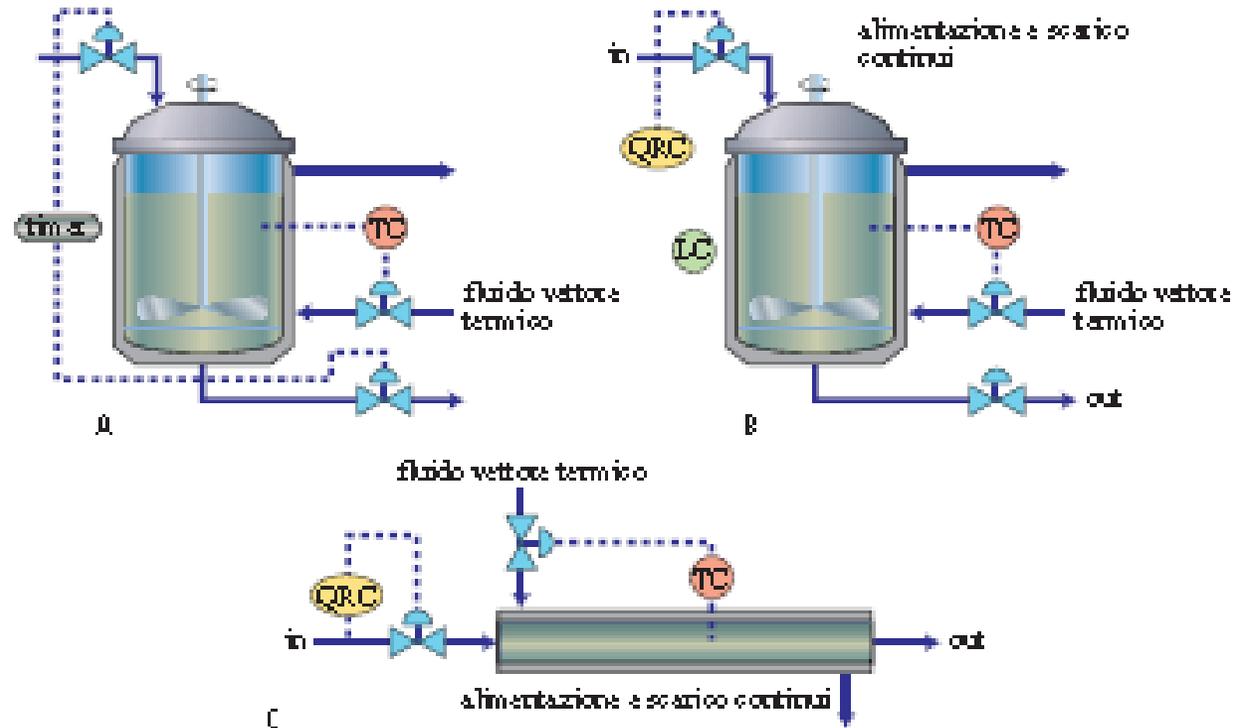


Simulation of BATCH and PFR reactors: EXERCISES

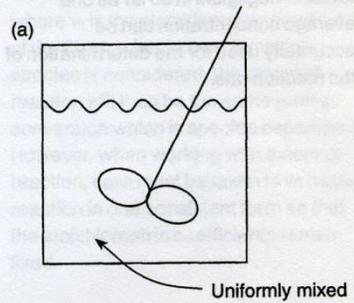
Carlo Pirola
Federico Galli



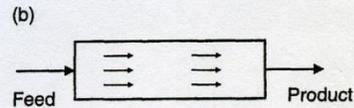
Mass balances for chemical reactors

- The following mass balance is always valid. If we consider a unit of volume or a small time interval, the balance for every compound is:
- **Accumulation_i = moles entering_i - moles exiting_i - (+) moles reacted_i**
- In particular cases some terms could be equal to zero (for example in a batch reactor the second and the third term)

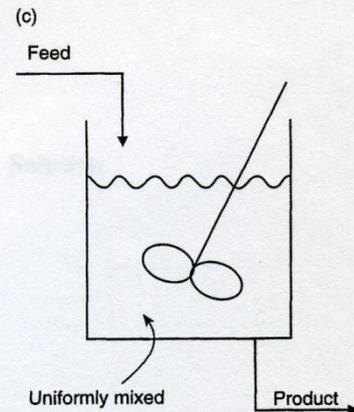
(2.1)



BATCH: All the reagents are charged at the beginning. There is NO addition or subtraction of products during the reaction. It is assumed that inside the reactor no temperature and concentration gradients are present.



PFR: tubular reactor. Reactants are continuously fed and the products continuously removed. The system is not stirred, and the flow profile is flat (PLUG)



CSTR: similarly to PFR, because reactants are continuously fed and the products continuously removed. Due to the stirring *Data l'agitazione* NO TEMPERATURE AND CONCENTRATION GRADIENTS ARE PRESENT (like batch reactor).

Fig. 2.1 Schematic representation of: (a) a batch reactor; (b) a plug flow reactor; (c) a continuous stirred tank reactor.

BATCH REACTORS

- 1) Time dependent
- 2) inside the reactor the mixture is considered homogeneous (in every point same concentrations)
- 3) Temperature constant in every part of the reactor
- 4) Constant volume assumption (what can vary is the pressure)

Starting from the general mass balance previously reported, and being:

- N_a the moles of A in the volume unity V;
- r_a the reaction rate defined as:

(A moles)/(time*Volume)

And being:

Moles accumulated = $N_a(t+dt) - N_a(t)$

Moles reacted = $r_a * V * dt$

The mass balance **Accumulation_i = moles entering_i - moles exiting_i - (+) moles reacted_i**

Becomes $N_a(t+dt) - N_a(t) = 0 + 0 - r_a * V * dt$

For $t \rightarrow 0$

$$r_a = - \frac{1}{V} \frac{dN_a}{dt}$$

Which is the design equation of the batch reactor

$$r_A = -\frac{1}{V} \frac{dN_A}{dt}$$

'Equation design' for BATCH reactor

THE TIME NEEDED FOR REACHING A CERTAIN CONVERSION can be calculated integrating this equation with the initial conditions $t=0$; $N_A=N_{A0}$

$$\int_0^t dt = - \int_{N_{A0}}^{N_A} \frac{1}{V} \frac{dN_A}{r_A}$$

The reaction proceeds until:

- a) The chemical equilibrium is reached
- b) One of the reagents is finished
- c) The mixture is discharged

THE CONVERSION required in the reactor is usually expressed as x_a defined as:

$$x_a = -\frac{N_{a0} - N_a}{N_{a0}}$$

If conversion is equal to zero: $N_A = N_{A0}$

If conversion is equal to 1: $N_A = 0$

Deriving this expression, we obtain

$$dx_a = -\frac{dN_a}{N_{a0}}$$

And inserting this one in the previous equation we obtain $\int_0^t dt = -\int_{N_{A0}}^{N_A} \frac{1}{V} \frac{dN_A}{r_A}$

$$\int_0^t dt = \int_0^{x_A} \frac{N_{A0}}{V} \frac{dx_A}{r_A}$$

Example1: first order irreversible, $A \rightarrow B$, conducted in a batch reactor with rate equation: $r_A = kC_A$. Given $k = 0,01 \text{ s}^{-1}$, calculate the time needed for reaching the 30% conversion.

It is useful to express the reaction rate in terms of moles: $r_A = kC_A = kN_A/V$

$$t = - \int_{N_{A0}}^{N_A} \frac{1}{V} \frac{dN_A}{r_A} = - \int_{N_{A0}}^{N_A} \frac{dN_A}{kN_A} = - \frac{1}{k} \ln \frac{N_A}{N_{A0}}$$

$$x_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A}{N_{A0}}$$

$$t = - \frac{1}{k} \ln(1 - x_A) = 35,7 \text{ secondi}$$

Plug Flow Reactors (PFR) REACTORS

The tubular reactors are used for the production in large scale, especially if the reactants are gases:

- Homogeneous reactions: eg $O_2 + 2 NO \rightarrow 2 NO_2$ (HNO₃ production from NH₃)
- Heterogeneous reactions (the reactor is filled with catalyst): $CO + 2 H_2 \rightarrow CH_3OH$ or $N_2 + 3 H_2 \rightarrow 2 NH_3$

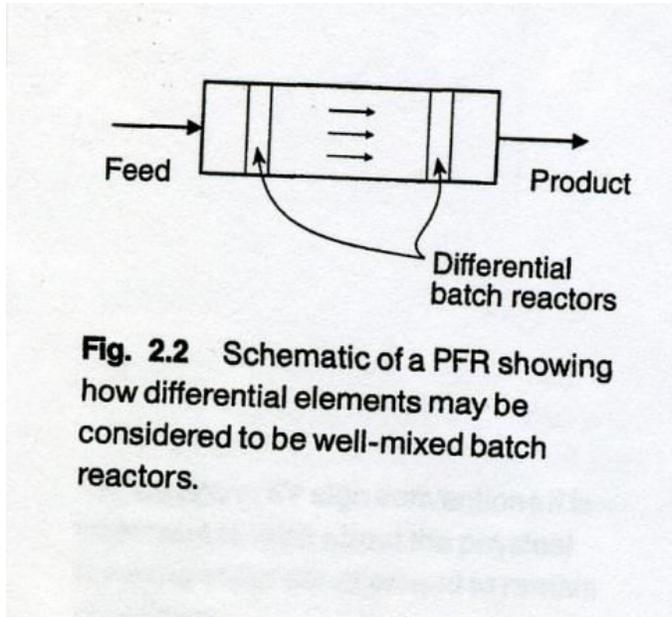
In these reactors, there is a constant flow of the reactants in a given direction and there is no type of 'induced' agitation. In order to simplify the fluid-dynamics in this type of reactors it is possible to introduce a simplification assuming a "piston" flow (plug flow). This simplification means:

- The flow velocity and flow properties are uniform for each section normal to the direction in the reactor;
- The axial mixing (due to diffusion or convection) is negligible.

These assumptions meet the reality if:

$Re > 10^4$, ie if there is a good radial mixing

Length reactor / reactor diameter > 50 , i.e., the axial mixing is negligible



If you consider a differential element in the reactor, PFR can be assimilated to a micro batch reactor.

In a PFR reactor the composition changes with the position but at a given position does not change with time.

Bilancio materiale sul PFR

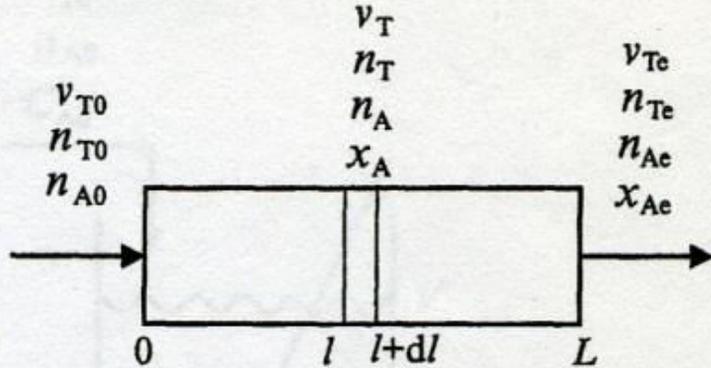


Fig. 2.3 Schematic of a PFR with nomenclature and showing a differential element used in the formulation of the material balance.

Observing what happens in a differential element that is located in a certain position along the reactor.

We can define the following symbols:

l : length (m)

L : total length of the reactor (m)

V : volume of the reactor (m³)

A : section of the reactor (m²)

n_A : total molar flux of component A (mol / s)

n_T : total molar flow (mol / s)

v_T : volumetric flow rate (m³ / s)

0: conditions of entry

e: output conditions

Accumulation_i = moles entering_i - moles exiting_i - (+) moles reacted_i

The accumulation is always equal to zero because the reactor at steady state (not time dependent). The input and output of the elements are the molar flows of the various components and the reagent is given by the rate of reaction (which is a specific volume (moles / volume) multiplied by the volume of the element dz , then:

$$0 = n_A(l) - n_A(l+dl) - r_A dV$$

Dividing by the length element

$$0 = -\frac{dn_A}{dl} - r_A \frac{dV}{dl}$$

Dividing by the section A

$$0 = -\frac{dn_A}{A dl} - r_A \frac{dV}{A dl} \qquad -\frac{dn_A}{A dl} = r_A \frac{dV}{A dl}$$

Remember! $A dl = dV$

$$r_A = -\frac{dn_A}{dV}$$

PFR 'equation design'

The higher the rate of reaction, the lower the A flux is increasing the length of the reactor or its volume.

In a BATCH reactor the composition is time dependent, while in a PFR the output composition is dependent by the reactor volume.

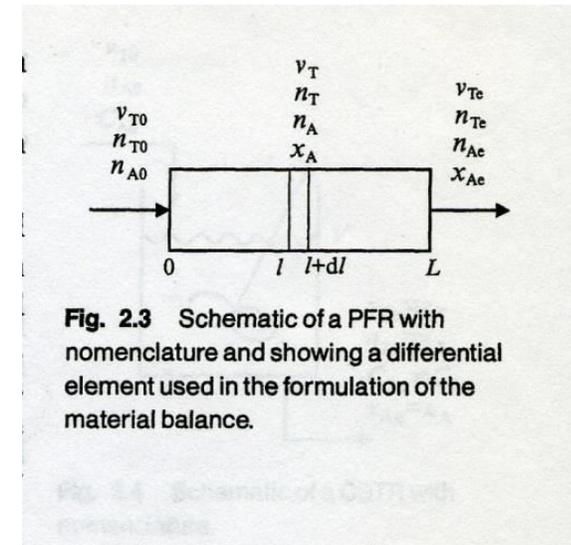


Fig. 2.3 Schematic of a PFR with nomenclature and showing a differential element used in the formulation of the material balance.

$$r_A = -\frac{1}{V} \frac{dN_A}{dt}$$

The PFR 'equation design' can be expressed also considering the product B:

$$r_B = + \frac{dn_B}{dV}$$

The volume dependence can be found by integrating the equation:

$$r_A = - \frac{dn_A}{dV} \longrightarrow \int_0^V dV = V = - \int_{n_{A0}}^{n_A} \frac{dn_A}{r_A}$$

From the definition of conversion in terms of molar flows:

$$x_A = \frac{n_{A0} - n_A}{n_{A0}} \quad \text{deriving:} \quad dx_A = - \frac{dn_A}{n_{A0}}$$

And substituting:

$$V = \int_0^{x_A} \frac{n_{A0} dx_A}{r_A}$$

Example 2: an irreversible first order reaction, $A \rightarrow B$, is conducted in a PFR : $r_A = kC_A$. Given $k = 0,01 \text{ s}^{-1}$ and the volumetric flow $v_T = 10^{-3} \text{ m}^3 \text{ s}^{-1}$. Calculate the reactor volume and the residence time needed to reach the 30% of conversion.

From the integrated form of the PFR equation $\int_0^V dV = V = - \int_{n_{A0}}^{n_A} \frac{dn_A}{r_A}$

$$r_A = k C_A = k \frac{n_A}{v_T}$$

\uparrow \nwarrow
 mol_A/s m^3/s

$$V = - \frac{v_t}{k} \int_{n_{A0}}^{n_A} \frac{dn_A}{n_A} = - \frac{v_t}{k} \ln \frac{n_A}{n_{A0}} = - \frac{v_t}{k} \ln(1 - x_A) = 3,57 \times 10^{-2} \text{ m}^3$$

Residence time: $\tau = \frac{V}{v_T} = 35,7 \text{ s}$

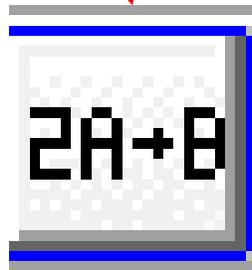
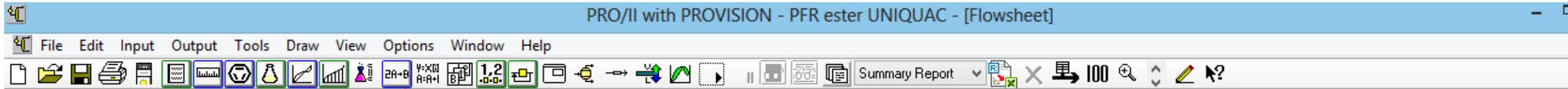
Comparing the example for the batch it could be observed that the residence time in the two reactors is the same. From this point of view the two reactors are equivalent: in the batch we have the actual time while in the PFR the residence time. The difference is that in the batch composition changes over time while in the PFR over space.

How can we simulate BATCH and PFR reactors using PRO II?

We should give to PRO II the kinetic parameters.

In PRO II it is possible to simulate both the reactors.

To insert the kinetic parameter we use the button here highlighted



Referring to the lesson in which we discussed the paper by Gmehling (Ind.Eng.Chem.Res. 39(2000)2601-2611)

In the window we have to write the forward and reverse reaction.
For each of them, then we set the kinetic model and write the numeric parameters.

We consider that these reactions are correctly represented with the pseudo-homogeneous model. More complex models, such as the autocatalytic or adsorption based require programming PRO II using the FORTRAN language.

Reaction Data - Reaction Definitions

UOM Range Help

Reaction Set: ESTER

Description:

Data Entry Legend
Heat of Reaction - H...
Equilibrium Data - E...
Kinetic Data - K...

Kinetic Rate Calculation

Calculation Method: Power Law Procedure Name:

Cut	Name	Definition	H...	E...	K...
Insert	1 DIR	$C_2H_4O_2 + CH_4O = H_2O + C_3H_6O_2$	H...	E...	K...
Reset	2 INV	$H_2O + C_3H_6O_2 = C_2H_4O_2 + CH_4O$	H...	E...	K...
	3	Reactants = Products	H...	E...	K...
	4	Reactants = Products	H...	E...	K...
	5	Reactants = Products	H...	E...	K...
	6	Reactants = Products	H...	E...	K...

OK Cancel

Exit the window after saving all data

Reaction Data - Kinetic Reaction Data

UOM Range Help

Reaction Set: ESTER

Reaction Name: DIR

Reaction: $C_2H_4O_2 + CH_4O = H_2O + C_3H_6O_2$

Define Kinetic Data

Kinetic Data

Power Law:

Rate = A . exp [-E/RT] . Tⁿ . Π (Activity)^{Order}

Units

Temperature: [K](#)

Weight: [g](#)

Volume: [liter](#)

Pressure: [kPa](#)

Time: [sec](#)

Pre-exponential Factor (A):

1.1246e+006

Activation Energy (E):

0.0491900 x10³ kJ/g-mol

Temperature Exponent (n):

0.00000

Reaction Order and Activity Basis

Default Phase:

Liquid

Liquid Activity Basis:

Activity

Vapor Activity Basis:

Molar Concentration

Reaction Order
&
Activity Phase...

OK

Cancel

Exit the window after saving all data

**PAY ATTENTION
TO UOM!!!**

$$\text{Rate} = A \cdot \exp(-E/RT) \cdot T^n \cdot \Pi (\text{Activity})^{\text{Order}}$$

$$r = \frac{1}{\nu_i} \frac{dn_i}{dt} = m_{\text{cat}} (k_1 a_{\text{HOAc}} a_{\text{MeOH}} - k_{-1} a_{\text{MeOAc}} a_{\text{H}_2\text{O}})$$

$$k_i = k_i^0 \exp\left(\frac{-E_{A,i}}{RT}\right)$$

$$r_A = -\frac{1}{V} \frac{dN_A}{dt}$$

Batch reactor

TABLE 11. Parameters and Residual Errors of the Different Kinetic Models Used To Fit the Experimental Data with Amberlyst 15 as the Catalyst

model	mean relative error (%)	k_1^0 (mol·g ⁻¹ ·s ⁻¹)	$E_{A,1}$ (kJ·mol ⁻¹)	$k-10$ (mol·g ⁻¹ ·s ⁻¹)	$E_{A,-1}$ (kJ·mol ⁻¹)
pseudohomogeneous, ideal liquid phase	14.6	1.648×10^4	47.98	1.161×10^5	58.60
pseudohomogeneous, activities by UNIQUAC	13.9	2.961×10^4	49.19	1.348×10^6	69.23
Song's model with original parameters, activities by UNIQUAC	10.4	3.985×10^6	52.28	use K_a given by Song et al.	
Song's model, parameters fitted, activities by UNIQUAC	6.7	5.312×10^7	58.25	use K_a from this work	
eq 16	5.4	8.497×10^6	60.47	6.127×10^5	63.73

The pre-exponential factor must be numerically multiplied by the grams of catalyst and divided by the volume of the reactor, in our case it corresponds to the amount of reactants.

$$\text{Rate} = A \cdot \exp(-E/RT) \cdot T^n \cdot \Pi (\text{Activity})^{\text{Order}}$$

$$r_A = -\frac{dn_A}{dV}$$

PFR REACTOR

$$r = \frac{1}{\nu_i} \frac{dn_i}{dt} = m_{\text{cat}} (k_1 a_{\text{HOAc}} a_{\text{MeOH}} - k_{-1} a_{\text{MeOAc}} a_{\text{H}_2\text{O}})$$

$$k_i = k_i^0 \exp\left(\frac{-E_{A,i}}{RT}\right)$$

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Song's model, parameters fitted, activities by UNIQUAC	6.7	5.312×10^7	58.25	use K_a from this work	
eq 16	5.4	8.497×10^6	60.47	6.127×10^5	63.73

The pre-exponential factor should be numerically multiplied by the grams of catalyst but **not** divided by the volume of the reactor, to be defined according to the residence time we want.

From the article you can do exercises on all RUN conducted by the authors.

USE THE SUPPORTING INFORMATIONS!!!!

PER ESEMPIO LA RUN 7

Table 8. Summary of the Experiments with Amberlyst 15 as Catalyst

run number	temperature (K)	mass of dry catalyst (g)	duration (h)	initial mole numbers (mol)			
				HOAc	MeOH	MeOAc	H ₂ O
1	304.25	18.27	23.4	1.557	1.557	0	1.014
2	303.45	31.54	23.3	1.993	2.012	0	0
3	313.63	8.84	2.0	1.621	1.618	0	0.542
4	313.14	3.81	23.4	1.646	1.608	0	0.234
5	313.00	5.76	31.6	3.589	1.591	0	0.354
6	323.00	7.17	5.6	1.997	1.999	0	0.427
7	323.15	7.71	6.4	2.031	1.982	0	0
8	323.00	7.31	4.8	1.996	2.090	0	0.441
9	323.00	6.70	5.0	2.006	2.017	0	0.363
10	323.00	23.80	5.1	2.003	2.049	0	1.485
11	323.08	8.18	17.7	1.656	1.626	0	0.502
12	323.06	8.55	18.8	1.642	1.621	0	0.524
13	323.06	17.10	21.1	1.632	1.627	0	1.049
14	323.00	3.54	23.0	2.050	1.019	0	0.217
15	323.00	8.67	3.2	1.539	2.921	0	0.531
16	323.15	7.15	5.9	0.428	3.588	0	0.440
17	333.14	4.25	23.2	1.669	1.642	0	0.261
18	333.12	8.19	20.3	1.670	1.646	0	0.502
19	333.13	17.71	20.1	1.661	1.604	0	1.087
20	333.20	23.38	4.9	1.562	1.549	0	1.230
21	304.25	18.66	23.4	0	0.367	1.614	1.546
22	313.30	17.61	19.7	0	0	1.621	2.801
23	313.00	5.70	95.1	0	0	2.539	4.156
24	323.08	17.13	18.5	0	0	1.648	2.698
25	323.15	29.52	3.7	0	0.432	1.812	1.897
26	333.03	17.78	20.9	0	0	1.623	2.785
27	323.15	12.97	6.5	2.001	2.009	0	0
28	323.15	27.61	6.5	2.012	2.008	0	0
29	323.15	36.95	6.5	2.003	1.992	0	0
30	323.15	46.35	6.5	2.015	1.998	0	0
31	323.15	55.37	3.7	2.004	2.015	0	0
32	323.15	5.02	6.5	0.246	4.761	0	0
33	323.15	7.20	6.2	0.431	3.579	0	0
34	323.15	6.14	7.1	1.008	4.073	0	0
35	323.15	5.61	5.4	2.721	0.730	0	0
36	323.15	11.19	6.2	3.590	0.387	0	0
37	323.15	5.89	1.8	3.088	0.142	0	0
38	323.15	4.32	70.6	0	0	0.595	5.400
39	323.15	4.35	24.6	0	0	1.005	3.991
40	323.15	6.65	5.4	0	0	1.997	0.499
41	323.15	5.27	4.5	0	0	1.795	0.198
42	313.15	20.73	24.5	0	0	0.898	9.362
43	323.15	20.54	5.4	0.897	0.901	0	8.454
44	323.15	59.68	1.3	0	0	0.613	5.417
45	333.15	20.49	5.4	0	0	0.904	9.366
46	343.15	21.18	3.5	0.894	0.901	0	8.517
47	313.49	17.60	21.1	1.483	0	0.640	1.477
48	313.45	17.58	19.0	1.012	0	0.956	2.328
49	333.05	17.66	15.8	0.654	1.580	0.800	1.281
50	333.09	17.58	19.0	0.459	0.149	0.934	3.866

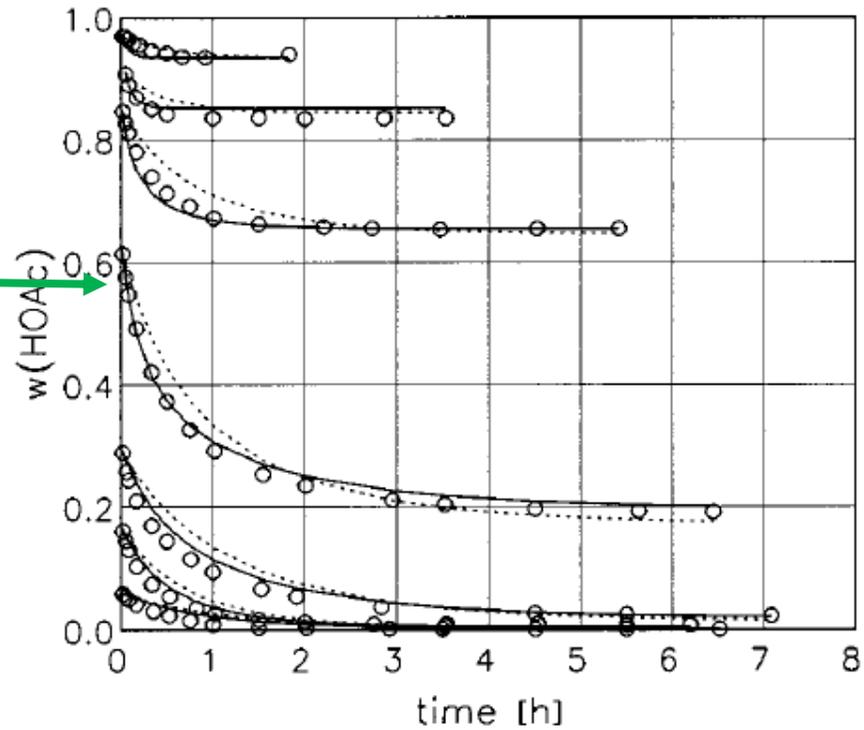


Table S-2b.07 Run 7

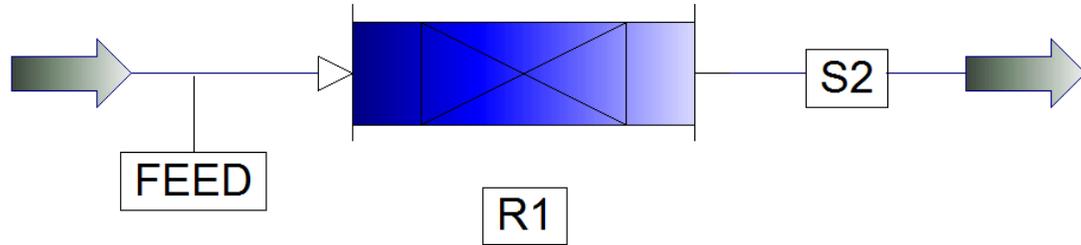
time [s]	w(HOAc) [mg/g]	sample size [g]
60	614.06	1.1556
180	575.98	1.1370
300	547.53	0.7275
600	491.65	0.7567
1200	420.98	0.7578
1800	373.13	0.8177
2700	326.40	0.7947
3660	291.95	0.9383
5561	253.38	0.8641
7230	235.28	0.8065
10630	211.12	0.8211
12675	204.20	0.7789
16210	196.91	1.1371
20280	192.65	0.7645
23205	191.42	1.1900

RUN #7

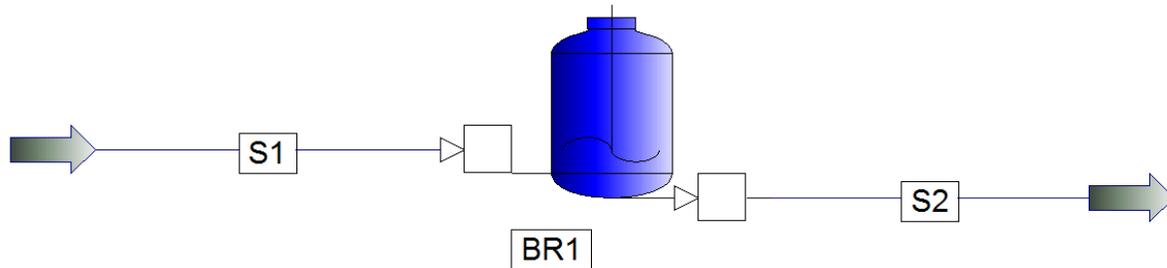
run number	temperature (K)	mass of dry catalyst (g)	duration (h)	initial mole numbers (mol)			
				HOAc	MeOH	MeOAc	H ₂ O
7	323.15	7.71	6.4	2.031	1.982	0	0



PFR



We have to set the size of the reactor and the flow of reagents to determine consequently the residence time of the reactants within the reactor



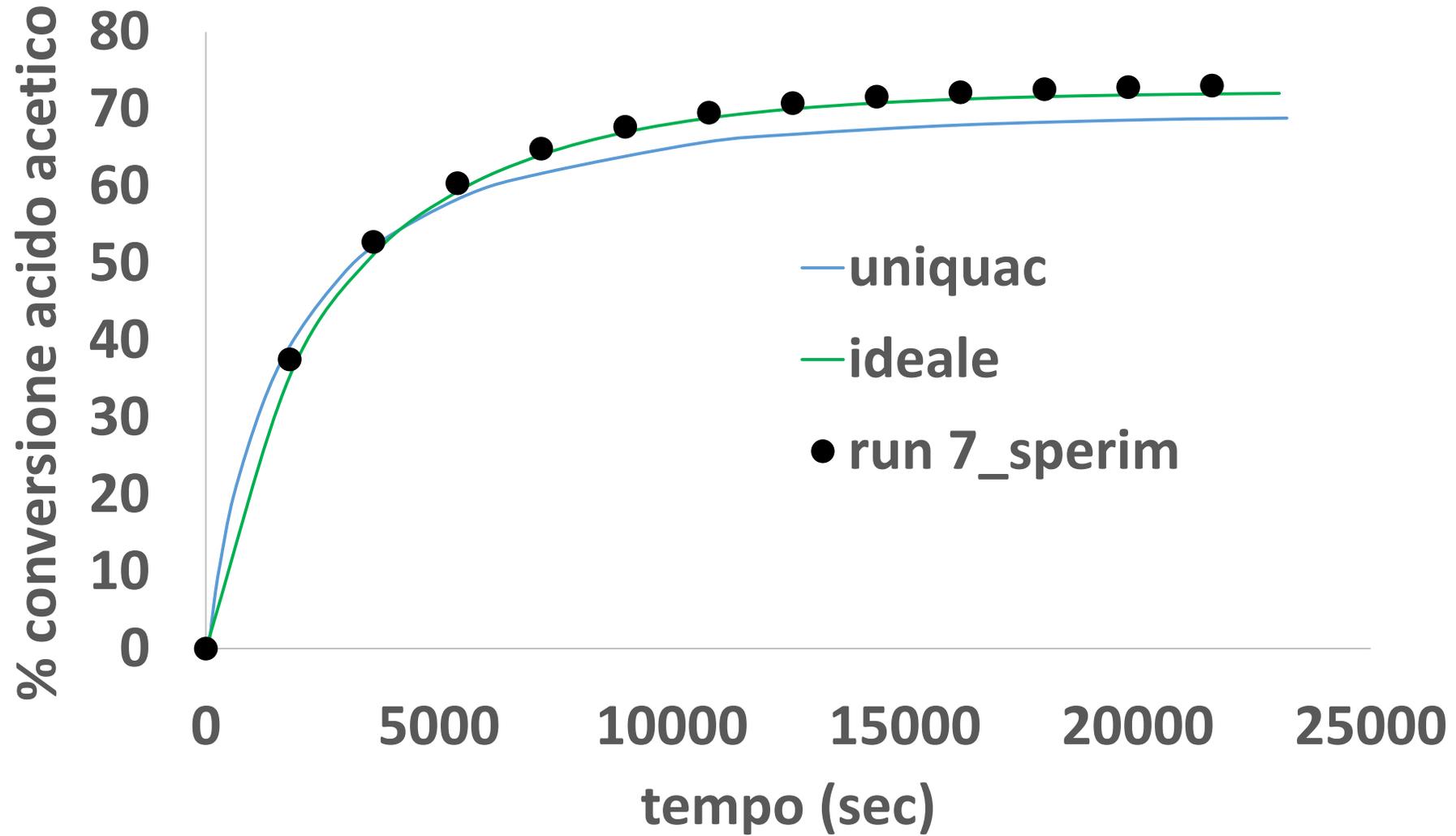
We have to input all the batch steps of the reactor:

1. Charge
2. Heating
3. Reaction

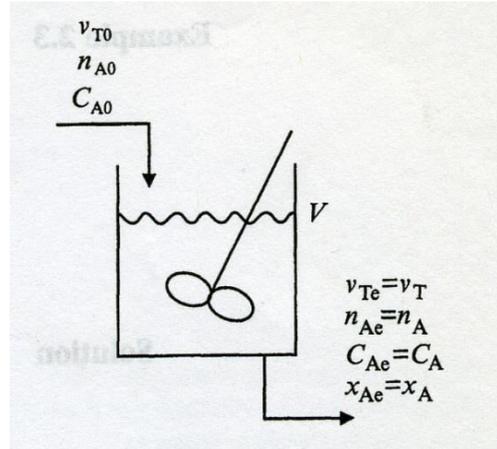
The volume of the reactor corresponds to the mass loaded.

BATCH

RUN 7



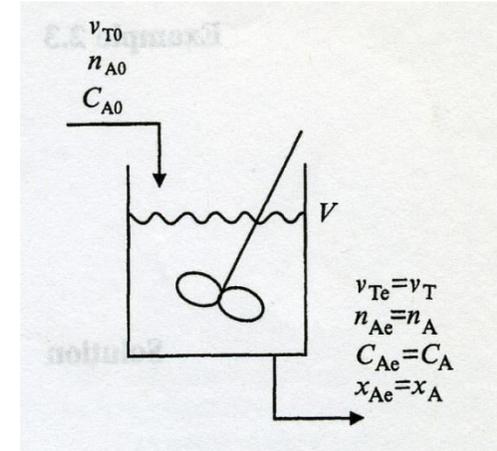
Continuous stirred tank (CSTR) REACTORS



The main feature of the CSTR is the perfect mixing within the reactor. This means that the properties of the mixture are uniform in all parts and identical to the properties of the mixture exiting the reactor. Furthermore, the mixing of the incoming flow with the mass reagent is instantaneous.

Also we assume steady state conditions, i.e. the reaction rate is the same in each time and time independent.

Since the properties of the mixture are uniform throughout the reactor, we can set a material balance for the component A for the whole reaction volume V. Therefore:



Accumulation_i = moles entering_i - moles exiting_i - (+) moles reacted_i

As in the case PFR, there is no accumulation being the reactor in stationary conditions. The input and output of the elements are the molar flows of the various components and the reagent is given by the rate of reaction (which is a specific volume (moles / volume) multiplied by the volume of the reactor.

$$0 = n_{A0} - n_{Ae} - r_A V \qquad r_A = \frac{n_{A0} - n_{Ae}}{V}$$

There is no distinction between n_A and n_{Ae} , therefore: $r_A = \frac{n_{A0} - n_A}{V}$

This is the CSTR "equation design'

$$r_A = \frac{n_{A0} - n_A}{V}$$

the 'design equation' for the CSTR IS NOT A DIFFERENTIAL EQUATION as in the case of BATCH and PFR reactors. The need for a differential equation arises in the case of BATCH because the composition changes over time and in the case of PFR because the composition changes in length. In the case of the CSTR instead the composition does not change nor as a function of time or space.

But then if there are no changes in the composition or function of time or space, how CSTR can be a reactor? What reacts if it 'changes nothing'? The answer is that there is a discontinuity between what goes in and what comes out of this reactor. We assume that at the time of entering into the reactor reagent composition change, instantly.

Example 3: an irreversible reaction of first order, $A \rightarrow B$, is conducted in a CSTR with first order kinetics: $r_A = kC_A$. If $k = 0.01 \text{ s}^{-1}$ and the flow rate v_T is $10^{-3} \text{ m}^3 \text{ s}^{-1}$. Calculate the volume of the reactor and the residence time it takes to reach 30% conversion.

From the 'equation design' of CSTR: $r_A = \frac{n_{A0} - n_A}{V}$

$$V = \frac{n_{A0} - n_A}{r_A} \quad r_A = k C_A = k n_A / v_T$$

$$V = \frac{n_{A0} - n_A}{k \frac{n_A}{v_T}} = \frac{v_T}{k} \left(\frac{n_{A0}}{n_A} - 1 \right) \quad \text{ma} \quad x_A = 1 - \frac{n_A}{n_{A0}}$$

$$V = \frac{v_T}{k} \left[\frac{1}{(1 - x_A)} - 1 \right] = \frac{v_T}{k} \frac{x_A}{(1 - x_A)} = 4,29 \times 10^{-2} \text{ m}^3$$

Residence time: $\tau = V / v_T = 42,9 \text{ s}$

Comparison between BATCH- PFR- CSTR (examples 1, 2, 3)

From the numerical exercises carried out in the previous slides it can be observed how, for the same reaction with the same kinetics, the volume or the residence time required for a conversion in the CSTR is equal than that required in the reactors BATCH or PFR. The motivation lies in the fact that when we introduce fresh supply in the CSTR we dilute immediately to the concentration output, and then the reaction rate (which depends on the concentration of the reactants) decreases. Unlike in the other two reactors, the dilution of the reagents is not instantaneous but progressive and therefore the reaction rate is generally higher.

You may see this concept imagining color mixtures: if I inject red in a CSTR becomes immediately pink, in the PFR becomes progressively advancing in the tube becomes pink and in the BATCH turns pink gradually over time.

However, not always the reaction rates are higher with higher concentrations of reagents. You sometimes have kinetic mechanisms for which a reaction rate is inversely proportional to the concentration of a certain reagent. In these cases therefore the CSTR requires time (or volumes) lower than a batch or a PFR to achieve the same conversion.

CHEMICAL REACTORS: PART 2

'equations design' of batch, PFR, CSTR, extensions

1) BATCH reactors: generalizing the equations

Taking the two fundamental equations of the batch

$$r_A = -\frac{1}{V} \frac{dN_A}{dt} \qquad \int_0^t dt = \int_0^{x_A} \frac{N_{A0}}{V} \frac{dx_A}{r_A}$$

In a general irreversible reaction $A \rightarrow B$ with a reaction rate $r = k C_A^n$, esprimibile anche come:

$$r_A = k C_A^n = k \frac{N_A^n}{V^n} = k \frac{N_{A0}^n (1 - x_A)^n}{V^n}$$

That substitute in the equation gives

$$t = \frac{1}{k N_{A0}^{n-1}} \int_0^{x_A} V^{n-1} \frac{dx_A}{(1 - x_A)^n}$$

In this eq. N_{A0} is constant and k is constant (we assume that the reactor T does not change when changing the conversion)

$$t = \frac{1}{kN_{A0}^{n-1}} \int_0^{x_A} V^{n-1} \frac{dx_A}{(1-x_A)^n}$$

If the number of moles of the product are different from the number of reagent (obviously depending on the stoichiometry of the reaction) there will be a change in the total number of moles of the system. For a gas phase reaction, this means that:

Reactor at constant volume → change reactor pressure

Reactor at constant pressure → changes the volume of the reactor

In the first case I can consider constant (and thus carry out the integral) the volume; in the second case I will not be able to take it out and I'll have to look for a relationship between the volume of the reactor and the degree of conversion

We see the first case, i.e. in the gas phase batch reactor with constant volume:

$$t = \frac{V^{n-1}}{kN_{A0}^{n-1}} \int_0^{x_A} \frac{dx_A}{(1-x_A)^n} = \frac{1}{kC_{A0}^{n-1}} \int_0^{x_A} \frac{dx_A}{(1-x_A)^n}$$

for $n \neq 1$:

$$t = \frac{-1}{kC_{A0}^{n-1}(1-n)} \{ [(1-x_A)^{1-n} - 1] \}$$

If otherwise $n=1$ I have:

$$t = \frac{1}{k} \ln \frac{1}{1 - x_A} \quad \text{con} \quad x_A = 1 - e^{-kt}$$

This means that for an irreversible reaction of the first order at infinite residence times the conversion of the reactor will tend to 1 (100%) with exponential trend.

Or, alternatively, whether express the same equations in terms of moles of A present we will have:

$$t = \frac{1}{k} \ln \frac{N_{A0}}{N_A} \quad N_A = N_{A0} e^{-kt}$$

2) PFR reactors: extensions to a more general cases

Taking the two fundamental equations of the PFR

$$r_A = -\frac{dn_A}{dV} \quad \int_0^V dV = V = -\int_{n_{A0}}^{n_A} \frac{dn_A}{r_A} \quad \text{being} \quad dn_A = -n_{A0} dx_A$$

Substituting the kinetics of order n, as in the case of the batch reactor:

$$r_A = kC_A^n = k \frac{n_A^n}{v_T^n} = k \frac{n_{A0}^n (1 - x_A)^n}{v_T^n}$$

I obtain:

$$V = \int_0^{x_A} \frac{v_T^n dx_A}{kn_{A0}^{n-1} (1 - x_A)^n}$$

Similarly to the previous case the volumetric flow v_T will be constant for a reaction in the liquid phase or in gas phase where the number of moles, and therefore the pressure, does not change. Again, if we are not in these conditions it is necessary to derive a relationship between flow rate and conversion.

As in the case of the batch reactor, considering the equations for volumetric flow constant and $n = 1$ (Reaction of the first order). In this case we get:

$$V = \frac{v_T}{k} \ln \frac{1}{(1 - x_A)} \quad \text{Therefore:} \quad \frac{1}{(1 - x_A)} = \exp\left(\frac{kV}{v_T}\right) = \exp(k\tau)$$

Being τ the residence time in the reactor (reactor volume / flow rate)

You can isolate x_A :

$$x_A = 1 - e^{-k\tau}$$

That is, in a PFR the conversion will tend to 1 (100%) with increasing residence time in an exponential manner.

The same equations can be derived in terms of molar flow of reactant A:

$$V = \frac{v_T}{k} \ln \frac{n_{A0}}{n_A} \quad n_A = n_{A0} e^{-k\tau}$$

3) CSTR reactor: extensions to a more general cases

Returning to the fundamental equation of the CSTR and the kinetics of order n

$$r_A = \frac{n_{A0} - n_A}{V}$$

I obtain:

$$V = \frac{n_{A0} - n_A}{r_A} = \frac{n_{A0}x_A}{kC_A^n} = \frac{n_{A0}x_A v_T^n}{kn_A^n} = \frac{n_{A0}x_A v_T^n}{kn_{A0}^n(1-x_A)^n}$$

As in previous cases, if I have the gas phase and a change in the number of moles I need a correlation between flow rate and degree of conversion.

$$V = \frac{n_{A0} - n_A}{r_A} = \frac{n_{A0}x_A}{kC_A^n} = \frac{n_{A0}x_A v_T^n}{kn_A^n} = \frac{n_{A0}x_A v_T^n}{kn_{A0}^n(1-x_A)^n}$$

In the case of reactions at constant volume and for $n = 1$ is obtained:

$$\tau = \frac{V}{v_T} = \frac{1}{k} \frac{x_A}{1-x_A} \quad \text{Where, as in the PFR, } \tau \text{ is the average residence time in the reactor}$$

therefore:

$$x_A = \frac{k\tau}{1+k\tau}$$

So in a CSTR the conversion approaches the value 1 (100%) in a dependent way from the reciprocal of the average residence time.

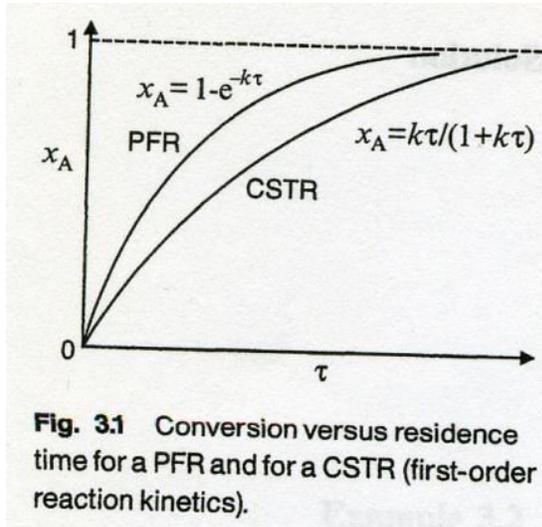
Expressing the same equations in terms of the molar flow of the reagent A, is obtained:

$$\tau = \frac{1}{k} \frac{n_{A0} - n_A}{n_A} \quad n_A = \frac{n_{A0}}{1+k\tau}$$

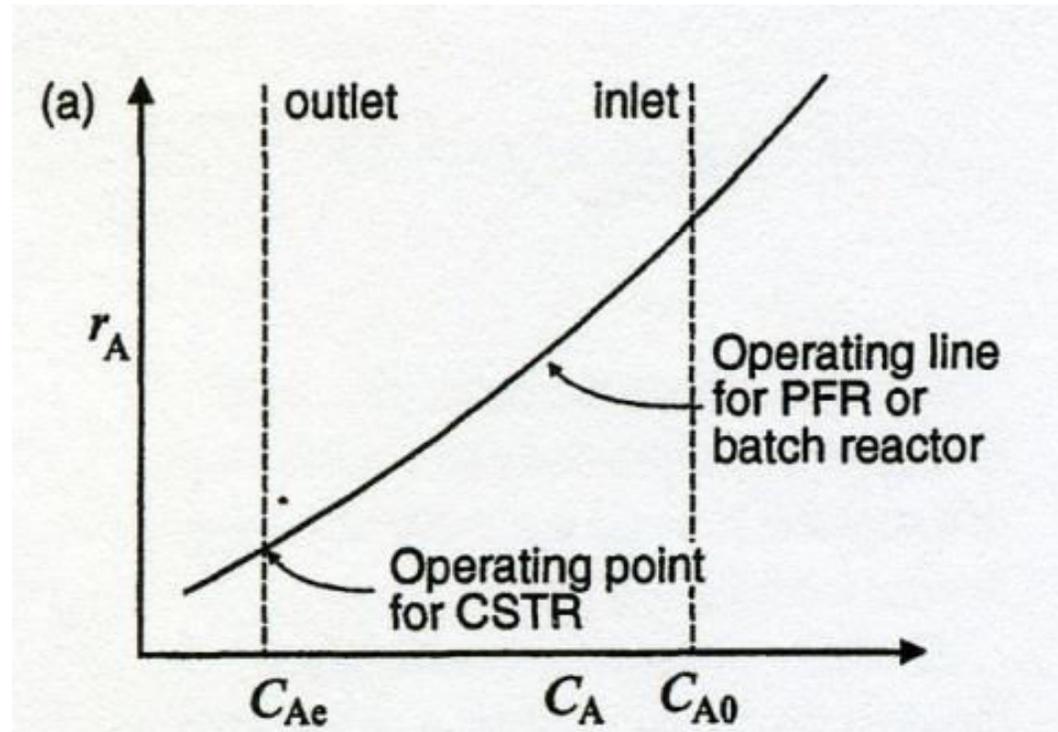
Comparison PFR-CSTR

PFR: $x_A = 1 - e^{-k\tau}$

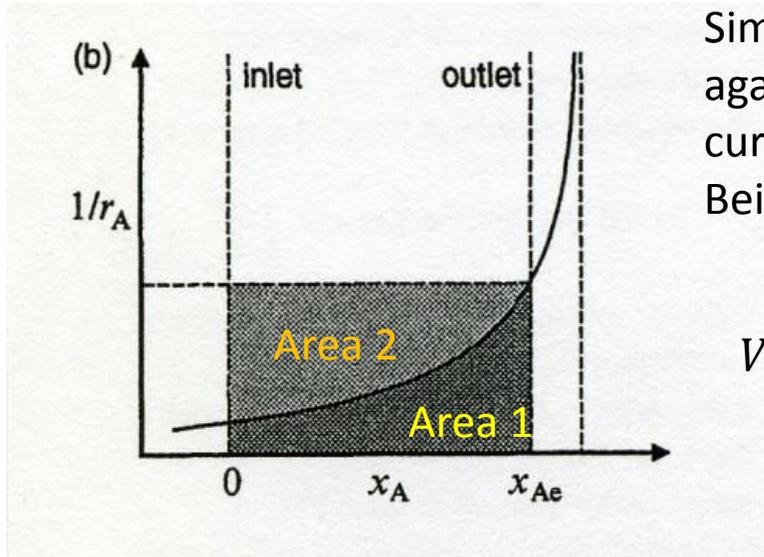
CSTR: $x_A = \frac{k\tau}{1 + k\tau}$



For kinetics of the first order a PFR will always require residence times lower to achieve a certain conversion respect to a CSTR (or for a certain residence time will always ensure a greater conversion).



This figure shows the reaction rate as a function of concentration of reagent A. Obviously the exit has a concentration of A lower than the entrance. A CSTR will operate with a concentration equal to that of output (operating POINT), while the PFR requires to be represented by a curve (operating LINE), because the concentration of A varies in its interior.



Similarly, it can be to plot the inverse of the reaction rate against conversion. Again the PFR is represented by a curve and a point from the CSTR.

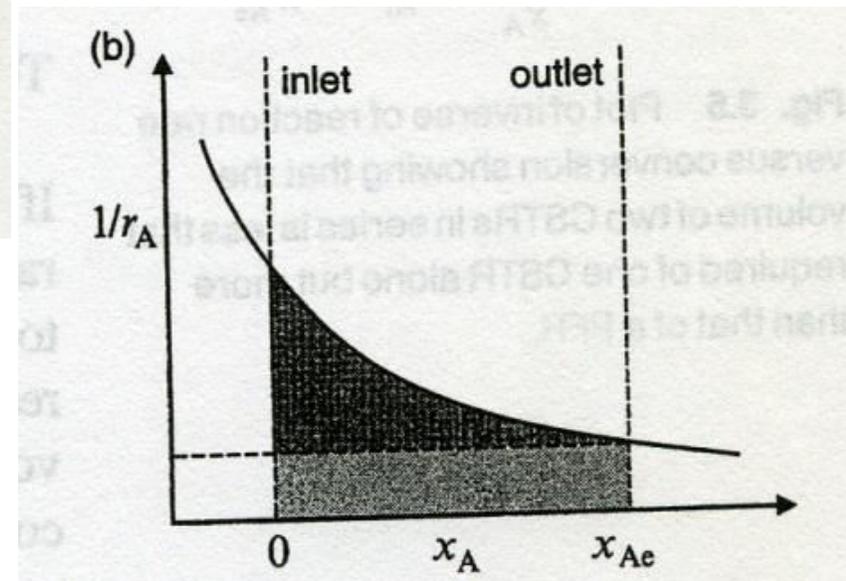
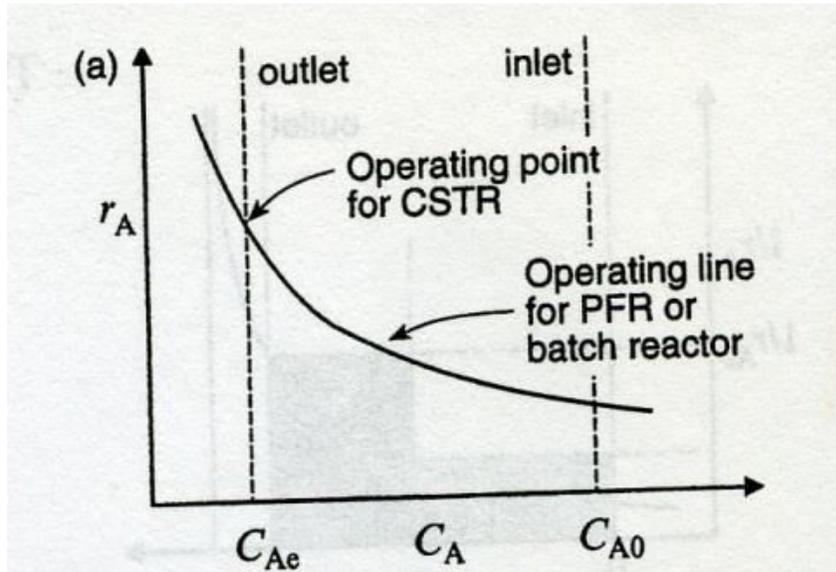
Being that the volumes of the two reactors depend on:

$$V_{PFR} = n_{A0} \int_0^{x_{Ae}} \frac{dx_A}{r_A} \quad V_{CSTR} = n_{A0} \frac{x_{Ae}}{r_A}$$

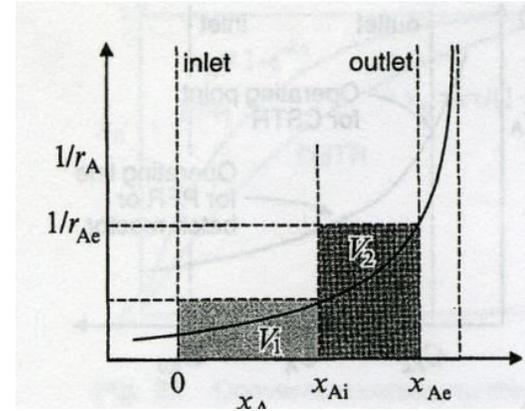
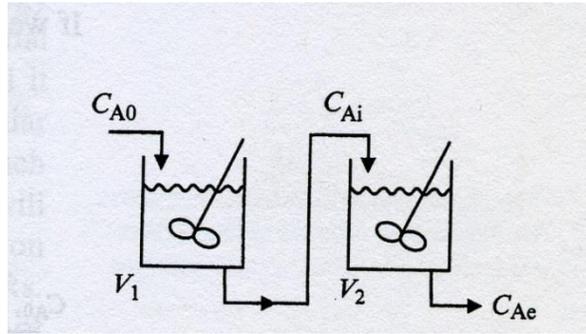
It is obtained that the volume of the PFR is proportional to the area under the "operating line" (Area 1), while the volume of the CSTR is proportional to the rectangular (Area 1 + Area2).

So the volume of the PFR will always be less than the volume of a CSTR.

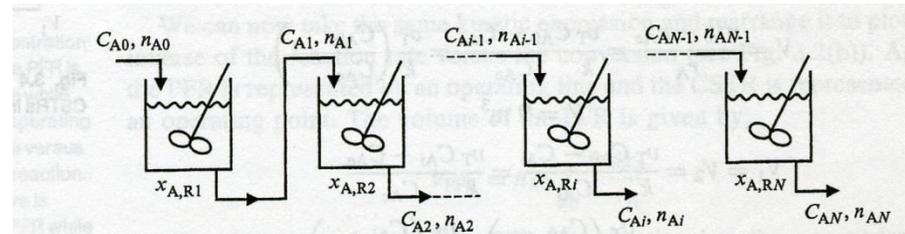
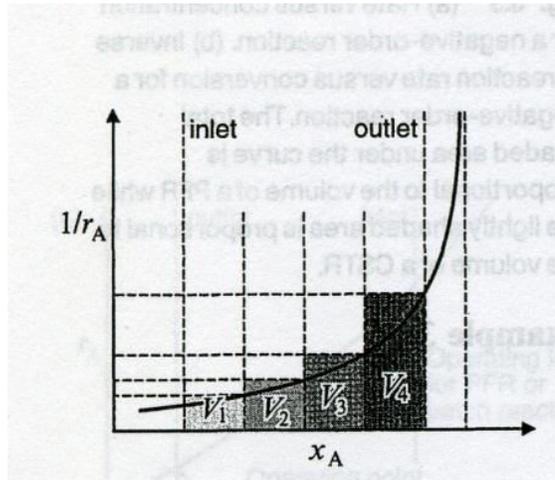
This discussion is valid for orders of reaction > 1 , for the reasons discussed. HOWEVER, IF we treat reaction orders lower than one, and therefore the higher the concentration of reagents is less than the speed of the reaction, the speech is reversed and the reactor with less volume required becomes the CSTR. The figures seen before become:



REACTOR IN SERIES: CSTR OF EQUAL VOLUME



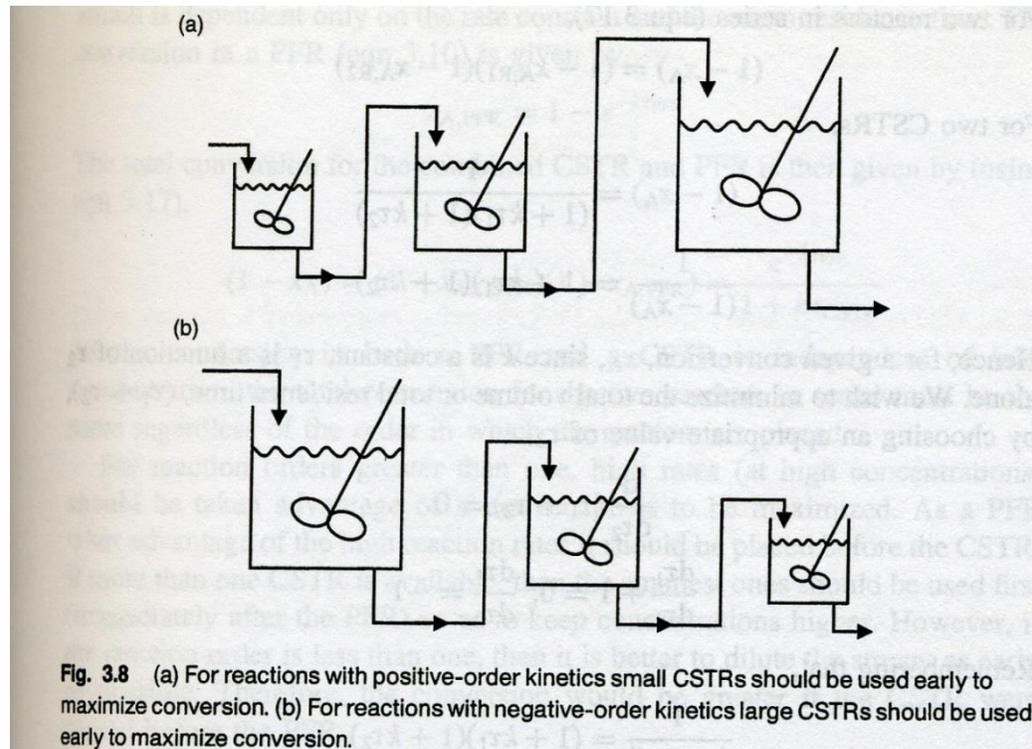
2 CSTR in series will have a lower volume than a single CSTR to obtain the same conversion, but will always be greater than the volume required by a PFR. Increasing the number of CSTR in series tends to reach (for infinite CSTR) the same volume required by PFR. Then n CSTR in series tend to the behavior of the PFR.



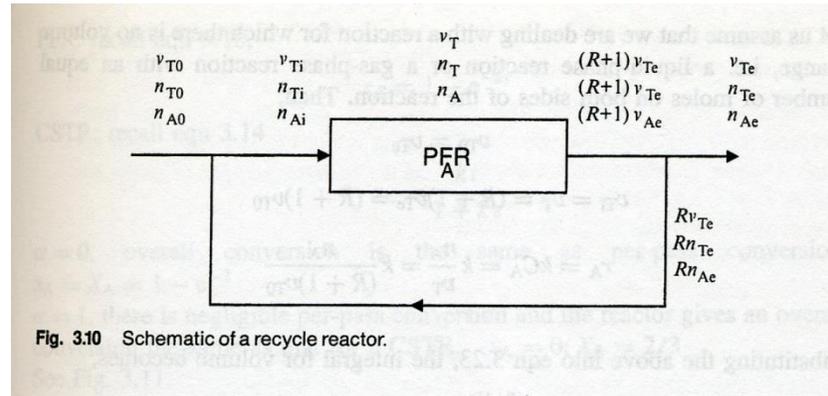
REACTOR IN SERIES: CSTR OF DIFFERENT VOLUME

How to maximize the total conversion of n CSTR operating on their single volume? It all depends on the order of the reaction kinetics.

If $n = 1$ then the order of the reactors is irrelevant, if $n > 1$ should operate with small reactors at the beginning (to maintain the highest concentrations of the reactants is favorable), if $n < 1$ should operate with larger reactors at the beginning (preferably as soon as possible to lower the concentrations of the reactants).



RECYCLE



The fresh feed is mixed with a stream of recycle and then sent to the PFR. The output of the reactor is divided between output and recycling. It defines recycle ratio:

$$R = \frac{\text{moli rientranti}}{\text{moli uscenti dal sistema}}$$

IF **R tends to zero** the reactor behaves like a **PFR**

IF **R tends to infinite** the reactor behaves like a **CSTR**, because an infinite recycling is equivalent to a perfect mixing

RECYCLE

For an irreversible reaction of the first order the conversion step (x_A) and the total conversion (X_A) can be expressed as a function of the fraction recycled, as indicated in the following chart:

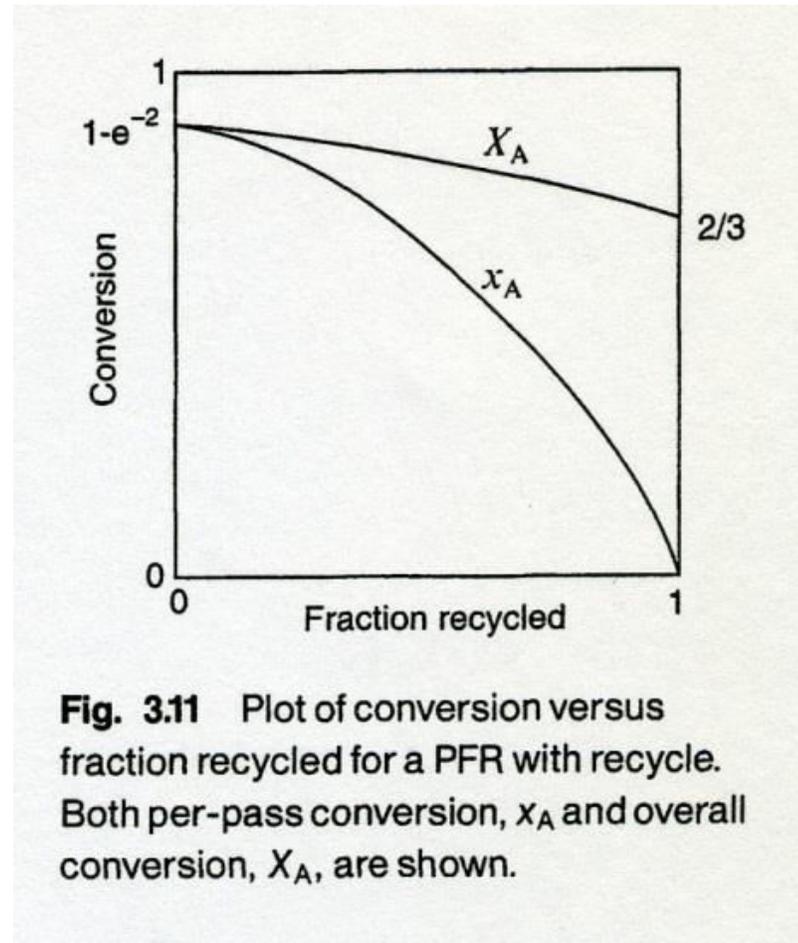


Fig. 3.11 Plot of conversion versus fraction recycled for a PFR with recycle. Both per-pass conversion, x_A and overall conversion, X_A , are shown.

Consecutive reactions: $A \rightarrow R \rightarrow S$

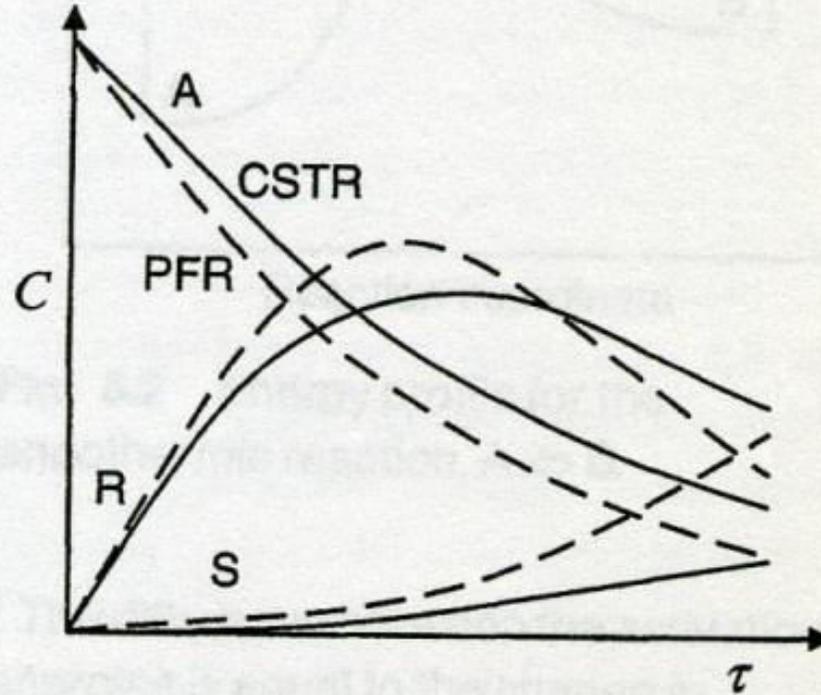


Fig. 4.6 Concentrations (not to scale) of species involved in a series reaction, $A \rightarrow R \rightarrow S$, in a PFR and a CSTR.

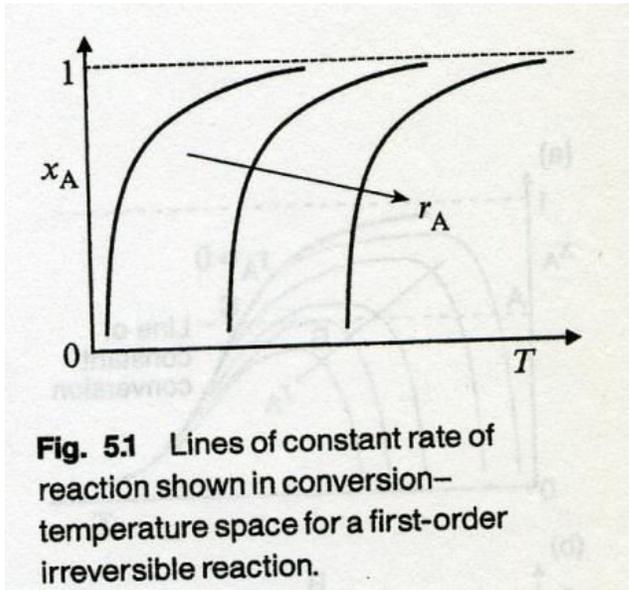
Temperature dependence

IRREVERSIBLE reaction: you can replace the k with its temperature dependence, namely:

$$r_A = kC_A = k' \exp\left(-\frac{\Delta E}{RT}\right) C_{A0}(1 - x_A)$$

k' =pre-esponenzial factor

ΔE = activation energy



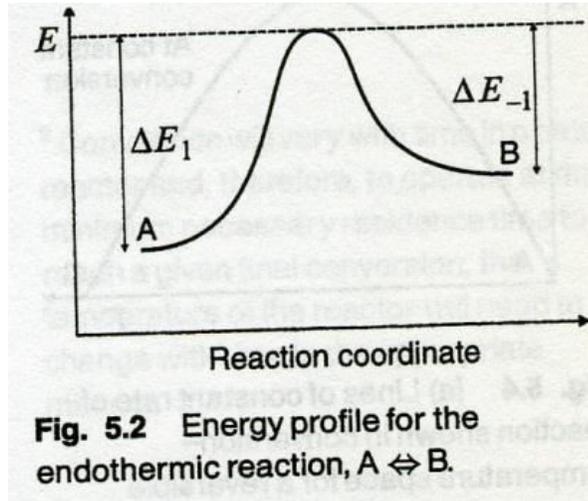
The reaction rate varies as a function of temperature and conversion:

If T increases, increases reaction speed

If the conversion goes down, the rate of reaction too the reactant concentration of the reagent is larger

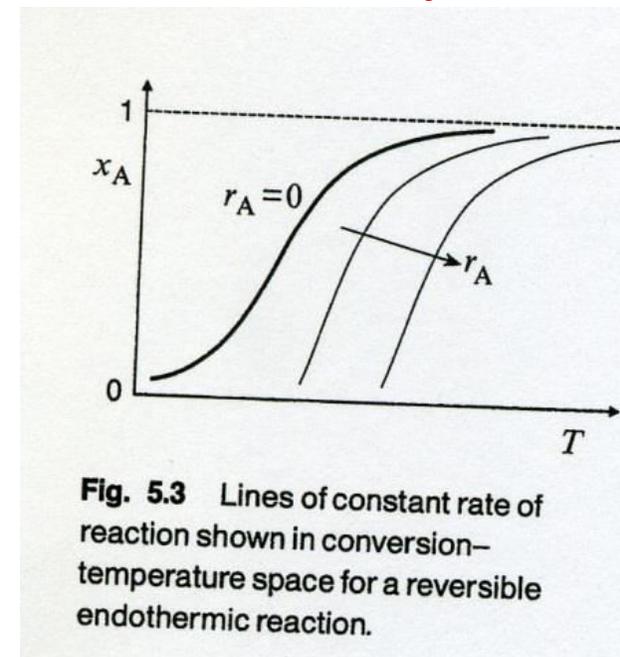
High conversions are therefore favoured by high T .

ENDOTHERMIC IRREVERSIBLE REACTION



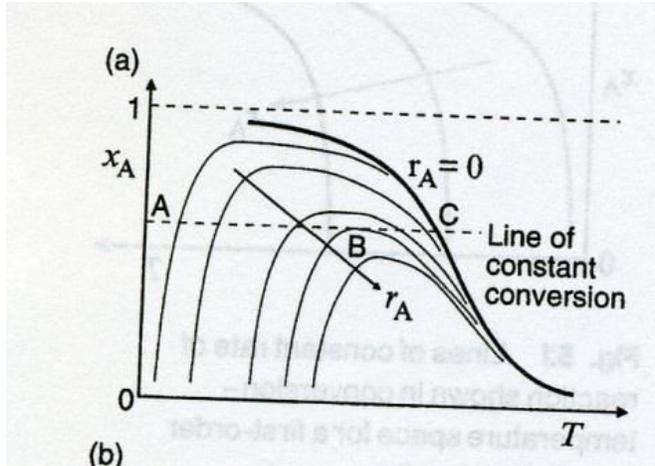
You have direct reaction (k_1) and reverse reaction (k_{-1}). The relationship between these two k is the equilibrium constant K . As the temperature increases the value of K increases for endothermic reactions and therefore also the value of the conversion of A.

High conversions are therefore favored by high T.



REVERSIBLE EXOTHERMIC reaction

If the reaction is instead EXOTHERMIC, the equilibrium constant decreases as the temperature increases, and then decreases the conversion of equilibrium.



There is an optimum operating temperature, a compromise between thermodynamic (equilibrium constant which falls with increasing T) and issues kinetics (rate constant that rises with increasing T).

