n = number of molecules associating
R = gas constant
T = temperature, °K.
V = molar volume of the liquid, ml./g. mole
δ = solubility parameter $= \left(\dfrac{\Delta H - RT}{V}\right)^{1/2}$
γ = molal activity coefficient of hydrochloric acid
γ_w = activity coefficient of solute in water phase

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Continuous Stirred Tank Reactors:

Designs for Maximum Conversions of Raw Material to Desired Product. Homogeneous Reactions

P. J. TRAMBOUZE and EDGAR L. PIRET

University of Minnesota, Minneapolis, Minnesota

It is shown in a series of illustrative examples how the conversion efficiency of many reactions can be markedly affected by the type of reactor used, even though the temperatures, catalyst, and basic kinetics are already fixed by the chemistry of the process. For such purpose graphical and analytic criteria are developed which permit the selection of a continuous stirred tank or tubular reactor system to obtain the most advantageous conversion of raw material to desired product. When a continuous stirred tank reactor process is preferable, the optimum number of reactor stages for maximum conversion is one. An example is given of a case where a combination of a continuous stirred tank and a tubular reactor is advantageous.

A new graphical method of reactor design for simple or complex reactions is also introduced. This method utilizes continuous stirred tank reactor data directly rather than batch data or kinetics analyses.

Reactions are classified according to the kinetic and stoichiometric characteristics which determine the allowable design procedures and the differences in the composition paths occurring in batch, tubular, or continuous stirred tank reactors.

The mathematical analysis of continuous stirred tank reactor systems for complex reactions leads to a set of difference equations. For cases of zero- or first-order reactions these are readily solved as illustrated in examples, even when several independent components influence the reaction kinetics.

Even when identical feed compositions are used, the concentrations of the chemical components flowing from any one reactor of a continuous stirred tank reactor system may or may not be the same as the concentration obtainable from a batch process or from a tubular reactor design. Consequently in many cases the engineer can markedly improve the conversion efficiency of an important reaction by selecting the proper type and arrangement of reactor system. The possibility of effecting a gain, however, depends upon the characteristics of the reaction.

From the stoichiometric viewpoint a

P. J. Trambouze is with Institut Francais du Petrole, Rueil-Malmaison, France, and Edgar L. Piret is at the American Embassy, Paris France.

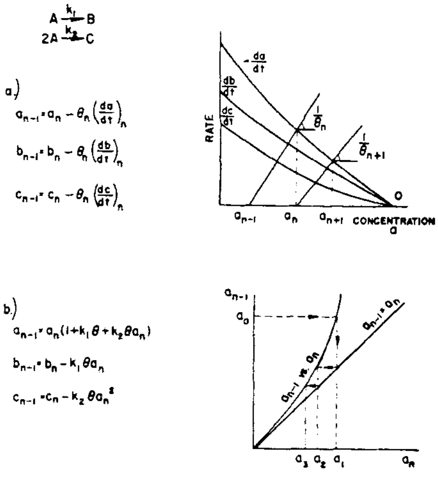

Fig. 1. Design procedures for kinetically simple reactions.

reaction is called *simple* if the evolution of the system can be represented by a single stoichiometric equation (*1*). In other cases the reaction is *stoichiometrically complex.*

From the point of view of kinetics a reaction system is called *simple* if its instantaneous rate depends on the concentration of only one component; it is called *complex* in other cases. A stoichiometrically simple reaction is always kinetically simple, but not vice versa.

It will be seen that the stoichiometric classification of a reaction determines whether or not the conversion can be affected by the choice of reactor type, that is tubular or batch reactor vs. continuous stirred tank reactor. On the other hand the kinetic classification determines whether or not certain convenient procedures may be used in the design of continuous stirred tank reactor processes (Table 1).

For a clear delineation of the areas of application of the several methods, previously published theory on the design of continuous stirred tank reactor systems for homogeneous reactions will first be briefly summarized and also extended.

KINETICALLY SIMPLE REACTIONS

Graphical and algebraic design methods are applicable. In a simple graphical procedure which requires only the availability of batch data giving the concentrations of the components of interest as a function of time, the rates of reaction are obtained by graphical or numerical differentiation of these data. The rates are then plotted as shown in Figure 1a (*7*). The example is for the kinetically simple but stoichiometrically complex reaction

$$\left\{\begin{matrix} A \xrightarrow{k_1} B \\ 2A \xrightarrow{k_2} C \end{matrix}\right\}$$

When one assumes constant volumetric flow rate and adequate mixing, the material balances lead to the three equations shown. The intersections of the rate curves with the straight line of slope $1/\theta_n$, drawn from the feed concentration a_{n-1}, provides the rates of reaction in the n^{th} reactor. These rates with the known feed compositions a_{n-1}, b_{n-1}, c_{n-1} and holding time θ_{n-1} allow by the use of the material balances, for example

$$a_{n-1} = a_n - \theta_n(da/dt)_{a=a_n},$$

the calculation of the desired reactor effluent concentrations a_n, b_n, c_n. The process can be repeated stage by stage for systems of reactors of equal or unequal volumes by simply drawing from each subsequent feed composition shown on the axis the straight lines of slope θ_n, θ_{n+1}, θ_{n+2}, etc.

If the reaction rate constants are known, however, algebraic procedures or the graphical technique illustrated in Figure 1b can be used (*6*). Again material balances lead to the three equations shown in the example. In this case insertion of arbitrary values of a_n into the first equation conveniently allows the plotting of the a_n vs. a_{n-1} curve; then since the effluent of a reactor is the feed to the next reactor in the chain, the step-by-step procedure illustrated provides the concentration of a in each reactor of the chain. Substitution of feed concentrations b_{n-1}, c_{n-1} and of the concentration a_n into the second and third equations allows the calculation of the concentrations of b_n, c_n in the n^{th} reactor, and so on down the chain. In this case equal-volume reactors have been assumed. This graphical technique (or a trial-and-error algebraic solution) is applicable even when, as illustrated above, the difference equations are nonlinear. Analytical solutions for linear systems will be illustrated later.

KINETICALLY COMPLEX REACTIONS

The methods mentioned above are not applicable to kinetically complex reactions, in which their use will lead to error.

Graphical Methods

Batch data known. A graphical design method for complex reactions recently developed is convenient and does not require knowledge of the reaction-velocity constants but directly uses batch-composition—vs.—time data (*1*). In this method the batch-composition paths are plotted on a concentration space representation (Figure 4a). If the product given by a continuous stirred tank reactor stage has the composition (*P*), then, since the instantaneous conversion rates are proportional to the direction cosines of the tangents to the batch curves, the possible compositions of the feeds to this stage at this point will be on a line going through the product-composition point and drawn tangent to the batch-composition path.

The method is applicable when only two and at most three independent components affect the rate of formation of the products of interest and is especially suitable when recycles or side streams are used. If the holding times in each stage are to be equal, a trial-and-error procedure is required.

Continuous stirred tank reactor data known. It is of interest for design purposes to carry out kinetic investigations in the laboratory by the use of a continuous stirred tank reactor rather than batch methods. In this case the effluent compositions from a single stage continuous stirred tank reactor using various feed compositions F_1, F_2 $\cdots$ etc., and different holding times are conveniently plotted as shown in Figure 2a or on rectangular coordinates. On such a chart a straight line which joins a feed-composition point and any one of its continuous stirred tank reactor product

TABLE 1

Classification		Definition	Typical stoichiometric and kinetic equations	Consequences
Stoichiometry	Simple	Single reaction	$A + B \rightarrow C$ $-da/dt = -db/dt = dc/dt = kab$	Tubular and continuous stirred tank reactor composition paths* are identical.
	Complex	Several reactions	$A + B \rightarrow C$ $A + C \rightarrow D$ $-da/dt = kab + k_1ac$ $-db/dt = kab$	Tubular and continuous stirred tank reactor composition paths are different
Kinetics	Simple	Rate depending on only one component	$A \rightarrow B + C$ $2A \rightarrow D$ $-da/dt = ka + k_1a^2$.	Continuous stirred tank reactor design methods of Figure 1 are applicable.
	Complex	Rate depending on more than one component	$A + B \rightarrow C$ $A \rightarrow D$ $-da/dt = kab + k_1a$	Continuous stirred tank reactor design methods of Figure 1 are *not* applicable.

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*By the composition path of a reaction is meant the evolution of the concentrations of the components of interest with respect to time or length in the case of a batch or a tubular reactor in plug flow or with respect to the holding time in a continuous stirred tank reactor.

composition points is tangent at its intersection with the curve to a batch composition path (dotted curve on Figure 2b).

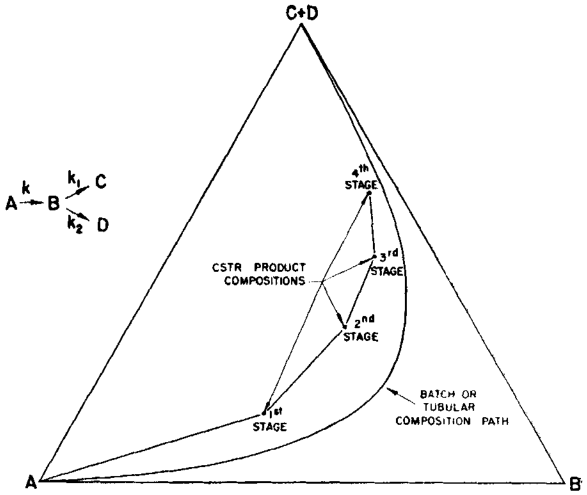

Fig. 3. Results of analytical solution for continuous stirred tank reactor design (illustration 1).

The performance of a continuous stirred tank reactor chain can be readily predicted from the triangular plot as follows. The feed to the first stage is assumed to be F_1 and its product P_1 (Figure 2c). A straight line drawn through P_1 and for example F_2 will intersect at P_2 the continuous stirred tank reactor composition path beginning at F_2. P_2 will then be the product of a second stage, of which the feed is P_1. The straight line $F_2P_1P_2$, it will be noted, is tangent at P_2 to some batch-composition path (dotted curve). Hence as seen before, the feed composition of the continuous stirred tank reactor stage giving the product P_2 can be any point on this tangent line, and thus P_1 may be this feed. The construction can be continued in the same way for other stages. The holding time in each stage can be conveniently found by the addition of a time grid, as illustrated by the θ_1', θ_2' curves shown in Figure 2c. The holding time of the first stage is directly given by the time grid for the single-stage operations, that is $\theta_1' - \theta_1$. The holding time of the second stage is obtained as follows.

From the chart:

θ_2': holding time of a single stage giving the product P_2 from the feed F_2
a_1: concentration of component A in the product P_1
a_2: concentration of component A in the product P_2
a_2^0: concentration of component A in the single stage feed F_2.

From the relation $(da/dt)_{P_2}\theta_2' = a_2 - a_2^0$ the rate of reaction (da/dt) at P_2 can be calculated. Then the holding time of the second stage is obtained from

$$\theta_2 = \frac{a_2 - a_1}{\left(\frac{da}{dt}\right)_{P_2}}$$

The use of several reactors in series affords a means of determining whether components other than A, B, C affect the kinetics and need be considered. Generally interpolation will be required for the synthesis of single-stage curves when data obtained from a multistage laboratory unit are used.

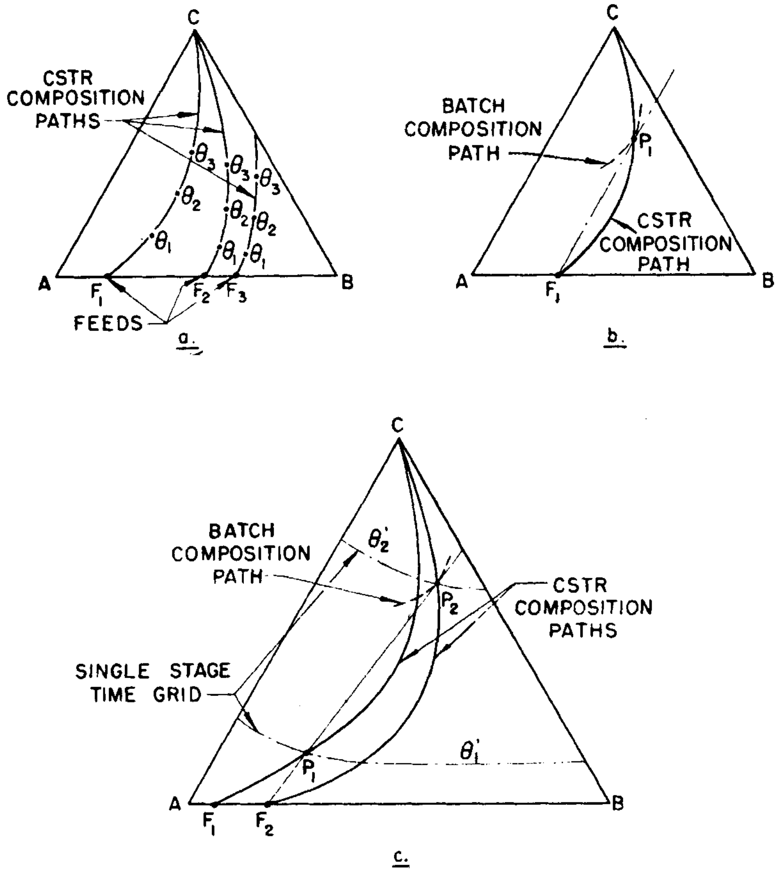

Fig. 2. Design procedure for complex reactions, single-stage, continuous stirred tank reactor composition paths used.

Analytical Method

The reaction rate constants must be known.

The algebraic procedures of reference (*6*) can be used, and the design equations for a variety of complex as well as simple reactions have been tabulated. The algebraic procedures, which for complex reactions are always step by step and frequently require trial-and-error solutions become more tedious as the number of stages increases. In such cases the analytical methods which follow are advantageous.

The design of a tubular reactor for complex reactions leads to a set of first-order differential equations. Similarly, the continuous stirred tank reactor systems design for such reactions requires the solution of a set of first-order difference equations. If all the reactions involved are chemically of zero or first order (for example $da/dt = k$ or $da/dt = k_1a + k_2b$), the problem can easily be solved analytically, since the difference equations in the set are then linear and have *constant* coefficients if the holding times are the same in each stage. The mathematical treatment of such equations is well known (*10*, *11*).

Illustration 1

$$A \xrightarrow{k} B \begin{matrix} \overset{k_1}{\nearrow} C \\ \underset{k_2}{\searrow} D \end{matrix}$$

This case will illustrate that the optimum number of stages required to obtain the maximum concentration of desired product (for fixed operating conditions, for example, given feed composition and fixed nominal holding time) can be immediately calculated from the analytical relations. In this illustration the reactions are assumed to be of order one.

If the holding time, in each stage is the same, and $k\theta = \alpha$; $k_1\theta = \beta$; $k_2\theta = \gamma$, then the material balances are

$$a_{n-1} = a_n(1 + \alpha) \qquad (1a)$$

$$b_{n-1} = b_n(1 + \beta + \gamma) - \alpha a_n \qquad (1b)$$

$$c_{n-1} = c_n - \beta b_n \qquad (1c)$$

$$d_{n-1} = d_n - \gamma b_n \qquad (1d)$$

The solutions are, if $\beta + \gamma \neq \alpha$,

$$a_n = \frac{G_2}{\alpha}(\beta + \gamma - \alpha)\rho_2^{\,n} \qquad (2a)$$

$$b_n = G_1\rho_1^{\,n} + G_2\rho_2^{\,n} \qquad (2b)$$

$$c_n = \frac{\beta G_1}{1 - 1/\rho_1}\rho_1^{\,n} + \frac{\beta G_2}{1 - 1/\rho_2}\rho_2^{\,n} + G_3 \qquad (2c)$$

$$d_n = \frac{\gamma G_1}{1 - 1/\rho_1}\rho_1^{\,n} + \frac{\gamma G_2}{1 - 1/\rho_2}\rho_2^{\,n} + G_4 \qquad (2d)$$

where

$$\rho_1 = \frac{1}{1 + \beta + \gamma} \quad \text{and} \quad \rho_2 = \frac{1}{1 + \alpha}$$

If the feed is pure A at concentration a_0 in an inert solvent so that $b_0 = c_0 = d_0 = 0$, the constants G_1, G_2, G_3, and G_4 are determined by

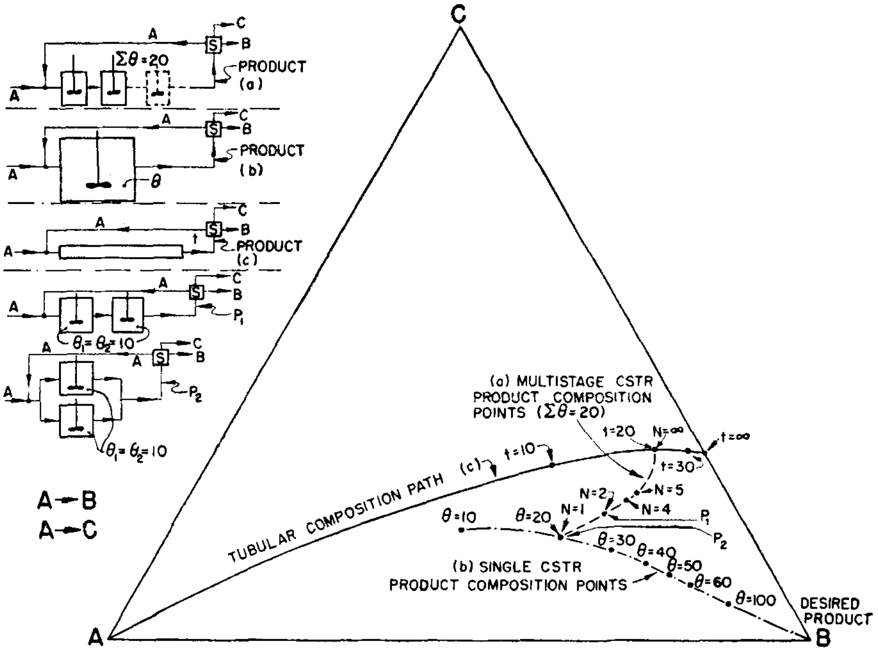

Fig. 5. Comparison of tubular and continuous stirred tank performances. The reaction $A \to C$ is second order.

$$G_1 = -G_2 = \frac{-\alpha a_0}{\beta + \gamma - \alpha}$$

$$G_3 = \beta G_1\left(\frac{1}{1 - 1/\rho_2} - \frac{1}{1 - 1/\rho_1}\right)$$

$$G_4 = \gamma G_1\left(\frac{1}{1 - 1/\rho_2} - \frac{1}{1 - 1/\rho_1}\right)$$

If, however, $\beta + \gamma = \alpha$, then $\rho_1 = \rho_2 = 1/(1 + \alpha) = \rho$, and the solutions, again for $b_0 = c_0 = d_0 = 0$, are

$$a_n = a_0\rho^n \qquad (3a)$$

$$b_n = \frac{\alpha a_0}{1 + \alpha} n\rho^n \qquad (3b)$$

$$c_n = \left(-\frac{\beta}{\alpha}a_0 - \frac{\beta}{1 + \alpha}a_0 n\right)\rho^n + \frac{\beta}{\alpha}a_0 \qquad (3c)$$

$$d_n = \left(-\frac{\gamma}{\alpha}a_0 - \frac{\gamma}{1 + \alpha}a_0 n\right)\rho^n + \frac{\gamma}{\alpha}a_0 \qquad (3d)$$

The value of n to obtain a maximum concentration of B for a fixed-stage holding time can be found by differentiating (2b) with respect to n, so that if $\beta + \gamma \neq \alpha$, at the maximum

$$(\rho_1/\rho_2)^n = \frac{\log \rho_2}{\log \rho_1} \qquad (4)$$

Similarly, if $\beta + \gamma = \alpha$,

$$n = \frac{1}{\log_e(1 + \alpha)} \qquad (5)$$

As a numerical example, $k = 0.1$, $k_1 = 0.02$, $k_3 = 0.02$, and $a_0 = 1$. Two equal-volume reactors in series are to be used, and a value of the holding time is desired which will give the maximum concentration of B in the product. Since $k \neq k_1 + k_2$, relation (4) may be used, and solving for $n = 2$ (θ being the variable) one obtains the value $\theta = 10$. Then $\rho_1 = 0.71$, $\rho_2 = 0.5$ and $G_1 = 0.166$, $G_2 = -0.166$.

When one substitutes into Equations (2), the concentrations of A and B in a four-stage continuous stirred tank reactor chain are

$$b_0 = 0 \qquad a_0 = 1$$

$$b_1 = 0.35 \qquad a_1 = 0.5$$

$$b_2 = 0.41 \qquad a_2 = 0.25$$

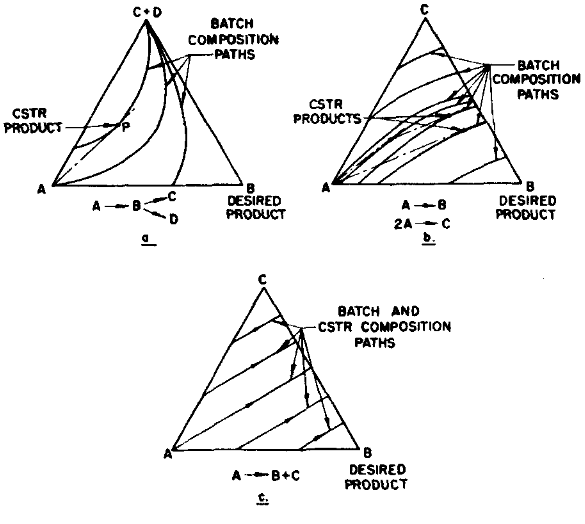

Fig. 4. Reactor-systems selection for optimum conversion based on batch-composition paths: (*a*) tubular reactor preferable, (*b*) continuous stirred tank reactor preferable, (*c*) either system.

$$b_3 = 0.39 \qquad a_3 = 0.12$$

$$b_4 = 0.31 \qquad a_4 = 0.06$$

The maximum tabulated concentration of B occurs, as required, at $n = 2$. These results are represented by Figure 3.

This particular illustration will be of interest in a subsequent paper for a process wherein solvent streams are introduced.

If among the reactions some are chemically of second or higher order, then nonlinear difference equations will appear on the set of material balances. When in the nonlinear difference equations only one variable is present, each of these can be easily solved graphically by the procedure indicated in Figure 1b. Then the remaining set of linear difference equations is solved analytically.

TABLE 2. PRODUCT COMPOSITIONS AND CONVERSIONS FOR SEVERAL CONTINUOUS STIRRED TANK REACTOR SYSTEMS AND FOR A TUBULAR REACTOR

$$A \rightarrow B$$
$$A \rightarrow C$$

The rate equations are $db/dt = ka$ and $dc/dt = ka$..

a. Multistage Continuous Stirred Tank Reactor—Total holding time constant, $\Sigma\theta = 20$

	Product composition			Conversion per pass	Over-all conversion
	a	b	c		
$N = 1$	0.28	0.56	0.16	0.56	0.77 ← P_2
2	0.19	0.60	0.21	0.60	0.74 ← P_1
4	0.15	0.625	0.225	0.625	0.73
5	0.13	0.63	0.24	0.63	0.72
∞*	0.070	0.62	0.31	0.62	0.66

*or tubular reactor in plug flow or batch process

b. Single Continuous Stirred Tank Reactor with variable holding time ($N = 1$)

	a	b	c	Conversion per pass	Over-all conversion
$\theta = 10$	0.41	0.41	0.18	0.41	0.70
20	0.28	0.56	0.16	0.56	0.77 ← P_2
30	0.21	0.64	0.15	0.64	0.81
40	0.175	0.70	0.125	0.70	0.84
50	0.15	0.74	0.11	0.74	0.87
60	0.13	0.78	0.09	0.78	0.90
100	0.085	0.85	0.065	0.85	0.93
∞	0	1.00	0.00	1.00	1.00

c. Tubular reactor or batch process

	a	b	c	Conversion per pass	Over-all conversion
$t = 10$	0.23	0.48	0.29	0.48	0.62
20	0.070	0.62	0.31	0.62	0.66
30	0.020	0.670	0.31	0.67	0.685
∞	0.00	0.69	0.31	0.69	0.69

Illustration 2

$$A \xrightarrow{k} B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C$$

$$A \underset{k_3}{\longrightarrow} D$$

In this example the rate of formation of D is expressed by $dd/dt = k_3a^2$.

$$a_{n-1} = a_n(1 + k\theta + k_3\theta a_n) \qquad (6a)$$

$$b_{n-1} = b_n(1 + k_1\theta) - k_2\theta c_n - k\theta a_n \qquad (6b)$$

$$c_{n-1} = c_n(1 + k_2\theta) - k_1\theta b_n \qquad (6c)$$

$$d_{n-1} = d_n - k_3\theta a_n^{\,2} \qquad (6d)$$

Equation (6*a*) is nonlinear, but since only one variable appears, it can be solved graphically for a_n. Then d_n is determined directly from (6*d*).

Letting $\alpha = k\theta$, $\beta = k_1\theta$, $\gamma = k_2\theta$, $\delta = k_3\theta$, one obtains from (6*b*) and (6*c*)

$$(1 + \beta + \gamma)c_n - (2 + \beta + \gamma)c_{n-1} + c_{n-2} = \alpha\beta a_n \qquad (7)$$

The solution of the homogeneous equation is readily obtained as before:

$$c_n = G_1 + G_2\rho^n$$

where

$$\rho = \frac{1}{1 + \beta + \gamma}$$

The general solution of (7) can be written directly as

$$c_n = G_1 + G_2\rho^n + \sum_{p=0}^{n} \alpha_{p,n}a_p \qquad (8)$$

By substituting (8) into (6) one finds the following relations between the $\alpha_{p,n}$:

$$\alpha_{p,n-2} - K\alpha_{p,n-1} + H\alpha_{p,n} = 0 \quad \text{for} \quad 0 \le p < n$$

where $K = 2 + \beta + \gamma$ and $H = 1 + \beta + \gamma$

$$\alpha_{n,n} = \frac{\alpha\beta}{H} \quad \text{for} \quad n = p$$

and

$$\alpha_{p,n} = 0 \quad \text{for} \quad p < 0 \quad \text{or} \quad p > n$$

Then

$$\alpha_{n-1,n} = \frac{K\alpha\beta}{H^2}$$

$$\alpha_{n-2,n} = \frac{\alpha\beta}{H^3}K[K^2 - H]$$

$$\alpha_{n-3,n} = \frac{\alpha\beta}{H^4}K[K^2 - 2H] \quad \text{etc.}$$

By the substitution of (8) into (6*c*)

$$\beta b_n = \gamma G_1 - \beta G_2\rho^n + \sum_{p=0}^{n} [(1 + \gamma)\alpha_{p,n} - \alpha_{p,n-1}]a_p \qquad (9)$$

COMPARISON OF THE CONVERSION EFFICIENCY OF TUBULAR REACTORS AND CONTINUOUS STIRRED TANK REACTOR SYSTEMS

A reaction is considered in which operating temperature, catalyst concentration, feed composition, and basic kinetics are fixed by the chemistry of the process and for which a suitable tubular or continuous stirred tank reactor design is sought. Before the tubular and continuous stirred tank reactors for several cases are compared, however, it is desirable to define a measure of the efficiency of the process. If, for example, compounds A and B are the starting materials of one or several reactions in a process giving various products, among which C and D are desired, an over-all stoichiometric equation may be written:

$$\alpha A + \beta B \rightarrow \gamma C + \delta D + \text{waste product} \qquad (10)$$

The over-all stoichiometric coefficients and may or may not be constant and are generally dependent upon the conditions of operation.

If the values of compounds A, B, C, and D are respectively V_A, V_B, V_C, and V_D (dollars/mole for instance), an economic efficiency may be defined by

$$E = \frac{\dfrac{a_0F}{\alpha}(\gamma v_C + \delta v_D)}{\dfrac{a_0F}{\alpha}(\alpha v_A + \beta v_B) + (\text{H.C.})} = \frac{\gamma v_C + \delta v_D}{\alpha v_A + \beta v_B + \dfrac{\alpha}{a_0F}(\text{H.C.})} \qquad (11)$$

Since for stoichiometrically simple reactions the coefficients are constant, then for a given temperature the use of a tubular or a continuous stirred tank reactor system will affect the value of E, only as the hourly charges differ. On the other hand if the reaction is stoichiometrically complex, the coefficients, as explained before, can also be influenced by the choice of the type of reactor, and, as will be seen, this can markedly affect the value of E.

For simplicity in the following it is considered that in the reaction $\alpha A = \beta B +$ waste, where B is the desired product, the hourly charges are small compared with the value of the starting material; then from (*11*)

$$E = \frac{v_B\beta}{v_A\alpha} = \frac{v_B}{v_A}f \qquad (12)$$

The conversion in such a case can be taken as the basis of comparison between various processes.

If a stoichiometrically complex reaction is considered (for instance the cases *a* and *b* of Figure 4), it can be seen that since a straight line cannot be drawn from the same feed tangent to the batch or tubular path (*1*), a continuous stirred tank reactor system cannot give the same product as a tubular reactor operating in plug flow with the same feed. However the composition paths of stoichiometrically simple reactions, carried out in idealized tubular or a single stage continuous stirred tank reactor, will be straight lines on such a diagram (Figure 4c) and will coincide, so that either system can be used to obtain the same products and conversion when the same feed composition is used. The continuous stirred tank reactor volume will be larger for the same hourly production.

If B is the desired product in the case of Figure 4, the tubular reactor has an advantage over the continuous stirred tank reactor system in case *a*, but in case *b* the continuous stirred tank reactor system will give a better yield of B than the tubular reactor. MacMullin (*9*), Corrigan (*2*), and Denbigh (*3*, *4*, *5*) have given industrially important examples of such effects.

A general rule can be used to determine whether a tubular or continuous stirred tank reactor system will give the higher conversion efficiency for a particular reaction. The continuous stirred tank reactor system will be better if the concavity of the batch-composition paths is turned toward the desired product-representation point, that is point B. On the other hand if the convexity is turned toward B, the tubular reactor will be preferable.

The analytical and general expressions of these conditions are as follows: for any values of a, b, and c where $\partial^2 b/\partial a^2 < 0$, the tubular reactor is preferable (case *a*). For any values of a, b, and c where $\partial^2 b/\partial a^2 > 0$, the continuous stirred tank reactor system is superior (case *b*).

If, for any values of a, b, and c, $\partial^2 b/\partial a^2 = 0$, the composition paths are straight lines and the two types of reactors will give the same conversion, when the same feed composition is used (case *c*).

If $\partial^2 b/\partial a^2$ is positive in a certain range of values of a, b, and c and negative in another range, a combination of a tubular reactor and continuous stirred tank reactor system may be envisaged, the point of change of design being preferably at $\partial^2 b/\partial a^2 = 0$.

In Figure 4b, it appears that the maximum conversion of A to B for the same feed composition will be obtained when the continuous stirred tank reactor product-composition point is as distant as possible from the batch-composition path. This occurs when only one reactor stage is used. If more than one continuous stirred tank reactor stage is used, then for the same consumption of A less desired product B will be obtained.

The above condition may be understood from another point of view; $-\partial b/\partial a$ is the instantaneous conversion f_i, and as a simple case this is only dependent on a. If $\partial^2 b/\partial a^2 > 0$, f_i is increasing when a decreases, and then

$$f_{CSTR} = \frac{1}{a_0 - a_N} \sum_{i=1}^{N} f_i \cdot \Delta a_i$$

will be larger than

$$f_{\text{tub.}} = \frac{1}{a_0 - a(t)} \int_0^t f_i a \, dt,$$

where

$$a(t) = a_N$$

Furthermore f_{CSTR} will be maximum (for the same values of a_0 and a_N) When $N = 1$, that is when the system uses only one reactor stage.

In some instances of course the volume of the single reactor required to drive a reaction to near completion may be so large that the economic balance, which includes hourly charges, Equation (11), will indicate the use of reactor series even for cases where $\partial^2 b/\partial a^2 > 0$. The over-all economic optimum arrangement of number and sizes of reactors must be determined for each specific case.

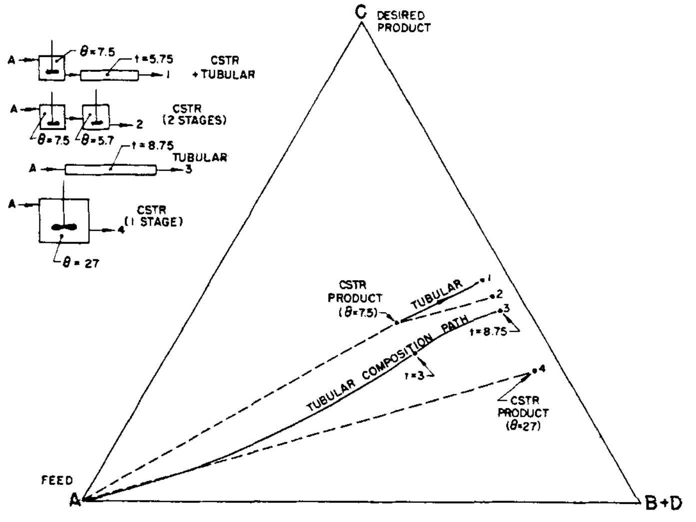

Fig. 6. Combined continuous stirred tank reactor and tubular design for maximum conversion.

As the number of reactors to be used in series is increased, the continuous stirred tank reactor product composition approaches (but does not coincide with) that of the tubular reactor. In reactions where a tubular design produces the highest conversion, a continuous stirred tank reactor design may nevertheless be imposed by other considerations, for example if a high agitation level, independent of flow rates, is required to increase heat transfer rates or to maintain a suspension of heavy particles or liquid- or gas-phase droplets. In such cases the continuous stirred tank reactor system should be multistage to approach the optimum conversion as closely as needed.

In the case of stoichiometrically simple reactions, for which idealized tubular reactors operating in plug flow and continuous stirred tank reactors systems can give the same conversion, the choice of the type of reactor will depend only upon the hourly charges [Equations (*11*)]. The tubular reactor has a higher volumetric efficiency, since it operates at higher mean concentration levels than a continuous stirred tank reactors system (*4*, *8*); however agitation requirements, stability, or other considerations also enter into the choice.

Illustration 3

This illustration shows the marked effect on conversion which can be arrived at by an engineering design of a reactor assembly.

The envisaged reaction is

$$A \begin{array}{l} \overset{k}{\nearrow} B \quad (\text{order } n) \\ \underset{k_1}{\searrow} C \quad (\text{order } m) \end{array}$$

the desired product being B.

$$\frac{db}{dt} = ka^n \quad \text{and} \quad -\frac{da}{dt} = ka^n + k_1 a^m$$

Then

$$\frac{\partial b}{\partial a} = -\frac{ka^n}{ka^n + k_1 a^m}$$

and

$$\frac{\partial^2 b}{\partial a^2} = \frac{kk_1 a^{m+n-1}(m - n)}{(ka^n + k_1 a^m)^2}$$

If

$$m > n, \; \partial^2 b/\partial a^2 > 0,$$

the continuous stirred tank reactor system will be superior.

If

$$m < n, \; \partial^2 b/\partial a^2 < 0,$$

the tubular reactor will be the more efficient.

As a numerical example, $n = 1$, $m = 2$, with $k = k_1 = 0.1$ and $a_0 = 1$; $b_0 = c_0 = 0$.

Table 2 and Figure 5 compare the performances of a tubular reactor and of a continuous stirred tank reactor system (with the same feed of pure A and inert solvent) with various numbers of stages, holding times, and reactor arrangements. For each case the over-all conversion is calculated on the assumption of a complete recycle of component A present in the reaction product. It is apparent that for this case the continuous stirred tank reactor system is markedly superior in conversion efficiency over a tubular reactor and that furthermore for a given total holding time the single stage continuous stirred tank reactor gives the highest conversion. The limiting conversion for large holding times indeed approaches 1.00 for a single continuous stirred tank reactor system but is only 0.69 for a tubular reactor. Thus it is seen in this example how by proper design of a reactor system a reaction can advantageously be forced in a desired direction.

Illustration 4

The following is a case of a batch-composition path having a double curvature. Taking the reaction

$$\begin{array}{lll} A \xrightarrow{k} B & & \text{zero order} \\ \underset{k_1}{\searrow} C & & \text{first order} \\ \underset{k_2}{\searrow} D & & \text{second order} \end{array}$$

where C is the desired product and A the starting material, one has the relations

$$-\frac{da}{dt} = k + k_1a + k_2a^2$$

$$\frac{dc}{dt} = k_1a$$

Then

$$\frac{\partial^2 c}{\partial a^2} = \frac{k_1a(k_1 + 2k_2a) - k_1(k + k_1a + k_2a^2)}{(k + k_1a + k_2a^2)^2}$$

This quantity is $= 0$ when $a^2 = k/k_2$

> 0 when $a^2 > k/k_2$

< 0 when $a^2 < k/k_2$

As a numerical example, $k = 0.025$, $k_1 = 0.2$ and $k_2 = 0.4$, $a_0 = 1$, $b_0 = c_0 = d_0 = 0$

$$\frac{\partial^2 c}{\partial a^2} = 0 \quad \text{when} \quad a = 0.25$$

$$> 0 \quad \text{when} \quad a > 0.25$$

$$< 0 \quad \text{when} \quad a < 0.25$$

The design possibilities shown in Figure 6 are one continuous stirred tank reactor stage followed by a tubular reactor, two continuous stirred tank reactors stages, tubular reactor, or single stage continuous stirred tank reactor. The conversions which are obtained, when the same utilization of A is assumed, are $f_1 = 0.49$, $f_2 = 0.45$, $f_3 = 0.42$, and $f_4 = 0.29$. It is seen that the combination of a continuous stirred tank reactor stage and a tubular reactor gives the highest conversion to C and hence is the design having maximum conversion efficiency.

The case of two compounds of value in the feed A and B and two desired products C and D will now be briefly considered. The efficiency of such a process is defined by Equation (11). By differentiating (11) with respect to a and considering the hourly costs to be small enough to be neglected, one has the relation

$$\frac{\partial E}{\partial a} = \frac{(v_A + \beta/\alpha v_B)\left[v_C \dfrac{\partial(\gamma/\alpha)}{\partial a} + v_D \dfrac{\partial(\delta/\alpha)}{\partial a}\right] - \left(\dfrac{\gamma}{\alpha} v_C + \dfrac{\delta}{\alpha} v_D\right) \dfrac{\partial(\beta/\alpha)}{\partial a} v_B}{\left(v_A + \dfrac{\beta}{\alpha} v_B\right)^2}$$

in which appear the conversions of A to C, that is γ/α, of A to D, that is δ/α and also β/α, the ratio of the moles of the components disappearing by reaction.

Whenever E increases when a decreases, that is if $\partial E/\partial a < 0$, the continuous stirred tank reactor system will be superior. On the other hand if $\partial E/\partial a > 0$, a tubular reactor will be more efficient.

More generally a chemical process ($\sum \nu_i Ai = \sum \mu_i Pi$ + waste) the efficiency of which has been defined(for example by $E = \sum \mu_i v_{Pi} / \sum \nu_i v_{Ai}$) will be considered. If in the range of concentration of the components which are of interest from either a kinetic or cost viewpoint, the efficiency increases as the reaction advances, a continuous stirred tank reactor process (with only one stage) will be the more efficient design. On the other hand wherever along the reaction path E decreases as the reaction proceeds, the tubular reactor will give the higher efficiency. It is clear that even when the temperature, catalyst, and basic kinetics have been fixed by the chemistry of the process, considerable gains in conversion efficiency may accrue from the proper application by the engineer of the techniques of reactor systems design such as described herein. Obviously all costs of separation and recirculation or side stream units, if used, must be included in the economic analysis.

Reactor-systems engineering encompasses the selection of the type, size, and arrangement of the reactors and of the separation, recirculation, and control system considered as a whole. It also is concerned with operating conditions such as temperature, pressure, catalyst concentration, etc. Numerical examples have been given here to illustrate some of the effects which can be achieved by the selection of the type and arrangement of reactors used.

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NOTATION

A, B, C, D = compounds A, B, C, D

a, b, c, d = molar concentrations of compounds A, B, C, D

a_0 = molar concentration of A in feed to system

E = economic efficiency

F = volumetric rate of flow

f = conversion (mole/mole)

$(H.C.)$ = hourly charges on entire production unit, including recirculation costs, amortization, labor, burden rates, and costs of any separation process in the system

k = specific reaction velocity constant

N = number of reactor stages operated in series

t = time

V = vessel volume occupied by reaction medium

v = market value

$\alpha, \beta, \gamma, \delta$ = stoichiometric coefficients or constants

$\theta = V/F$ = nominal holding time

Subscripts

A, B, C, D = components A, B, C, D

n = n^{th} reactor stage

0 = feed to the system (initial conditions)

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