a PFR:

$$\frac{F_{P_{(non-stoich)}}}{F_{P_{(stoich)}}} = \frac{\frac{1.8x_A V}{\ln\left(\frac{2-x_A}{2(1-x_A)} - \frac{x_A}{2(2-x_A)}\right)}}{\frac{\frac{3.6x_A}{1-x_A}}{\frac{1}{(1-x_A)^2} - 1}} = \frac{\frac{1}{(1-x_A)^2} - 1}{2\left[\ln\left(\frac{2-x_A}{2(1-x_A)} - \frac{x_A}{2(2-x_A)}\right)\right]}$$

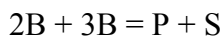
Specifically for  $x_A = 0.95$  we get

$$\frac{F_{P_{(non-stoich)}}}{F_{P_{(stoich)}}} = \frac{\frac{1}{0.05^2} - 1}{2\left[\ln\frac{1.05}{2 \times 0.05} - \frac{0.95}{2 \times 1.05}\right]} \frac{199.5}{2\left(\ln 10.5 - \frac{0.75}{2.10}\right)} = \frac{199.5}{\ln 10.5 - 0.45228045} = 105.0$$

For a CSTR

$$\frac{F_{P_{(non-stoich)}}}{F_{P_{(stoich)}}} = \frac{3.6(1-x_A)(2-x_A)^2}{3.6(1-x_A)^3} = \frac{(2-x_A)^2}{(1-x_A)^2} = \left(\frac{2-0.98}{1-0.98}\right)^2 \frac{F_{P_{(non-stoich)}}}{F_{P_{(stoich)}}} = \left(\frac{1.05}{0.05}\right)^2 = 21^2 = 441$$

Let us examine the situation when the reaction just considered occurs at  $P = \text{const}$ ,  $T = \text{const}$  in the gaseous phase. Then due to stoichiometry we have



$$\sum \nu_j = 1 + 1 - 2 - 3 = -3$$



Consider stoichiometric feed of reactants at  $C_{B_0}/C_{A_0} = 3/2$ .

$$y_{A_0} = \frac{2}{5} = 0.4 \quad (-\nu_A) = 2$$

$$\varepsilon_A = y_{A_0} \frac{\sum \nu_j}{(-\nu_A)} = \frac{0.4^{(-3)}}{2} = -0.6$$

$$C_A = C_{A_0} \frac{1-x_A}{1-0.6x_A} \quad C_B = C_{A_0} \frac{\frac{C_{B_0}}{C_{A_0}} - \frac{3}{2}x_A}{1-0.6x_A}$$

$$-R_A = 0.2x C_{A_0}^3 \left(\frac{3}{2}\right)^2 \frac{(1-x_A)^3}{(1-0.6x_A)^3} = 3.6 \frac{(1-x_A)^3}{(1-0.6x_A)^3}$$

### CSTR

$$F_P = \frac{(-R_A)}{2} V$$

$$V = \frac{2F_P}{-R_A} = \frac{2x10(1-0.6x0.95)^3}{3.6(1-0.95)^3}$$

$$V = \frac{10}{1.8} \frac{(1-0.57)^3}{0.05^3} = 44,444x0.43^3 = 3,534(L)$$

Tremendous reduction in required volume compared to the  $\varepsilon_A = 0$  case occurs!

### PFR

$$V = F_{A_0} \int_0^{x_A} \frac{dx_A}{-R_A} = \frac{2F_P}{x_A} \int_0^{x_A} \frac{(1-0.6x)^3 dx}{3.6(1-x)^3}$$

$$V = \frac{F_P}{1.8x_A} \int_0^{x_A=0.95} \frac{(1-0.6x)^3}{(1-x)^3} dx = \frac{10}{1.8x0.95} \int_0^{0.95} \left(\frac{1-0.6x}{1-x}\right)^3 dx$$

$$V = 125.6(L)$$

Again a significant reduction in PFR reactor volume requirement is observed. Why?

## 2.4 Graphic Comparison of PFR and CSTR

$$\left(\frac{V}{F_{A_0}}\right)_{CSTR} = \frac{x_A}{(-R_A)_{exit}}$$

$$\left(\frac{V}{F_{A_0}}\right)_{PFR} = \int_0^{x_{A_0}} \frac{dx_A}{-R_A}$$

The graphic representation of the above two design equations is represented below for an n-th order reaction. Clearly, for fixed feed conditions and feed rate and for chosen desired conversion the volume of the CSTR will always be larger than or equal to the PFR volume.

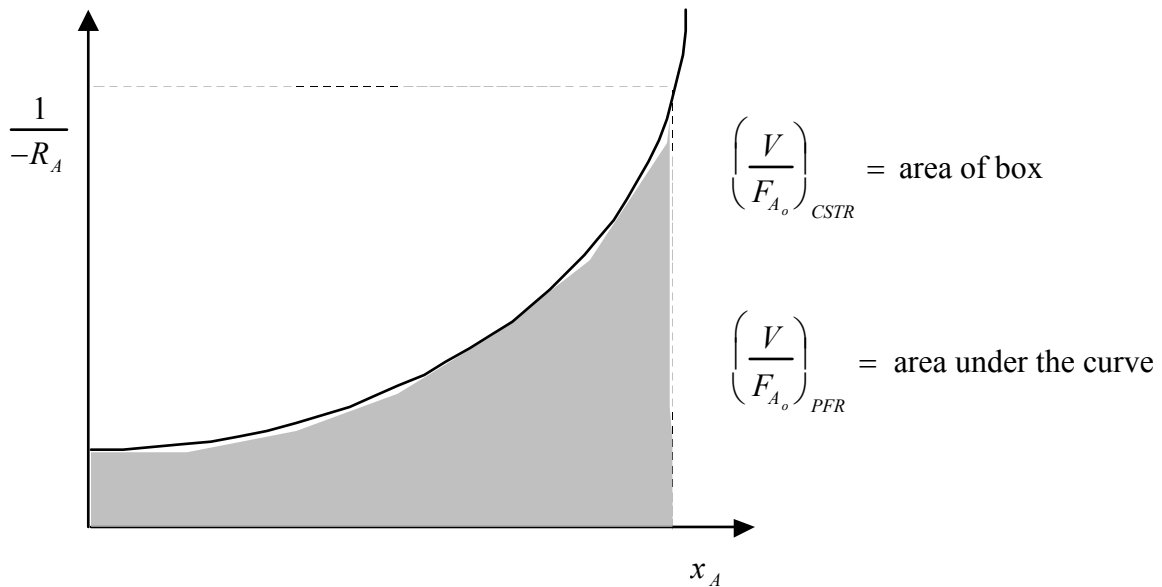


FIGURE 2-4: Graphical Comparison of CSTR and PFR