

The theory of continuously operated chemical reactors to which part of the reaction mixture leaving the reaction zone is recycled and which are finding ever wider application in chemical and petrochemical processes, was developed in papers [1-5]. The authors derived analytical equations describing the statics (macro-kinetics) of the various important irreversible, reversible, and autocatalytic processes in the reactors. Analysis of the results enabled us to find interesting properties of recycled chemical reactors.

In particular, it was established that in many cases (simple irreversible first-order reactions etc.), the capacity of flow reactors to which the product is recycled is intermediate between the capacities of ideally-mixed and ideal prop flow reactors. It was further established that, if autocatalytic first-order reactions are carried out in such reactors, there may be found an optimum degree of recycling at which the capacity of the recycled reactor exceeds that of ideally-mixed and ideal prop flow reactors.

Below we report a graphical method for calculation of recycled reactors. A typical feature by which the graphical method differs from the analytical calculation method is that with the former one has not to use an analytical expression for the kinetic plot from the experimental data. The method is simple and graphical. It enables the optimum degree of recycling to be rapidly calculated with a minimum amount of computation work. It contributes to a better understanding of the specific operation of a recycled reactor, permits evaluating the position of this reactor type relative to that of ideally-mixed and ideal prop flow reactors from the shape of the original kinetic plot.

We shall discuss the very general case that a simple kinetic reaction takes place in the apparatus. Such a process can be described by a single differential equation of the type:

$$\frac{dx}{d\tau} = \varphi(x), \quad (1)$$

where  $x$  denotes the concentration of one of the reaction products (key component);  $\varphi(x)$  is the kinetic function determined by the reaction type.

Figure 1 shows a diagram of a flow reactor to which the products are recycled. We shall use the following simplifying assumptions: the reaction takes place without causing a change in volume, no radial velocity gradient exists in the apparatus, the hydrodynamical regime of ideal prop flow establishes, and the system is operated isothermally. The mass balance taken over the total current and the reaction product in the point where the fresh current is mixed with the recycled stream then reads:\*

$$\Phi_{vmf} = \Phi_v + \Phi_{vr}, \quad (2)$$

$$\Phi_{vmf}x_{mf} = \Phi_v x_n + \Phi_{vr} x_k, \quad (3)$$

where  $\Phi_v$  denotes the volume of fresh material supplied per unit time to the reactor,  $\Phi_{vr}$  the flow rate of the recycled current,  $\Phi_{vmf}$  the total flow rate (after mixing of the fresh and recycled currents) of the current entering the reactors;  $x_n$ ,  $x_k$ ,  $x_{mf}$  denote the concentrations of the key component in the fresh, recycled, and total streams, respectively.

Introducing the notation  $r = \Phi_{vr}/\Phi_v$ , where  $r$  denotes the degree of recycling, we derive

$$\Phi_{vmf} = \Phi_v (1 + r), \quad (4)$$

$$x_{mf} = x_k - (x_k - x_n)/(1 + r). \quad (5)$$

\* The principles of the derivation of macrokinetic relationships for recycled reactors are discussed in more detail in papers [2, 5].

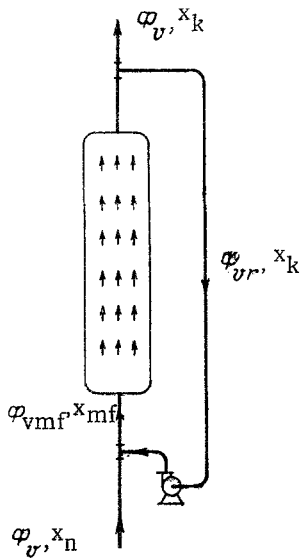


Fig. 1. Diagram of a recycled reactor.

The mean residence time of the reactant liquid  $\tau_r$  in the apparatus equals

$$\tau_r = \frac{O_p}{\Phi_v} = \frac{O_p}{\Phi_{vmf}}(1+r) = \tau_{mf}(1+r), \quad (6)$$

where  $O_p$  denotes the effective reactor volume,  $\tau_{mf}$  the residence time of the mixed flow in the apparatus (the recycled part being taken into account). To find  $\tau_{mf}$ , we return to the kinetic Eq. (1). We shall introduce the parameter

$$\frac{d\tau}{dx} = \frac{1}{\psi(x)} = \psi(x), \quad (7)$$

which may be considered as the differential time increment needed for increasing the conversion from the concentration  $x$  to  $x + dx$ .

The residence time of the flow  $\tau_{vmf}$  in the apparatus then equals

$$\tau_{mf} = \int_{x_{mf}}^{x_k} \psi(x) dx,$$

hence it follows that

$$\tau_r = (1+r) \int_{x_{mf}}^{x_k} \psi(x) dx. \quad (8)$$

$$x_{mf} = x_k - \frac{x_k - x_n}{1+r}$$

We now assume that the plot of the differential time  $\psi$  versus  $x$  is known (Fig. 2).

The differential reaction time  $\psi = d\tau/dx$ , which is the reverse of the true reaction rate, has quite often been used in graphical kinetic calculations by Hougen and Watson and other authors. Plots of  $\psi$  versus  $x$  can be constructed in two ways. First, by graphical differentiation of experimental  $x-\tau$  plots taken either in a batch reactor or in a continuously operated ideal prop flow reactor. Second, by starting from  $x-\theta$  plots taken in an ideally-mixed reactor to which a current without the key component (reaction product) is supplied ( $\theta$  denotes the mean nominal residence time). In the latter case the plot needed is constructed by applying the relationship  $\theta/x = d\tau/dx = \psi(x)$ .

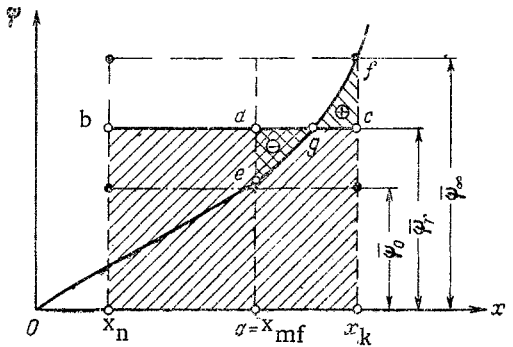


Fig. 2. Graphical calculation of the reactor in the general case of a monotonously increasing function  $\psi = \psi(x)$ .

Let the points  $x_n$  and  $x_k$  on the axis of abscissas (Fig. 2) represent the concentrations of the key component at the inlet and outlet of the reactor system. To find the position of the point  $x_{mf}$ , we divide the line segment  $x_n x_k$  in the ratio  $r : 1$ , so that  $\overline{x_n a} : \overline{a x_k} = r$ . The length of the segment  $a x_k$  will then be equal to  $r + 1$  times the length of the segment  $x_n x_k$ , i.e.,  $\frac{ax_k}{x_n x_k} = \frac{ax_k}{x_n a + ax_k} = \frac{1}{1+r}$ . Consequently, the abscissa of point  $a$ , or the length of segment  $Oa$ , equals

$$\overline{Oa} = \overline{Ox_k} - \overline{ax_k} = \overline{Ox_k} - \frac{\overline{x_n x_k}}{1+r} = x_k - \frac{x_k - x_n}{1+r}.$$

Hence, it follows that point  $a$  represents the concentration  $x_{mf}$ .

We shall now graphically determine the mean value of function  $\psi(x)$  in the interval  $x_{mf} - x_k$ . The mean value of function  $\psi(x)$  in the interval  $x_{mf} - x_k$  equals

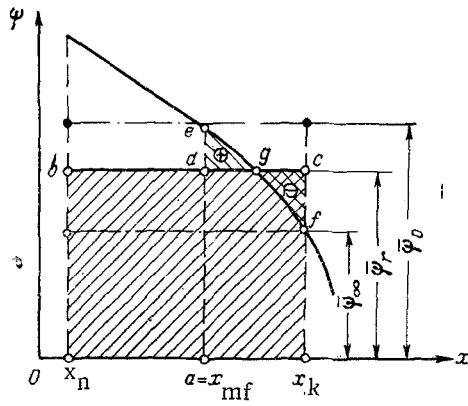


Fig. 3. Graphical calculation of a reactor for the hypothetical case of monotonously decreasing function  $\psi(x)$ .

Taking into account that  $\frac{x_n x_k}{a x_k} = r + 1$ , we find

$$S_{x_n b c x_k} = (1 + r) \int_{x_{mf}}^{x_k} \psi(x) dx = \bar{\psi}_r (x_k - x_n) = \tau_r, \quad (11)$$

in other words, as follows from a comparison of Eq. (10) and formula (8), the area of rectangle  $x_n b c x_k$  is numerically equal to the mean residence time of the original liquid reactant in the reactor.

We shall now discuss how the required reaction times in ideally-mixed and ideal prop flow reactors can be determined by applying the same procedure. In the first reactor type  $r = \infty$ , and, therefore, the length of segment  $a x_k$  tends to zero, while the point  $x_{mf}$  coincides with the point  $x_k$  (see Fig. 2). The corresponding mean value of function  $\psi(x)$  will then equal  $\psi_\infty = \psi(x_k)$ . This can easily be demonstrated by means of formula (9),

$$\bar{\psi}_\infty = \lim_{r \rightarrow \infty} \bar{\psi}_r = \lim_{x_k - x_n \rightarrow 0} \frac{\int_{x_{mf}}^{x_k} \psi(x) dx}{x_k - x_n} = \lim_{\Delta x \rightarrow 0} \frac{\int_{x_k - \Delta x}^{x_k} \psi(x) dx}{\Delta x} = \psi(x_k).$$

The corresponding value of the mean residence time is given by

$$\tau_\infty = \Theta = \bar{\psi}_\infty (x_k - x_n) = \psi(x_k) (x_k - x_n). \quad (12)$$

If the reactor is operated in the regime of ideal prop flow, then,  $r = 0$ , the point  $x_{mf}$  coincides with the point  $x_n$ , and parameter  $\bar{\psi}_0$  is represented by the mean ordinate of curve  $\psi(x)$  in the range  $x_n - x_k$ ,

$$\bar{\psi}_0 = \frac{\int_{x_n}^{x_k} \psi(x) dx}{x_k - x_n}.$$

Consequently, the reaction time required will equal

$$\tau_0 = \bar{\psi}_0 (x_k - x_n) = \int_{x_n}^{x_k} \psi(x) dx. \quad (13)$$

$$\bar{\psi}_r = \frac{\int_{x_{mf}}^{x_k} \psi(x) dx}{x_k - x_{mf}}. \quad (9)$$

The graphical interpretation of this formula is that parameter  $\bar{\psi}_r$  is represented by the height of rectangle  $a d c x_k$ , whose area equals the area under the  $\psi(x)$  curve in the interval  $x_{mf} - x_k$ , i.e., equals the area  $a e f x_k$ . In other words, the horizontal line  $bc$  must be so drawn that the areas of the curved triangles  $deg$  and  $f g c$  are equal.

The area of rectangle  $x_n b c x_k$  with basis  $x_n x_k$  and height  $\bar{\psi}_r$  then equals

$$S_{x_n b c x_k} = (x_n - x_k) \bar{\psi}_r = \frac{x_k - x_n}{x_k - x_{mf}} \int_{x_{mf}}^{x_k} \psi(x) dx = \frac{x_n x_k}{a x_k} \int_{x_{mf}}^{x_k} \psi(x) dx. \quad (10)$$

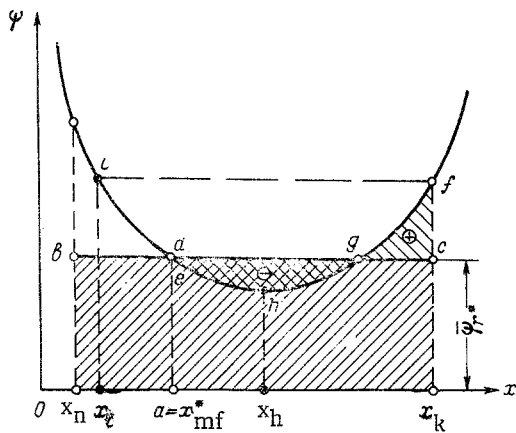


Fig. 4. Calculation of a recycled reactor for the case that the differential time increment passes through an extreme.

if the curve rises monotonously (this holds, for example, for irreversible and reversible  $n^{\text{th}}$  order reactions at  $n > 0$ , both when the reagents are present in the stoichiometric ratio and when they are present in other ratios, etc.), then,  $d\psi/dx > 0$ . Hence we easily derive the following inequalities:  $\bar{\psi}_\infty > \bar{\psi}_r$  and  $\bar{\psi}_r > \bar{\psi}_0$ , which hold for any finite degree of recycling. Under these conditions the regime of restricted recycling will always take a position intermediate between the regimes of ideal mixing and ideal prop flow ( $\pi_\infty < \pi_r < \pi_0$ ).

In the hypothetical case of a monotonously-decreasing function, the differential quotient  $d\psi/dx < 0$  [this would formally correspond to a hypothetical reaction of negative order ( $n < 0$ ) and to regions of the kinetic  $\psi$ - $x$  curves in which the inverse reaction rate drops with increasing concentration, as it does in autocatalytic reactions]; in this case the sequence of the specific mean rates would be reversed; at any final degree of recycling the regime of restricted recycling is less efficient than the regime of ideal mixing, but more efficient than the regime of ideal prop flow, i.e.,  $\bar{\psi}_\infty < \bar{\psi}_r < \bar{\psi}_0$  (Fig. 3) and  $\pi_0 < \pi_r < \pi_\infty$ .

If the plot of function  $\psi$  is a straight line parallel to the axis of abscissas, or  $d\psi/dx = 0$  (which corresponds to a zero-order reaction), all three regimes are equally efficient:  $\bar{\psi}_\infty = \bar{\psi}_r = \bar{\psi}_0$  and  $\pi_0 = \pi_r = \pi_\infty$ .

Analysis of the more complicated situation where the function  $\psi(x)$  is a nonmonotonous function of the concentration  $x$  in the operation range, is of considerable interest. We suppose that the curve  $\psi$  is unimodal, has a single minimum, and that its two branches are monotonous (Fig. 4). Autocatalytic reactions of the first and second orders etc., yield a curve of this shape.

From general considerations we may suppose that here, unlike in the cases considered previously, we may find a degree of recycling  $r = r^*$  at which the capacity of the recycled reactor is higher than that attainable with the regimes of ideal-mixing and ideal prop flow, i.e.,  $\pi_{r^*} > \pi_0$  and  $\pi_{r^*} > \pi_\infty$  or  $\bar{\psi}_{r^*} < \bar{\psi}_0$  and  $\bar{\psi}_{r^*} < \bar{\psi}_\infty$ .

We shall derive a general relationship which enables us to find the concentration  $x_{mf} = x_{mf}^*$  (or the degree of recycling  $r = r^*$ ) corresponding to the maximum specific mean rate  $\pi_r$ , or to the minimum residence time  $\tau_r$  for a given conversion range  $x_n - x_k$ . Utilizing Eq. (11), we transform (9) into

$$\tau_r = (x_k - x_n) \bar{\psi}_r(x_{mf}) = (x_k - x_n) \frac{\int_{x_n}^{x_k} \psi(x) dx}{x_k - x_{mf}}$$

The necessary condition for the minimum of the residence time reads

$$\frac{d\tau_r}{dx_{mf}} = \frac{d\bar{\psi}_r(x_{mf})}{dx_{mf}} = 0,$$

utilizing formula (9), we find

From the constructions mentioned above it is evident that it depends on the ratio between parameters  $\bar{\psi}_0$ ,  $\bar{\psi}_r$ , and  $\bar{\psi}_\infty$ , i.e., on the mean increment of the resistance time, what regime will be the most suitable. In the example considered the specific mean rate (reactor capacity), which is defined as

$$\pi_r = \frac{x_k - x_n}{\tau_r} = \frac{1}{\bar{\psi}_r},$$

and equals the inverse mean increment of the residence time, will be highest in the regime of ideal prop flow; at a finite degree of recycling  $r$  it will have an intermediate value, since the following inequality holds:  $\bar{\psi}_\infty > \bar{\psi}_r > \bar{\psi}_0$  (see Fig. 2). The specific mean rate generally depends on the shape of the  $\bar{\psi}(x)$  curve in the concentration interval  $x_n - x_k$ , and on the position of the point  $x_{mf}$  in this interval, i.e., on the degree of recycling.

In many cases it can a priori be concluded from the shape of the  $\psi = \psi(x)$  curve what regime will be the most suitable for a given reaction. This problem is easy to solve, in particular, when the curve is a monotonous one. In fact,

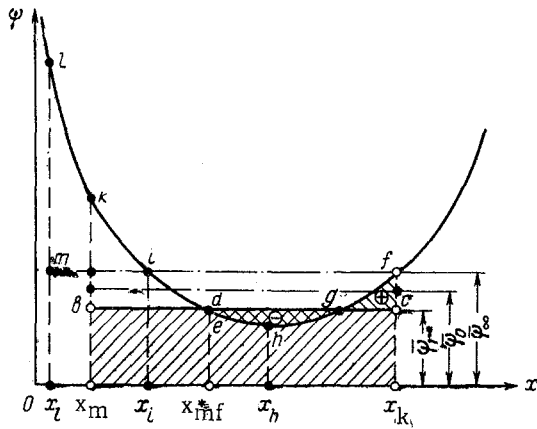


Fig. 5. Operation at the optimum degree of recycling compared with operation under the regimes of ideal mixing and ideal prop flow for cases where function  $\psi$  passes through an extreme.

abscissa  $a = x_{mf}^*$ . We shall now consider how condition (14) can be satisfied in the graphical construction. We write:

$$\int_{x_{mf}^*}^{x_k} \psi(x) dx = (x_k - x_{mf}^*) \psi(x_{mf}^*).$$

The integral at the left-hand side of this equality equals the area of the figure

$$S_{aehgfc} = S_{aehgck} + S_{gfc}.$$

The product at the right-hand side equals the area

$$S_{adgck} = S_{aehgck} + S_{ehg}.$$

Consequently,

$$S_{gfc} = S_{ehg},$$

i.e., the areas of the hatched figures must be equal. It follows, therefore, that to meet condition (14) in the graphical construction and to find the optimum point  $x_{mf}^*$ , it suffices to find such a point  $e$  on the left-hand branch of the curve that the areas of the figures  $gfc$  and  $ehg$  enclosed by the horizontal line through this point, the  $\psi(x)$  curve, and the vertical line  $x = x_k$ , are equal. The abscissa of this point equals  $x_{mf}^*$ .

We shall now prove that the degree of recycling thus found warrants a higher efficiency than the regimes of ideal-mixing and ideal prop flow. We first remark that relationship (14) was derived on the assumption that the point  $x_{mf}^*$  lies in the interval  $x_n - x_k$  and  $x_{mf}^* > x_n$ . In the opposite case ( $x_{mf}^* < x_n$ ) the optimum degree of recycling found by means of formula (15) would be negative, which is physical nonsense.

Figure 5 shows the graphical calculation of reactors operated under the regimes of ideal-mixing and ideal prop flow, or at the optimum degree of recycling. From the graphical construction it is quite evident that parameters  $\bar{\psi}_\infty$  is always larger than  $\psi_{r^*}$ , so that  $\pi_{r^*} > \pi_\infty$ . Parameters  $\pi_0$  will be smaller than  $\pi_{r^*}$ . In fact, the residence time for the optimum degree of recycling will equal the area of the figure

$$\tau_{r^*} = S_{x_n b d g c x_k} = S_{x_n b e h g f x_k}$$

and the residence time for the regime of ideal prop flow is given by

$$\tau_0 = S_{x_n k d h g f x_k} = S_{x_n k e h g f x_k} + S_{b k d},$$

Hence it follows that

$$\tau_0 = \tau_{r^*} + S_{b k d},$$

viz.,  $\tau_{r^*} < \tau_0$ ,  $\pi_{r^*} > \pi_0$ .

$$\psi(x_{mf}^*) = \frac{\int_{x_{mf}^*}^{x_k} \psi(x) dx}{x_k - x_{mf}^*} = \bar{\psi}_{r^*}. \quad (14)$$

From the equation thus derived we can determine the optimum concentration  $x_{mf}^*$ . The corresponding optimum degree of recycling is found by means of Eq. (5); this yields:

$$r^* = \frac{x_{mf}^* - x_n}{x_k - x_{mf}^*}. \quad (15)$$

Condition (14) implies that the mean differential time increment over the range of conversions  $x_{mf}^* - x_k$  achieved in the reactor at the optimum degree of recycling equals the differential time increment corresponding to the concentration  $x = x_{mf}^*$  at the inlet of the reaction zone. Hence, it follows that the horizontal line  $bc$  for the optimum degree of recycling must intersect the curve in the point with abscissa

The difference between the efficiency achieved at the optimum degree of recycling and the efficiencies attained with the regimes of ideal mixing and ideal prop flow depends on how much  $\bar{\psi}_\infty$  and  $\bar{\psi}_0$  exceed parameter  $\bar{\psi}_I$ . The latter ratios are actually determined by the shape of the curve in the interval  $x_\Pi - x_K$ .

The following relationships are easily derived for the relative efficiencies of the regimes of ideal mixing and ideal prop flow. If  $x_\Pi < x_I$  (where the point  $x_I$  is defined by the condition  $S_{mI} = S_{ihf}$ , see Fig. 5), then,  $\bar{\psi}_0 > \bar{\psi}_\infty$ . If  $x_\Pi = x_I$  then  $\bar{\psi}_0 = \bar{\psi}_\infty$ , and if  $x_\Pi > x_I$  the inequality  $\bar{\psi}_0 < \bar{\psi}_\infty$  holds.

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