University of Anbar

College of Engineering

Chemical and Petrochemical Engineering Department

Chemical Reacior Design

Third Year

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Lecture No. 13

Autocatalytic Reactions:

In our approach we deal exclusively with their $1/(-r_A)$ versus X_A curves with their characteristic minima, as shown in Fig. 6.18.

Plug Flow Versus Mixed Flow Reactor, No Recycle. For any particular rate-concentration curve a comparison of areas in Fig. 6.19 will show which reactor is superior (which requires a smaller volume) for a given job. We thus find

1. At low conversion the mixed reactor is superior to the plug flow reactor.
2. At high enough conversions the plug flow reactor is superior.

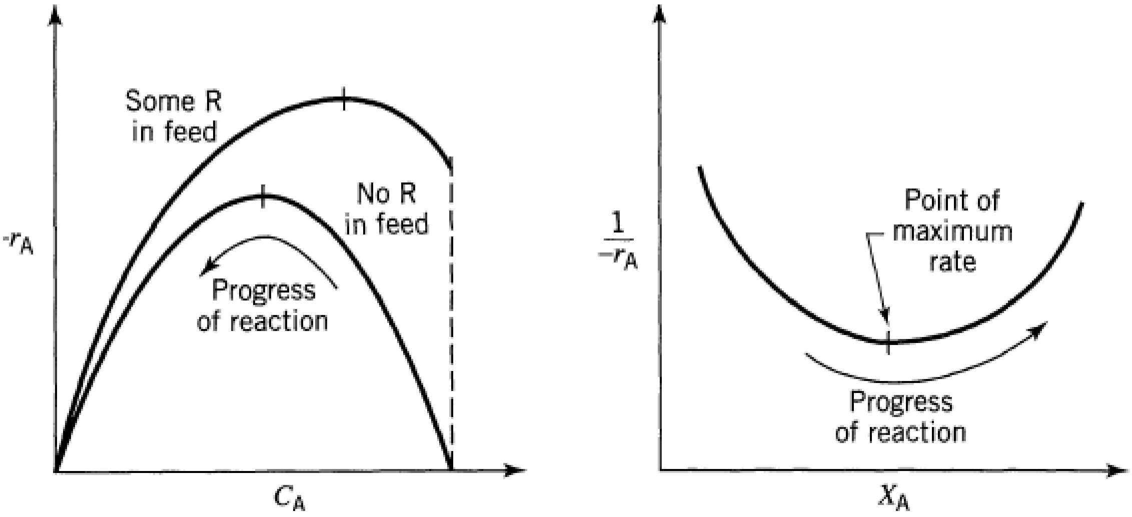


Figure 6.18 Typical rate-concentration curve for autocatalytic reactions, for example:

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

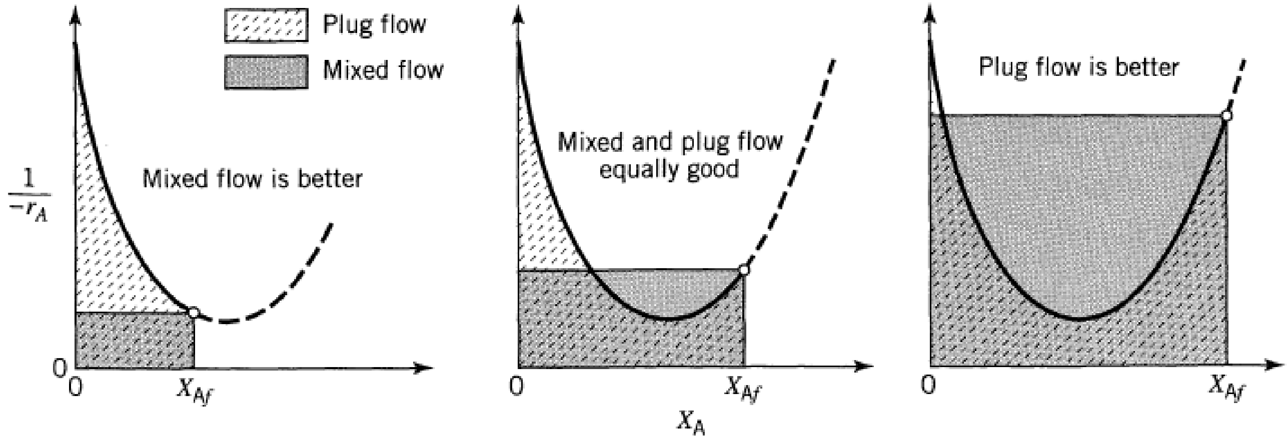


Figure 6.19 For autocatalytic reactions mixed flow is more efficient at low conversions, plug flow is more efficient at high conversions.

These findings differ from ordinary nth-order reactions ($n > 0$) where the plug flow reactor is always more efficient than the mixed flow reactor.

In addition, that a plug flow reactor 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.

Optimum Recycle Operations. When material is to be processed to some fixed final conversion X_{Af} in a recycle reactor, reflection suggests that there must be a particular recycle ratio which is optimum in that it minimizes the reactor volume or space-time. Let us determine this value of $\boldsymbol{R}$.

The *optimum recycle ratio* is found by differentiating Eq. 21 with respect to $\boldsymbol{R}$ and setting to zero, thus

$$\text{take} \quad \frac{d(\tau/C_{A0})}{d\boldsymbol{R}} = 0 \quad \text{for} \quad \frac{\tau}{C_{A0}} = \int_{X_{Ai}=\frac{\boldsymbol{R}X_{Af}}{\boldsymbol{R}+1}}^{X_{Af}} \frac{\boldsymbol{R}+1}{(-r_A)}\, dX_A \qquad \textbf{(25)}$$

This operation requires differentiating under an integral sign. From the theorems of calculus, if

$$F(\boldsymbol{R}) = \int_{a(\boldsymbol{R})}^{b(\boldsymbol{R})} f(x, \boldsymbol{R})\, dx \qquad \textbf{(26)}$$

then

$$\frac{dF}{d\boldsymbol{R}} = \int_{a(\boldsymbol{R})}^{b(\boldsymbol{R})} \frac{\partial f(x, \boldsymbol{R})}{\partial \boldsymbol{R}}\, dx + f(\mathrm{b}, \boldsymbol{R})\frac{db}{d\boldsymbol{R}} - f(a, \boldsymbol{R})\frac{da}{d\boldsymbol{R}} \qquad \textbf{(27)}$$

For our case, Eq. 25, we then find

$$\frac{d(\tau/C_{A0})}{d\boldsymbol{R}} = 0 = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)} + 0 - \left.\frac{\boldsymbol{R}+1}{(-r_A)}\right|_{X_{Ai}} \frac{dX_{Ai}}{d\boldsymbol{R}}$$

where

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

Combining and rearranging then gives for the optimum

$$\boxed{\left.\frac{1}{-r_A}\right|_{X_{Ai}} = \frac{\displaystyle\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}}{(X_{Af} - X_{Ai})}} \qquad \textbf{(28)}$$

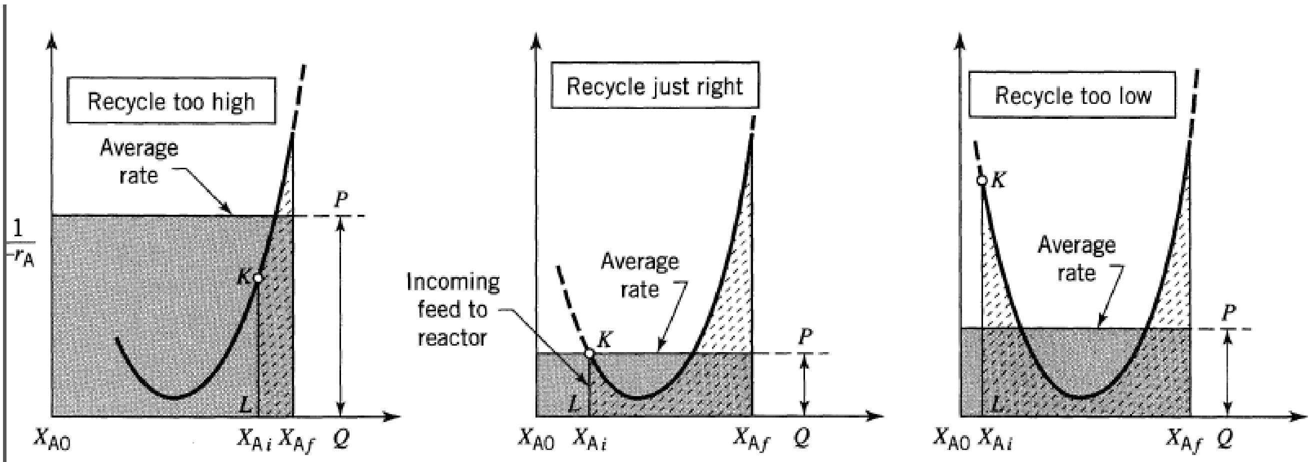


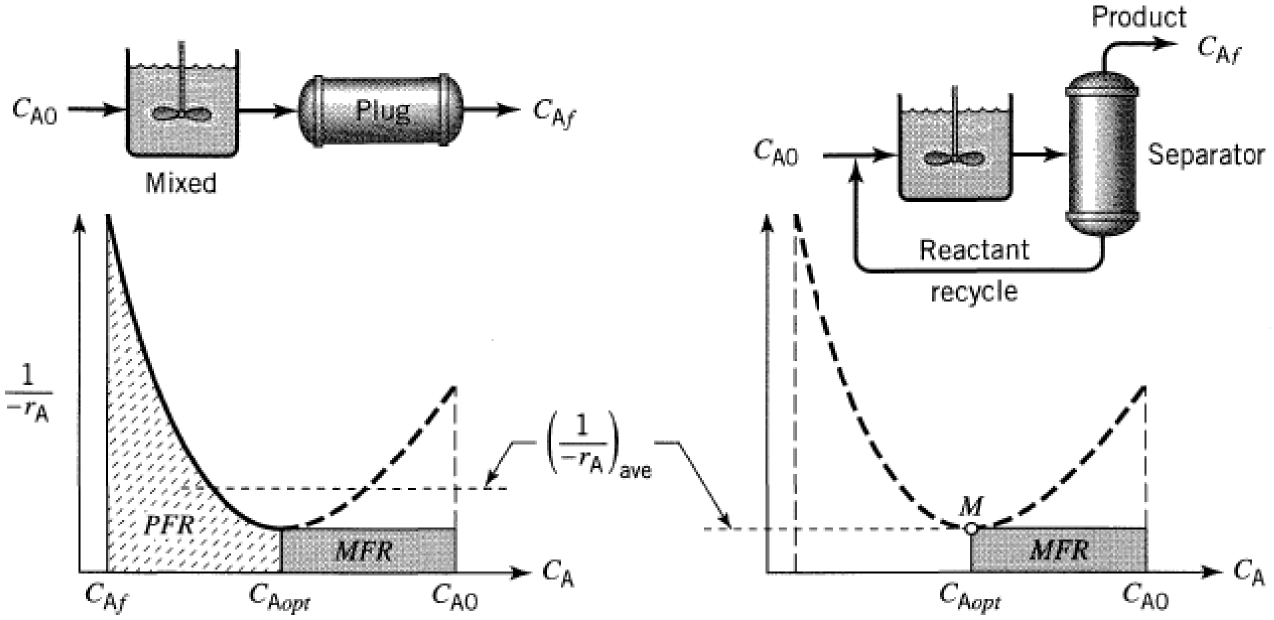
Figure 6.20 Correct recycle ratio for an autocatalytic reaction compared with recycle ratios which are too high and too low.

Reactor Combinations

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. 6.21 one should always try to reach point *M* in one step (using mixed flow in a single reactor), then follow with plug flow or as close to plug flow as possible. This procedure is shown as the shaded area in Fig. 6.21a.

When separation and reuse of unconverted reactant is possible, operate at point *M* (see Fig. 6.21*b*).

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.



(*a*) (*b*)

Figure 6.21 (*a*) The best multiple reactor scheme. (*b*) The best scheme when unconverted reactant can be separated and recycled.

EXAMPLE 6.3 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 mixed flow reactor 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 $C_{A0} = 10$ $mmol/m^3$ 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 cubic meters per minute (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?
- **(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.

SOLUTION

First calculate and tabulate $1/-r_A$ at the measured C_A. This is shown as the last line of Table E6.3. Next, draw the $1/-r_A$ vs. C_A curve. This is seen to be U-shaped (see Figs. E6.3*a*, *b*, *c*) so we must prepare to deal with an autocatalytic type reacting system.

Table E6.3

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
$\frac{1}{-r_A} = \frac{\tau}{C_{A0} - C_A}, \frac{m^3 \cdot min}{mmol}$	20	0.5	10	2	0.8	5	2.5	0.2

Part* (a) *Solution. From the $-1/r_A$ vs. C_A curve we see that we should use plug flow with recycle. From Fig. E6.3*a* we find

$$C_{Ain} = 6.6 \text{ mmol/m}^3$$

$$\boldsymbol{R} = \frac{10 - 6.6}{6.6 - 1} = 0.607$$

$$V = \tau v_0 = \text{area}\,(v_0) = [(10-1)(1.2)](0.1) = \underline{\underline{1.08\ \text{m}^3}}$$

$$v_R = v_0 R = 0.1(0.607) = \underline{\underline{0.0607\ \text{m}^3/\text{min}}}$$

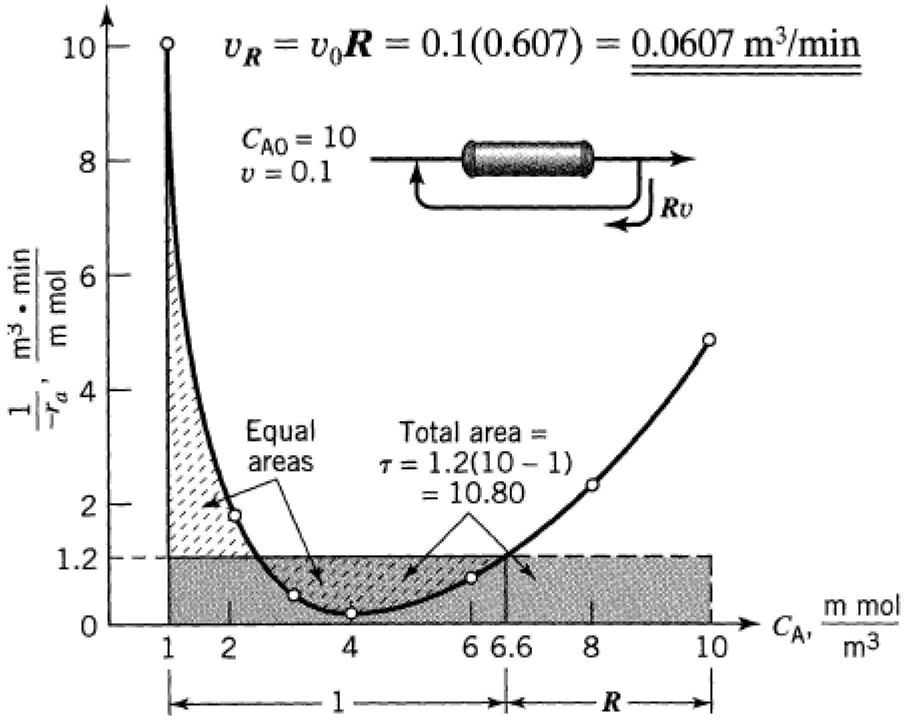


Figure E6.3*a* Plug flow with recycle.

Part* (b) *Solution. Drawing slopes and diagonals according to the method of maximization of rectangles we end up with Fig. E6.3*b*.

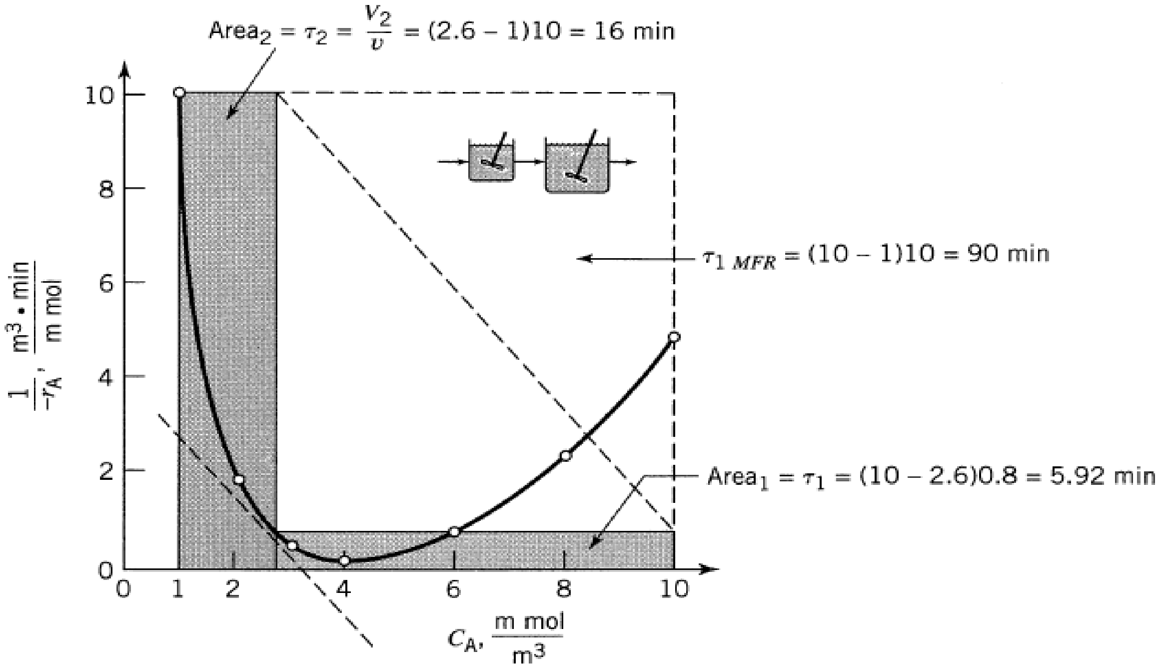


Figure E6.3*b* One and two mixed flow reactors in series.

For 1 tank $\quad V = \tau v = 90(0.1) = \underline{\underline{9.0\ \text{m}^3}}$

$$\text{For 2 tanks} \quad \left.\begin{aligned} V_1 &= \tau_1 v = 5.92(0.1) = 0.59 \\ V_2 &= \tau_2 v = 16(0.1) = 1.6\ \text{m}^3 \end{aligned}\right\} V_{\text{total}} = \underline{\underline{2.19\ \text{m}^3}}$$

Part* (c) *Solution. Following the reasoning in this chapter we should use a mixed flow reactor followed by a plug flow reactor. So with Fig. E6.3*c* we find

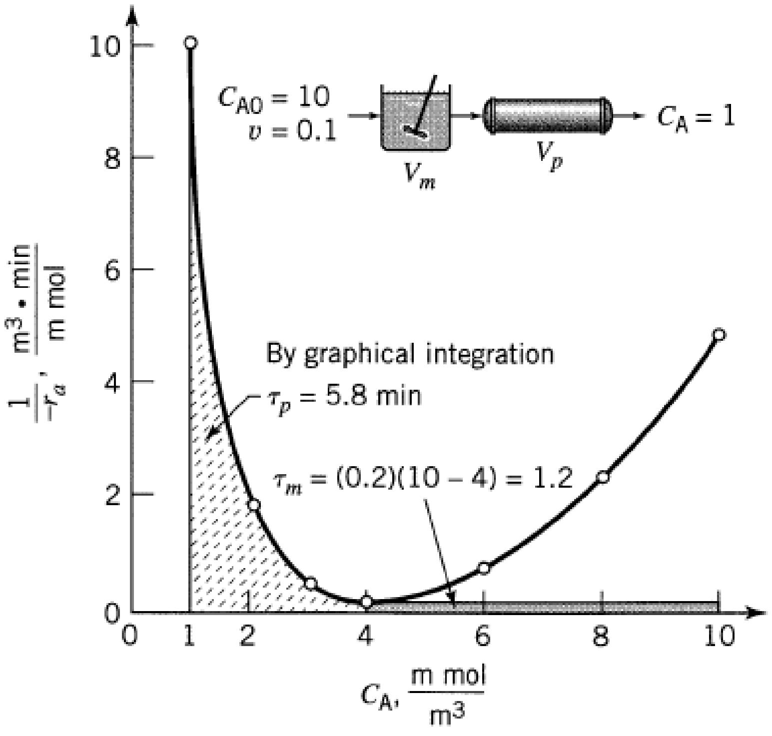


Figure E6.3*c* Arrangement with smallest volume.

$$\left.\begin{array}{ll}\text{For the MFR} & V_m = \upsilon\tau_m = 0.1(1.2) = 0.12\ \text{m}^3 \\ \text{For the PFR} & V_p = \upsilon\tau_p = 0.1(5.8) = 0.58\ \text{m}^3\end{array}\right\} V_{\text{total}} = \underline{\underline{0.7\ \text{m}^3}}$$

Note which scheme (a) or (b) or (c) gives the smallest size of reactors.

what should be the mean residence time of gas in this tube for the same extent of radioactive decay?