CHAPTER 7

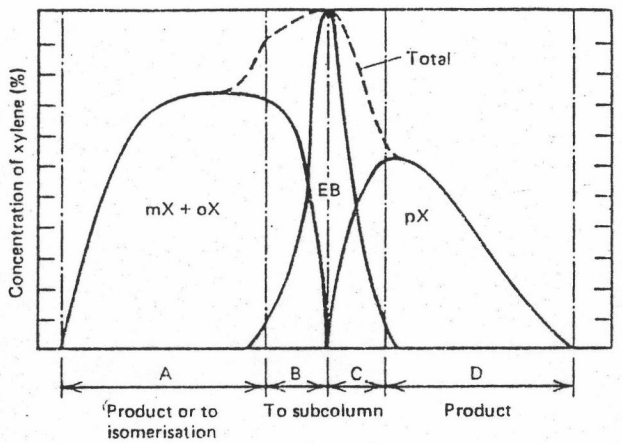
FUNDAMENTAL DESIGN OF ADSORPTION UNIT

An analytic chromatograph can provide highly efficient separation of even very similar molecule species and the possibility of scaling up such processes for large-scale production has therefore attracted much attention. Some interest process applications include a chromatographic process for separation of C_8 aromatic isomers recently developed by Asahi (see Fig. 7.1) and an "Elf-N-Iself" chromatographic process for separation of linear paraffins from light naphtha, as an alternative to the conventional type of cyclic batch "Iso-Siv" process.

7.1 Process Description

A simplified flow sheet for a preparative scale chromatography is shown in Figure 7.2 . Since the system is, in essence, a batch process, it is common practice to use several columns, operating in parallel, in order to provide a more or less continuous flow of product. An automatic timing system controls the injection valves so that a pulse of feed is injected into each column in turn, according to a preprogrammed sequence. The injection cycle is adjusted so that by the time the injector is ready to introduce a second pulse into the first column, the first pulse has progressed far enough along the column that an acceptable separation is maintained.

The effluent from the column is directed alternately to the appropriate traps or receivers in which the products are separated and



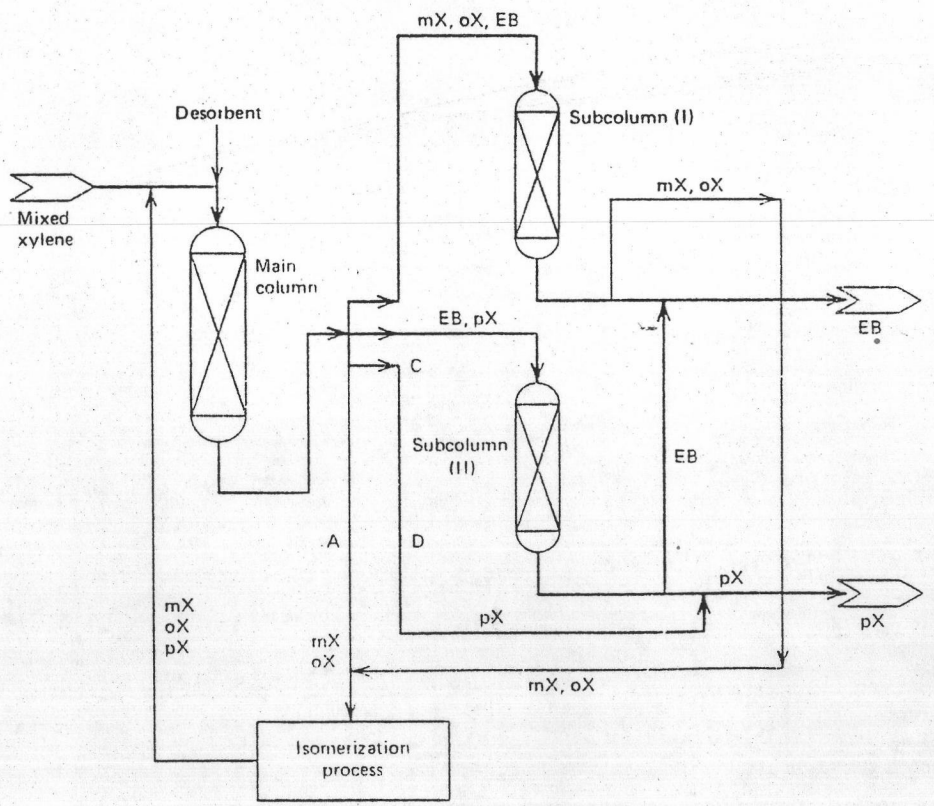


Fig. 7.1 Schematic diagram of Asahi process for separation of C_8 aromatic isomers.

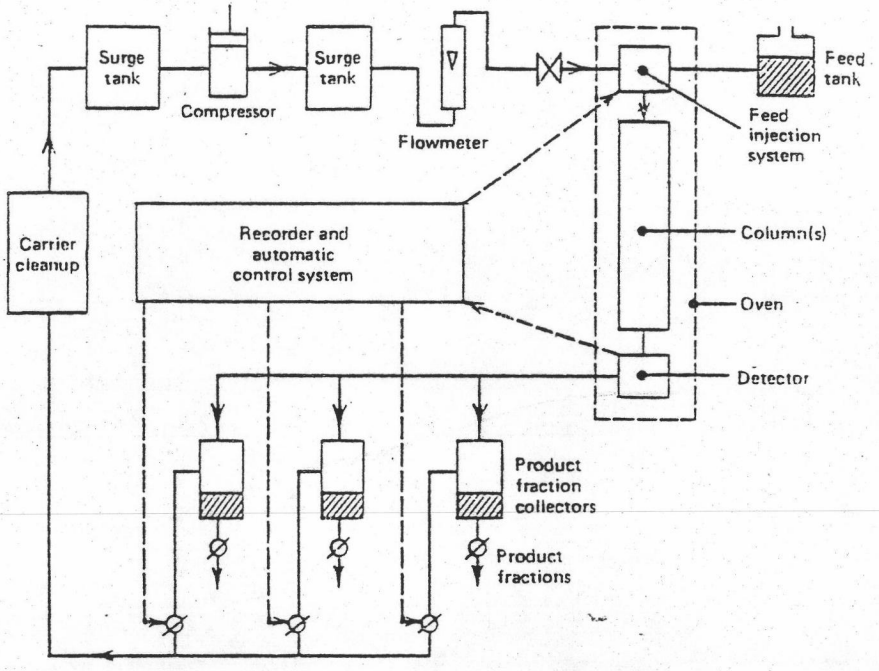


Fig. 7.2 Schematic diagram of production scale chromatographic process.

the carrier is then recycled to the inlet. The process scheme is essentially the same for both gas and liquid operation.

7.2 Column Efficiency

The separating power of a chromatographic process arises because during passage through the column each molecule of an adsorbable species is equilibrated many times between the mobile and stationary phases. Each equilibration is equilivalent to one "equilibrium stage" or "theoretical plate". Even though the separation factor between two components may be small, with sufficient "theoreticaL plates", any desired resolution may be achieved. The great advantage of a chromatographic system is that many theoretical plates can be contained within a column of moderate length.

The height equivalent to a theoretical plate (HETP) for a chromatographic column, representing a hypothetical equilibrium stage in the plate theory of chromatography, can be related to the moments of the chromatographic peak:

$$H = \frac{\sigma^2}{\mu^2} L = 2\frac{D_L}{v} + 2v\left(\frac{\epsilon}{1-\epsilon}\right)\frac{1}{kK} \tag{7.1}$$

where, K >> 1.0 and

$$\frac{1}{kK} = \left(\frac{R_p^2}{3D_m} + \frac{R_p^2}{15\epsilon_p D_p} + \frac{r_c^2}{15K_p D_c}\right)$$

The axial dispersion coefficient, D_L, may be represented by

$$D_L = \gamma_1 D_m + \gamma_2 2R_p v \tag{7.2}$$

where γ_1 and γ_2 are constants. Combining this equation with equation

(7.1) yields an expression of the same general form as the van Deemter equation:

$$H = A + \frac{B}{v} + Cv \tag{7.3}$$

where,

$$A \approx 2\gamma_2 R_p \qquad B \approx 2\gamma_1 D_m \qquad C \approx \frac{2\epsilon}{(1-\epsilon)kK}$$

The minimum value of H occurs at

$$v = \left(\frac{B}{C}\right)^{1/2} = \left[2\left(\frac{1-\epsilon}{\epsilon}\right)\gamma_1 D_m kK\right]^{1/2} \tag{7.4}$$

and is given by

$$H_{\min} = 2\gamma_2 R_p + 2\left[\frac{2\gamma_1 \epsilon D_m}{(1-\epsilon)kK}\right]^{1/2} \tag{7.5}$$

In order to access the magnitude of H_{min} and its dependence on the size of the adsorbent particles, we may consider the three extreme cases of external film, macropore diffusion, and intracrystalline diffusion control.

External film

$$\frac{H_{\min}}{2} \geqslant \gamma_2 R_p + \left(\frac{2\gamma_1 R_p \epsilon}{1-\epsilon}\right)^{1/2} \approx R_p + \sqrt{R_p} \tag{7.5}$$

where we have assumed the typical values $\gamma_2 \sim 1.0$, $\gamma_1 = 0.7$, and $\epsilon = 0.4$.

Macropore diffusion

$$\frac{H_{\min}}{2} \geqslant \gamma_2 R_p + R_p\left(\frac{2\gamma_1 \epsilon \tau}{15(1-\epsilon)\epsilon_p}\right)^{1/2} \approx 1.8 R_p \tag{7.6}$$

where we have again assumed $\gamma_2 \sim 1.0$, $\gamma_1 = 0.7$, $\epsilon = 0.4$, $\epsilon_p = 0.3$, and $\tau = 3.0$.

Intracrystalline diffusion

$$\frac{H_{\min}}{2} = \gamma_2 R_p + r_c \left(\frac{2\gamma_1 \epsilon D_m}{15(1-\epsilon)KD_c} \right)^{1/2} \tag{7.7}$$

The role played by the particle size is now less important since the second term depends only on the crystal size.

7.3 Operating conditions

In selecting operating conditions for analytical chromatograph it is generally desirable to maximize the resolution, subject to some restriction on the maximum acceptable retention time. In preparative chromatography the constraints are more complex since the objective is generally to maximize the production rate with a given column or to minimize the column volume required for a given production rate, subject to allowable limits on product purity. In addition, for a true economic optimization it is necessary to consider, as well as, the capital cost which is determined mainly by the column volume, the energy costs, which are determined mainly by the carrier flow rate and the pressure drop.

Since the production rate increases directly with the quantity of feed injected in each pulse, as well as with the injection frequency, it is common practice to run a preparative column under overload conditions (i.e., outside the Henry's law region) and to inject the sample as a square pulse of finite duration rather than as an ideal delta function. The column is also operated close to the minimum acceptable resolution and successive pulses of feed are injected as frequently as possible subject to the constraint imposed by minimum resolution requirements. It is evident that the basic assumptions of ideal chromatography (linear system, perfect pulse injection) are

violated to a greater or lesser extent in a preparative system and conclusions deduced from the idealized theory will not be quantitatively correct. Nevertheless, the idealized theory provides useful approximate guidance concerning the optimal choice of operating conditions.

It may be shown that, provided the width ($4\sigma_i$) of a rectangular injection pulse is less than about 40% of the width of the response peak measured between the intersections of the tangents at the inflection points with the axis ($4\sigma_A$ or $4\sigma_B$), the standard deviation of the response peak (σ_A or σ_B) will not differ by more than 10% from the standard deviation for an ideal pulse injection. Under these conditions the number of theoretical stages in the column is given, approximately, by

$$N = \left(\frac{\bar{t}_A}{\sigma_A}\right)^2 = \left(\frac{\bar{t}_B}{\sigma_B}\right)^2 \tag{7.8}$$

The resolution between two adjacent peaks is defined by

$$R_{AB} = \frac{\bar{t}_A - \bar{t}_B}{4\sigma_{AB}}, \qquad \sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{7.9}$$

At $R_{AB} = 1.0$ successive peaks are almost resolved while resolution is essentially complete for $R_{AB} \geqslant 1.5$. The number of theoretical stages required to achieve a given resolution in an ideal system is given by

$$N_0 \equiv \frac{L}{H} = 4R_{AB}^2\left(\frac{\alpha + 1}{\alpha - 1}\right)^2 \tag{7.10}$$

while $\alpha = \bar{t}_A/\bar{t}_B$ For strongly adsorbed species (K $\gg$ 1.0), defined in this way is equivalent to the separation factor for the distillation

column. In the case of a rectangular injection pulse, as illustrated in Figure 7.3. The number of theoretical stages required to achieved the same degree of resolution is given by

$$N = N_0\left(1 + \frac{\sigma_i}{\sigma_{AB}R_{AB}}\right)^2 = 4R_{AB}^2\left(\frac{\alpha+1}{\alpha-1}\right)^2\left(1 + \frac{\sigma_i}{\sigma_{AB}R_{AB}}\right)^2 \tag{7.11}$$

Assuming the same minimum separation between peaks introduced in successive injections as between the peaks for adjacent components in the same injection, the time interval between successive injections is given by

$$T = 2(\bar{t}_A - \bar{t}_B) = 8(\sigma_i + R_{AB}\sigma_{AB}) \tag{7.12}$$

and the relative duration of the injection pulse is given by

$$\theta = \frac{4\sigma_i}{T} = \frac{1}{2(1 + R_{AB}\sigma_{AB}/\sigma_i)} \tag{7.13}$$

Using equations (7.11) and (7.13), the required number of theoretical stages may be expressed as a function of θ with α and R_{AB} as parameters:

$$N(\theta) = 4R_{AB}^2\left(\frac{\alpha+1}{\alpha-1}\right)^2(1-2\theta)^{-2} \tag{7.14}$$

The column length is given by $N(\theta)H(v)$ and the production rate (per unit cross-sectional area) by $\theta v\epsilon$ so that the production rate per unit column volume is given by

$$\frac{\theta v\epsilon}{NH} = \frac{\epsilon}{4R_{AB}^2}\left(\frac{\alpha-1}{\alpha+1}\right)^2\frac{v}{H(v)}\theta(1-2\theta)^2 \tag{7.15}$$

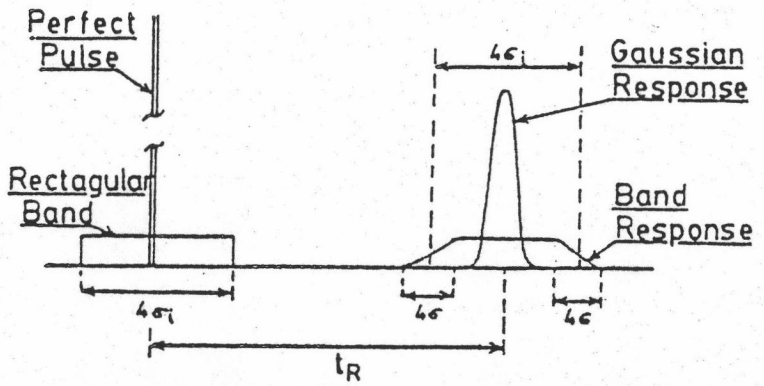


Fig. 7.3 Idealized chromatographic response to (a) a perfect pulse injection and (b) a rectangular pulse injection.

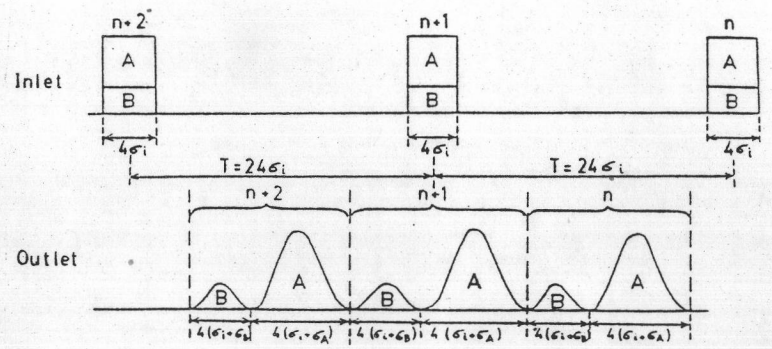


Fig. 7.4 Optimal pulse sequence for production chromatography.

It is evident that, in order to maximize this quantity, θ should be chosen to maximize the function $\theta(1-2\theta)^2$, while the velocity should be chosen to minimize $H(v)/v$. This gives, the optimal value of θ, $\theta = \frac{1}{6}$. More detailed analysis shows that under several different sets of simplifying assumptions, the requirement to minimize power consumption also suggests an optimal value of θ close to one-sixth. The optimal situation is shown in Figure 7.4.

From equation (7.1) it is clear that the requirement to minimize $H(v)/v$ leads to the conclusion that the fluid velocity should be as large as possible. Under these conditions

$$\frac{H(v)}{v} \approx \frac{2\epsilon}{(1-\epsilon)kK} \tag{7.16}$$

The particle size should be as small as possible to maximize k, but the benefits of the reduction in the column volume must be balanced against the greater energy costs arising from the higher pressure drop with small adsorbent particles.

7.4 The design example of the fundamental adsorption unit

The adsorption experiments were carried out at various flow rates and temperatures (as shown below) for the propane and n-butane gases to find the condition which gives the value of R_{AB} (the resolution between two peaks) $\geq$ 1. The NaY zeolite was selected because of its lower adsorption ability of n-butane gas compared to the Offretite/Erionite zeolite at the same temperature (as discussed in the previous chapter).

Some examples of the experimental run are shown.

1. At T = 150^{o}C and flow rate = 6.82 cm^3/min

   Propane $\bar{t}_A$ = 9.4604 min and σ_A = 1.4744 min

n-Butane $\bar{t}_B$ = 10.2314 min and σ_B = 1.7860 min

R_{AB} (from equation(7.9)) = 0.1182

2. At T = 100°C and flow rate = 15.46 cm^3/min

Propane $\bar{t}_A$ = 12.8698 min and σ_A = 1.4848 min

n-Butane $\bar{t}_B$ = 15.3361 min and σ_B = 1.7978 min

R_{AB} (from equation(7.9)) = 0.3756

3. At T = 75°C and flow rate = 24.5 cm^3/min

Propane $\bar{t}_A$ = 14.2437 min and σ_A = 2.02 min

n-Butane $\bar{t}_B$ = 23.9081 min and σ_B = 2.55 min

R_{AB} (from equation(7.9)) = 1.05766

The above results, at T = 75°C, which give the satisfied value of R_{AB} will now be used to design the fundamental adsorption unit for LPG separation. First, the size of the rectangular pulse was assumed.

$$4\sigma_i = 4.832 \text{ min}$$

The time interval between successive injection is calculated from the equation (7.12).

$$T = 29 \text{ min}$$

The number of theoretical stages required to achieve the same degree the same degree of resolution is determined from the equation (7.14)

$$N = 71.239$$

The height equivalent to theoretical plate, H, generally depends on the fluid velocity through the column, and can be calculated from the first and second moments of the chromatographic curve.

$$H = \frac{\sigma^2}{\mu^2} L \qquad (7.17)$$

If the velocity in the above experiment is used, the calculated value of H can be calculated from the equation (7.17), H = 0.24 cm.

Then the length of the chromatographic column required for LPG separation can be approximated.

$$L = H.N = 17.28 \text{ cm}$$

The inside diameter of the column is 3.34 mm. and the particle size is 0.212 mm