CHEN 416: CHEMICAL REACTION ENGINEERING II

AUTOCATALYTIC REACTIONS

LEARNING OBJECTIVES

- At the end of this lecture, students should be able to:
  - Explain what autocatalytic reactions are
  - Determine optimum recycle ratio for autocatalytic reactions
  - Determine the best combination of reactors for autocatalytic reactions.

AUTOCATALYTIC REACTION

- In a batch reactor, when material reacts, its rate of disappearance is rapid at the start when the concentration of reactant is high. This rate then slows progressively as reactant is consumed.
- An autocatalytic reaction is one in which a product of the reaction catalyzes or promotes further reaction of the reactant.

$$A + R \rightarrow R + R \qquad -r_A = kC_A^a C_R^r$$

- In an autocatalytic reaction, the rate at the start is low because little product is present; it increases to a maximum as product is formed and then drops again to a low value as reactant is consumed. Figure 7-1 shows a typical situation for the reaction:

AUTOCATALYTIC REACTION

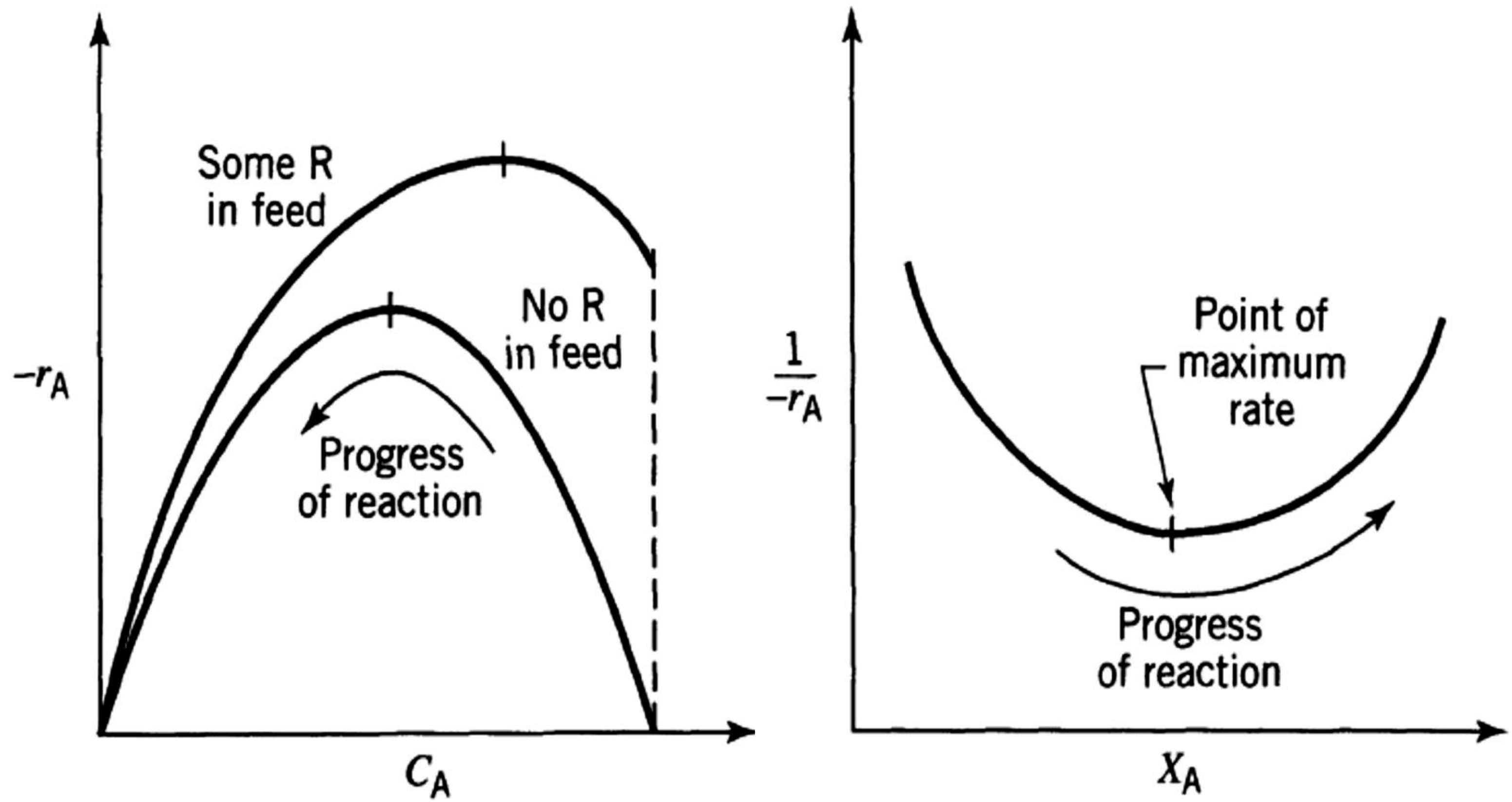

Figure 7-1 Typical rate-concentration curve for Autocatalytic reaction.

- ❑ Reactions with such rate-concentration curves lead to interesting optimization problems.

AUTOCATALYTIC REACTION

- Comparing a PFR with a MFR for autocatalytic reaction in which there is no recycle, Fig. 7-2 shows which reactor is superior (which requires a smaller volume) for a given job of any particular rate-concentration curve.

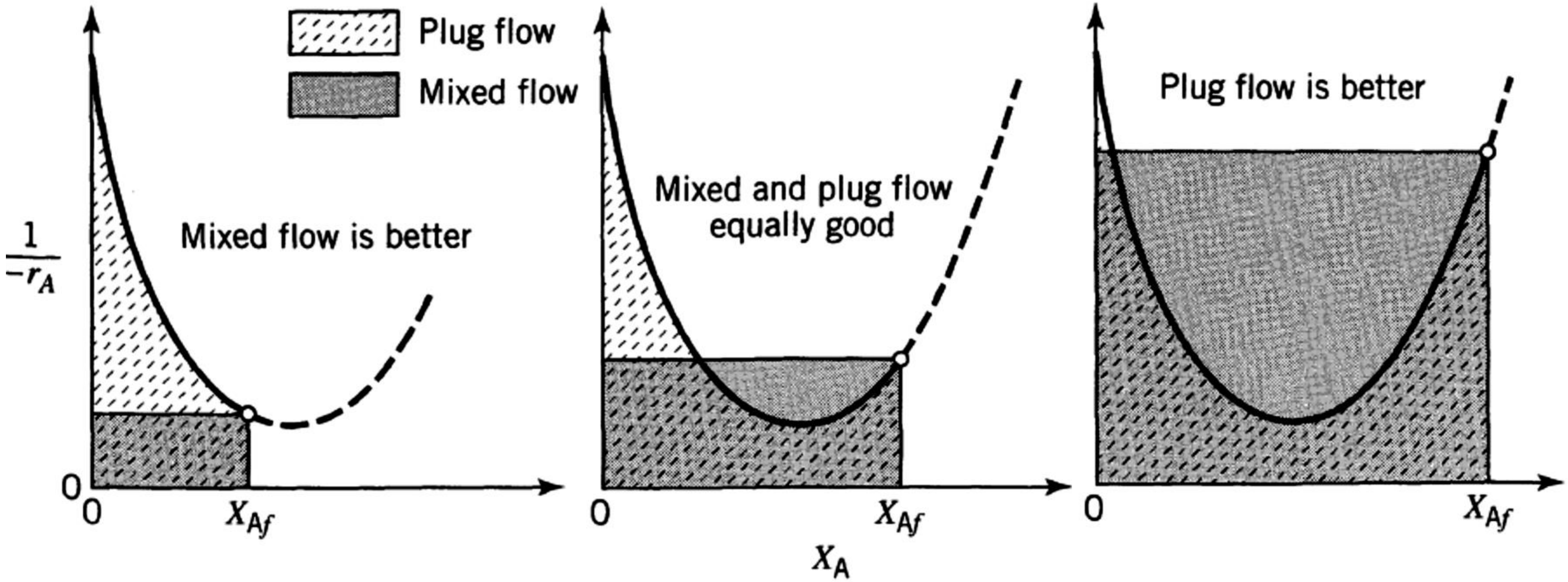

Figure 7-2 MFR vs PFR for autocatalytic reactions

- Thus:

1. At low conversion the MFR is superior to the PFR.
2. At high enough conversions the PFR is superior.

OPTIMUM RECYCLE OPERATION FOR AUTOCATALYTIC REACTION

- These findings differ from ordinary nth-order reactions (n > 0) where
  - the PFR is always more efficient than the MFR.
- In addition, a PFR in autocatalytic reaction will not operate at all with a feed of pure reactant.
  - In such a situation the feed must be continually primed with product, an ideal opportunity for using a recycle reactor.
- When material is to be processed to some fixed final conversion X_{Af} in a recycle reactor, there must be a particular recycle ratio R, which is optimum so as to minimize the reactor volume or space-time.
- The *optimum recycle ratio* is found by differentiating the performance equation for recycle reactor, Eqn.7-1 with respect to R
- $$\text{for} \quad \frac{\tau}{C_{A0}} = \int_{X_{Ai}=\frac{RX_{Af}}{R+1}}^{X_{Af}} \frac{R+1}{(-r_A)}\, dX_A \qquad \text{7-1}$$
- and setting the differential to zero, thus

$$\text{take} \quad \frac{d(\tau/C_{A0})}{dR} = 0$$

OPTIMUM RECYCLE OPERATION

- This operation requires differentiating under an integral sign. From the theorems of calculus, if
- $$F(\boldsymbol{R}) = \int_{a(\boldsymbol{R})}^{b(\boldsymbol{R})} f(x, \boldsymbol{R})\, dx \qquad \text{7-2}$$
- Then
  - $$\frac{dF}{d\boldsymbol{R}} = \int_{a(\boldsymbol{R})}^{b(\boldsymbol{R})} \frac{\partial f(x, \boldsymbol{R})}{\partial \boldsymbol{R}}\, dx + f(\mathrm{b}, \boldsymbol{R}) \frac{db}{d\boldsymbol{R}} - f(a, \boldsymbol{R}) \frac{da}{d\boldsymbol{R}} \qquad \text{7-3}$$
- For our case of Eqn.7-1, we then find
  - $$\frac{d(\tau/C_{A0})}{d\boldsymbol{R}} = 0 = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)} + 0 - \left.\frac{\boldsymbol{R}+1}{(-r_A)}\right|_{X_{Ai}} \frac{dX_{Ai}}{d\boldsymbol{R}} \qquad \text{7-4}$$
- Where

$$\frac{dX_{Ai}}{d\boldsymbol{R}} = \frac{X_{Af}}{(\boldsymbol{R}+1)^2}$$

- Combining and rearranging then gives for the optimum
- $$\left.\frac{1}{-r_A}\right|_{X_{Ai}} = \frac{\displaystyle\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}}{(X_{Af} - X_{Ai})} \qquad \text{7-5}$$

OPTIMUM RECYCLE OPERATION

- The optimum recycle ratio introduces to the reactor a feed whose $1/(-r_A)$ value (KL in Fig. 7-3) equals the average $1/(-r_A)$ value in the reactor as a whole (PQ in Fig. 7-3).
- Figure 7-3 compares this optimum with conditions where the recycle is either too high or too low.

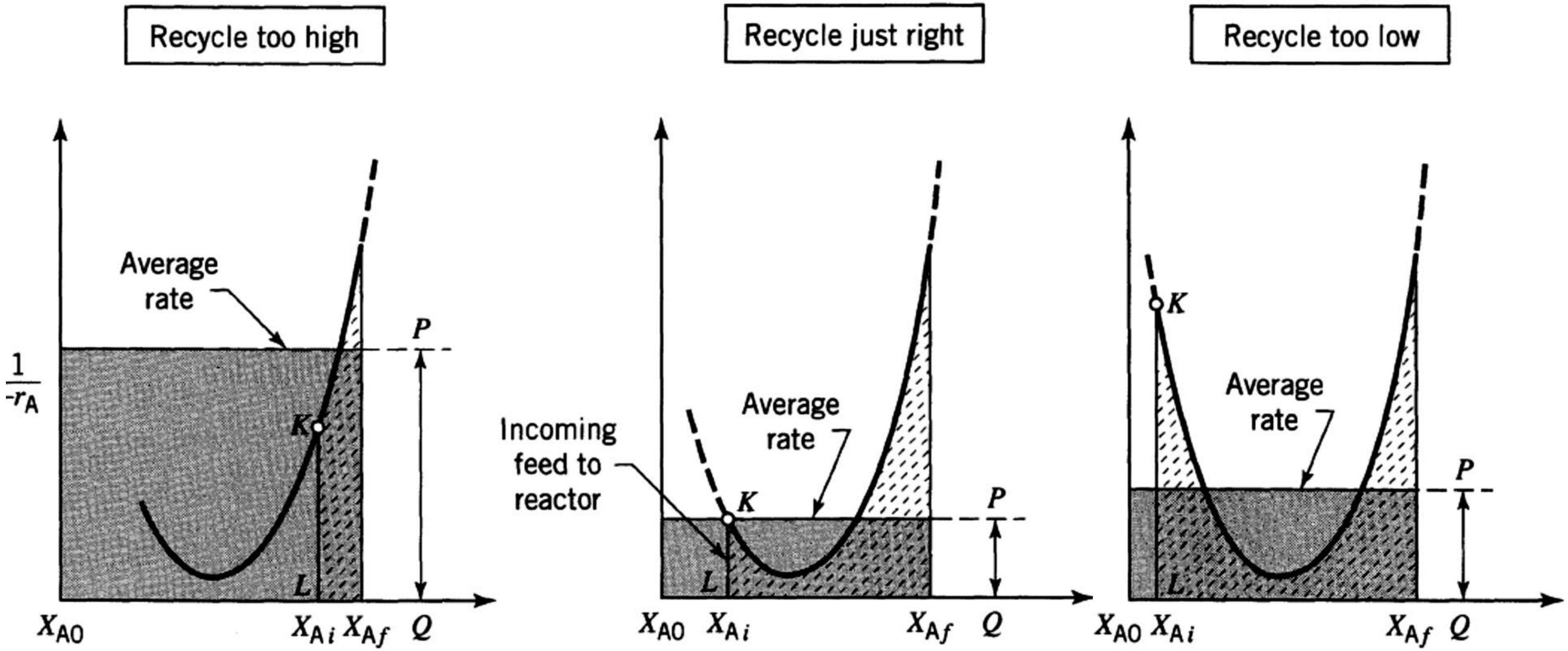

Figure 7-3 Correct recycle ratio for an autocatalytic reaction compared with recycle ratios which are too high and too low.

OCCURRENCE OF AUTOCATALYTIC REACTIONS

- The most important examples of autocatalytic reactions are the broad class of fermentation reactions which result from the reaction of microorganism on an organic feed.
- Another type of reaction which has autocatalytic behavior is the exothermic reaction (say, the combustion of fuel gas) proceeding in an adiabatic manner with cool reactants entering the system.
- In such a reaction, called ***auto-thermal,*** heat may be considered to be the product which sustains the reaction.
  - with plug flow the reaction will die.
  - with MFR the reaction will be self-sustaining because the heat generated by the reaction can raise fresh reactants to a temperature at which they will react.
- Auto-thermal reactions are of great importance in solid catalyzed gas-phase systems.

REACTORS COMBINATION FOR AUTOCATALYTIC REACTIONS

- For autocatalytic reactions all sorts of reactor arrangements are to be considered if product recycle or product separation with recycle is allowable.
- In general, for a rate-concentration curve as shown in Fig. 7-4 one should always try to reach point M in one step (using MFR in a single reactor), then follow with PFR or as close to PFR as possible. This procedure is shown as the shaded area in Fig. 7-4a.
- When separation and reuse of unconverted reactant is possible, operate at point M (see Fig. 7-4b).
- The volume required is now the very minimum, less than any of the previous ways of operating.
- However, the overall economics, including the cost of separation and of recycle, will determine which scheme is the optimum overall.

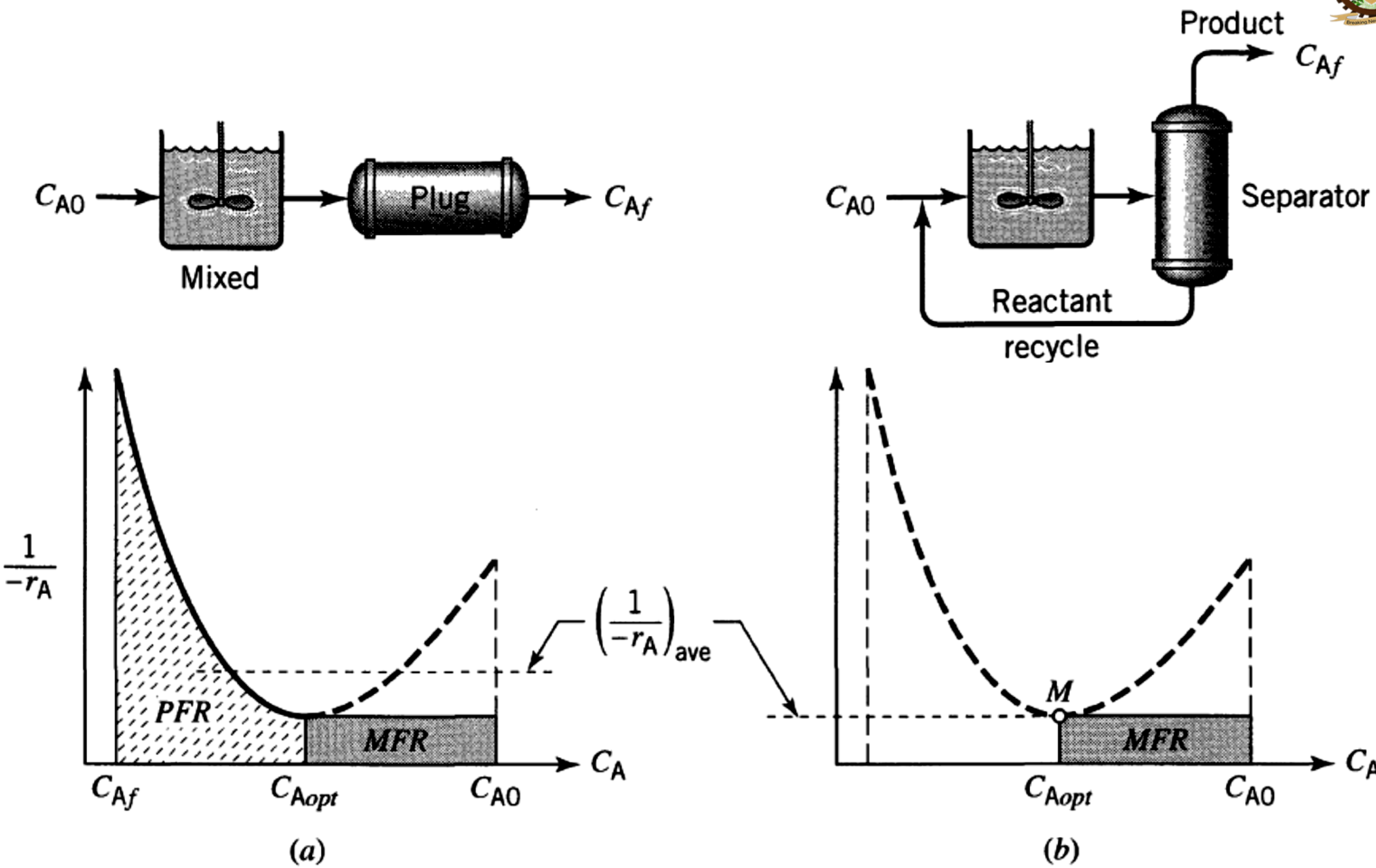

Figure 7-4 *(a)* The best multiple reactor scheme. (b) The best scheme when unconverted reactant can be separated and recycled.

QUESTION ON FINDING THE BEST REACTOR SETUP

In the presence of a specific enzyme E, which acts as a homogeneous catalyst, a harmful organic A present in industrial waste water degrades into harmless chemicals. At a given enzyme concentration C_E tests in a laboratory MFR give the following results:

C_{A0}, mmol/m^3	2	5	6	6	11	14	16	24
C_A, mmol/m^3	0.5	3	1	2	6	10	8	4
τ, min	30	1	50	8	4	20	20	4

We wish to treat 0.1 m^3/min of this waste water having, C_{A0} = 10mmol/m^3 to 90% conversion with this enzyme at concentration C_E.

(a) One possibility is to use a long tubular reactor (assume plug flow) with possible recycle of exit fluid. What design do you recommend? Give the size of the reactor, tell if it should be used with recycle, and if so determine the recycle flow rate in (m^3/min). Sketch your recommended design.

(b) Another possibility is to use one or two stirred tanks (assume ideal). What two-tank design do you recommend, and how much better is it than the one-tank arrangement?

EXAMPLE ON FINDING THE BEST REACTOR SETUP

(c) What arrangement of plug flow and mixed flow reactors would you use to minimize the total volume of reactors needed? Sketch your recommended design and show the size of units selected. We should mention that separation and recycle of part of the product stream is not allowed.

THANK YOU
FOR
YOUR
ATTENTION!
ANY QUESTIONS?