# Continuous Stirred Tank Reactors: A New Graphical Method for Complex Reactions and Reflux Designs

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**The usual graphical CSTR design methods are not adequate for the case of complex reactions involving competing or consecutive steps; therefore graphical design method based on the representation of batch data on a triangular diagram is given and illustrated by several examples. This method does not require a complete analysis of the kinetics of the reaction. Since material balances are easily represented on concentration spaces, the method is especially useful when the design includes recycling, or feed additions along a reactor chain.**

Experiments on chemical reactions are most often performed batchwise in the laboratory, and design methods are needed to calculate the requirements for continuous operation. As there are important limitations to the available techniques for graphical design of stirred flow reactors, these methods require further development and clarification.

The available graphical methods (*3, 4, 7, 10*) all assume that a material balance on a single chemical component is sufficient for design purposes and, for instance, allows the complete determination of the outlet-stream composition when the feed-stream composition is known. This is true when the reaction taking place in the vessel is represented by a single relation, such as $A + B \rightarrow C$, but is not true in general when the reaction involves consecutive or parallel steps. It is therefore interesting to analyze in detail the case of consecutive or parallel reactions (which in the following discussion will be called "complex" reactions, as opposed to simple reactions) which are represented by a single relation like $A + B \rightarrow C$.

A graphical design method for the case of complex reactions has been developed as a result of this investigation. The method may be used when only batch data are available. It does not require a complete analysis for kinetics, as do the available algebraic methods (*3, 6, 8*), although a knowledge of the stoichiometry of the reaction is of course necessary. The method is especially suitable when recycles or side streams are used and might be extended to a three-dimensional space representation similar to representations employed for four-component extraction design.

## COMPARISON OF BATCH AND CSTR PROCESSES

A reaction may be carried out batchwise or continuously, for instance in a continuous stirred tank reactor. In the batch process the composition of the reacting mixture changes with time, and therefore the reaction rate usually is not constant during the run. In a continuous stirred flow process, on the contrary, the reacting mixture is maintained at a steady state composition through the inflow of fresh feed and the outflow of product. The reaction occurs therefore at constant rate. The concentrations in all parts of the reactor are maintained uniform by sufficient agitation.

Another difference between the two processes concerns reaction time. In a batch run all fractions of the reacting mixture are processed during an equal time. In the continuous stirred flow process the different fractions of feed coming into the reactor do not stay for the same length of time. There is thus a distribution in residence times, the average residence time being the reactor holding time. These differences between the two groups of processes were described in detail long ago (*6, 2*). The viewpoint here is somewhat different, and in the following discussion the first object is to compare the products of a batch process and a continuous stirred flow process operating on the same feed.

A reaction process in which the rate depends on the concentrations of the chemical species involved will be considered. The rate may depend also on a score of other factors such as pressure, temperature, catalysts, ionic strength, and so on. All these other factors shall be assumed identically the same in the batch and continuous stirred tank reactor processes which will be compared.

It is assumed that a certain batch process is in operation, with a process time $t$ and a certain feed introduced in totality at the beginning of the process. The problem may be summarized by the following question: Can one, using a feed of the same composition as the initial batch mixture, design a continuous stirred flow process, with a single tank operating with a holding time $\theta$ which will give a product stream of the same composition as the end product of the batch run? This is of course one of the first questions that arise whenever a reaction process is converted from batch to continuous operation. The answer is that such a conversion is possible for simple reactions and some special cases of complex reactions. In such cases there is, as will be seen, a definite relationship between $t$ and $\theta$, the batch process time and the equivalent CSTR holding time. When however the reaction scheme includes consecutive or parallel reactions, which are here called complex reactions, it is found generally that the batch product cannot be duplicated by continuous CSTR operation with the same feed, and thus the equivalent holding time cannot be defined. It is still possible, of course, in many ways to get the batch-product composition with a continuous stirred flow method, but a feed different from the batch process feed would be required.

A reaction described by a single relation, like $A + 2B \rightarrow C$, and proceeding in a batch system can be readily characterized by a degree of conversion $R(t)$ varying with time. Here $C_1$, $C_2$, $C_3$ will be called the concentration of the substances $A$, $B$, $C$ at a time $t$ after the start of the batch re-

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action and $C_{10}$, $C_{20}$, $C_{30}$ the initial concentrations of $A$, $B$, $C$ in the batch process feed. The degree of conversion $R(t)$ is defined as

$$R(t) = \frac{C_{10} - C_1}{1} = \frac{C_{20} - C_2}{2} = \frac{C_{30} - C_3}{-1}$$

The three terms on the right are equal because of the stoichiometric relations in the foregoing reaction scheme.

More generally, if one considers the reaction

$$\alpha_1 A_1 + \alpha_2 A_2 + \ldots + \alpha_p A_n \rightarrow \gamma P$$

where reactants $A_1, A_2 \ldots A_n$ contribute to the formation of a product $P$, one finds that

$$R(t) = \frac{C_{10} - C_1}{\alpha_1} = \frac{C_{20} - C_2}{\alpha_2} = \ldots + \frac{C_{no} - C_n}{\alpha_n} \qquad (1)$$

where, as before $C_{10}$ and $C_1$ are the concentrations of component $A_1$ at time zero and at time $t$.

Such a relation exists for all reactions which are stoichiometrically described by a single relation, that is to say by single irreversible reactions as shown above or single reversible reactions of the type

$$\alpha_1 A_1 + \alpha_2 A_2 + \ldots + \alpha_p A_p \rightleftarrows (-\alpha_{p+1}) A_{p+1} + \ldots + (-\alpha_{p+q}) A_{p+q}$$

The stoichiometric coefficients $\alpha_i$ on the product side are taken as negative in order to keep the form of relation (1) valid for product compounds also.

The criterion which determines whether or not a single function $R(t)$, as defined by Equation (1), will describe the evolution of all components of a batch reaction is of course evident: the rates of reaction for all substances concerned should be proportional to each other during the whole course of the reaction. This condition is satisfied for a reaction like $A + 2B \rightarrow C$, where $dA/dT = (\frac{1}{2}\, dB/2dt) = (-dC/dt)$. It is not satisfied in general for what have been called complex reactions, like the scheme $2A \rightarrow B \rightarrow C + D$.

Since the test of proportionality of rates or of concentration changes is used generally to ascertain reaction stoichiometry, the distinction between the two types of reactions is easily established from analystical laboratory data.

Some reaction schemes involving parallel reactions may exceptionally be described by a single relation like (1). An important case is given by the formation of isomers having the same rate dependence on the reactant concentrations for each isomer.

### Time Equivalence for Simple Reactions

If the concentrations present at various times in a batch process are plotted in concentration space, the result is a reaction path starting at the initial concentration point which can be graduated in terms of the reaction time $t$. A similar path, which will not necessarily coincide with the first, may be obtained by plotting, for different values of the reactor holding time $\theta$, the product concentrations of a stirred flow reactor which receives a feed of the same composition as the initial batch mixture.

Relation (1) states that the reaction path of the batch process for a simple reaction is a straight line in concentration space, its direction parameters being the stoichiometric coefficients $\alpha_1, \alpha_2, \ldots \alpha_p$.

For the continuous stirred flow process, the concentration change across the reactor is given by a mass balance

$$\frac{C_i - C_{io}}{\theta} = \left[\frac{dC_i}{dt}\right]_{batch} \qquad (2)$$

where $[dC_i/dt]_{batch}$ is the reaction rate for component $C_i$ for a batch process at the same composition and physical conditions as the steady state continuous process. Volume changes have been neglected for simplicity of presentation.

For the simple reaction the batch rate is, from relation (1),

$$\left[\frac{dC_i}{dt}\right]_{batch} = -\alpha_i \frac{dR(t)}{dt} \qquad (3)$$

Therefore, from relations (3) and (2) one can write for the CSTR path

$$\frac{C_{io} - C_i}{\alpha_i} = \theta \frac{dR(t)}{dt} \qquad (4)$$

TABLE 1.—TIME EQUIVALENCE FOR SEVERAL SIMPLE REACTIONS

| Reaction | Kinetics | Time equivalence |
|---|---|---|
| $A \rightarrow P$ | $\frac{dA}{dt} = -k$ | $k\theta = kt$ |
| $A \rightarrow P$ | $\frac{dA}{dt} = -kA$ | $k\theta = e^{kt} - 1$ |
| $2A \rightarrow P$ | $\frac{dA}{dt} = -kA^2$ | $C_o k\theta = C_o kt\,(1 + C_o kt)$ |
| $3A \rightarrow P$ | $\frac{dA}{dt} = -kA^3$ | $C_o^2\, k\theta = (1 + 2C_o^2\, kt)^{3/2} - (1 + 2C_o^2\, kt)$ |
| $nA \rightarrow P$ | $\frac{dA}{dt} = -kA^n$ | $C_o^{n-1} k\theta = (1 + (n-1)\, C_o^{n-1} kt)^{n/n-1} - (1 + (n-1)\, C_o^{n-1} kt)$ |
| $A \rightleftarrows B$ | $\frac{dA}{dt} = k_2 B - k_1 A$ | $(k_1 + k_2)\,\theta = e^{(k_1 + k_2)t} - 1$ |
| $\begin{cases} A \rightarrow B \\ A \rightarrow C \end{cases}$ | $\frac{dA}{dt} = -(k_1 + k_2)\,A$ | $(k_1 + k_2)\,\theta = e^{(k_1 + k_2)t} - 1$ |

NOTE: $C_0$ is the initial concentration of $A$.

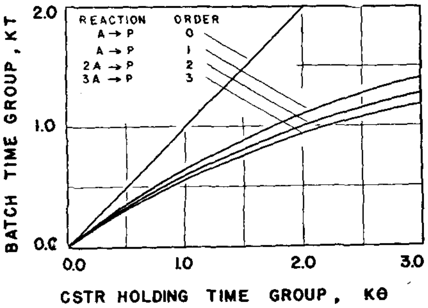

Fig. 1. Time equivalence for simple reactions. (The initial concentration of $A$ is taken as unity.)

And, since (4) can be written for any component in the CSTR,

$$\frac{C_{10} - C_1}{\alpha_1} = \frac{C_{20} - C_2}{\alpha_2} = \cdots \frac{C_{p_0} - C_p}{\alpha_p}$$

But this is the same relation as (1), which describes the batch process path. Therefore the plot of CSTR operation in concentration space for simple reactions is a straight line, which is the same as for the batch process. Hence for the case of simple reactions, the batch product composition may also be obtained by continuous operation. Some general relations for simple reactions readily follow from the foregoing equations. Thus, the relation between the batch process time and the equivalent continuous reactor holding time is obtained from relations (1) and (4):

$$R(t) = \theta \frac{dR(t)}{dt}$$

and therefore

$$\frac{1}{\theta} = \frac{d \ln R(t)}{dt} \qquad (5)$$

The volumetric-CSTR-to-batch-efficiency ratio $e$, which is defined as the ratio of the amounts of product obtained in the same tank volume in equivalent CSTR and batch processes, may also be expressed in terms of $R(t)$. Assuming no dead time in batch operation, one has

$$e = \frac{Ft}{V} = \frac{t}{\theta} = \frac{t}{R(t)} \frac{dR(t)}{dt}$$

Therefore

$$e = \frac{d \ln R(t)}{d \ln t} \qquad (6)$$

Thus the slope of a log-log plot of concentration vs. time affords a convenient means of rapidly evaluating volumetric efficiencies.

Some examples of the time-equivalence relation (5) are given in Table 1 and plotted on Figure 1. The curves for first-, second-, and third-order reactions lie closely together, especially for low conversion. Rough estimations of time equivalence are therefore possible even when the order of the simple reaction considered is not known.

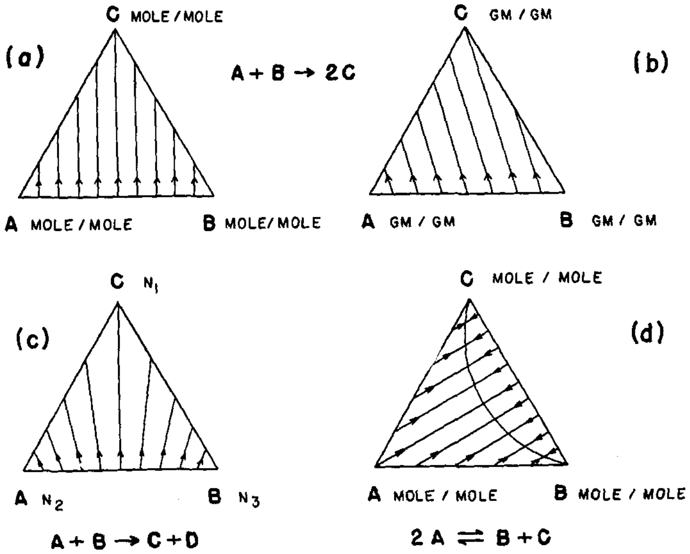

Fig. 2. Reaction paths for simple reactions.

### Complex Reactions

When the process involves reactions of the type which have here been called complex, the batch reaction path is no longer described by expression (1), as from the definition of complex reactions the reaction rates for the different substances are no longer proportional to each other.

The path is therefore no longer a straight line. The same holds for the CSTR reaction path. Examples of such cases are given later and show that batch and CSTR reaction paths for the same feed do not coincide in the case of complex reactions. Thus for the case of complex reactions, the batch and CSTR products from a given feed will never have the same composition. This fact should be recognized and duly taken into account in the design of stirred flow reactors operating on complex reactions and in the selection of batch pilot plant data for such a design.

Especially in order to duplicate rate conditions in the projected continuous reactor, batch pilot-plant data should be taken with an initial batch mixture different from the projected CSTR feed. This will be seen from the samples presented.

## PLOTTING OF REACTION PATHS

Below are some examples of batch reaction-path plots in concentration space representation. The design method for continuous operation is based on this type of plot.

The representation loses much of its practical interest when the number of independent components considered exceeds two. This allows the consideration of three linearly related components by means of a representation of the *triangular diagram type*. Usually the plotted quantities will be concentrations, expressed in mole/mole, gram/gram, or moles/liter of reactant mixture. Rectangular coordinates can also be used.

### Example 1, Simple Reactions

The reaction $A + B \rightarrow 2C$ will be considered. The diagram of the reaction paths, with concentrations expressed in mole fraction, is shown in Figure 2*a*. The reaction paths are straight parallel lines. The same reaction can be plotted with concentrations in grams/grams of mixture. If it is assumed for instance that the mole weights of $A$, $B$, $C$ are proportional to 1, 3, and 2, the diagram takes the form represented in Figure 2*b*.

Another example is the reaction $A + B \rightarrow C + D$, where $D$ is a waste product of no interest, for instance water. Representations may be done in mole fractions on a selected component basis, excluding $D$. This procedure may be generalized to exclude more than one component. If $C_1$, $C_2$, $C_3$ are the mole fractions of $A$, $B$, $C$ on the total basis, then the quantities to plot are

$$n_1 = \frac{C_1}{C_1 + C_2 + C_3},\ n_2 = \frac{C_2}{C_1 + C_2 + C_3},$$

$$n_3 = \frac{C_3}{C_1 + C_2 + C_3}$$

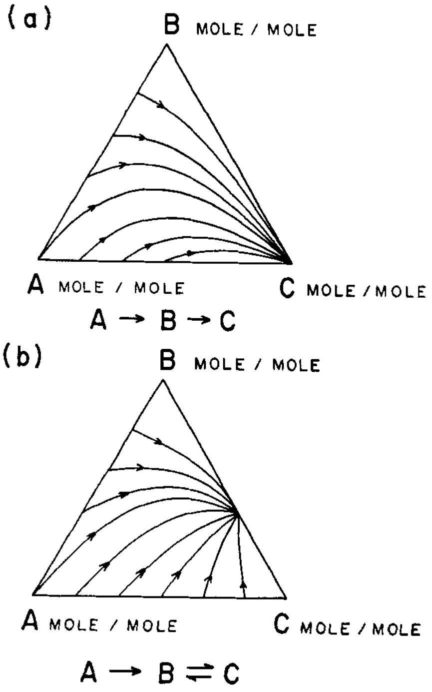

Fig. 3. Batch reaction paths for consecutive reactions.

The paths are given in Figure 2*c*. They converge at the point $n_1 = 1$, $n_2 = 1$, $n_3 = -1$. The existence of such a point is related to the stoichiometry of the reaction. Thus, for the reaction $\alpha A + \beta B \rightarrow \gamma C + \sigma D$ where $\alpha$, $\beta$, $\gamma$, $\sigma$ are the stoichiometric coefficients the coordinates of the common point of the reaction paths are

$$n_1 = \frac{\alpha}{\alpha + \beta - \gamma}, n_2 = \frac{\beta}{\alpha + \beta - \gamma},$$

$$n_3 = \frac{-\gamma}{\alpha + \beta - \gamma}$$

As a last case of simple reactions the scheme $2A \rightleftarrows B + C$ may be examined. This is a reversible reaction, and equilibrium concentrations are related by

$$\frac{[A]^2}{[B]\,[C]} = K$$

This represents an equilibrium line on the diagram, which is given in Figure 2*d*. The reaction paths are still straight, in accordance with the general analysis.

### Example 2, Consecutive Reactions

Until now the cases considered gave straight-line paths. The cases presented below are examples of curved paths. For instance the scheme $A \rightarrow B \rightarrow C$ will be considered. The paths plotted on a mole/mole basis are represented in Figure 3*a*. The curvature depends on the ratio of the rate constants in the two reactions.

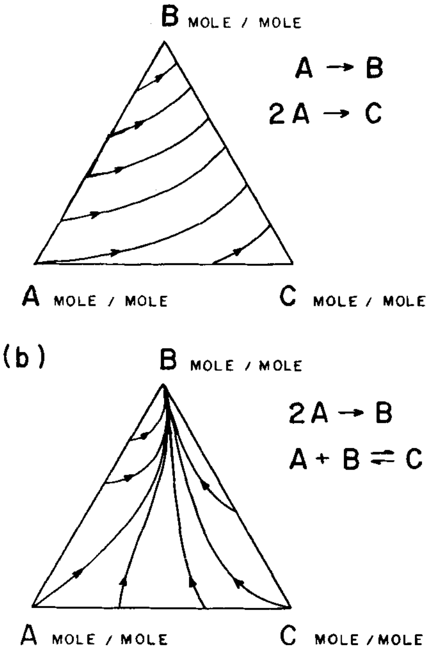

Fig. 4 Batch reaction paths for parallel reactions.

Another example is $A \rightarrow B \rightleftarrows C$. There is an equilibrium point, and the paths are curved (Figure 3*b*). Many variations could be found; however, the main features have been illustrated in Example 1, and the present example brings only the additional characteristic of curvature, which is also found below in the case of parallel reactions.

### Example 3, Parallel Reactions

The scheme

$$\begin{cases} A \rightarrow B \\ 2A \rightarrow C \end{cases}$$

where the reactions are assumed to have different orders, is represented in Figure 4*a*.

Another example is the scheme shown in Figure 4*b*,

$$\begin{cases} 2A \rightarrow B \\ A + B \rightleftarrows C \end{cases}$$

## GRAPHICAL DESIGN METHOD FOR THE CASE OF COMPLEX REACTIONS

The underlying assumption in the graphical CSTR design methods which have appeared in the literature is that the concentration vs. time plot taken during a batch process for one of the reaction components is enough to characterize the whole reaction.

From the general discussion, however, it appears, that this is true only for those kinetic schemes which have been classified as simple reactions. Eldridge and Piret have already pointed out(*5*) that their stepwise graphical procedure could not be used in all the cases. Instead they recommend an algebraic procedure for certain reaction schemes. A new graphical method can therefore be developed with advantage for the case of complex reactions. Such a method is presented below.

### Determination of Product and Feed Compositions

A reaction with curved paths may be represented on a triangular diagram (*A, B, C*) in terms of the concentrations $C_1$, $C_2$, $C_3$ of the three components of interest *A, B, C*. The mass balances over a stirred flow reactor of holding time $\theta$ operating on the represented reaction are

$$C_1 - C_{10} = \theta \left[\frac{dC_1}{dt}\right]_{batch} \qquad (7a)$$

$$C_2 - C_{20} = \theta \left[\frac{dC_2}{dt}\right]_{batch} \qquad (7b)$$

$$C_3 - C_{30} = \theta \left[\frac{dC_3}{dt}\right]_{batch} \qquad (7c)$$

With times eliminated, these relations may be written

$$\frac{[dC_1]}{C_1 - C_{10}} = \frac{[dC_2]}{C_2 - C_{20}} = \frac{[dC_3]}{C_3 - C_{30}} \qquad (8)$$

The geometrical interpretation of these relations is the following. The quantities $[dC_1]$, $[dC_2]$, $[dC_3]$ determine the direction of the tangent to the batch reaction path at the product composition point ($C_1$, $C_2$, $C_3$), and relations (8) mean that the vector which has the projections $C_1 - C_{10}$, $C_2 - C_{20}$, $C_3 - C_{30}$ lies along this tangent. Therefore the feed composition point ($C_{10}$, $C_{20}$, $C_{30}$) lies on the

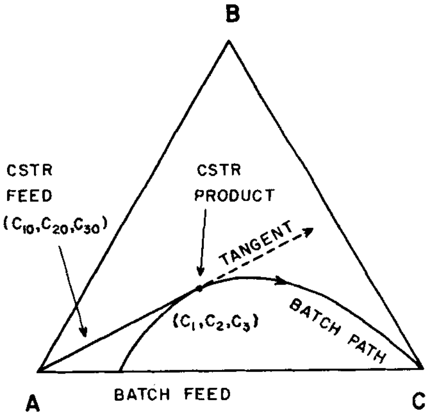

Fig. 5. Graphical CSTR design method.

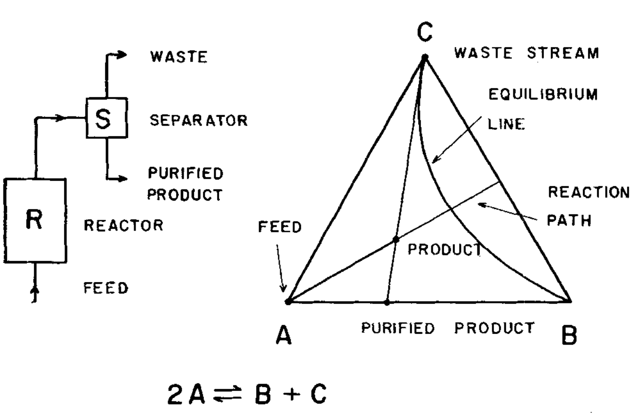

Fig. 6. CSTR design for the reaction $2A \rightleftarrows B + C$ (a single reactor).

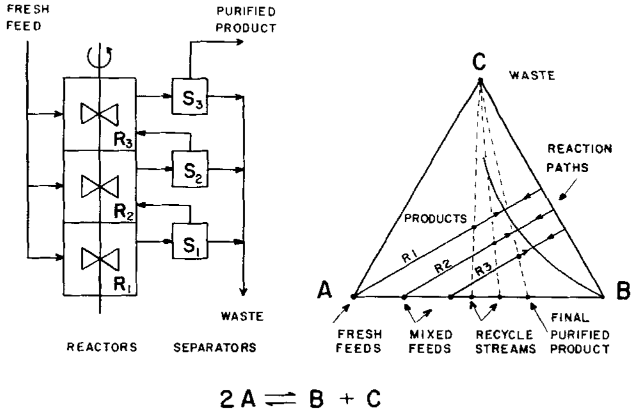

Fig. 8. CSTR design for the reaction $2A \rightleftarrows B + C$ (three reactors with purified product recycling).

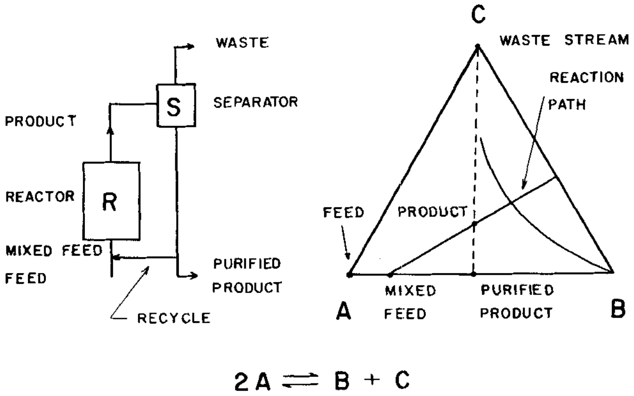

Fig. 7. CSTR design for the reaction $2A \rightleftarrows B + C$ (a single reactor with purified product recycling).

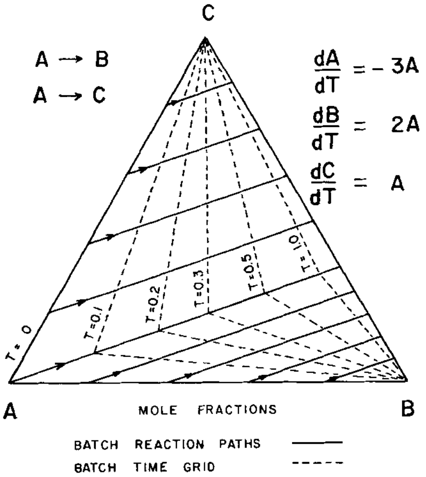

Fig. 9. Example of a batch reaction time grid.

tangent to the batch reaction path going through the desired product composition point $(C_1, C_2, C_3)$.

The construction is illustrated in Figure 5. Actually only points which lie on the backward portion of the tangent are physically acceptable as CSTR feed-composition points. Any feed represented by a point lying on this portion of the tangent may thus be used to obtain the CSTR product of composition $(C_1, C_2, C_3)$.

The construction holds as long as the mass balances (*7a*, *b*, *c*) are valid and generally is not affected by the method of plotting. Linear functions of the concentrations may be plotted instead of the concentrations themselves. The method is valid for instance if plotting is done on a selected-component basis. Thus for a reaction involving compounds *A*, *B*, *C*, *D*, a *D*-free representation of *A*, *B*, *C* in terms of the mole fractions may be used. Such a representation is of interest, however, only if *D*, or other excluded components, has no marked effect on reaction rates.

### Holding Times and Reactor Volumes

In this presentation the emphasis has been placed on the concentrations of the different components and not on reaction time. Time dependence of the reaction may be indicated on the plot of the batch reaction paths in two ways.

1. *Indication of Reaction Rate.* Reaction rate for a given component, for instance *A*, may be indicated along the reaction paths. If extensive design is to be made, it may prove interesting to plot the whole grid of equal reaction-rate curves. The CSTR holding time is then obtained from the CSTR mass balance as

$$\theta = \frac{\Delta C_A}{R_A}$$

where $\Delta C_A$ is the concentration drop in reactant *A* across the reactor (which is known or which can be measured from the plot) and $R_A$ is the reaction rate for component *A* at the desired CSTR product composition point. $R_A$ may be obtained by interpolation from the rate grid. In this representation it is desirable to choose as components of interest those which most influence the reaction rate.

2. *Indication of Reaction Time.* This representation is less handy but is preferable when only a simple design is needed. Direct laboratory data on reaction time are marked along the batch reaction paths. The rate is then obtained by graphical differentiation of the batch curve only at the points where it is needed for design. The CSTR mass balance is then used as above for the calculation of the holding time. Again, in the case of extensive design, it may prove interesting to plot the whole grid of the equal reaction-time curves, the starting points being chosen for instance along the sides of the triangle.

### ILLUSTRATIONS

The foregoing procedures may be illustrated by a few examples.

When design is concerned with simple reactions only, the triangular plots presented here are not necessary and other methods may be applied as well. Still even in these cases the triangular plot may be helpful for the presentation of data, especially when the design involves recycles or side streams, in close analogy with the methods in use in solvent-extraction and separation processes.

In the case, already examined, of the reaction $2A \rightleftarrows B + C$, it may be assumed that $C$ is a waste product which can be easily separated from the reacting mixture. It may be profitable then to recycle the purified product stream containing $A$ and $B$ only, in order to increase the conversion of $A$ and the concentration of $B$ in the reactor effluent. If the holding time proves too high, a series of reactors might be used, with side-stream addition of $A$ and subtraction of $C$. The following designs are illustrated: a single reactor with product purification (Figure 6), a single reactor with recycling of purified product (Figure 7), and a series of three reactors with intermediate purification (Figure 8).

As an example of a time grid and also of a case of parallel reactions which have straight paths, Figure 9 shows two parallel first-order reactions:

$$A \rightarrow B, \text{ with } k_1 = 2$$

$$A \rightarrow C, \text{ with } k_2 = 1$$

Initial compositions are taken along two sides of the triangle. The time grid is represented by straight lines. Rates calculated from the equations of reference (*1*) have been used to illustrate the case of a rate grid. Figure 10 represents the monosulfonation of benzene. The rate is indicated in grams/gram of mixture/hour of benzene–sulfonic acid formed at 140°C. under 1 atm. of benzene. The components indicated are sulfuric acid, water, and benzene–sulfonic acid. Since the reaction paths are plotted on a selected component basis (benzene is excluded), the paths converge at a certain point.

In Figure 10 and in some subsequent figures an equilateral triangular plot has not been used simply to illustrate the point that of course other coordinates and representations of concentration space *can be equally well* used for the graphical procedures presented here.

Several cases of reaction schemes with curved reaction paths are presented below. In the case of the reaction $A \rightleftarrows B \rightarrow C$ with all reactions first order, the rate constant of the first forward reaction is $k_1 = 3$, the reverse rate is $k_2 = 2$, and the second forward reaction has a rate $k_3 = 2$. The paths are presented in Figure 11. To show the difference between batch reaction paths and CSTR reaction paths, a CSTR reaction path corresponding to an initial feed of pure $A$ has been indicated.

It is seen from the figure that if $B$ is the product of interest, the CSTR process will always give a lower concentration of $B$ in its product than the batch process operating on the same feed.

If $B$ is the product of interest, then a CSTR design where $C$ is totally recycled will prevent any new formation of this waste component. Similar designs are possible whenever a waste compound is in equilibrium with a useful compound, provided that separation is economically feasible. Such an example is given in Figure 12 for the reaction $A \rightarrow B \rightleftarrows C$ with total recycling of $C$. Another instance where recycling may prove useful occurs for the case of reaction intermediates. The *recycling of* reaction intermediates maintains their concentration at the steady state value and prevents their loss in the effluent.

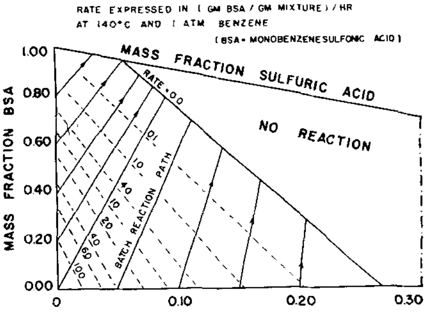

Fig. 10. Example of a rate grid [monosulfonation of benzene(*1*)].

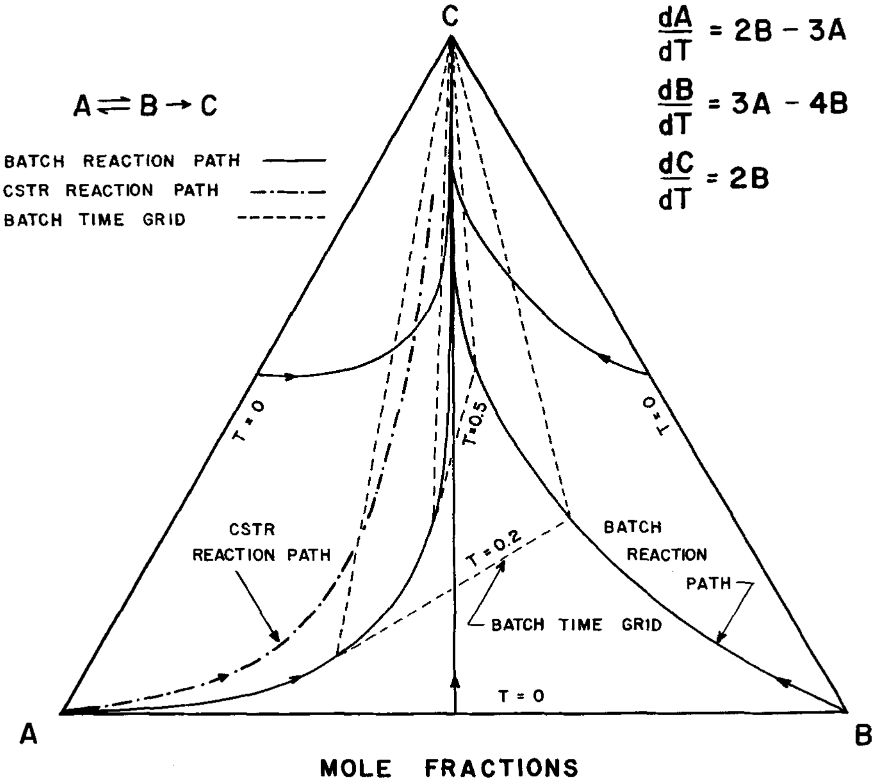

Fig. 11. Example of CSTR and batch reaction paths for a complex reaction.

TABLE 2.—GRAPHICAL DESIGN OF A STRAIGHT CSTR CHAIN

(Data from Figure 13)

| | Tank 1 | | | Tank 2 | | | Tank 3 | | | Tank 4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *A* | *B* | *C* | *A* | *B* | *C* | *A* | *B* | *C* | *A* | *B* | *C* |
| Feed composition, mole % | 100 | 0 | 0 | 48.5 | 25 | 26.5 | 25.5 | 20.5 | 54 | 14 | 13 | 73 |
| Product composition, mole % | 48.5 | 25 | 26.5 | 25.5 | 20.5 | 54 | 14 | 13 | 73 | 5 | 5 | 90 |
| Rate of production of *C* | 50 moles/hr. | | | 41 moles/hr. | | | 26 moles/hr. | | | 10 moles/hr. | | |
| Increase in *C* | 26.5 moles | | | 27.5 moles | | | 19 moles | | | 17 moles | | |
| Holding time | 0.53 hr. | | | 0.67 hr. | | | 0.73 hr. | | | 1.70 hr. | | |

Figure 13 shows the design of a straight chain of four continuous stirred tank reactors on the reaction $A \rightleftarrows B \rightarrow C$ the rate expressions of which are given in Figure 11. Table 2 shows the graphical data taken from Figure 13. The holding times are calculated as the ratio of the concentration increase of $C$ across the reactor to the rate of production of $C$. This rate is proportional in the example to the mole fraction of $B$. For illustrative purposes the rates have been multiplied by 100, times being expressed in hours.

As a last example and somewhat of a generalization of the method, the case of a copolymerization reaction will be considered. The two monomers are styrene ($S$) and β chlorethylacrylate ($A$).

The differential equation of the batch reaction paths is, from reference(*9*),

$$\frac{dS}{dA} = \frac{S}{A} \frac{r_1 S + A}{S + r_2 A} \qquad (9)$$

with

$$r_1 = 0.59$$

$$r_2 = 0.08$$

The quantities plotted in Figures 15 and 17 are the mole percentage of monomers $S$ and $A$ and of monomers polymerized. Other ingredients of the reactive emulsion, such as catalyst, soap, and water, are not considered. The rate of this reaction is practically independent of monomer concentrations and may be assumed in the example to be 10 mole % of monomer converted/hr. The reaction paths, calculated from Equation (9), are presented in Figure 14.

Since polymer composition varies with the composition of the generating monomer mixture, according to Equation (9), which is plotted

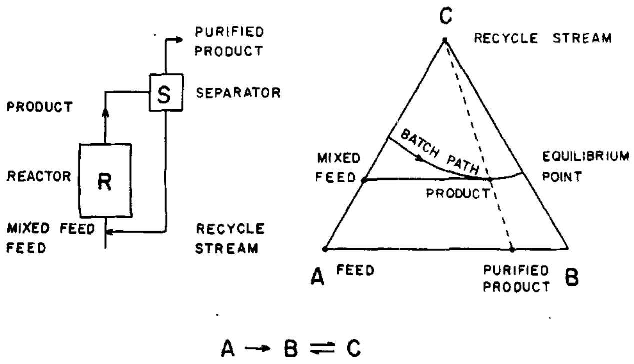

Fig. 12. Example of a CSTR design with recycling of waste.

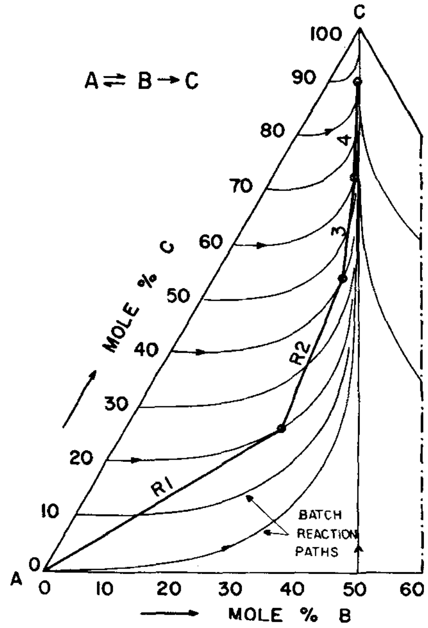

Fig. 13. Design of a straight chain of four CSTR's for the reaction $A \rightleftarrows B + C$.

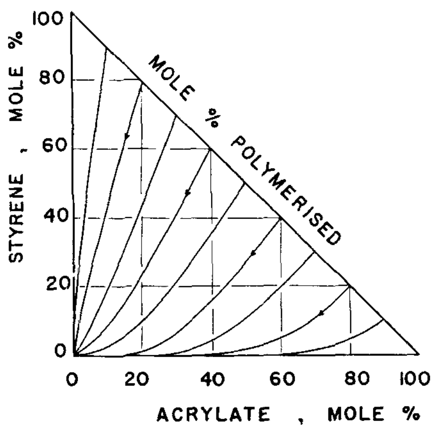

Fig. 14. Batch copolymerization reaction paths.

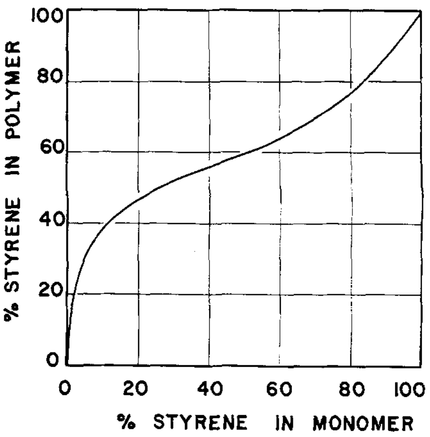

Fig. 15. Polymer-vs.-monomer-composition ratios for a copolymerization reaction.

TABLE 3.—GRAPHICAL DESIGN OF A CONTINUOUS COPOLYMERIZATION PROCESS

(Data from Figure 16)

| | Tank 1 | | | | Tank 2 | | | | Tank 3 | | | | Tank 4 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Data | Moles/hour | $S\%$ | $A\%$ | $P\%$ | Moles/hour | $S\%$ | $A\%$ | $P\%$ | Moles/hour | $S\%$ | $A\%$ | $P\%$ | Moles/hour | $S\%$ | $A\%$ | $P\%$ |
| Side stream | 0 | 0 | 0 | 0 | 8.3 | 100 | 0 | 0 | 8.7 | 100 | 0 | 0 | 5.8 | 100 | 0 | 0 |
| Total feed | 100 | 22.3 | 77.7 | 0 | 108.3 | 12.9 | 47.2 | 39.9 | 117.0 | 10.4 | 30 | 59.6 | 122.8 | 7.2 | 15.7 | 77.1 |
| Product | 100 | 5.7 | 51 | 43.3 | 108.3 | 3.6 | 32.3 | 64.1 | 117.0 | 1.83 | 16.5 | 81.7 | 122.8 | 0.55 | 5 | 94.5 |
| Conversion of monomer feed | | 43.3% | | | | 40.3% | | | | 54.7% | | | | 76% | | |
| Holding time based on monomer | | 4.33 hr. | | | | 4.03 hr. | | | | 5.47 hr. | | | | 7.6 hr. | | |

on Figure 15, it may be of interest, for example, to reduce viscosity and to control mixing or to design a chain of stirred low reactors with the same S/A monomer ratio in each vessel. As an illustration it may be assumed that one wishes to operate at a 10 mole % styrene concentration in the monomer, which yields from the plot of Figure 15 a polymer product with 38% styrene, 62% acrylate. The reactant mixture will be depleted in styrene, and therefore additional styrene side streams to each reactor are necessary. A final product containing 94.5% polymer is desired. The design for a chain of four reactors operating under such conditions, presented in Figure 16, is given as an example. Only the monomer and polymer flows have been determined, since they are the most important. Once these flows are determined, the other ingredients such as water, soap, and catalyst are added in known proportions, and the volume of the necessary tanks may be calculated. Thus, if one wishes to use tanks of equal size, a trial-and-error design should be made. Tabulated data from the graphical design of Figure 16 are presented in Table 3. Side-stream flows are calculated from a mass balance on styrene.

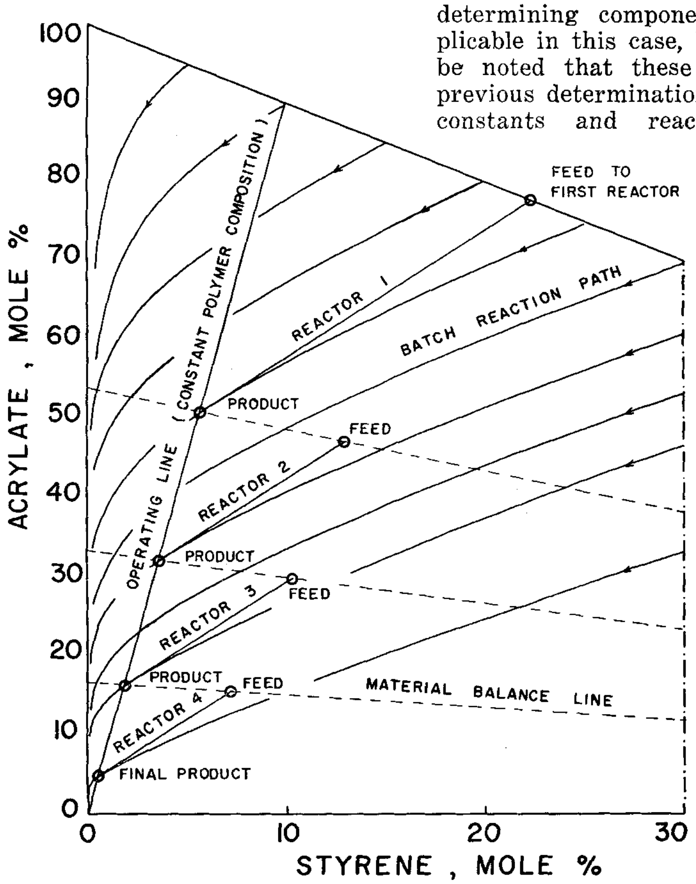

Fig. 16. Design of a CSTR chain for a copolymerization reaction.

## CONCLUSIONS

In this development the difference between batch and CSTR processes has been carefully examined from the viewpoint of product compositions.

It was found that for single reversible or irreversible reactions and some special cases of parallel reactions the product compositions given by the two methods of operation from the same feed were comparable and an equivalence could be defined between batch process time and CSTR holding time. On the contrary, for complex reaction schemes, generally represented by consecutive and parallel reactions, the complete product compositions for the two processes are essentially different and no simple time equivalence could be defined. Thus for these complex reactions, adjusting the holding time in a CSTR does not result in the same product compositions obtained in a batch reactor.

This difference calls for a special graphical design method for the case of complex reactions, where the usual graphical methods(*4, 7, 10*) are not valid. Of course the algebraic methods previously presented(*3*), which are based upon the simultaneous solution of material balances on the several rate-determining components, are applicable in this case, but it should be noted that these require the previous determination of the rate constants and reaction orders. These last are obviously not always easily accomplished and hence the advantage of the graphical method.

A graphical method valid for complex reactions was developed on the basis of the representation of the reaction paths in concentration space. Triangular and other representations can be employed. The method is useful especially when side streams or recycles are involved and when the reaction can be sufficiently described in terms of two independent concentrations.

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## APPENDIX

### Prediction of Continuous Stirred Tank Reactor Performance from Batch Reaction Data on Complex Reactions

Several batch reaction paths starting with various feed combinations are drawn on triangular coordinates. These paths are obtained by plotting the concentrations at different times of the three most important components of the reaction.

On this chart CSTR performance can be predicted. Beginning at the feed composition to be used in the continuous operation, any straight line is drawn, which is tangent to the one of the above-mentioned reaction paths. The coordinates found at the tangent point correspond to the composition of the CSTR product stream. The required holding time, and therefore the volume of the continuous reactor for a given production rate, is calculated from the batch rate of reaction data at this composition, i.e., $\theta = \Delta C_A / R_A$. For multistage CSTR design the procedure is repeated by drawing a series of tangent lines to the curves, each, of course, starting with the product composition of the previous reactor in the chain. The effects of recycle or side streams, if they are desired, may also easily be evaluated, as material balances appear as straight-line relations on these triangular plots.