Synthesis of Optimal Serial Reactor Structures for Homogeneous Reactions.

Part II: Nonisothermal Reactors

In Part I of this paper a methodology for the synthesis of optimal isothermal serial reactor structures for complex reactions was presented. This has been extended to nonisothermal systems in this paper.

A complete review of the relevant background has been included in this paper. A graphical procedure has been presented for Type II complex reactions and a computer program has been described for Type III complex reactions. Two cases for the Van de Vusse reaction scheme and a naphthalene oxidation example have been used to illustrate the synthesis approach.

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SCOPE

The objective of this research is to find rules and procedures which could be used in specifying the type and arrangement of reactor(s) to maximize product yield for complex reactions. In Part I of this paper the methodology presented was limited to isothermal systems. In this paper a methodology has been described for the synthesis of serial nonisothermal reactor systems.

CONCLUSIONS AND SIGNIFICANCE

In Part I of this paper reactions were classified into three basic types. Type I reactions were called simple reactions, and Types II and III were denoted complex reactions.

From a literature review summarized in this paper, it has been concluded that the rules presented in the literature for adiabatic and nonadiabatic reactor systems are only applicable for simple reactions and in general are not valid for complex reactions.

For Type II complex reactions a graphical procedure has been presented for obtaining the optimum temperature profile. Analytical results for obtaining the optimum serial reactor structure have been derived for Type II complex reactions. These results have been explained graphically in the form of a stepping procedure described in this paper.

For Type III reactions an optimization procedure based on the modified complex method has been used to obtain the optimal serial reactor structure. The dominant eigenvalue method is used to converge the calculations.

INTRODUCTION

In Part I of this paper a synthesis strategy was proposed for obtaining the optimum serial reactor structure consisting of isothermal reactors, for a Type II complex reaction scheme. An optimization strategy and a computer program was also described for obtaining an optimum serial reactor structure for Type III complex reactions.

As noted in Part I, the objective of our research is to find rules and procedures which could be used in specifying the type and arrangement of the reactor(s) to maximize product yield for complex reactions.

In this paper, the methodology presented earlier for isothermal serial structures will be extended to nonisothermal reactor systems. Although preliminary decisions can be made concerning operating temperature and reactor type based on isothermal operation, ultimately it is important to analyze the nonisothermal nature of the system. All industrial reactions are either exothermic or endothermic, and the associated heat effects can have a significant impact on reactor design and operation.

General suggestions based on temperature sensitivity have been made for adiabatic and nonadiabatic reactor systems (Rase, 1977). The effects of temperature on some typical Type I (simple) reactions have been summarized in Table 1 (Rase, 1977). These rules in general are not valid for complex (Type II and Type III) reactions (Chitra and Govind, 1985).

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TABLE 1. TEMPERATURE STRATEGIES FOR SOME TYPICAL SIMPLE REACTIONS (RASE, 1977).

Reaction System	Recommended Temperature Strategies
1. $\begin{tikzcd}[row sep=small] A+B \arrow[r, "E_1"] \arrow[dr, "E_2"'] & R \\ & S \end{tikzcd}$ or $\begin{tikzcd}[row sep=small] A \arrow[r, "E_1"] \arrow[dr, "E_2"'] & R \\ & S \end{tikzcd}$	If $E_1 > E_2$ use high temperature to favor R. If $E_1 < E_2$ use low temperature to favor R. For maximum yield use low temperature initially (high concentrations) and higher temperatures as rate decreases.
2. $A \xrightarrow{E_1} R \xrightarrow{E_2} S$	Same as 1 to favor R for maximum yield if $E_2 > E_1$ use high temperature initially and then decreasing temperature.
3. $\begin{tikzcd}[row sep=small] A+B \arrow[r, "E_1"] & R \arrow[r, "E_2"] \arrow[dr, "E_3"'] & S \\ & & P \end{tikzcd}$	If $E_3 > E_1 > E_2$, Reaction 1 is favored over Reaction 2 for high temperatures. Reaction 1 is favored over Reaction 3 at low temperatures

It should be noted that our research has only concentrated on determining the optimal reactor structure. The problems of stability and operability have not been addressed in our methodology. This can be formalized in the evaluation step to follow the synthesis procedure.

BACKGROUND

There is a proliferation of papers in the reaction engineering literature on nonisothermal reactor systems. The relevant literature, classified in Table 2, indicates that extensive studies have been conducted for simple reactions (irreversible first order, second order, reversible, etc.) in specified reactor types such as plug flow reactors (*PFR*), continuous stirred tank reactors (CSTR), and recycle reactors. Levenspiel (1962) reported heuristic rules on yield and selectivity in stirred tank and tubular reactors. For simple reactions, nonisothermal single reactors have been analyzed by Aris (1961).

Russell and Buzzeli (1969) studied a consecutive reaction scheme and investigated product yield for nonisothermal conditions. A number of industrial reactions can be represented by a consecutive reaction scheme.

For simple reactions, known combinations of CSTR and PFR have been analyzed in the literature. Combinations of PFR and CSTR for irreversible first and second order reactions under endothermic and exothermic adiabatic conditions also have been studied (Cholette and Blanchet, 1961).

Aris (1961c) has optimized combination of reactors for simple reaction schemes using dynamic programming. The different configurations include optimal sequences of isothermal stirred tank reactors, adiabatic CSTRs, multistage adiabatic reactors, and reactors with cold shots.

In Table 3 the literature papers classified in Table 2 have been summarized. Our research, including this paper can be classified in boxes C and D in Table 2.

OPTIMAL TEMPERATURE PROFILE

It is known that for simple reactions the reaction rate is only a function of temperature and conversion. The optimum temperature profile for such reactions is obtained by selecting the temperature at which the rate is maximum at each conversion. However, for complex reactions (Type II and Type III) the reaction rate is a function of product concentration, reactant conversion, and temperature. Hence, it is necessary to find a rule which enables the optimal (maximum product concentration) temperature profile to be determined for complex reactions.

Consider a plug flow reactor, shown in Figure 1, in which the reactor is subdivided into reactor elements (shaded in Figure 1). For the ith reactor element operating at temperature T_i and exit product concentration p_i, we can write the basic equation for Type II reactions as

$$p_{i,T_i} = p_{i-1,T_{i-1}} + \int_{x_{i-1}}^{x_i} \phi_M(p_i,x_i,T_i)dx \qquad (1)$$

where

$$\phi_M(p_i,x_i) = \frac{dp}{dx}(p_i,x_i)$$

and

$$x_i = 1 - r_i \qquad (2)$$

For maximum product concentration, p_i

$$\frac{\partial p_{i,T_i}}{\partial x_{i-1}} = \frac{\partial p_{i-1,T_{i-1}}}{\partial x_{i-1}} - \phi_M \bigg|_{x=x_{i-1},T_i} = 0 \qquad (3)$$

TABLE 2. LITERATURE CLASSIFICATION FOR NONISOTHERMAL REACTOR SYSTEMS

Type	Simple Reaction	Complex Reactions
Single Reactor		
a. PFR	Levenspiel (1962)	Gillespie & Carberry (1966)
b. CSTR	Aris (1961a)	Aris (1960c)
c. Recycle		Padmanabhan & Bankoff (1969)
Known Combination of Reactors		
a. Mixed Multistage Reactors	Aris (1960d) Kubota et al. (1961) Aris (1961b) Fan et al. (1965)	Aris (1960a) Mah & Aris (1964)
b. Adiabatic Multibed Reactors	Aris (1960b) Rafal & Dranoff (1966) Lee & Aris (1963) Malenge & Villermaux (1967) Hellinckx & Van Rompay (1968) Bhandarkar & Narsimhan (1969) Malenge (1969) Dyson & Horn (1969) Malenge & Vincent (1972) Caha et al. (1973) Brusset et al. (1978) Burghardt & Patzek (1978)	
c. Mixed Tubular/Tubular Mixed Reactor	Cholette & Blanchet (1961) Aris (1962) King (1965)	
Optimum Combination of Reactors	Box *C*	Box *D*

TABLE 3. SUMMARY OF RELEVANT LITERATURE REFERENCES

Author	Summary
Aris (1960a)	A dynamic programming strategy was used to optimize the product yield for the Denbigh reaction in a serial n-CSTR system, each reactor operating isothermally at a different temperature.
Aris (1960b)	A dynamic programming procedure was used to maximize conversion and minimize reactor volume for a single reaction conducted in a serial combination of adiabatic PFR reactors with interstage cooling.
Aris (1960c)	Using the dynamic programming method, the optimum temperature was obtained for a single PFR for the case of a consecutive first order reaction.
Aris (1960d)	Using the dynamic programming method, a profit function described for a serial combination of nonadiabatic nonisothermal reactors was maximized for a single reaction.
Aris (1961a)	For single reactions, a graphical procedure was described for a serial combination of CSTRs.
Kubota et al. (1961)	Calculus of variations was used to minimize reactor volume at a fixed outlet conversion for single reactions. The reactor system was a completely mixed multistage reactor.
Aris (1961b)	For single reactions, using dynamic programming, the profit function was maximized for a sequence of CSTRs to find the optimum volume, temperature, and by-pass rates.
Cholette & Blanchet (1961)	For single reactions, the performance of mixed-tubular and tubular-mixed reactors was compared. A graphical method applicable for mixed tubular reactors was developed.
Aris (1962)	An extension of Cholette and Blanchet (1961). A general procedure with graphical conditions for the optimality of mixed-tubular reactors is derived. It was shown that a CSTR design is always stable.
Lee and Aris (1963)	The scheme presented in Aris (1961b) is used for the SO_2 oxidation example using dynamic programming.
Mah & Aris (1964)	The optimal temperature policy for a series of CSTRs was obtained for a first order consecutive reversible reaction.
King (1965)	Using the discrete principle of optimality, a simultaneous solution is developed for the operating conditions of mixed-tubular reactors. Provisions are made for cooling in the mixed stage and an intercooler between stages.
Fan et al. (1965)	The discrete maximum principle is used to optimize the profit function with respect to holding time and temperature for single reactions.
Rafal & Dranoff (1966)	Based on a combination of an analytic criteria for optimum and a dynamic programming formulation, an efficient algorithm is developed for optimization of multi-bed adiabatic reactor sequence.
Malenge & Villermaux (1967)	Pointed out a theoretical modification of Lee and Aris (1963) and confirmed this numerically by improving the pseudooptimum using the direct search method.
Hellinckx & Rompay (1968)	Showed improvement in the result of Malenge and Villermaux by using the discrete maximum principle.
Bhandarkar & Narsimhan (1969); Narsimhan (1969)	Proposed a method for the optimization of an adiabatic reactor sequence with cold shot cooling, by allowing the problem to be solved by successive optimization of single variable functions.
Malenge (1969)	Proposed a correction for Bhandarkar and Narsimhan (1969) by indicating that the first derivatives vanish at the optimum.
Dyson & Horn (1969)	For a single reversible exothermic reaction, an algorithm is proposed for determining the minimum mass of catalyst required by an N-stage adiabatic tubular reactor with feed preheater and cold shot cooling by feed bypass.
Padmanabhan & Bankoff (1969)	For a consecutive first order reaction conducted in an adiabatic tubular reactor with a single cold shot injection, Pontryagin's methods were applied to the variational problem.
Malenge & Vincent (1972)	For a sequence of adiabatic reactors with cold shot cooling, proposed optimization of several single variable functions.
Caha et al. (1973)	For simple reactions and multi-bed adiabatic reactors, proposed an optimization method using numerical solution of the reactor bed.
Brusset et al. (1978)	Considered the application of dynamic programming to complex problems in which the objective function depends on several decision variables such as input temperature, reactive gas injection, and fresh air injection between stages.
Burghardt & Patzek (1978)	For simple reactions, optimal conditions are derived with and without inequality constraints on temperature of each bed.

or

$$\frac{\partial p_{i-1},T_{i-1}}{\partial x_{i-1}} = \frac{\partial p_{i-1},T_i}{\partial x_{i-1}} \tag{4}$$

From the definition of ϕ (Eq. 2), it follows from Eq. 4 that the intersection point of the ϕ vs. x curve at temperature T_{i-1} and the ϕ vs. x curve at temperature T_i must lie on the optimum temperature profile. For a series of such isothermal reactor elements, each element operating at a different temperature, Eq. 4 can be applied to obtain the optimal temperature profile for Type II complex reactions.

This can be illustrated graphically on the instantaneous yield plot shown in Figure 2. The instantaneous yield, ϕ, has been plotted versus the reactant conversion, x, for different temperatures. Points a, b, c, d are located on the plot in Figure 2 as the points of intersection of two ϕ curves at two slightly different temperatures as derived in Eq. 4. By connecting these points of intersection, the optimal temperature profile is obtained. Once this profile has been obtained, the procedure for finding the optimal serial reactor structure is as derived in the following section.

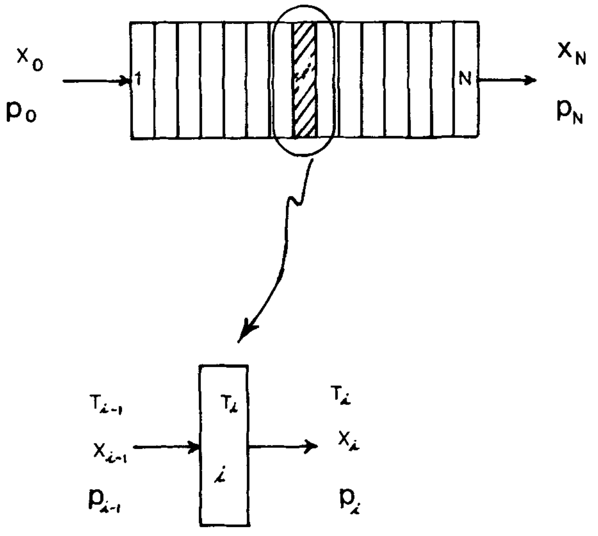


Figure 1. Plug flow reactor with N elements along the reactor length, and detail of element. Each element is maintained at a constant temperature.

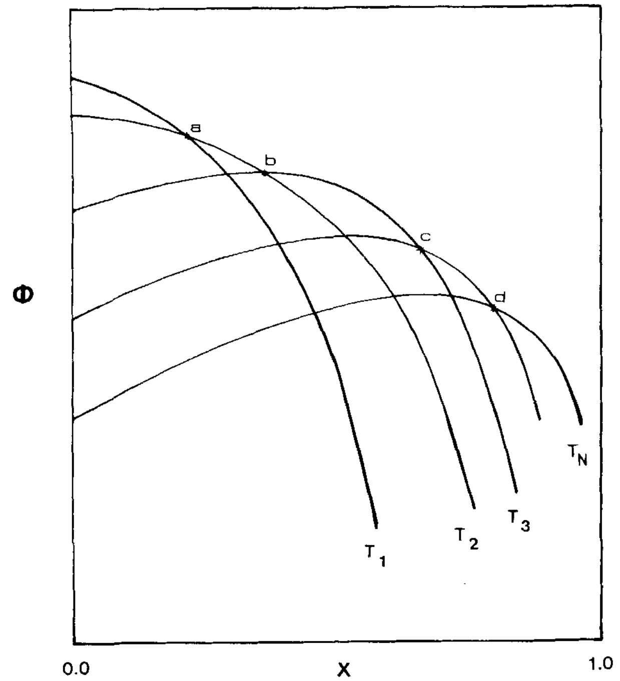


Figure 2. Graphical procedure to obtain optimal temperature profile for Type II complex reactions.

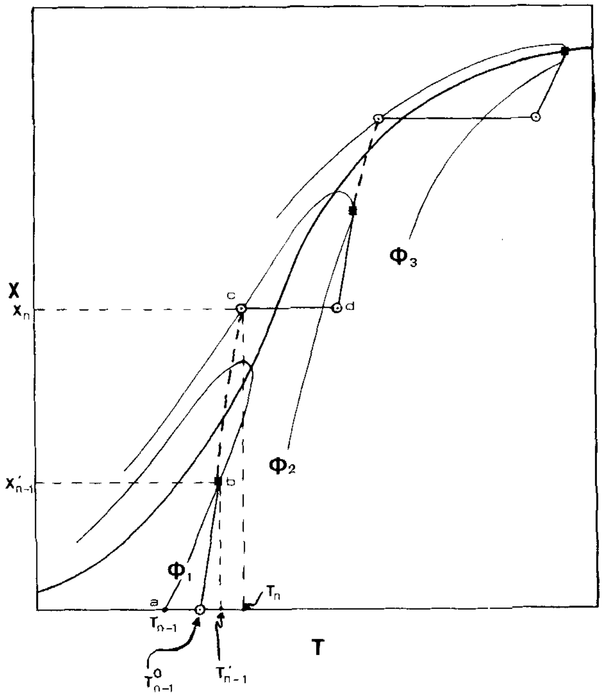
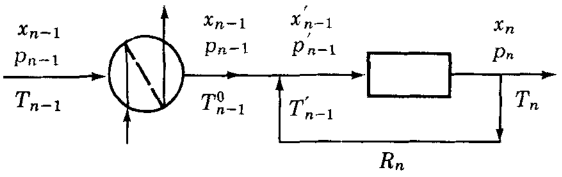


Figure 3. Stepping procedure to obtain optimum serial reactor configuration for Type II complex reactions.

THE OPTIMAL SERIAL REACTOR STRUCTURE

Consider the nth heat exchanger and recycle reactor combination shown below.



The product yield, p_n, is given by

$$p_{n,T_n} = p_{n-1,T_{n-1}} + (R_n + 1) \int_{x'_{n-1},T'_{n-1}}^{x_n,T_n} \phi_R \, dx \tag{5}$$

For maximum product yield, p_n, the following necessary conditions are obtained

$$\frac{\partial p_{n,T_n}}{\partial x_{n-1}} = 0 \tag{6}$$

$$\frac{\partial p_{n,T_n}}{\partial R_n} = 0 \tag{7}$$

$$\frac{\partial p_n}{\partial T^0_{n-1}} = 0 \tag{8}$$

It should be noted that Eqs. 6 and 7 are due to Eq. 8 in Part I of this paper.

In Part I it was shown that Eq. 6 results in the following necessary condition, which is identical to Eq. 11 in Part I:

$$\phi_R \Big|_{\substack{x=x_{n-1}\\ T=T_{n-1}}} = \phi_R \Big|_{\substack{x=x'_{n-1}\\ T=T'_{n-1}}} \tag{9}$$

Also, from Eqs. 5 and 7 the necessary condition becomes

$$- \int_{\substack{x'_{n-1}\\ T'_{n-1}}}^{\substack{T_n\\ x_n}} \phi_R \, dx + \frac{\partial x_n}{\partial R_n} [R_n \phi_R(x'_{n-1}) - (R_n + 1)\phi_R(x_n)] + \frac{(x_n - x_{n-1})\phi_R(x'_{n-1})}{(R_n + 1)} = 0 \tag{10}$$

This results in the area rule shown by Eq. 16 in Part I (Chitra and Govind, 1985). From Eqs. 5 and 8 we get

$$\int_{\substack{x'_{n-1}\\ T'_{n-1}}}^{\substack{T_n\\ x_n}} \frac{\partial \phi_R}{\partial T} dx = 0 \tag{11}$$

From Eqs. 9, 10, and 11 the following stepping procedure has been developed (Figure 3).

1. Given the feed composition and temperature, the point a in Figure 3 is located. Note that in this case the reactant conversion x in the feed is assumed to be zero, i.e., pure feed. In general point a will have the coordinates (T_{n-1}, x_{n-1}).
2. Plot different yield plots on the $x - T$ graph in Figure 3 such that the constant ϕ curve passes through the point a located in step 1.
3. Assume a point b on the constant ϕ curve obtained in step 2, as given by Eq. 9. Point b will have the coordinates (T'_{n-1}, x'_{n-1}).
4. Find point c on another ϕ curve such that Eq. 11 is satisfied for the point b assumed in step 3.
5. If Eq. 10 is also satisfied for the points b and c, then the assumed point b is correct. Otherwise, assume a different point b and repeat steps 4 and 5. The coordinates of point c will be (T_n, x_n).
6. Calculate the recycle ratio R_n, from the following component balance equation

$$R_n = \frac{x_{n-1} - x'_{n-1}}{x'_{n-1} - x_n} \tag{12}$$

Calculate the intermediate temperature T^0_{n-1} from the following energy balance equation, assuming constant specific heats

$$T^0_{n-1} = T'_{n-1}(R_n + 1) - T_n R_n \tag{13}$$

The above procedure is then repeated, starting from point c to find the next reactor system, until the final conversion is obtained.

Note that the above procedure is only valid for Type II complex reactions. For Type III complex reactions, the problem can be formulated using the structure discussed in the following sections.

GENERALIZED SERIAL REACTOR CONFIGURATION

The generalized serial reactor configuration is shown in Figure 4. It consists of a series of adiabatic recycle reactors with heaters/coolers between the reactors and in the recycle stream of each reactor. While this configuration is capable of representing a wide

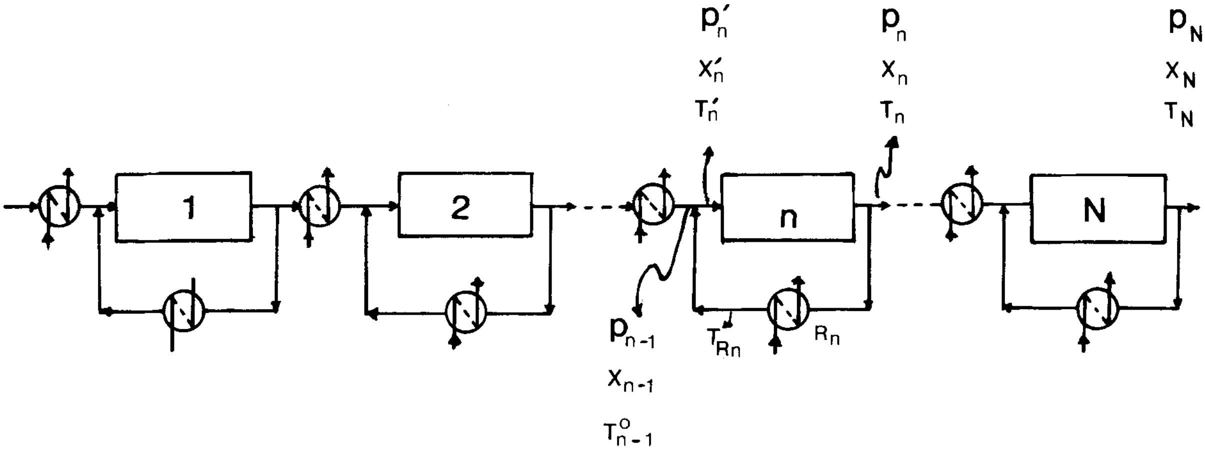


Figure 4. Generalized serial reactor configuration consisting of adiabatic recycle reactors with intercoolers/interheaters for Type III complex reactions.

variety of serial structures, it has the same drawbacks as the generalized reactor structure selected in Part I of this paper.

As argued in Part I and also discussed by Kondelik (1982), in most chemical reactors the operating costs of the reactor are negligible in comparison with the cost of raw materials. Hence, optimum reactor design is determined by product yield maximization.

For the generalized structure shown in Figure 4, the final product yield, p_n, can be written as

$$p_N = fn(x_0, T_0, x_n, T^0_{n-1}, R_n, T_{Rn}, n = 1 \ldots N) \tag{14}$$

subject to the following constraints for $n = 1 \ldots N$.

$$0 \leq x_n \leq 1.0 \tag{15}$$

$$T_{\min} \leq T^0_{n-1} \leq T_{\max} \tag{16}$$

$$0 \leq R_n \leq \infty \tag{17}$$

$$T_{\min} \leq T_{Rn} \leq T_{\max} \tag{18}$$

$$0 \leq (x_{n-1} - x_n) \leq 1.0 \tag{19}$$

The optimization procedure to obtain the optimum (maximum p_N) serial reactor structure is discussed in the following section.

OPTIMIZATION PROCEDURE

The objective is to maximize product concentration at the exit of the last reactor (p_N) by varying the recycle ratio, intermediate conversions, inlet temperature, and the recycle temperature of each recycle unit in the generalized serial structure shown in Figure 4. A nonlinear constrained search technique, such as the modified complex method (Umeda and Ichikawa, 1971) is used, since the objective function is highly nonlinear for most complex reactions.

In the original complex method for inequality constraints, if a trial point does not satisfy the constraints, it is moved halfway toward the centroid of the remaining points.

For equality constraints the original complex method corresponds to the simplex method (Spendley et al., 1962). The objective function is evaluated at vertices which form a simplex in the space of independent variables. After finding the worst value of the function, a new simplex is formed by replacing the worst vertex by a point α times as far from the centroid of the remaining points as the reflection of the worst point in the centroid. The procedure is repeated until a specified stopping criterion is satisfied.

In the modified complex method, a weighted centroid, $\bar{z}_{ij}$, is defined as follows

$$\bar{z}_{ij} = \frac{\sum\limits_{\substack{k=1 \\ k \neq w}}^{K} (\Delta h_{j,k})^{n'} z_{i,j,k}}{\sum\limits_{\substack{k=1 \\ k \neq w}}^{K} (\Delta h_{j,k})^{n'}} \tag{20}$$

where

$$\Delta h_{j,k} = \frac{h_{j,k} - h_{j,\min}}{h_{j,\max} - h_{j,\min}} \tag{21}$$

for maximization.

New trial points are determined by

$$\frac{(1 + \alpha) \sum\limits_{\substack{k=1 \\ k \neq w}}^{K} (\Delta h_{j,k})^{n'} z_{i,j,k}}{\sum\limits_{\substack{k=1 \\ k \neq w}}^{K} (\Delta h_{j,k})^{n'}} - \alpha z_{i,j,k} \tag{22}$$

Further, in the modified method, if a trial point does not satisfy inequality constraints, its new position is computed as follows

$$z_{i,j,k} = 0.5\, z_{i,j} + 0.5\, z_{i,j,w} \tag{23}$$

Based on experience with the modified complex method, the following computational algorithm has been recommended. In the first stage where the criterion $(h_{j,\max} - h_{j,\min})/h_{j,\max} \leq 0.05$ is not satisfied, the modified complex method is applied, and in the second stage, which is a final step to an optimal point, the original complex method ($n' = 0$) is applied (Umeda and Ichikawa, 1971).

In our problem the values selected for the expansion factor α and the exponent of the function values, n', are

$$\alpha = 1.3 \text{ and } n' = 1.0$$

To converge the calculations, the dominant eigenvalue method proposed by Orbac and Crowe (1971) is used. The calculations are carried out first by the Wegstein method (1958) and the dominant eigenvalue is estimated by the following equation

$$|\lambda_1|_j = \frac{|(\Delta \bar{z})_j|}{|(\Delta \bar{z})_{j-1}|} \tag{24}$$

where

$$(\Delta \bar{z})_j = (\bar{z})_j - (\bar{z})_{j-1}$$

= vector deviations of variables of two consecutive iterations.

If in two consecutive iterations, the estimate of λ_1 differs by less than 0.001, a new solution approximation is calculated by the following equation:

$$(\bar{z})_{j+1} = (\bar{z})_{j-1} + t' \frac{(\bar{z})_j - (\bar{z})_{j-1}}{1 - (\lambda_1)_j} \tag{25}$$

In our calculation, a damping factor, t, of 0.7 was used to converge the recycle calculations.

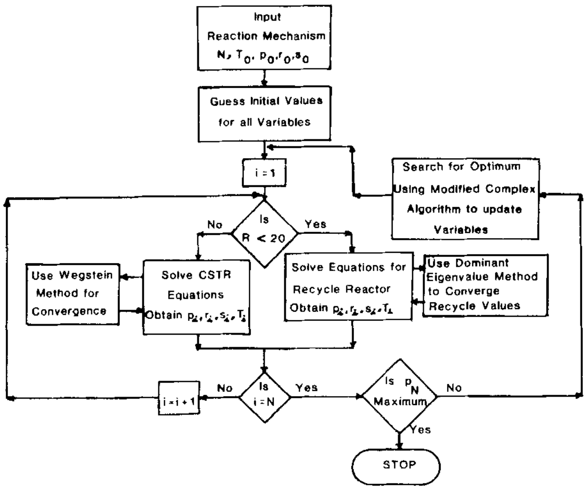


Figure 5. Overall procedure to obtain the optimum serial nonisothermal reactor configuration for any Type III reaction.

DESCRIPTION OF THE COMPUTER PROGRAM

Based on the above optimization procedure, a computer program has been developed to calculate the optimal serial reactor structure (maximize final yield, p_N), starting with the generalized structure shown in Figure 4. The overall procedure used by the program is shown in Figure 5. The feed concentration, flow rate, and temperature, together with the reaction mechanism and kinetic constants, are inputs to the program. The procedure begins with the first reactor by assuming a value of the recycle ratio, R_1, feed temperature, and recycle temperature. If the recycle ratio is high, resulting in a CSTR, the CSTR equations are used in conjunction with the convergence procedure, described in the previous section, to obtain the exit product concentration, reactant conversion, and temperatures. If the recycle ratio is not high, the exit values for the variables are obtined by using recycle reactor equations. The procedure is repeated until the final exit product concentration, p_N is obtained.

The assumed values of the variables are varied to maximize the final product concentration, p_N, based on the modified complex method discussed in the previous section.

Example 1.

Van de Vusse reaction (Van de Vusse, 1964):

$$A \xrightarrow{(1)} B \xrightarrow{(2)} C \qquad A + A \xrightarrow{(3)} D$$

The desired product is B; k_1, k_2, k_3 are kinetic constants for the respective reactions.

For the adiabatic recycle reactor the following equations can be written

$$\frac{dp}{dr} = \frac{-(k_1 r - k_2 p)}{(k_1 r + k_3 A_0 r^2)} \tag{26}$$

$$\frac{dt}{dr} = \frac{-(\beta_1 k_1 r + \beta_2 k_2 p + \beta_3 k_3 A_0 r^2)}{(k_1 r + k_3 A_0 r^2)} \tag{27}$$

For the nth order unit, the boundary conditions are

$$r_n' = \frac{r_{n-1} + r_n R_n}{(R_n + 1)}$$

or

$$x_n' = \frac{x_{n-1} + x_n R_n}{(R_n + 1)} \tag{28}$$

$$p_n' = \frac{p_{n-1} + p_n R_n}{(R_n + 1)} \tag{29}$$

$$t_n' = \frac{t_{n-1} + t_n R_n}{(R_n + 1)} \tag{30}$$

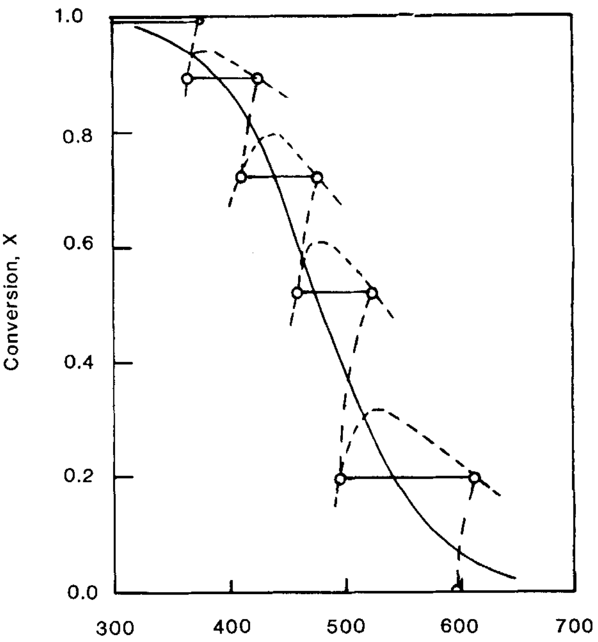


Figure 6. Stepping procedure to obtain optimum adiabatic reactor configuration for Van de Vusse reaction, Case 1, with β_1 = 0.28, β_2 = 0.36, and β_3 = 0.20.

Equations 26 and 27 are solved simultaneously with the initial-condition Eqs. 28, 29, and 30 for each recycle unit. The calculation procedure is continued until the final product yield, p_N, is obtained.

Two cases were considered for the Van de Vusse reaction:

Case 1:
$k_{10} = 5.4 \times 10^9\ \mathrm{h}^{-1}$ $\quad E_1 = 15{,}840$ cal/gmol
$k_{20} = 1.6 \times 10^{12}\ \mathrm{h}^{-1}$ $\quad E_2 = 23{,}760$ cal/gmol
$k_{30} = 3.6 \times 10^5 \cdot \mathrm{gmol}^{-1} \cdot \mathrm{h}^{-1}$ $\quad E_3 = 7{,}920$ cal/gmol

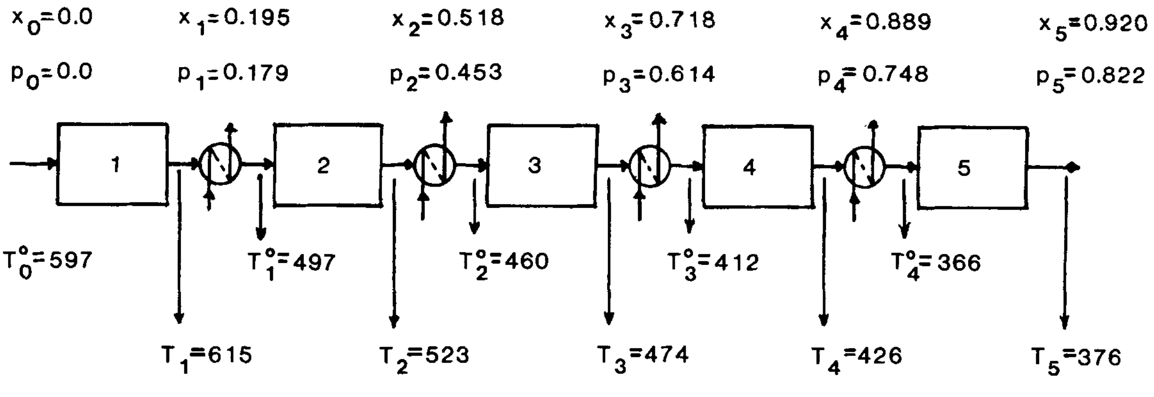
Case 2:
$k_{10} = 5.4 \times 10^9\ \mathrm{h}^{-1}$ $\quad E_1 = 15{,}840$ cal/gmol
$k_{20} = 3.6 \times 10^5\ \mathrm{h}^{-1}$ $\quad E_2 = 7{,}920$ cal/gmol
$k_{30} = 1.6 \times 10^{12} \cdot \mathrm{gmol}^{-1} \cdot \mathrm{h}^{-1}$ $\quad E_3 = 23{,}760$ cal/gmol

For Case 1 of the Van de Vusse reaction, the reaction conversion x is plotted versus the temperature T with the curves for constant instantaneous yield ϕ. The initial feed conversion x_0 is zero and the initial feed temperature T_0 is 300 K. The optimal temperature profile obtained from the ϕ vs. x curve, as discussed in this paper, is plotted on the x vs. T plot, as shown in Figure 6. The optimal serial reactor structure is obtained by the procedure presented in this paper. The optimum configuration is a combination of five PFRs in series as shown in Figure 7.

Qualitatively, this result can be explained from the optimal temperature profile. As the temperature increases the reaction conversion decreases, and since increased conversion is the objective, intercoolers have to be used between the reactor units. Further, mixing of the recycle stream at a high temperature with the feed, as in a recycle unit, is not compatible with the conversion vs. temperature plot. Hence all the reactors are PFRs.

For Case 2 the conversion vs. temperature plot is shown in Figure 8. As the temperature increases the conversion also increases, since the optimum temperature profile has a positive slope. Hence, increasing the reaction mixture temperature by recycling the hot exit stream, as in a recycle unit, is favorable for increased conversion. From the x vs. T plot, based on the procedure developed in this paper, a serial combination of five recycle reactors with recycle ratio ranging from $R = 0$ (PFR) to $R = \infty$ (CSTR), shown in Figure 9, is found to be the optimal serial structure.

This result is also supported by DeVera and Varma (1979), where the entire kinetic parameter space has been classified based on maximum product yield and recycle ratio for a single isothermal



All Temperatures are in °Kelvin

Figure 7. Optimal serial adiabatic reactor structure obtained by stepping procedure for reaction data in Fig. 6.

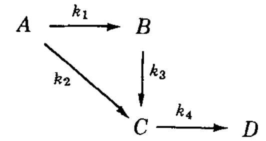
recycle reactor. The result from their paper is shown in Figure 10.

In the optimal serial structure shown for Case 2 in Figure 9, as the temperature increases the kinetic parameters change. These changes can be shown as in Figure 10. The optimal kinetic parameter profile starts from the PFR region and moves into the CSTR region as conversion is increased. This agrees with the result obtained from the procedure for Case 2.

For Case 1, the optimum kinetic parameter profile plotted in Figure 10 (DeVera and Varma, 1979), starts from the CSTR region and moves into the PFR region. However, the optimal structure in this case is a series of five PFR's, since the mixing of the recycle stream with the feed stream is incompatible with the optimum temperature strategy, as discussed earlier.

Example 2.

Naphthalene Oxidation:



where A = Naphthalene, B = Naphthaquinone,
C = Phthalic anhydride D = $CO_2 + H_2O$

This is a highly exothermic reaction of such a velocity that heat and mass transfer limitations both prevail throughout the reactor.

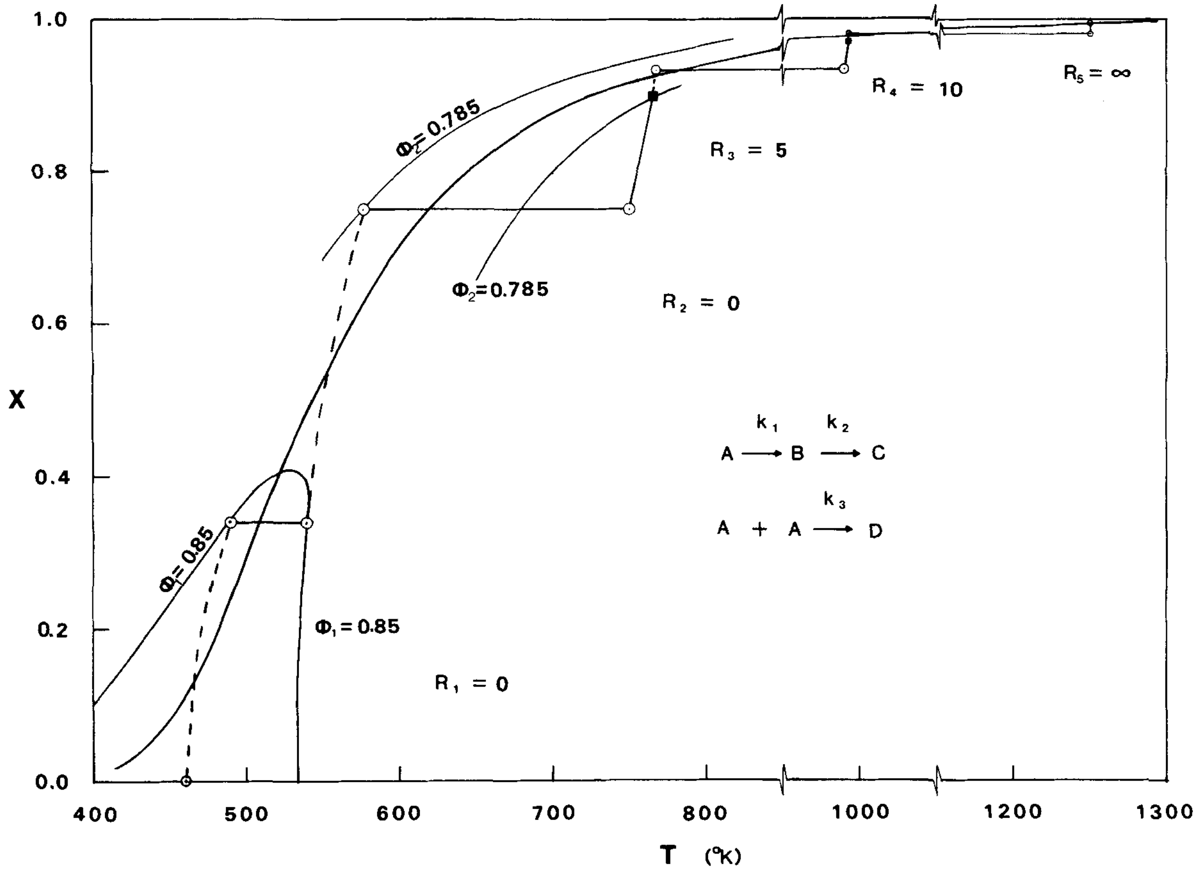


Figure 8. Stepping procedure to obtain optimum adiabatic reactor configuration for Van de Vusse reaction, Case 2, β_1 = 0.28, β_2 = 0.36, and β_3 = 0.20.

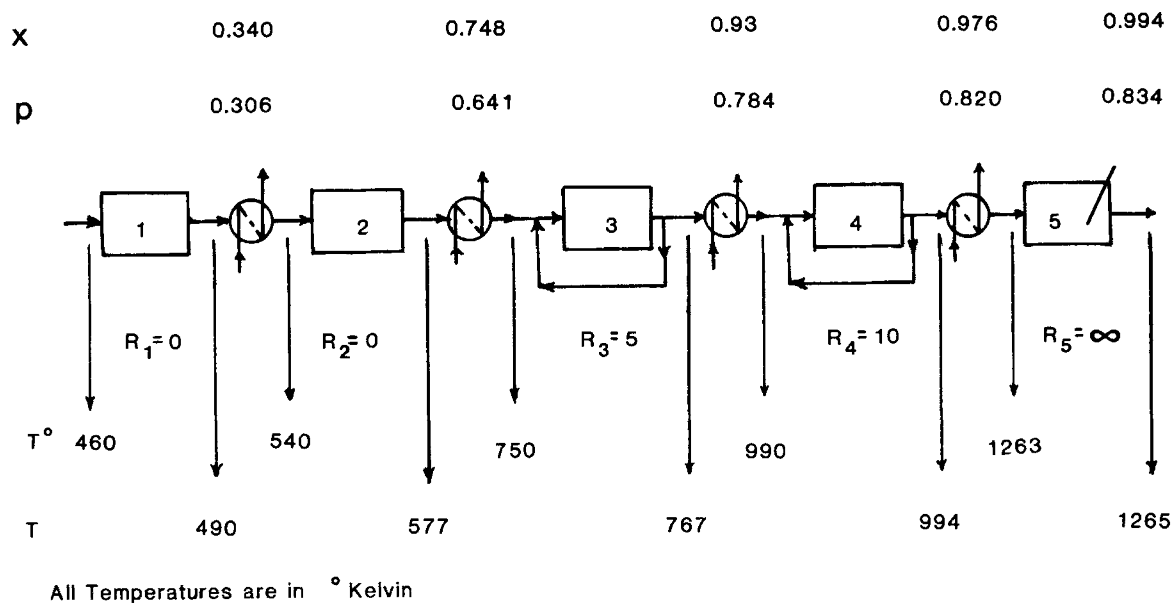


Figure 9. Optimal serial adiabatic reactor structure obtained by stepping procedure for data in Fig. 8.

For simplicity, radial interparticle dispersion of heat and mass are neglected in this analysis.

The following rate equations are used for this case study. The kinetic data presented by DeMaria et al (1961) in their report on simulation of fluidized bed isothermal oxidation of naphthalene are used to obtain the values of the rate coefficients

$$r_1' = r_2' = 2 \times 10^{13}\,\mathrm{Exp}(-38{,}000/RT)A$$
$$r_3' = 8.15 \times 10^{17}\,\mathrm{Exp}(-50{,}000/RT)B$$
$$r_4' = 2.1 \times 10^{5}\,\mathrm{Exp}(-20{,}000/RT)C$$

For plug flow adiabatic homogeneous tubular reactor with recycle, the continuity equations are

$$\frac{db}{df} = -\frac{(k_1f - k_3b)}{(k_1 + k_2)f} \tag{31}$$

$$\frac{dc}{df} = -\frac{(k_1f + k_3b - k_4c)}{(k_1 + k_2)f} \tag{32}$$

$$\frac{dt}{df} = -\frac{(\beta_1k_1f + \beta_2k_2f + \beta_3k_3b + \beta_4k_4c)}{(k_1 + k_2)f} \tag{33}$$

with initial conditions as

$$f_n' = \frac{f_{n-1} + R_nf_n}{(R_n + 1)} \tag{34}$$

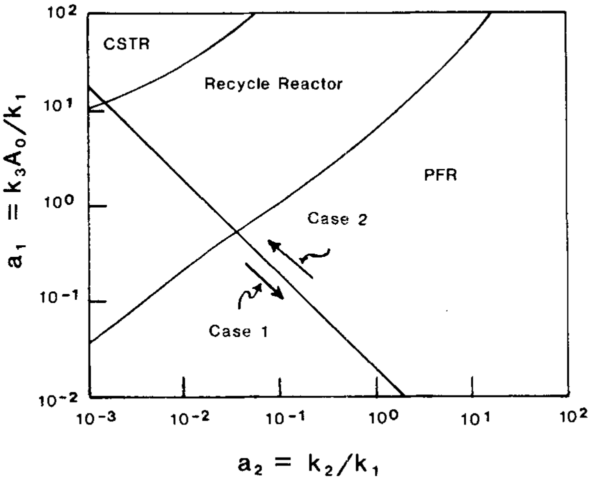


Figure 10. Optimal kinetic parameter profile obtained for Van de Vusse reaction, Case 1 and Case 2, on the kinetic parameter (a_1 and a_2) space plot (DeVera and Varma, 1979).

$$b_n' = \frac{b_{n-1} + R_nb_n}{(R_n + 1)} \tag{35}$$

$$c_n' = \frac{c_{n-1} + R_nc_n}{(R_n + 1)} \tag{36}$$

$$t_n' = \frac{t_{n-1} + R_nt_n}{(R_n + 1)} \tag{37}$$

Equations 31, 32, and 33 can be solved simultaneously with the initial conditions given by Eqs. 34 through 37. These equations are solved for each recycle reactor to obtain the final product yield.

Optimization of the serial generalized reactor system for the phthalic anhydride reaction using the computer program resulted in a configuration consisting of four plug flow reactors shown in Figure 11. The final product yield is 0.999 and conversion is 0.995.

NOTATION

b	$= B/A_0$, dimensionless concentration of naphthaquinone, Eq. 31
c	$= C/A$, dimensionless concentration of phthalic anhydride, Eq. 32
C_p	= average specific heat of the reaction mixture
E_1,E_2,E_3	= activation energy values for different reaction steps of Van de Vusse reaction
f	$= A/A_0$, dimensionless concentration of naphthalene, Eq. 31
h	= objective function value, Eq. 21
j	= iteration number
$k = w$	= denotes worst point
k_{10},k_{20},k_{30}	= Arrhenius constants for different reaction steps of Van de Vusse reaction
k_1,k_2,k_3	= reaction rate constants for different reaction seps of Van de Vusse reaction
K	= number of vertices of simplex, Eq. 20
n'	= exponent of the function values, Eq. 22
N	= number of reactors in reactor train
p	= dimensionless product concentration
$p_0,p_1 \ldots p_N$	= dimensionless product concentrations at different locations of the reactor configuration, Figure 4
r	= dimensionless concentration of the limiting reactant
r_1',r_2',r_3',r_4'	= reaction rates

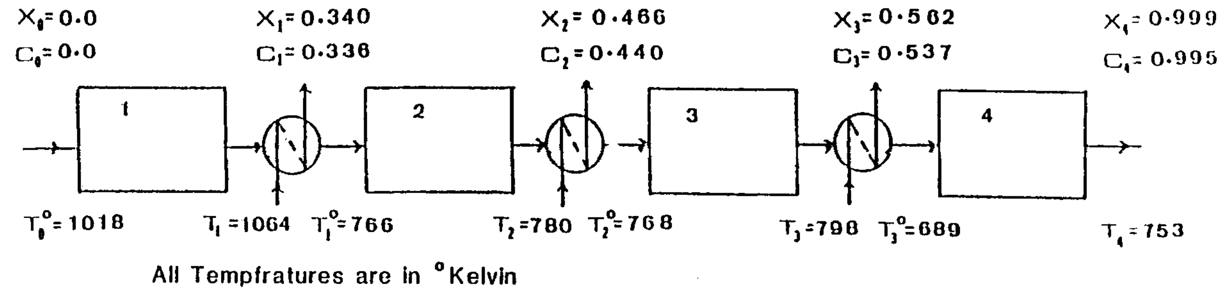


Figure 11. Optimal serial adiabatic reactor configuration obtained by the overall procedure of Fig. 2 for naphthalene oxidation reaction with $\beta_1 = 0.12$, $\beta_2 = 0.43$, $\beta_3 = 0.36$, and $\beta_4 = 0.78$. (Temperatures in K.)

$r_0, r_1 \ldots r_N$ = dimensionless concentration of the limiting reactant at different locations of the reactor configuration, Figure 4
R = recycle ratio; ratio of volumetric recycle stream flow rates to volumetric feed rate
$R_1, R_2 \ldots R_N$ = recycle ratio values for different reactor in the generalized reactor configuration, Figure 4
R' = gas constant
t' = damping factor used for convergence, Eq. 25
t = T/T_0, dimensionless temperature, Eq. 27
T = temperature
$T_0, T_1 \ldots T_n$ = temperature values at different locations of the reactor configuration
x = conversion of the limiting reactant
$x_0, x_1 \ldots x_N$ = conversion of the limiting reactant at different locations of the reactor configuration, Figure 4
z = independent variable used for optimization, Eq. 20

Greek Letters

α = expansion factor used in modified complex method, Eq. 22
β = dimensionless heat of reaction parameter = $(-\Delta H_i)A_o/\rho c_p T_o$, Eq. 27
ΔH_i = heat of reaction for the ith reaction step, Eq. 27
λ_1 = dominant eigenvalue, Eq. 24
ϕ = instantaneous yield
ϕ_M = instantaneous yield for a mixer reactor
ϕ_R = instantaneous yield for recycle reactor.

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Gas-Liquid Mass Transfer in Fluidized Particle Beds

Gas/liquid mass transfer has been studied in air/water fluidized beds of 0.05–8 mm glass spheres in a 0.14 m diameter reactor. The volumetric mass transfer coefficients k_La were independent of bed height, and, for particle diameters up to 1 mm, decreased linearly with solids concentration. Low solids loadings as well as large diameter particles significantly increased k_L and a, respectively, as compared to the two-phase system.

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SCOPE

In gas-liquid fluidization, a particle bed is fluidized by cocurrent upwards gas and liquid flows. Small particles can also be fluidized by gas-induced liquid motion alone in a bubble column slurry reactor. Applications of three-phase bubble column reactors are numerous including catalytic hydrogenations and oxidations, synthesis gas conversion processes, and coal liquefaction. Usually, mass transfer can be modelled by the concept of resistances in series: i.e., gas-liquid and liquid-solid mass transfer and the chemical reaction at the solid surface are noninteracting steps. Nevertheless, the presence of the solids hydrodynamically affects the gas-liquid mass transfer. Since this transfer step may considerably contribute to the overall resistance, solids effects on the volumetric mass transfer coefficients k_La are an important information for the design of three-phase reactor.

Previous studies concentrated on large particle diameters. Glass spheres of about 1 mm diameter were found to decrease oxygen-water mass transfer, whereas at diameters exceeding 3 mm, k_La significantly increased as compared to the air/water system. Confusing results on axial variation of k_La and on effects of liquid flow rates have been reported that may partly refer to inadequate experimental design and modelling.

It is the objective of this study to provide reliable data for the solids effects on gas-liquid mass transfer in a wide range of particle diameters (0.05–8 mm) and gas and liquid superficial velocities. The measurements were carried out in a 0.14 m diameter reactor and air/water fluidized beds of 0.38–2.65 m height. Volumetric mass transfer coefficients were determined from the steady-state axial profiles of the oxygen liquid-phase concentration accounting for dispersion in the liquid phase. Emphasis was laid on the effects of small-sized particles because of their greater range of application in industry and the lack of reported data.

CONCLUSIONS AND SIGNIFICANCE

The volumetric gas-liquid mass transfer coefficients k_La were independent of the bed height and the axial position within the bed. At same liquid flow rate, k_La ran through a minimum with increasing particle size. Spheres of diameters exceeding 3 mm increased the gas-liquid mass transfer by factors up to 4 at low gas velocities. Most previously reported results agreed reasonably under these conditions. At high gas velocities the bubble disintegration effect of the particles was less pronounced, thus rendering the process energetically inefficient.

It was observed that in the case of small particles the effect of the particle diameter and the influence of the liquid flow variations can be combined into one characteristic factor which is the solids fraction ϕ_S in the suspension. The volumetric mass transfer coefficients in the presence of small fluidized particles were found to be merely a linear function of the solids fraction in the suspension. Comprehensive data for four different particle diameters from 0.05 to 1 mm at five different liquid flow rates and superficial gas velocities of 0.02 to 0.16 m·s⁻¹ were empirically correlated by the relation:

$$k_La''' = 0.39\left(1 - \frac{\bar{\phi}_S}{0.58}\right)\bar{u}_G^{0.67}$$

$$(\mathrm{s}^{-1}) \qquad\qquad\qquad (\mathrm{m}\cdot\mathrm{s}^{-1})$$

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