Screening Multiphase Reactors for Nonisothermal Multiple Reactions

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A screening procedure developed synthesizes a multiphase reactor and the accompanying heat-transfer devices desired for a given reaction scheme. It is an extension of a procedure, previously described for isothermal systems with a single reaction to multiple reactions involving heat effects. The three key elements to this approach include a generic reactor model, an accompanying sensitivity model, and a knowledge base consisting of heuristics, as well as correlations on hydrodynamics, heat, and mass transport. The generic reactor model is extended to include various topologies and reactor constituent parts for heat and mass transfer. The sensitivity model quantifies the potential impact of various reactor parameters on reactor performance. The knowledge base is expanded to tackle multiple, nonisothermal reactions. In this procedure, reactor attributes and constituent parts are aggregated to form a reactor for the specific reaction under consideration. It is especially useful at the early stage of process development, when there is a great deal of uncertainty regarding reaction kinetics, and potential limitations of heat and mass transfer.

Introduction

Multiphase reactors are used for a large class of catalytic and noncatalytic reactions including oxidation, hydrogenation, alkylation, and halogenation. These reactions are often highly exothermic and are accompanied by several side reactions. Table 1 shows a few such multiple reaction schemes and the corresponding industrial examples. For these reactions, maximization of selectivity is a key issue in commercialization. In addition to selection of the best reactor type, proper heat management is essential, especially for systems with significantly different activation energies for the various individual reactions.

There is a rich literature on the analysis and design of multiphase reactors including several notable texts and monographs (Shah, 1979, 1991; Ramachandran and Chaudhari, 1983; Doraiswamy and Sharma, 1984; Gianetto and Silveston, 1986; Mills et al., 1992). However, relatively little is available on how to systematically synthesize multiphase reactors. Systematic techniques including graphical optimization procedures (Chitra and Govind, 1985a,b), nonlinear and mixed integer nonlinear programming (Achenie and Biegler, 1990; Schweiger and Floudas, 1999), and attainable region analysis (Glasser et al., 1987; Hildebrandt and Biegler, 1995) have been developed by researchers in the process systems engineering community. However, these studies are limited to homogeneous systems, without considering the complexities presented by interfacial transfer, phase equilibria, and multiphase flow. Further, the focus is on the use of a network of individual reactors for optimizing reaction performance.

The need for a systematic procedure for synthesizing a single optimal multiphase reactor is being met by some recent work. Krishna and Sie (1994) proposed selecting reactors based on three levels: catalyst design, injection and dispersion strategy, and choice of hydrodynamic flow regime. Schembecker et al. (1995) employed a heuristic-numeric consulting scheme for selection of multiphase reactors. In the approach taken by Mehta and Kokossis (1997, 1998), a superstructure is reduced using a stochastic optimization technique to identify an optimal multiphase reactor. The screening procedure of Kelkar and Ng (1998) approaches the problem from the opposite direction. Reactor attributes and constituent parts are aggregated to form a reactor for the specific reaction under consideration. A sensitivity model provides the possible impact of the various reactor parame-

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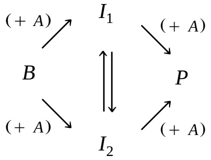
Table 1. Some Basic and Complex Gas-Liquid Reaction Schemes*

Classification	Reaction Scheme	Examples
Independent parallel reactions	$A_1\ (+B) \longrightarrow P$ $A_2\ (+B) \longrightarrow X$	Simultaneous absorption of H_2S and CO_2 in aqueous alkali; absorption of HCN and CO_2 in alkali.
Parallel reactions	$A\ (+B_1) \longrightarrow P$ $A\ (+B_2) \longrightarrow X$	Co-oxidation of organic compounds (such as acetaldehyde and cyclohexane) with air or O_2; chlorination or alkylation of mixed cresols.
Consecutive reactions	$A \xrightarrow{(+B)} I \xrightarrow{(+B)} P$ and $A \xrightarrow{(+B)} P \xrightarrow{(+B)} X$	Ethynylation of formaldehyde to butynediol with propargyl alcohol as intermediate.
Parallel-consecutive reactions	$A\ (+B) \longrightarrow P$ $A + P \longrightarrow X$	Chlorination of para-cresol to 2-chloro-4-methylphenol, and subsequent chlorination to 2,6-dichloro-4-methylphenol.
Complex reactions		Hydrogenation of cottonseed oil (I_1, I_2 are the cis- and trans- mono unsaturated isomers, respectively.)
	$A_1\ (+B) \longrightarrow I$ $A_2 + I \longrightarrow P$	Absorption of Cl_2 and CO_2 in caustic soda.

*A_i, B_i are the dissolved gaseous reactants and liquid-phase reactants, respectively; I_i, P and X are the intermediate, desirable, and the undesirable liquid-phase products, respectively. Parentheses imply that a species may or may not take part in the reaction.

ters on reactor performance. It is especially useful when there is a great deal of uncertainty regarding reaction kinetics, and potential limitations of heat and mass transfer. The procedure, previously limited to isothermal systems with a single reaction, is extended to multiple reactions involving heat effects in this article.

A review is made of the framework with which conventional multiphase reactors are decomposed into four classes of common features. Then, the additional phase attributes, reactor characteristics, constituent parts, and model parameters that are required in each class for nonisothermal multiple reactions are described. The accompanying heuristics and knowledge base are also provided, followed by a discussion of a generic reactor model, as well as a companion sensitivity model. Examples are used to illustrate the screening procedure.

Deconstructing a Generic Multiphase Reactor

It was shown that the seemingly different multiphase reactors can be compared on the basis of four classes of common features or attributes. Figure 1 shows how these four elements combine to form a generic multiphase reactor.

- *Phase distribution attributes* describe the characteristics of the gas, liquid and solid phases which are distributed in the reactor. A phase in general can be classified as being *dispersed*, *fluidized*, *packed*, or *continuous*, depending on its volume fraction in the multiphase reactor. A generic *Volume Fraction Map* shows the ranges of gas, liquid, and solid holdups in a multiphase reactor for phase attributes ranging from dispersed to continuous. Other phase attributes include a description of the state of motion and mixedness of the phase, the physical form of the phase, and quantitative descriptions such as its flow rate, the bubble and drop-size distribution, the interfacial area between phases, and so on.

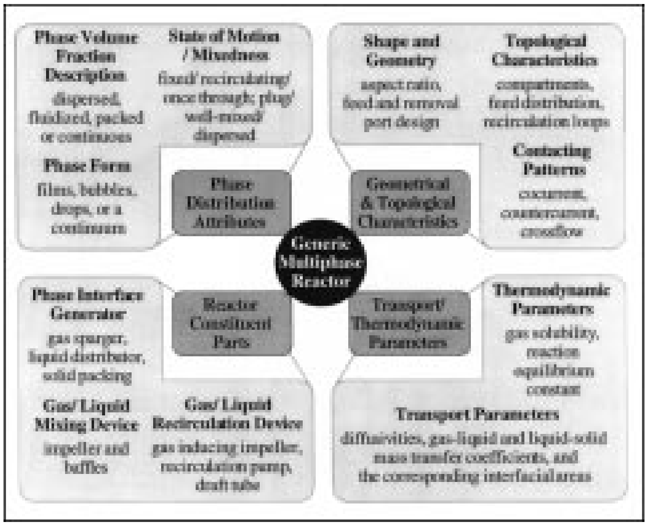


Figure 1. Four classes of common features in a generic multiphase reactor.

Typical features (in bold) in each class along with examples of such features are presented.

- *Topological and geometrical characteristics* describe the physical features of the reactor. These include information about the overall geometry of the reactor, its topology, as well as the nature of the contacting patterns for the fluid phases.
- *Reactor constituent parts* include devices such as the gas-liquid interface generating device, and the gas and liquid recirculation and mixing devices. The structure of the solid phase in the reactor can also be considered to be a part of this class, because the nature of the gas-liquid interface is different when the solid is packed in the reactor, than when it is dispersed in the form of powder.
- *Transport and thermodynamic parameters* form the fourth class of common features in a generic multiphase reactor. The values of various reactor parameters such as the gas-liquid mass-transfer coefficient in different reactors are not a property of the reactors themselves, but primarily of the constituent part generating the parameter value. *Generic Transport Parameter Maps* are used to identify the ranges of these transport parameter values for each reactor part.

The decomposition framework shown in Figure 1 is not rigid, and new features and information can be added to expand its applicability. For synthesis of multiphase reactors with nonisothermal, multiple reactions, the information needed in addition to that for a single isothermal reaction is presented below.

Phase distribution attributes

For multiple reactions with heat effects, the following additional phase distribution attributes can be defined:

- For reactions using different catalysts, what is the size and relative fraction of each catalyst? For example, consecutive reactions may be carried out in staged packed beds with a different catalyst in each stage to improve selectivity.
- Is a phase reacting or nonreacting? For example, the gas phase may only serve to supply the gaseous reactant to the liquid phase where the reaction takes place. In other cases, as in the hydrogenation of crotonaldehyde in a trickle bed (Sedriks and Kenney, 1973), the reaction may take place on the surface of the solid catalyst, as well as in the gas phase. Sometimes, in the case of a gas-liquid reaction catalyzed by a solid, simultaneous, noncatalytic side reactions may occur in the liquid phase, leading to a lower selectivity to the desired product.
- Does a phase undergo a phase change, either within or outside the reactor? For example, a liquid phase is transformed into a solid phase in a reactive crystallizer (Kelkar and Ng, 1999). In a boiling reactor, the liquid phase leaves the reactor in vapor form (Khinast et al., 1998).
- Is there a mass-transfer agent such as a phase-transfer catalyst which ferries components from one phase to another (Naik and Doraiswamy, 1998)?
- Does the phase selectively retain or reject one or more components from it? For example, in a liquid-liquid extractive reaction, the selectivity to the desired product can be improved by a judicious choice of the solvent (Samant and Ng, 1998a,b,c).

Reactor topological and geometrical characteristics

By manipulating these characteristics, the designer can change various attributes such as the level of mixedness of each phase, the concentrations of individual species, and the temperature profile in the reactor:

- Is there heat transfer inside or outside of the reactor? For example, Figures 2a to 2c show reactors with internal heat transfer, Figure 2d shows an ebullated bed using an external stream for heat removal, with the dark circles representing the solid phase, while Figure 2e shows a reactor which involves heat removal by boiling the liquid, followed by a reflux condenser and a liquid recycle.
- Is there any interstage addition of feed? Figure 2f shows a multistaged adiabatic packed bed reactor, with an intermediate addition of cold feed.
- Is there selective removal of one or more species from the reaction mixture? A membrane reactor is such an example (Guha et al., 1995).
- Do the reactants flow axially or radially relative to the reactor? For example, although an axial flow is the most commonly used, a radial flow packed-bed reactor gives a lower pressure drop and also prevents hot spots for highly exothermic reactions, due to a short length of the bed (Balakotaiah and Luss, 1981).

Figure 3 shows how these characteristics manifest themselves into a geometrical representation. Figure 3a shows a single reactor with an internal heat-transfer mechanism. Note that it can represent a dispersed, fluidized or packed reactor, depending on the solid volume fraction. Figures 3b and 3c represent a reactor with external recirculation and heat transfer. Figure 3d shows a reactor with heat transfer involving a phase change, and recirculation of the cold reflux. Figure 3e shows a multistaged reactor with preheating of the feed, and interstage heat exchange, whereas Figure 3f shows a similar reactor with interstage injection of feed. Note that these representations can be combined to yield additional reactor topologies. For example, combining the topologies of Figures 3a and 3f, we have a multistaged reactor with internal heat transfer in each stage, as well as a distributed feed. Figure 3g shows the possibility of removing some of the components through a side stream by using a selective mass-transfer device. Some heuristics for selecting the reactor topology are given below.

- Because of the simplicity, use a jacketed reactor for heat removal, if possible.
- Use an external recirculation loop for highly exothermic reactions for which the capacity of internal heat-transfer de-

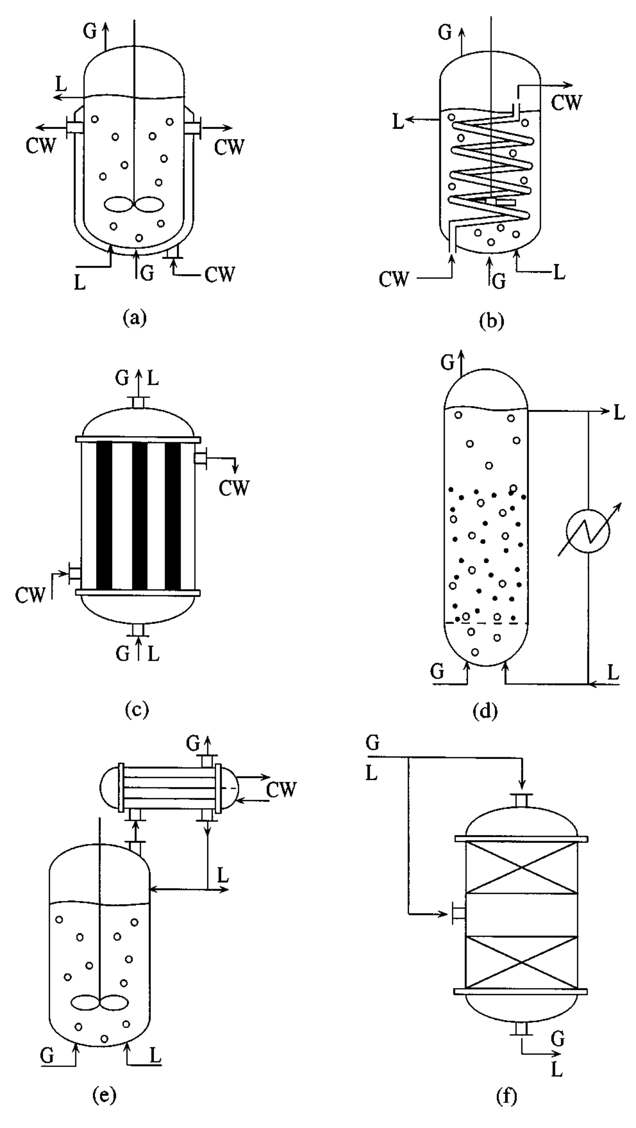


Figure 2. Selected multiphase reactors with the accompanying heat-transfer schemes.

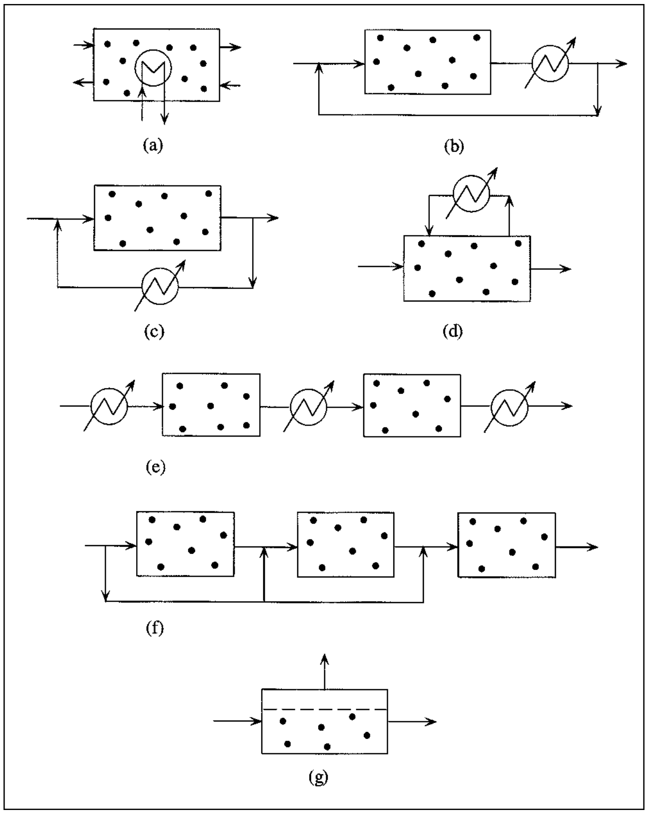


Figure 3. Selected topologies for multiphase reactors.

vices is inadequate. Watch out for fouling, plugging, unintended reactions, and so on in the external loop.

- Use interstage injection of cold reactants as an alternative to using heat-transfer devices, if it is easy to recover and recycle the reactant.
- Use multiple-tube reactors if the presence of radial temperature gradients is deleterious to reactor performance.
- Use compartments to allow interstage injection of a reactant to improve selectivity.
- Use a selective mass-transfer device for the preferential removal of some components as a means for improving yield/selectivity.

Reactor constituent parts

Many attributes of the reactor are determined by distinct reactor parts. The gas-liquid interface generating device, the gas and liquid recirculation device, and so on were described previously (Kelkar and Ng, 1998). Some additional constituent parts are discussed below:

- Devices for selective mass transfer: A membrane reactor features such a device to selectively remove some components to enhance selectivity or overcome equilibrium limitations (Park et al., 1998).
- Devices for internal heat exchange: Some of the devices can be seen in Figure 2: a jacket (Figure 2a) and internal cooling coils (Figure 2b) in a multiphase stirred tank, and a shell-and-tube heat exchanger configuration for a tubular packed reactor (Figure 2c).
- Devices for external heat exchange: Heat exchangers (Figure 2d) and fired heaters can be used for external heat transfer. If the heat transfer involves a phase change, a condenser (Figure 2e) may be used.

Transport and thermodynamic parameters

Various parameters for mass transfer, such as the gas-liquid and liquid-solid mass-transfer coefficients, along with phase distribution parameters such as the corresponding interfacial areas, were previously identified and their ranges mapped in the *Generic Transport Parameter Maps*. Similar maps can be developed for the heat transport parameters in a reactor, such as the overall heat-transfer coefficient and the heat-transfer area (Figures 4a and 4b). The overall coefficient for a jacketed vessel can range from about 50 to 1,000 $W/m^2 \cdot K$, whereas it ranges from about 100 to 2,000 $W/m^2 \cdot K$ for a shell-and-tube heat exchanger, and can be as high as 5,000 $W/m^2 \cdot K$ in a three-phase fluidized bed. Similarly, the heat-transfer area in a jacketed vessel is low, about 0.4 to 4 m^2/m^3 reactor, whereas it can range from 5 to 500 m^2 in an external shell-and-tube heat exchanger. Another characteristic of a heat-transfer scheme is the heat load that it can handle (Figure 4c). Depending on the exothermicity of the reactions involved, the heat generated in an exothermic reactor can range from about 10^3 to 2×10^6 W/m^3 reactor volume. The heat load which can be removed using an internal heat-transfer scheme is low. For example, it ranges from 10^3 to 10^5 W/m^3

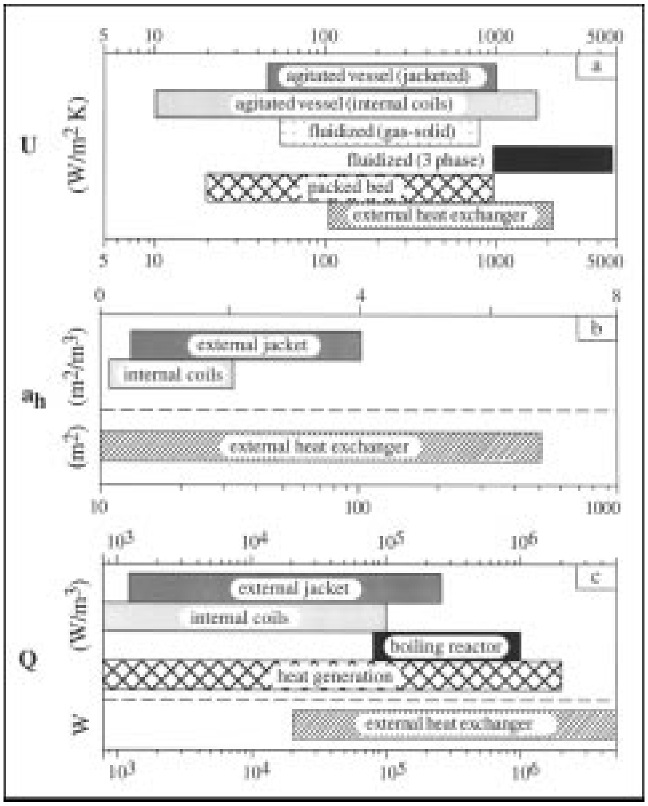


Figure 4. Overall heat-transfer coefficient, heat-transfer area, and the heat load capacity for different heat-transfer schemes.

reactor volume using internal coils. The boiling reactor performs much better, and can remove a heat load ranging anywhere from 10^5 to 10^6 W/m^3 reactor volume. The external heat exchanger, in theory, has no limitations on its size and, hence, can handle much higher heat loads. In practice, this may lead to an unacceptably large recirculation stream.

Generic Multiphase Reactor Model

In this synthesis procedure, the reactor model is not meant to simulate the reactors in details; rather, it distinguishes between different reactors and reactor parts, based on the aforementioned attributes. Any model which can represent a broad class of reactors from trickle beds to slurry reactors may be used. Network models are computationally tractable, and, hence, popular for reactor modeling (Wen and Fan, 1975). For example, Mann (1986) used a network of stirred tanks to represent a single agitated tank, while Ramachandran and Smith (1979) used it to represent a trickle-bed reactor. Dassori (1998) recently used a modified tanks in series model to represent a three-phase slurry reactor. A network model accounting for interphase mass-transfer serves as the generic model in this study.

Figure 5 shows some example networks which can be used to model the flows of the gas, liquid, and solid phases in a multiphase reactor. Figures 5a, 5b, and 5c are the three basic units, or *cells* which describe the varying degrees of mixedness of the gas and liquid phase in the reactor. Additional basic units may be considered to represent situations such as a stagnant zone of fluid (Deans and Lapidus, 1960; van Swaaij et al., 1969), or a nonuniform radial distribution of fluid (Hanika et al., 1978). Although such details provide a better representation of the reactor residence time, they introduce mathematical complexity that may be unnecessary at such a preliminary stage of reactor synthesis. Figure 5d shows the basic unit for representing either internal or external heat transfer in the reactor model, while Figure 5e represents a device for the selective removal of one or more components from the reaction mixture. These five basic units can be interconnected in various ways to yield reactor networks of varying complexity. Figure 5f shows a reactor with the gas and liquid being axially dispersed, and an internal heat-transfer device. Figure 5g shows an N-cell network with a well-mixed liquid phase and a gas phase in plug flow in each cell, an interstage injection of gas, and no heat-transfer arrangement. N can vary from one to a high number so as to allow a representation of a mixing pattern ranging from well-mixed to plug flow in the reactor. Figure 5h represents an N-cell network with well-mixed gas and liquid phases and an internal heat-transfer arrangement in each cell. There is also a recycle for both phases. By adjusting the recirculation ratios, the mixedness of the gas and liquid phases can be independently varied over a wide range, from relatively plug flow to relatively well-mixed. Finally, Figure 5i represents a reactor with interstage, as well as external heat transfer. An advantage of network models is that it is possible to switch from one network to another as the screening procedure proceeds, without too much additional modeling effort. For example, starting with the network shown in Figure 5h, which features an internal heat-transfer arrangement, it is easy to change to an interstage heat-transfer arrangement instead. Such changes allow us to evaluate the effect of different heat-transfer arrangements on reactor performance, and will be illustrated in the examples in a later section.

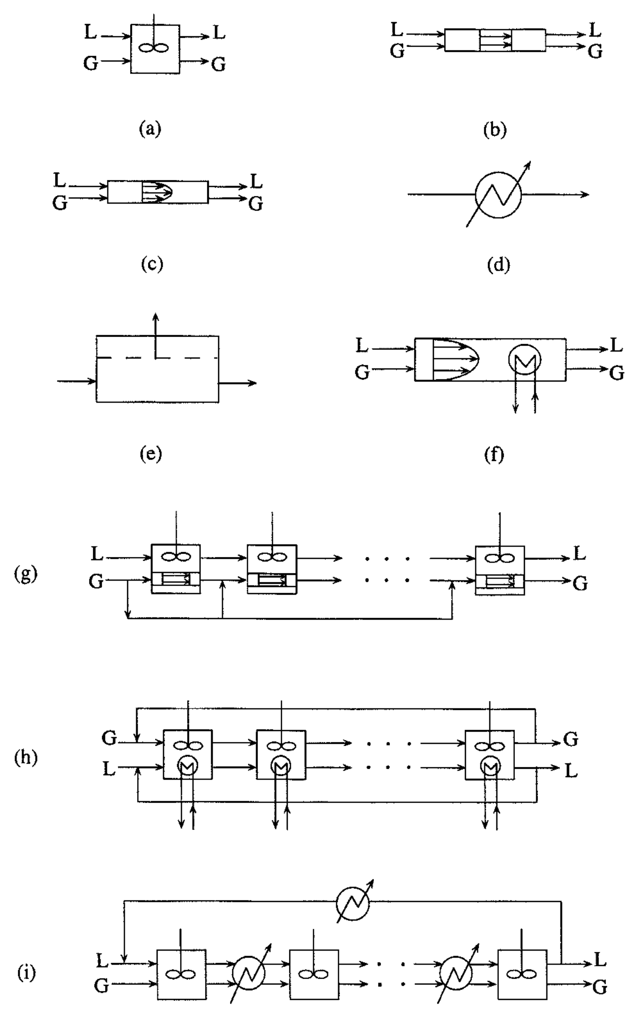


Figure 5. Examples of network models for reactor simulation.

Let us consider a multiple reaction scheme involving gas-liquid, liquid-liquid or gas-liquid-solid (catalytic) reactions

$$\sum_i \nu_{ik} A_i = 0 \qquad k = 1, \ldots, R \tag{1}$$

Each reaction may be reversible in general, and is associated with a heat of reaction ΔH_k. Assuming that some basic information such as estimates of activation energies, gas solubilities, diffusion coefficients, and so on is known about this reaction scheme, our task is to synthesize alternative reactor types that are appropriate for the reaction under consideration. After the network model has been chosen by interconnecting some of the basic units of Figure 5, the set of equations for simulating such a network can be compiled using standard heat and mass balance equations for each cell and mixing point in the network, as well as for transfer across the gas-liquid and liquid-solid interfaces. The resulting system of equations describes the concentrations of all species and temperature throughout the network. Thus, for a one-dimensional steady-state reacting system, the bulk phases can be described by the following general equations

$$f\left(\frac{d^2c}{dz^2}, \frac{dc}{dz}, c, T; z, \boldsymbol{\alpha}, \boldsymbol{\beta}\right) = \mathbf{0} \tag{2}$$

$$g\left(\frac{d^2T}{dz^2}, \frac{dT}{dz}, c, T; z, \boldsymbol{\alpha}, \boldsymbol{\beta}\right) = \mathbf{0} \tag{3}$$

with the appropriate boundary conditions. Here, c is the vector of concentrations of all the species in all the phases, T is the vector of temperatures in all the phases at all the points in the network, $\boldsymbol{\alpha}$ is the vector of phase distribution attributes such as ϵ_G, ϵ_L, ϵ_S, a and a_S, and $\boldsymbol{\beta}$ is the set of transport and thermodynamic parameters such as k_L, k_S, H_i, D_i, U and a_h. The general equation can be greatly simplified, depending on the structure of the chosen model. For example, for a gas-liquid system, represented with only well-mixed tanks with internal heat transfer, and no reaction in the gas-liquid film, the model equations are nonlinear algebraic equations.

In addition to the network model for representing the flows of the three phases, the two film theory (Lewis and Whitman, 1924) is used to model gas-liquid interface transport. Thus, the cells in Figures 5a to 5c represent the mixedness only in the bulk of the gas and liquid phases, not in the films. The liquid-solid mass transfer is modeled using a mass-transfer coefficient, which is usually correlated in terms of the Reynolds and the Schmidt numbers (Dharwadkar and Sylvester, 1977; Nienow, 1975). For reaction within a catalyst pellet, an intraparticle diffusion resistance may lead to a nonuniform concentration profile within the catalyst. In that case, the model will include the differential equations describing the simultaneous diffusion and reaction of the chemical species within the catalyst, or an approximate solution involving the catalyst effectiveness factor.

Sensitivity analysis

An integral part of this screening procedure is a sensitivity model which accompanies the reactor model. The relative impact of the different variables and model parameters on reactor performance can be assessed. The direct differential method (Rabitz et al., 1983) is used for the sensitivity model, which involves sensitivity equations obtained by differentiating Eqs. 2 and 3, with respect to the parameter of interest α_j

$$\left(\frac{\partial f}{\partial c''}\right)_{\boldsymbol{\alpha},\boldsymbol{\beta},T}\frac{d^2 s_j}{dz^2} + \left(\frac{\partial f}{\partial c'}\right)_{\boldsymbol{\alpha},\boldsymbol{\beta},T}\frac{ds_j}{dz} + \left(\frac{\partial f}{\partial c}\right)_{\boldsymbol{\alpha},\boldsymbol{\beta},T} s_j + \left(\frac{\partial f}{\partial \alpha_j}\right)_{\boldsymbol{\alpha}_i[i\neq j],c,\boldsymbol{\beta},T} = \mathbf{0} \tag{4}$$

$$\left(\frac{\partial g}{\partial T''}\right)_{\boldsymbol{\alpha},\boldsymbol{\beta},c}\frac{d^2 s_j^T}{dz^2} + \left(\frac{\partial g}{\partial T'}\right)_{\boldsymbol{\alpha},\boldsymbol{\beta},c}\frac{ds_j^T}{dz} + \left(\frac{\partial g}{\partial T}\right)_{\boldsymbol{\alpha},\boldsymbol{\beta},c} s_j^T + \left(\frac{\partial g}{\partial \alpha_j}\right)_{\boldsymbol{\alpha}_i[i\neq j],c,\boldsymbol{\beta},T} = \mathbf{0} \tag{5}$$

The vectors of sensitivity coefficients are defined as

$$s_j = \left(\frac{\partial c}{\partial \alpha_j}\right) \quad \text{and} \quad s_j^T = \left(\frac{\partial T}{\partial \alpha_j}\right) \tag{6}$$

Although some of the transport parameters $(\boldsymbol{\beta})$ may depend on phase parameters $(\boldsymbol{\alpha})$, they are treated as mathematically independent in the sensitivity analysis for two reasons. First, a correlation between two such parameters that is generally applicable to all multiphase reactors is often not available. For example, there exists a correlation which shows how the solid-liquid mass-transfer coefficient k_S (m/s) increases with decreasing particle size in a stirred tank, but it is not applicable for a trickle-bed reactor. Second, treating the two parameters as independent does not affect the conclusion of the screening procedure. This is because the dependency is implicit in the *Generic Transport Parameter Maps* described earlier. For example, consider a case where the sensitivity model predicts an improvement in the reactor performance with a higher k_S, but does not indicate a high sensitivity to d_p because the two parameters were not correlated in the model. The screening procedure will then guide the user to a slurry reactor which has better mass-transfer characteristics than a packed reactor, and, which incidentally uses particles with a smaller d_p. Obviously, if a correlation between certain transport and phase distribution parameters is available, it should be incorporated explicitly into the reactor and sensitivity model.

The solution of the sensitivity equations (Eqs. 4 and 5) gives us the sensitivity of the concentrations and the reactor temperature to the reactor parameters. Usually, a more useful performance index, such as the conversion, selectivity, or total cost, is desired. For single irreversible reactions, the productivity of the reactor is determined by the amount of reactant converted in the reactor. The reactant conversion is thus an appropriate performance index, because maximizing the conversion is equivalent to minimizing the reactor size for a given production rate. For multiple reactions, however, the product distribution, or more specifically, the selectivity to the desired product, is the overriding concern. Kondelik (1982) showed that, only for a very inexpensive raw material, a very expensive reactor, or a very low production rate will the reactor cost be more significant to the raw material cost. In process synthesis, although the ultimate objective is always to minimize the cost of the total plant, it is common to optimize subsets of the plant, such as the reactor, or the reactor plus the separation system, individually. The appropriate performance index is different, depending on the focus of the synthesis procedure, and some guidelines for selecting the performance index are summarized in Table 2.

If the chosen performance index can be written as a function of reactor concentrations and temperature, the parame-

Table 2. Guidelines for Choosing a Performance Index During Reactor Synthesis

- If possible, use the total cost of the complete plant as the performance index.
- For multiple reactions, the conditions for maximum selectivity often run contrary to those for maximum conversion. If the unreacted reactant can be separated and recycled cheaply, use selectivity as the sole performance index. Else, use the yield of the product (based on the total amount of key reactant charged) as the performance index.
- For reactions with expensive catalysts (or with catalysts which deactivate rapidly), include the catalyst cost (or the catalyst regeneration costs) as part of the performance index.
- For systems where the recovery of the product, byproducts, reaction solvent or catalyst is expensive, include the cost of the corresponding separation system as part of the performance index.
- For reactions requiring expensive materials of construction for the reactor such as titanium, include the reactor cost as part of the performance index.

ters $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, and some other variables q,

$$P = P(c, T; \boldsymbol{\alpha}, \boldsymbol{\beta}, q) \tag{7}$$

then the sensitivity of the performance index $\Psi(\alpha_j)$ can be obtained as

$$\Psi(\alpha_j) = \frac{\partial P}{\partial \alpha_j} = \left(\frac{\partial P}{\partial c}\right) s_j + \left(\frac{\partial P}{\partial T}\right) s_j^T + \frac{\partial P}{\partial \alpha_j} + \left(\frac{\partial P}{\partial q}\right)\left(\frac{\partial q}{\partial \alpha_j}\right) \tag{8}$$

Here, q includes all the external variables required to relate the performance index to the concentrations and the temperature, and may depend on $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$. For example, if the performance index is taken to be the reactor cost, P depends on the reactor volume which, in turn, depends on the reactor effluent concentrations for a given conversion. In this case, q would include parameters which reflect the cost of construction and auxiliary equipment for the reactor.

The sensitivity coefficients are normalized using the maximum expected variation in the parameter value. This allows a comparison of the sensitivity coefficients on an equal basis

$$\overline{\Psi}(\alpha_j) = \frac{\partial P}{\partial(\alpha_j/\Delta\alpha_{j,\max})} = \Psi(\alpha_j)\Delta\alpha_{j,\max} \tag{9}$$

Here, $\Delta\alpha_{j,\max}$ is the maximum expected range of α_j. Thus, the larger the magnitude of the normalized sensitivity coefficient, the more impact it has on the performance index. When the sensitivity coefficients are negative, the performance index increases with a *decrease* in the parameter value. For positive sensitivity coefficients, the performance index can be improved by *increasing* the value of the corresponding parameter. The generic reactor and sensitivity model are illustrated below for a multiple gas-liquid reaction scheme.

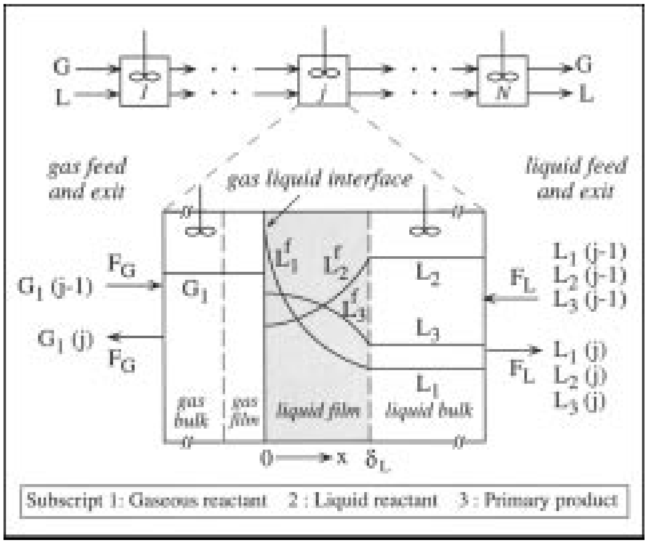


Figure 6. Stirred-tanks-in-series flow model with a film-theory model for the gas-liquid contact.

Model Illustration

Let us consider a network of N isothermal well mixed tanks in series. There are m_G reactants present in the gas feed, m_L reactants in the liquid feed, and m_P products of reaction in the liquid. The gas-liquid mass transfer is modeled using the stagnant film theory. We assume that the reactions take place only in the liquid phase and that the gas phase presents a negligible resistance to mass transfer. We further assume that the liquid phase is of a constant density and that the liquid reactants and products are nonvolatile. The network and the gas-liquid interface is shown in Figure 6. For each cell, we have the bulk gas-phase material balances, the bulk liquid phase material balances, and the differential equations describing the diffusion and reaction of the chemical species through the liquid film. Gas-phase material balances for the species i in the jth cell are as follows

$$F_G(G_i(j-1) - G_i(j)) + V k_L a\left(\frac{D_i}{D_A}\right)\left(\frac{dL_i^f(j)}{dX}\right)_{X=0} = 0 \qquad i = 1, \ldots, m_G \tag{10}$$

Here, $G_i(j)$ is the gas-phase concentration of the ith gaseous species; $L_i^f(j)$, the concentration of the ith gaseous species in the liquid film, is a function of the dimensionless distance X in the film given as

$$X = \frac{x}{\delta_L} \tag{11}$$

D_i is the diffusion coefficient of the ith gaseous species in the liquid phase (m^2/s). D_A is the diffusion coefficient for the primary gaseous component, which is used to define the mass-transfer coefficient as

$$k_L = \frac{D_A}{\delta_L} \tag{12}$$

Thus, throughout this article, k_L refers to the mass-transfer coefficient (m/s) for the primary diffusing gaseous species.

The mass-transfer coefficients for any other species, such as the ith gaseous species, is given simply by $k_L(D_i/D_A)$.

For the m_G gaseous species diffusing through the liquid film, the steady-state material balance is given by

$$\frac{d^2 L_i^f(j)}{dX^2} = \left(\frac{D_A^2}{D_i k_L^2}\right)\mathbf{\Phi}_i^f(j) \qquad i = 1, \dots, m_G \tag{13}$$

where $\mathbf{\Phi}_i^f(j)$ is the rate of consumption of the ith gaseous species per unit volume of the liquid film, obtained by summing over all the reactions in the reaction scheme. One boundary condition for Eq. 13 is obtained by specifying the conditions at the interface, while the other is obtained by specifying the concentration of the gaseous species in the liquid bulk $L_i(j)$. Thus,

$$L_i^f(j) = \frac{G_i(j)}{H_i} \quad \text{at } X = 0 \quad i = 1, \dots, m_G \tag{14}$$

$$L_i^f(j) = L_i(j) \quad \text{at } X = 1 \quad i = 1, \dots, m_G \tag{15}$$

We have similar equations to describe the diffusion and reaction of the $m_L + m_P$ liquid reactants and products in the liquid film

$$\frac{d^2 L_i^f(j)}{dX^2} = \left(\frac{D_A^2}{D_i k_L^2}\right)\mathbf{\Phi}_i^f(j) \qquad i = m_G + 1, \dots, m_G + m_L + m_P \tag{16}$$

with boundary conditions

$$\frac{dL_i^f(j)}{dX} = 0 \quad \text{at } X = 0 \qquad i = m_G + 1, \dots, m_G + m_L + m_P \tag{17}$$

$$L_i^f(j) = L_i(j) \quad \text{at } X = 1 \qquad i = m_G + 1, \dots, m_G + m_L + m_P \tag{18}$$

where $L_i(j)$ is the concentration of the liquid reactant or product species in the liquid bulk.

The bulk liquid-phase mass balances for the dissolved gaseous and liquid reactants, and the liquid products are

$$F_L\big(L_i(j-1) - L_i(j)\big) - V k_L a \left(\frac{D_i}{D_A}\right)\left(\frac{dL_i^f(j)}{dX}\right)_{X=1} - V\epsilon_L\left(1 - \frac{aD_A}{\epsilon_L k_L}\right)\mathbf{\Phi}_i(j) = 0 \qquad i = m_G + 1, \dots, m_G + m_L + m_P \tag{19}$$

$\mathbf{\Phi}_i(j)$ is the rate of consumption of the ith species per unit volume of the bulk liquid phase. This is obtained by summing the rate expressions for each species over all the reactions in the reaction scheme. Equations 10 to 19 represent a system of $m_G + m_L + m_P$ coupled ODEs, with the corresponding $2(m_G + m_L + m_P)$ boundary conditions for each cell. The boundary value problems may be numerically solved by the shooting method. The entire network can be simulated by progressively solving the system of equations for each cell. The above model is used as the generic reactor model for Examples 1 and 2 later in this article.

Equations 10 to 19 can be easily simplified to the case where reaction in the liquid film is negligible. (For example, see Kelkar and Ng (1998) for such a model, although the gas-liquid reaction is catalyzed by a solid.) Under these conditions, we can write an overall energy balance for the jth cell as follows

$$(F_L\rho_L C_L + F_G\rho_G C_G)\big(T(j-1) - T(j)\big) + V k_L a \sum_{i=1}^{m_G}\left(\frac{D_i}{D_A}\right)\left(\frac{G_i(j)}{H_i} - L_i(j)\right)\Delta H_{i,\text{abs}} + V\epsilon_L \sum_{k=1}^{R}\Theta_k(j)\Delta H_k - \sum Q_{\text{ext}} = 0 \tag{20}$$

where $\Delta H_{i,\text{abs}}$ is the heat of absorption for the ith gaseous reactant, ΔH_k is the heat of reaction for the kth reaction, $\Theta_k(j)$ is the rate of the kth reaction per unit volume of the liquid phase in the jth cell in the network, and ΣQ_{ext} accounts for the heat transfer due to all heat-transfer arrangements. Here, the heat of gas absorption is assumed to be released in the liquid bulk. All the phases in each cell are assumed to be at the same temperature, and the thermophysical properties of the reaction medium are assumed to be constant. The above model, with inclusion of heat effects, but no reaction in the film will be used in Examples 3 and 4.

Sensitivity model

The sensitivity model for the isothermal reactor is obtained by differentiating the reactor model (Eqs. 10 and 13 to 19) with respect to the parameters of interest. The parameters we may like to consider include the transport and thermodynamic parameters (k_G, k_L, k_S, H_i, D_i, and so on), the phase distribution attributes (ϵ_G, ϵ_L, ϵ_S, a, a_S, and so on), the reaction rate constants k_k, and the temperature. For example, with k_L as parameter, the sensitivity equations are as follows

Gas Phase

$$F_G\big(s_i^G(j-1) - s_i^G(j)\big) + V k_L a\left(\frac{D_i}{D_A}\right)\left(\frac{ds_i^f(j)}{dX}\right)_{X=1} + Va\left(\frac{D_i}{D_A}\right)\left(\frac{dL_i^f(j)}{dX}\right)_{X=1} = 0 \qquad i = 1, \dots, m_G \tag{21}$$

Liquid Film (Gaseous Species)

$$\frac{d^2 s_i^f(j)}{dX^2} = \left(\frac{D_A^2}{D_i k_L^2}\right)\mathbf{\Phi}_i^{f'}(j) - 2\left(\frac{D_A^2}{D_i k_L^3}\right)\mathbf{\Phi}_i^f(j) \qquad i = 1, \dots, m_G \tag{22}$$

with boundary conditions

$$s_i^f(j) = \frac{s_i^G(j)}{H_i} \quad \text{at } X = 0, \quad i = 1, \ldots, m_G \tag{23}$$

$$s_i^f(j) = s_i^L(j) \quad \text{at } X = 1, \quad i = 1, \ldots, m_G \tag{24}$$

Liquid Film (Liquid Reactants and Products)

$$\frac{d^2 s_i^f(j)}{dX^2} = \left(\frac{D_A^2}{D_i k_L^2} \right) \mathbf{\Phi}_i^{f'}(j) - 2 \left(\frac{D_A^2}{D_i k_L^3} \right) \mathbf{\Phi}_i^f(j)$$

$$i = m_G + 1, \ldots, m_G + m_L + m_P \tag{25}$$

with boundary conditions

$$\frac{ds_i^f(j)}{dX} = 0 \qquad \text{at } X = 0$$

$$i = m_G + 1, \ldots, m_G + m_L + m_P \tag{26}$$

$$s_i^f(j) = s_i^L(j) \quad \text{at } X = 1$$

$$i = m_G + 1, \ldots, m_G + m_L + m_P \tag{27}$$

Bulk Liquid Phase (Reactants and Products)

$$F_L\left(s_i^L(j-1) - s_i^L(j) \right) - V k_L\, a \left(\frac{D_i}{D_A} \right) \left(\frac{ds_i^f(j)}{dX} \right)_{X=1} - Va \left(\frac{D_i}{D_A} \right) \left(\frac{dL_i^f(j)}{dX} \right)_{X=1} - V\epsilon_L \left(1 - \frac{aD_A}{\epsilon_L k_L} \right) \mathbf{\Phi}_i'(j) - V\epsilon_L \left(\frac{aD_A}{\epsilon_L k_L^2} \right) \mathbf{\Phi}_i(j) = 0$$

$$i = m_G + 1, \ldots, m_G + m_L + m_P \tag{28}$$

Screening Method

This screening procedure is applicable to a gas-liquid, liquid-liquid, or gas-liquid-solid catalytic reaction. The following scenario is considered. The proposed reaction is being investigated by the chemist in a laboratory reactor such as a bench-scale reactor or a microreactor. The information regarding the chemistry and kinetics of the reaction is likely to be incomplete, and may be unreliable as well. It is assumed, however, that the molar ratio of the reactants and an approximate reaction time for the primary reactants is known. Additionally, the reaction scheme with approximate rate expressions has been identified. An estimate of the heat of reaction is available. The phases involved at the temperature and pressure of the reaction, as well as the composition of the reactor feed is known. Some desirable physicochemical properties of the reaction mixture can also be estimated, such as the solubilities of gaseous reactants, diffusivities in the liquid phase as well as in the catalyst pores as in the case of a solid catalyzed reaction, and so on. The production rate has been specified.

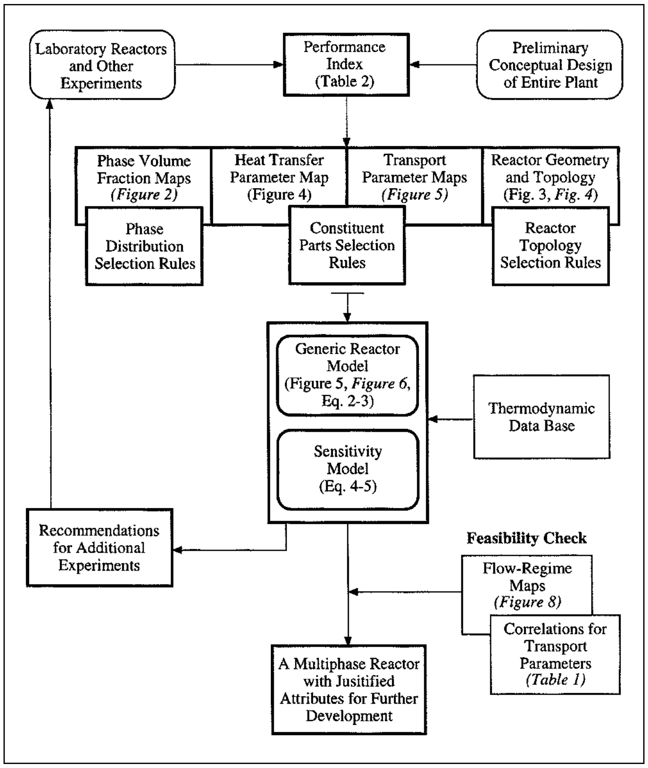


Figure 7. Algorithm for the reactor screening/synthesis procedure.

Italicized text refers to the figures and tables in Kelkar and Ng (1998).

The task of the screening procedure is to identify the dominant variables affecting the performance of the reactor, and suggest reactor types suitable for further process development. The procedure was previously described for single, isothermal reactors. The procedure for multiple reactions with heat effects, summarized in Figure 7, is discussed below. It can be suitably modified by the user for situations different from the one described here, and in light of the information that the user may or may not have.

Step 1: Using the heuristics given in Table 2, select the appropriate performance index for screening.

Step 2: Set Up the Generic Reactor Model.

(a) Using all known information concerning the reaction, select a suitable network model such as those shown in Figure 5. If selectivity is the desired performance index, the interconnections in the network model may be selected using the heuristics in Table 3. For example, for a parallel reaction scheme where the order of the desired reaction is lower than that of the undesired reaction, heuristic 3a in Table 3 suggests that an interstage addition of the corresponding reactant would improve selectivity. This should therefore be included in the network model. For reaction schemes where such heuristics cannot be easily applied, choose a network model having a complexity commensurate with the accuracy of the available reactor parameters and reaction kinetics.

(b) In general, all possible heat-transfer arrangements shown in Figure 3 are included as part of the network. The appropriate ones are activated as the screening proceeds. For

Table 3. Heuristics for Enhancing the Selectivity for the Basic Gas-Liquid Reaction Schemes*

(1) Selection of flow type (N in the Reactor Network)
  (a) For parallel reactions, if the main reaction is of a higher order in a certain reactant than the side reaction, plug flow gives a higher selectivity; if it is of lower order, mixed flow gives a higher selectivity.
  (b) For consecutive reactions, if the desirable product is an intermediate, plug flow always gives a higher selectivity than mixed flow.
(2) Effect of Mass-Transfer Limitations (Gas-Liquid-Interface Generating Device)
  (a) For parallel reactions, if the main reaction is of a higher order in a certain reactant than the side reaction, the selectivity decreases with increasing mass-transfer limitations for that reactant. Hence, operate in the kinetic controlled regime. The reverse is true when the main reaction is of a lower order than the side reaction.
  (b) For consecutive reactions, if the desirable product is an intermediate, the selectivity increases with increasing mass-transfer limitations.
(3) Concentration of Primary Reactant (Feed Concentration and Distribution)
  (a) For parallel reactions, if the order of the main reaction is higher than that of the side reaction, a higher concentration enhances selectivity, and vice versa.
  (b) For consecutive reactions, if the desirable product is an intermediate, a higher reactant concentration enhances selectivity.
(4) Temperature of Operation (Heat-Transfer Topology) (Considering the Temperature Effect only on the Reaction Rate Constants)
  (a) For parallel or consecutive reactions, if the activation energy of the main reaction is greater than that of the side reaction, operate at the highest acceptable temperature, irrespective of the type of the reactor, or the level of conversion.
  (b) For parallel or consecutive reactions, if the activation energy of the main reaction is less than that of the undesired reaction, the selectivity increases with decreasing temperature; hence, operate at a temperature which gives the best tradeoff between conversion and selectivity.
(5) Level of reactant conversion
  (a) For parallel reactions if the main reaction is of a lower order in a certain reactant than the side reaction, the selectivity increases with increasing conversion of that reactant, and vice versa.
  (b) If the desirable product is an intermediate in a consecutive reaction, the selectivity decreases with increasing conversion.

*Following the recommendation of the Working Party on Chemical Reaction Engineering, E.F.Ch.E. (Villermaux, 1984), selectivity is defined as the ratio of the amount of key reactant converted to desirable product to that converted to undesirable product.

example, if a phase change occurs in the reactor (such as, if a component has a bubble point which is lower than the temperature of operation), then the corresponding heat-transfer topology (Figure 3d) has to be activated.

(c) Select a model for gas-liquid interphase transport. For gas-liquid reactions, an analysis of the Hatta number (for example, $Ha = \sqrt{kD_A/k_L^2}$ for a reaction which is first order in the concentration of gaseous reactant A; see Westerterp et al. (1984) for a more general definition) may be used to decide whether a simultaneous solution of the diffusion-reaction equations close to the gas-liquid interface is necessary; else, only reactions in the liquid bulk need be considered. For heterogeneous catalytic reactions, also select a suitable model for the liquid-solid interphase transport and the transport within the porous catalyst.

(d) Alternatively, use a generic model which reflects the laboratory or existing production reactor.

(e) Set up the reactor model (Eqs. 2 and 3) for the generic reactor network created above.

Step 3: Set Up the Sensitivity Model.

(a) Identify a set of parameters with respect to which the sensitivity analysis is to be carried out.

(b) Set up the sensitivity model (Eqs. 4 to 9).

Step 4: Generate a Base Case.

(a) Assign base case values for the gas, liquid and solid holdups, the mass-transfer coefficients and interfacial areas, and the various heat-transfer coefficients and heat-transfer areas. If selectivity is the chosen performance index, the heuristics given in Table 3 may be used to identify whether the base case values for some reactor parameters such as the mass-transfer coefficients should be chosen from the higher or the lower end of their ranges. However, a good base case reactor, while helpful, is not critical because the screening procedure will eventually lead to the best reactor type. Additionally, choose a temperature for the feed(s) and for the heat-transfer medium.

(b) For the examples in this article, the reactor screening is carried out on the basis of a known liquid residence time, which is fixed throughout the screening. From the production rate and the liquid residence time, estimate a base case reactor volume. Also, assign the base case values for all other parameters in the model, such as the number of stirred tanks in series, choice of internal or external heat-transfer device, and recycle ratios for various streams, if any. The heuristics given in Table 3, if appropriate, may again be used to help choose the values for some of these parameters. Although several heat-transfer arrangements are included in the reactor model, it is recommended that the base case be chosen to be adiabatic, that is, without activating any heat-transfer scheme. This way, if the performance predicted in Step 5 below is satisfactory, then the reaction can be carried out adiabatically.

(c) Alternatively, if an existing laboratory or production reactor is used in Step 2d above, use the corresponding parameter values as the base case.

Step 5: Screen the Parameters.

(a) Determine the predicted reactor performance, as well as the sensitivity coefficients for the chosen generic reactor. With the base case being adiabatic, examine the temperature change across the reactor. If the temperature change is unacceptable, or if the performance index is sensitive to temperature, select a suitable heat-transfer scheme as part of the reactor network.

(b) Identify the parameter with the highest magnitude of sensitivity. This is the dominant parameter. If the sensitivity coefficient is positive, increase the parameter value to minimize the limitations due to this parameter. As the parameter value is increased in successive iterations, the sensitivity of the performance index to this parameter decreases, until eventually, some other parameter begins to dominate.

(c) If the sensitivity coefficient is negative, decrease the parameter value. This may make the sensitivity to that parameter more negative in the next iteration. In this case, decrease the parameter value until some other parameter is more dominant, or until some other overriding considerations are encountered. For example, for consecutive gas-liquid reactions, if the desired product is the intermediate, the selectivity increases with decreasing gas-liquid interfacial area a (Table 3, heuristic 2b). However decreasing a too much may lead to an unacceptably low conversion. Steps 5a to 5c are continued until the performance index is sufficiently high, or it is no longer sensitive to any of the chosen alterable reactor parameters.

(d) As the parameter values are adjusted, two types of constraints should be recognized. A hard constraint such as $(\epsilon_S + \epsilon_G + \epsilon_L > 1)$ is unacceptable and has to be avoided. A soft constraint is one in which the parameter values do not conform to those of a conventional multiphase reactor and is resolved by changing two or more parameter values simultaneously. For example, consider a base case that begins with a single reactor with a dispersed solids phase, and an internal heat-transfer scheme. The screening procedure has reached a point where the performance index (such as the selectivity to the desired product) is dominated by reactor temperature. The sensitivity coefficients indicate that the selectivity can be improved by lowering the reactor temperature, and, thus, by increasing heat removal from the reactor. This can be achieved by increasing the value of the available heat-transfer area. However, the current conditions are those of an internal heat-transfer device and there is an upper limit to its area. This soft constraint can be resolved by switching from an internal to an external heat-transfer topology, and, simultaneously, increasing the heat-transfer area.

Step 6: Identify Reactor Type and Constituent Parts.

(a) From the phase holdup values at the end of the screening procedure, identify the phase distribution in the reactor; from the values of the mass-transfer coefficients and interfacial areas, identify the type of gas-liquid interface generating device (see Kelkar and Ng, 1998). Similarly, from the type of heat-transfer coefficients, heat-transfer areas, and the heat loads handled (W/m^3), identify the type of heat-transfer scheme, and the corresponding constituent parts (Figure 4).

(b) Based on the heat-transfer scheme as decided above, and the value of the parameter N (that is, the number of tanks in reactor model), decide whether to use a single reactor, or multiple reactors arranged in a network. For example, consider a reactor with $N = 5$, a dispersed solid phase, a high gas-liquid mass-transfer coefficient, and an internal heat-transfer device. These can be translated into the following alternatives: (a) a cascade of stirred tanks in series with a cooling jacket or coils for each tank; (b) a (single) tray column, with cooling coils on each tray; or (c) a tower reactor with cooling coils along the length of the tower. The final choice can be made after a more detailed modeling and cost analysis. Obviously, other things being the same, a single reactor would be much cheaper than a cascade of reactors.

(c) Note that the parameter values may be such that step b above may lead to a reactor type not conventionally observed, or even a reactor with mutually conflicting parameter values (soft constraints). In such a case back up to the last set of parameter values resulting in a feasible reactor or a new reactor configuration.

In Steps 7 and 8, we verify the flow regime and check for reactor feasibility. This has been described previously, and is not repeated here. The screening procedure is illustrated with the following examples.

Examples

The first two examples deal with maximizing the selectivity under isothermal conditions. The next two examples examine the selectivity to the desired product, while taking into account the heat effects in the reactors. The reactions are fictitious, but the data used are close to those for the real reactions identified in each example.

Example 1: isothermal consecutive-parallel reaction scheme

Consider the following reaction scheme, where the gaseous species A undergoes a liquid-phase reaction with the liquid reactant B. The desired product P further reacts with B to form the undesired byproduct X. The scheme is thus a consecutive reaction scheme with respect to A and a parallel scheme with respect to B

$$\begin{aligned} &A_{(g)} \longrightarrow A_{(l)} \\ &A_{(l)} + B_{(l)} \xrightarrow{k_1} P_{(l)} \qquad \text{Rate} = k_1 A_{(l)} B_{(l)} \\ &B_{(l)} + P_{(l)} \xrightarrow{k_2} X_{(l)} \qquad \text{Rate} = k_2 B_{(l)} P_{(l)} \end{aligned}$$

A similar scheme has been observed in the ethynylation of formaldehyde to butynediol (Kale et al., 1981), with P being an intermediate (propargyl alcohol), and X being the product (butynediol). Similarly, the CO_2−monoethanolamine system is known to proceed according to such a reaction scheme. For a detailed analysis of the selectivity issues in the scheme, see Brian and Beaverstock (1966).

Step 1: The overall selectivity to P, given in this case by the ratio [amount of P formed]/[amount of X formed], is chosen as the performance index during screening.

Step 2: Generic Model. The rate expressions for the reactions are as shown above. A network of N well-mixed tanks in series is chosen as the flow model. The gas-liquid mass transfer is modeled using the stagnant film theory. The modeling of this network was illustrated earlier (Eqs. 10−19). No heat-transfer topology is incorporated into the model at this stage. Example 3 will illustrate the screening procedure for a similar reaction scheme with heat effects.

Step 3: Sensitivity Model. The parameters of interest are k_L, a, k_1, k_2 and ϵ_L. The sensitivity model for the parameter k_L was given earlier (Eqs. 21 to 28). The sensitivity of the performance index (selectivity, P/X) to the parameter k_L is related to the concentration sensitivity coefficients as follows

$$\Psi(k_L) = \frac{\left[L_X(N) s_X^L(N) - L_P(N) s_P^L(N)\right]}{\left[L_X(N)\right]^2} \qquad (29)$$

The sensitivity coefficients with respect to the other parameters can be set up similarly. The reactor model and sensitivity equations are solved simultaneously for every parameter.

Step 4: Generate Base Case. The input data for this example, typical values for gas-liquid reactions, are summarized in Table 4. The base case is chosen to be a bubble column reactor, with a gas and liquid holdup of 0.3 and 0.7, respectively.

Table 4. Base-Case Parameters for Example 1

F_G	0.04 m^3/s	k_L	5×10^{-5} m/s
F_L	0.0015 m^3/s	D_A	1×10^{-9} m^2/s
τ_L	200 s	D_B	1.2×10^{-9} m^2/s
ϵ_G	0.3	D_P, D_X	0.5×10^{-9} m^2/s
ϵ_L	0.7	Feed Conditions	
k_1	0.02 $m^3/mol\cdot s$	G_A	40 mol/m^3
k_2	5×10^{-5} $m^3/mol\cdot s$	L_B	1,000 mol/m^3
H_A	0.2 $(mol/m^3)_G/(mol/m^3)_L$	L_A, L_P, L_X	0 mol/m^3

The liquid phase has a residence time of 200 s, which will be kept constant throughout the screening procedure.

Step 5: Screen Parameters. The sensitivity coefficients are calculated for each set of parameter values, and, depending on the dominant coefficients (shown in bold), the parameter values are changed suitably. This process continues until the selectivity is no longer very sensitive to any alterable parameter, or until the resulting reactor is infeasible. The results are shown in Table 5. The leftmost column shows the iteration number. For each iteration, the numbers in alternate columns indicate the parameter values and the normalized sensitivity coefficient $\overline{\Psi}$ of the selectivity ratio P/X to these parameters. For comparison, the yield of P, defined as [amount of P formed]/[amount of B charged at the reactor inlet], is shown in column 3. The reactor corresponding to the parameter values at each iteration is shown in the far right column. In the first iteration, the selectivity ratio is a little over unity, which indicates that a lot of byproduct is being produced. Examination of the sensitivity coefficients reveals that $\overline{\Psi}(a)$ is the highest, followed by $\overline{\Psi}(k_L)$, indicating that the overall process is limited by the gas-liquid mass transfer. Note that $\overline{\Psi}(\epsilon_L)$ is negative, implying that the selectivity will improve with a decrease in liquid holdup. In iteration 2, a is increased to 1,000 m^2/m^3, and k_L to 1×10^{-4} m/s. Each parameter change is shown by a vertical arrow in the table. The selectivity improves to 4.75. The dominant sensitivity coefficients are $\overline{\Psi}(\epsilon_L)$ (at -4.8) and $\overline{\Psi}(a)$ (at 4.3). Therefore, in iteration 3, the liquid holdup is decreased to 0.3 to correspond to a liquid phase in the dispersed state, such as in a spray column. Simultaneously, a has to be decreased to the normal range of values observed in a spray column. A value of 500 m^2/m^3, which is high for a spray column, may be achieved by employing multiple spray nozzles. Iteration 3 shows some improvement in the selectivity ratio (5.1). $\overline{\Psi}(a)$ and $\overline{\Psi}(\epsilon_L)$ are both high, indicating that the selectivity can be improved by decreasing the liquid holdup and increasing the interfacial area. In iteration 4, we increase a to 1,500 m^2/m^3 and decrease ϵ_L to 0.2. The selectivity ratio is now 7.2, which is a considerable improvement over the base case reactor. The yield of P has also correspondingly gone up from 0.51 to 0.88. In iteration 4, the highest sensitivity coefficients are those related to the rate constants, which cannot be changed since temperature effects are ignored in this example. Also, the values of k_L and ϵ_L are close to their limits. The screening procedure is therefore terminated.

Step 6: Identify Reactor Type. The parameters in iteration 4 show that the desired reactor will have a low liquid holdup and a high gas-liquid mass transfer coefficient and interfacial area. The liquid holdup in iteration 4 corresponds to that observed in a packed column. The high interfacial area (1,500 m^2/m^3) may be achieved by operating in the spray regime. This is therefore recommended as the reactor for further consideration.

Steps 7 and 8: Flow Regime and Feasibility Check. The gas, liquid, and solid holdups used in iteration 4 are 0.3, 0.2, and 0.5, respectively. For a liquid residence time of 200 s, these correspond to a reactor volume of 1.5 m^3. Choosing a column height to diameter ratio of 20, the gas and liquid mass velocities are found to be 0.975 $kg/m^2\cdot s$ and 7.314 $kg/m^2\cdot s$, respectively. From the flow regime map of Turpin and Huntington (1967) for a cocurrent upflow packed reactor, the regime of operation is indeed found to be a spray flow regime, as assumed in Step 6 above. For cocurrent downflow packed beds, Reiss' (1967) correlation for the mass-transfer coefficient $k_L a$ is well known. For cocurrent upflow operation in the spray regime, Charpentier (1981) approximates $k_L a$ to be two times that obtained by using the above correlation. Using this approach, a $k_L a$ of 0.18 s^{-1} is obtained for the gas and liquid velocities under consideration. This is comparable to the one used in the screening procedure: hence, the packed bed operating in the spray regime is a feasible choice for a reactor.

Example 2: parallel reaction scheme

Consider the following reaction scheme where the dissolved gaseous species A reacts with the liquid reactant B to form the desired product P as well as the undesired byproduct X

$$A_{(g)} \longrightarrow A_{(l)}$$

$$A_{(l)} + B_{(l)} \xrightarrow{k_1} P_{(l)} \qquad \text{Rate} = k_1 A_{(l)} B_{(l)}$$

$$2\,A_{(l)} + B_{(l)} \xrightarrow{k_2} X_{(l)} \qquad \text{Rate} = k_2 A_{(l)}{}^2 B_{(l)}$$

Table 5. Sensitivity Analysis for an Isothermal Consecutive-Parallel Reaction Scheme (Example 1)

	P/X	Yield of P	k_L (m/s)	$\overline{\Psi}(k_1)$	a (m^{-1})	$\overline{\Psi}(a)$	k_1 ($m^3/mol\cdot s$)	$\overline{\Psi}(k_1)$	k_2 ($m^3/mol\cdot s$)	$\overline{\Psi}(k_2)$	ϵ_L	$\overline{\Psi}(\epsilon_L)$	Corresponding Reactor Type
1	**1.16**	0.51	5×10^{-5} ↓	**6.08**	300 ↓	**14.1**	0.02	0.77	5×10^{-5}	-0.94	0.7	-0.8	Bubble column
2	**4.75**	0.81	1×10^{-4}	3.4	1,000 ↓	**4.3**	0.02	3.88	5×10^{-5}	-3.95	0.7 ↓	$\mathbf{-4.8}$	Stirred tank reactor
3	**5.1**	0.82	1×10^{-4}	4.7	500 ↓	**16.0**	0.02	4.84	5×10^{-5}	-4.95	0.3 ↓	$\mathbf{-7.2}$	Spray column with multiple nozzles
4	**7.2**	0.88	1×10^{-4}	0.27	1,500	0.6	0.02	**8.23**	5×10^{-5}	$\mathbf{-11.8}$	0.2	-0.37	Packed column in spray regime

Table 6. Base-Case Parameters for Example 2

F_G	$0.04\ \text{m}^3/\text{s}$	k_L	$4\times10^{-5}\ \text{m/s}$
F_L	$0.0015\ \text{m}^3/\text{s}$	D_A	$1\times10^{-9}\ \text{m}^2/\text{s}$
τ_L	200 s	D_B	$1\times10^{-10}\ \text{m}^2/\text{s}$
ϵ_G	0.3	$D_P,\ D_X$	$1\times10^{-10}\ \text{m}^2/\text{s}$
ϵ_L	0.3	Feed Conditions	
k_1	$1\times10^{-3}\ \text{m}^3/\text{mol}\cdot\text{s}$	G_A	$40\ \text{mol/m}^3$
k_2	$1\times10^{-4}\ (\text{m}^3/\text{mol})^2/\text{s}$	L_B	$1{,}000\ \text{mol/m}^3$
H_A	$1.0\ (\text{mol/m}^3)_G/(\text{mol/m}^3)_L$	$L_A,\ L_P,\ L_X$	$0\ \text{mol/m}^3$

Step 1: The selectivity of P referred to the key reactant B, defined in this case by the ratio [amount of P formed]/[amount of X formed], is chosen as the performance index during the screening.

Step 2: Generic Model. The rate expressions are as given above. The desired reaction is first order in the concentration of the gaseous reactant, whereas the undesired reaction is second order. As before, a network of N well-mixed tanks in series is chosen as the flow model for the above gas-liquid reaction system. Applying heuristic 3a, Table 3, to the reaction scheme under consideration, we can see that the selectivity can be improved by keeping the concentration of dissolved A at a low level. The network model therefore allows the possibility of interstage injection of gas. The gas-liquid mass transfer is modeled using the stagnant film theory. The model equations are given by Eqs. 10 to 19, with an additional term for the interstage gas injection in the bulk gas-phase balances. No heat-transfer topology is incorporated into the model at this stage.

Step 3: Sensitivity Model. k_L, a, k_1, k_2, ϵ_L, and N are chosen as parameters for the sensitivity analysis.

Step 4: Generate Base Case. The kinetic data for the above reaction scheme are summarized in Table 6. Following Example 1, a packed column operating in the spray regime, with gas, liquid and solid holdups of 0.3, 0.3, and 0.4, respectively, is chosen as the base case.

Step 5: Screen Parameters. The values of the reactor parameters, as well as the normalized sensitivity coefficients of the performance index to these parameters, are shown in Table 7. For comparison, the conversion of liquid reactant x_B is also shown in column 3. The rate constants and the corresponding sensitivity coefficients are not shown for reasons of clarity. In the first iteration, the selectivity is low ($P/X = 1.68$), with $\overline{\Psi}(\epsilon_L)$ (0.47) being the highest sensitivity coefficient. Hence, in iteration 2, we change to an operation with liquid as the continuous phase ($\epsilon_L = 0.6$). Simultaneously, N is changed to 1 to reflect the considerable backmixing which would be present in such a reactor. This improves the selectivity to 2.0. In iteration 2, $\overline{\Psi}(k_L)$, $\overline{\Psi}(a)$ and $\overline{\Psi}(\epsilon_L)$ are all comparable, indicating that a decrease in k_L and a, and an increase in ϵ_L will improve the selectivity. Therefore, in iteration 3, k_L and a are decreased to 1×10^{-4} m/s and 400 m^2/m^3, respectively, and ϵ_L is increased to 0.75. This improves the selectivity to 4.2. In iteration 3, $\overline{\Psi}(a)$ is high (-6.31), indicating that the selectivity can be further improved by decreasing the gas-liquid interfacial area, though at the cost of liquid conversion x_B. Examination of heuristic 3a in Table 3 suggests that an interstage sparging of gas will lead to a lower concentration of dissolved gas, and, hence, a higher selectivity. Therefore, in iteration 4, we consider a five-stage reactor ($N = 5$) with an interstage injection of gaseous feed. This improves the selectivity to 4.55, while also increasing x_B slightly over that in iteration 3. The selectivity can be improved further by decreasing k_L or a or increasing ϵ_L. However, this will require examining the tradeoffs between conversion and selectivity, hence, the screening procedure is terminated at this stage.

Step 6: Identify Reactor Type. In iteration 4, the parameters correspond to a reactor with a large liquid holdup ($\epsilon_L = 0.75$), and a low gas-liquid mass-transfer coefficient ($k_L a = 0.04\ \text{s}^{-1}$). This indicates a gas-sparged reactor with liquid being the continuous phase. This may be interpreted as a cascade of stirred tanks in series. However, the relatively low values of k_L and a indicate that mechanical agitation may not be needed. Thus, the reactor in iteration 4 may be considered to be a bubble column with gas being sparged at 5 different locations along its height. A third alternative is a horizontal reactor with partitions along its length which extend over part of the reactor height, with gas being injected in each compartment, as in the alkylation of isobutane (Lerner and Citarella, 1991).

Steps 7 and 8: Flow Regime and Feasbility Check. The feasibility check is illustrated for a bubble column reactor with distributed gas feed. For the holdups used in iteration 4, the required liquid residence time can be obtained in a reactor of volume 0.4 m^3. Using a height to diameter ratio of 5 for the bubble column, the gas and liquid superficial velocities are calculated to be 0.23 m/s and 0.0087 m/s, respectively, at the top of the column. From the flow regime map for gas-liquid bubble columns (Ramachandran and Chaudhari, 1983), the above velocities correspond to churn turbulent flow. Using the correlation by Akita and Yoshida (1973), the overall volumetric mass-transfer coefficient is estimated to be 0.06 s^{-1}.

Table 7. Sensitivity Analysis for a Parallel Reaction Scheme (Example 2)

	P/X	x_B	k_L (m/s)	$\overline{\Psi}\ (k_L)$	a (m^{-1})	$\overline{\Psi}\ (a)$	ϵ_L	$\overline{\Psi}\ (\epsilon_L)$	N	Corresponding Reactor Type
1	**1.68**	0.65	4×10^{-4}	-0.17	1,200	-0.18	0.3 ↓	**0.47**	5 ↓	Packed column in spray regime
2	**2.0**	0.59	4×10^{-4} ↓	**$-$0.4**	1,200 ↓	**$-$0.45**	0.6 ↓	**0.56**	1	Stirred tank reactor
3	**4.2**	0.268	1×10^{-4}	-2.5	400	**$-$6.31**	0.75	2.1	1 ↓	Bubble column
4	**4.55**	0.272	1×10^{-4}	-2.6	400	-6.4	0.75	2.75	5	Bubble column with interstage gas injection

This compares well with the value used in iteration 4. Thus, a bubble column is a feasible reactor choice.

Example 3: nonisothermal parallel-consecutive reaction

Consider a reaction scheme similar to the one in Example 1. Here, the dissolved gaseous species A reacts with B to form the desired product P. This further reacts with A to form the undesired product X. The reaction scheme is thus of a parallel nature with respect to A, and of a consecutive nature with respect to B. Industrial examples following this scheme include gas-liquid systems such as chlorination of paracresol and sulfonation of benzene, and gas-liquid-solid catalytic systems such as the hydrogenation of 2,6-dinitrotoluene to 2,6-diaminotoluene. See Darde et al. (1983) for a detailed theoretical analysis of this reaction scheme in gas-liquid systems under isothermal conditions

$$\begin{aligned}
&A_{(g)} \longrightarrow A_{(l)} && && -\Delta H_{A,\mathrm{abs}}\\
&A_{(l)} + B_{(l)} \xrightarrow{k_1} P_{(l)} && \text{Rate} = k_1 A_{(l)} B_{(l)} && -\Delta H_1\\
&A_{(l)} + P_{(l)} \xrightarrow{k_2} X_{(l)} && \text{Rate} = k_2 A_{(l)} P_{(l)} && -\Delta H_2
\end{aligned}$$

Step. 1. The overall selectivity to P, given in this case by the ratio [amount of P formed]/[amount of X formed] is chosen as the performance index.

Step 2: Generic Model. A network of stirred tanks in series is chosen to model the reactions. An analysis of the Hatta numbers shows that the reactions are too slow for any reaction to occur in the liquid film. Hence, the model for gas-liquid contact simply uses a gas-liquid mass-transfer coefficient with a linear concentration profile in the liquid film (that is, it is not necessary to solve the differential equations for simultaneous diffusion and reaction). The heat-transfer topology consists of internal, external, as well as interstage heat transfer (a combination of Figures 5h and i). The selection of a particular heat-transfer device in the topology is determined by appropriate parameters in the model. Arrhenius expressions are used for the rate constants, and the temperature effect on the gas solubility is ignored.

Step 3: Sensitivity Model. The parameters of interest are k_L, a, k_1, k_2, T and the number of tanks N in the model.

Table 8. Base-Case Parameters for Example 3

F_G	0.04 m^3/s	$-\Delta H_{A,\mathrm{abs}}$	8×10^3 J/mol
F_L	0.002 m^3/s	$-\Delta H_1$	4×10^4 J/mol
τ_L	1,000 s	$-\Delta H_2$	2×10^4 J/mol
ϵ_G	0.3	Feed Conditions	
ϵ_L	0.7	G_A	35 mol/m^3
k_1	$6\times10^8 \exp(-83{,}140/\Re T) m^3/mol\cdot s$	L_B	2,000 mol/m^3
k_2	$5\times10^{11} \exp(-10^5/\Re T) m^3/mol\cdot s$	L_P, L_X	0 mol/m^3
H_A	0.3 $(mol/m^3)_G/(mol/m^3)_L$	T_{feed}	325 K
k_L	3×10^{-4} m/s	T_{coolant}	300 K

Step 4: Generate Base Case. A single stirred tank reactor without any heat removal mechanism is chosen as the base case for this reaction. The feed is assumed to be at a temperature of 325 K, and a temperature of 300 K is assumed for the coolant stream. The base case parameters are summarized in Table 8.

Step 5: Screen Parameters. The results of the screening procedure are shown in Table 9. The performance index P/X and the liquid reactant conversion x_B are shown in columns 2 and 3, respectively. The temperature T_{out} is that at the outlet of the reactor or the reactor cascade. The rate constants and the corresponding sensitivity coefficients are not shown for reasons of clarity. In any case, k_1 and k_2 can only be changed indirectly, by changing the temperature. In the base case, the adiabatic stirred tank has a large increase in temperature ($T_{\mathrm{out}} = 363$ K), leading to a very low selectivity to P ($P/X = 0.392$). $\overline{\Psi}(k_L)$, $\overline{\Psi}(a)$, and $\overline{\Psi}(T)$ are negative, meaning that a decrease in the gas-liquid mass-transfer coefficient, the interfacial area, or the temperature will improve the selectivity.

Since the temperature sensitivity is the dominant one, iteration 2 considers an internal heat removal scheme for the reactor. The temperature rise is still significant ($T_{\mathrm{out}} = 342$ K) and the selectivity is still poor (0.557). Also, an examination of the reaction scheme shows that a plug flow of B will improve the selectivity to P (heuristic 1b, Table 3). This can be approximated by using a number of tanks in the model. Therefore, iteration 3 considers a cascade of five tanks in series ($N = 5$) with an interstage heat removal scheme. This brings the reactor close to isothermal operation, with T_{out} being 325.7 K, but selectivity is still less than unity. The selectiv-

Table 9. Sensitivity Analysis for a Nonisothermal Parallel-Consecutive Reaction Scheme (Example 3)

	P/X	x_B	k_L (m/s)	$\overline{\Psi}(k_L)$	a (m^{-1})	$\overline{\Psi}(a)$	T_{out} (K)	$\overline{\Psi}(T)$	N	Corresponding Reactor Type
1	**0.392**	0.448	3×10^{-4}	-0.043	1,000	-0.051	363	**-0.274**	1	Stirred tank without heat transfer
2	**0.557**	0.446	3×10^{-4}	-0.055	1,000	-0.066	342	**-0.59**	1 ↓	Stirred tank with internal heat transfer
3	**0.65**	0.5	3×10^{-4} ↓	**-0.09**	1,000 ↓	**-0.11**	325.7	**-0.8**	5 ↓	Stirred tank cascade with interstage heat transfer
4	**1.17**	0.34	1×10^{-4} ↓	**-1.48**	400 ↓	**-1.48**	325.7	**-2.06**	1 ↓	Sparged column with internal heat transfer
5	**4.66**	0.157	4×10^{-5}	-20.8	200	-16.7	335.4	-4.6	5	Packed column without heat transfer
6	**5.31**	0.155	4×10^{-5}	-25	200	-20	325.3	-6.2	5	Staged packed column with heat transfer

ity could be improved by decreasing the temperature of the feed below 325 K, but this is not considered in this example. Since $\overline{\Psi}(k_L)$ and $\overline{\Psi}(a)$ are negative, in iteration 4 we decrease k_L to 1×10^{-4} m/s, and a to 400 m^2/m^3, with the liquid holdup being at the base case value of 0.7. These parameters correspond to a bubble column type of reactor, and, hence, N is changed back to 1, to reflect the considerable liquid-phase backmixing in such reactors. For a reactor with an internal heat-transfer device, iteration 4 shows a selectivity of 1.17. $\overline{\Psi}(T)$, at -2.06, is again the dominant sensitivity, followed by $\overline{\Psi}(k_L)$ and $\overline{\Psi}(a)$ at -1.48. Iteration 4 involves hardly any temperature rise ($T_{\text{out}} = 325.7$ K); hence, in iteration 5 we consider a reactor packed with inert solids (solid holdup = 0.5), with flow close to plug flow ($N = 5$), and a lower k_L (4×10^{-5} m/s) and a (200 m^{-1}). This improves the selectivity to 4.66. There is a 10°C temperature rise across the reactor. If this is not acceptable, a staged packed column with interstage heat removal could be used, as shown in iteration 6. This further improves the selectivity of P to 5.31. In iteration 6, the values of k_L and a are close to their lower limits. Also, since there is hardly any temperature rise across the reactor, the screening procedure is terminated at this stage.

Step 6: Identify Reactor Type. The above set of parameters indicate a reactor with a 50% solids holdup, a low gas-liquid mass-transfer coefficient and interfacial area, and with liquid in nearly plug flow. This corresponds to a cocurrent downflow, gas-liquid packed column reactor. If an isothermal operation is desired, a staged packed column with heat removal between the stages is recommended (iteration 6).

Steps 7 and 8: Flow Regime and Feasibility Check. The gas, liquid and solid holdups at the end of the screening are 0.3, 0.2, and 0.5, respectively. For a liquid residence time of 1,000 s, these correspond to a reactor volume of 10 m^3. For a height to diameter ratio of 8, the gas and liquid mass velocities are found to be 0.149 $kg/m^2\cdot s$ and 1.495 $kg/m^2\cdot s$, respectively. From the flow regime map for downflow packed beds proposed by Charpentier and Faviar (1975), this corresponds to an operation in the trickling flow regime. For a column packed with 1/2 in. Raschig rings, the energy dissipation for liquid flow is found to be less than 1 W/m^3. For such low energy dissipation rates, a mean value of 0.008 s^{-1} applies for $k_L a$ (Charpentier, 1981). This is comparable to the value used in the screening procedure (iterations 5, 6). Hence, the downflow packed column is a feasible reactor choice.

Example 4: exothermic reversible reaction

Consider a single exothermic reversible reaction as shown below.

$$A_{(g)} \longrightarrow A_{(l)} \qquad\qquad -\Delta H_{A,\text{abs}}$$

$$A_{(l)} + B_{(l)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P_{(l)} \qquad \text{Rate} = k_1 A_{(l)} B_{(l)} - k_2 P_{(l)} \qquad -\Delta H$$

An example of such a reaction is the dimerization of acetylene, which is the first step in the manufacture of chloroprene from acetylene. Since the reaction is exothermic, the equilibrium conversion drops with increasing temperature; hence, heat removal is critical. One way to achieve a high conversion is to carry out the reaction in multiple stages, with a falling temperature profile. The screening procedure will now be applied to the above reaction.

Table 10. Base-Case Parameters for Example 4

F_G	0.04 m^3/s	$-\Delta H_{A,\text{abs}}$	0.8×10^4 J/mol
F_L	0.002 m^3/s	$-\Delta H$	2×10^5 J/mol
τ_L	1,000 s	$-\Delta H_{\text{vap}}$	1×10^6 J/mol
ϵ_G	0.3	Feed Conditions	
ϵ_L	0.7	G_A	30 mol/m^3
k_1	$1.2\times10^7 \exp(-0.5\times10^5/\Re T)$	L_A, L_P	0 mol/m^3
k_2	$10^{35} \exp(-2.5\times10^5/\Re T)$	L_B	5,000 mol/m^3
k_L	1×10^{-4} m/s	T_{feed}	350 K
H_A	0.25 $(mol/m^3)_G/(mol/m^3)_L$	T_{coolant}	300 K

Step 1: Since we are dealing with a single reversible reaction, the conversion of liquid reactant B is an appropriate performance index.

Step 2: Generic Model. The forward reaction is of second-order overall, while the reverse reaction is first-order in the product concentration. Again, a network of stirred tanks in series, with no reaction in the liquid film, is chosen to model the reaction. As before, the heat-transfer topology consists of internal heat transfer, as well as interstage heat transfer, with appropriate parameters in the model selecting between the two. Arrhenius expressions are used for the rate constants.

Step 3: Sensitivity Model. k_L, a, k_1, k_2, T, and N are chosen as parameters of interest.

Step 4: Generate Base Case. A single stirred tank reactor without any heat removal mechanism is chosen as the base case for this reaction. The temperature of the feed is 350 K, while the coolant stream is assumed to be at 300 K. The base case parameters are summarized in Table 10.

Step 5: Screen Parameters. The results of the screening procedure are shown in Table 11. The performance index x_B, as well as the gas conversion x_A, are shown in columns 2 and 3, respectively. The temperature T_{out} is that at the outlet of the reactor or the reactor cascade. The rate constants and the sensitivity coefficients of x_B to the rate constants are not shown for reasons of clarity. In the base case, the adiabatic stirred tank gives a very low conversion ($x_B = 0.09$). The sensitivity coefficient of the highest magnitude is that with respect to the temperature [$\overline{\Psi}(T) = -0.39$]; hence, iteration 2 employs an internal cooling device to manage the heat of reaction. The temperature of operation is consequently lower at 394 K. However, the conversion is still low ($x_B = 0.23$) and is most sensitive to temperature. Iteration 3 considers a liquid recycle with a supplementary external heat removal device having a heat-transfer area of 20 m^2. This improves the conversion to 0.25, and the reaction is dominated by the gas-liquid mass transfer ($\overline{\Psi}(k_L)$ and $\overline{\Psi}(a)$ are high). Also, the reactor still operates 35°C above the feed temperature. To achieve a greater heat removal, iteration 4 considers the reaction to be carried out in a boiling reactor, with heat being removed by the vaporizing solvent. This involves an implicit assumption that the bubble point for the solvent is lower than the reactor temperature. It is also assumed that the reactants and products do not vaporize to a significant extent. Also, k_L and a are increased as shown by the downward pointing arrows in the table. This improves the conversion ($x_B = 0.267$), and also makes the reactor essentially isothermal ($T_{\text{out}} = 350.6$

Table 11. Sensitivity Analysis for a Reversible Exothermic Reaction (Example 4)

	x_B	x_A	k_L (m/s)	$\overline{\Psi}\,(k_L)$	a (m^{-1})	$\overline{\Psi}\,(a)$	T_{out} (K)	$\overline{\Psi}$ (T)	N	Corresponding Reactor Type
1	**0.09**	0.4	1×10^{-4}	0.004	1,000	0.009	415	**−0.39**	1	Stirred tank without heat removal
2	**0.23**	0.84	1×10^{-4}	0.10	1,000	0.045	394	**−0.24**	1	Stirred tank with internal heat transfer
3	**0.25**	0.88	1×10^{-4} ↓	**0.11**	1,000 ↓	**0.06**	385	−0.05	1	Stirred tank with internal and external heat transfer
4	**0.267**	0.95	2×10^{-4}	0.03	1,200	0.02	350.6	−0.001	1 ↓	Boiling reactor
5	**0.278**	0.97	2×10^{-4}	0.05	1,200	0.04	353	−0.002	5	Stirred tank cascade with interstage heat transfer

K). In case a boiling reactor is not suitable for the reaction under consideration, we proceed as follows. Since we have a single reaction, a plug flow would improve the conversion. Hence, in iteration 5 we use a cascade of 5 reactors (each having one-fifth the volume of the single reactor). Also, an interstage heat removal scheme is employed, where the outlet of each stage is cooled to 350 K before going to the next reactor in the cascade. The temperature at the outlet of the cascade is now 353 K, only three degrees above the feed temperature. This improves the conversion of B to 0.278. Simultaneously, the conversion of A has improved from 0.4 (iteration 1) to 0.97. The screening procedure is stopped at this stage, because the only way to improve the conversion further is to reduce the feed temperature, a decision which is beyond the scope of the screening procedure.

Step 6: Identify Reactor Type. Two possible reactor types can be identified by the screening procedure. Iteration 4 suggests a single boiling reactor, whereas iteration 5 suggests a cascade of 5 reactors, with interstage heat removal. Both reactors have high mass-transfer coefficients. Thus, the first alternative corresponds to stirred tank reactor with the solvent being continuously evaporated and refluxed, while the other alternative is a cascade of stirred tanks with interstage heat removal.

Steps 7 and 8: Flow Regime and Feasibility Check. For the boiling reactor of iteration 4, a feasibility check similar to that for the stirred tank reactor of Example 2 will be considered. The gas and liquid holdup used in iteration 4 are 0.3 and 0.7, respectively. For a liquid residence time of 1,000 s, these correspond to a reactor volume of 2.85 m^3. With a height to diameter ratio of 1, the gas and liquid superficial velocities are calculated to be 0.022 m/s and 0.0013 m/s, respectively. Using the correlation of Yagi and Yoshida (1975) for $k_L a$ in gas-liquid agitated reactors, the operating impeller speed required to obtain a $k_L a$ of 0.24 s^{-1} is found to be 5 rps. This corresponds to a power consumption of about 1.21 kW/m^3 (6 hp/1,000 gal). Thus, the boiling reactor is a feasible reactor choice. It is easy to show that the stirred tank cascade is also feasible.

Conclusions

In the initial phase of process development, information about the reaction is often incomplete and unreliable, and design of the process around the reactor is still in progress. Despite this uncertain environment, it is crucial that the best reactor be identified for further process development in a timely fashion. Indecision will hold back other design activities and prolong the development time. Yet a suboptimal choice, once built, will incur economic penalty on a continuous basis (Lerou and Ng, 1996).

To meet this need for reactor synthesis, a screening procedure for nonisothermal, multiple reactions has been developed. We limit ourselves to gas-liquid, liquid-liquid, and gas-liquid-solid catalytic reactions in nonfoaming systems. The conventional multiphase reactors are decomposed into the relevant attributes, geometries, and constituent parts. To handle heat effects, topologies and devices for heat management are also included. All of these are then reaggregated to form a generic reactor model and an accompanying sensitivity model. For a chosen performance index, the sensitivity analysis suggests values for reactor parameters such as phase volume fractions, mass-transfer coefficients, heat- and mass-transfer areas, which lead to the desirable alternative reactor types. Further, the sensitivity coefficients of reactor parameters, such as solubility and rate constants, reveal the potential impact of the uncertainty of these parameters. This will help prioritize the experimental effort for the determination of more exact parameter values.

The screening procedure can be extended in a number of directions. Suitable models and knowledge base for selective mass-transfer devices, such as membranes, are needed. The reactor model can be further generalized. For example, we can account for the possibility that reaction can occur in more than one phase, the liquid reactants and products are volatile, and so on. It is also possible to include high resolution models with additional parameters in the screening procedure. For example, in addition to macromixing, micromixing can be incorporated in the model (Baldyga et al., 1997; Samant and Ng, 1999). The temperature, flow rate, and concentration of the feed, as well as the liquid-phase residence time, which are fixed in this screening procedure, can be varied to achieve a superior performance. Also, it is highly desirable to develop a user-friendly computer code to help perform this screening procedure. Most of these efforts are underway.

Acknowledgment

Financial support from the National Science Foundation (grant No. 9807101) and Mitsubishi Chemical Co. is gratefully acknowledged. We appreciate the hospitality of our colleagues during our visit at the Mizushima Plant, Japan, where part of this work was performed.

Notation

a = gas-liquid interfacial area per unit volume of reactor, m^2/m^3
a_h = surface area for heat transfer
a_S = solid surface area per unit volume of reactor, m^2/m^3
A_i = concentration of ith species taking part in reaction (Eq. 1)
c', c'' = first and second differentials of c with respect to z
C_G, C_L = heat capacity of the gas and liquid streams, respectively, $J/kg \cdot K$
D_i = diffusion coefficient of species i in the liquid phase, m^2/s
F_G, F_L = flow rate of gas and liquid phase fresh feed, m^3/s
$G_i(j)$, $L_i(j)$ = concentration of species i in the gas and liquid bulk phase, respectively, in the jth cell, mol/m^3
H_i = solubility coefficient for species i, $(mol/m^3)_{gas}/(mol/m^3)_{liquid}$
k = reaction rate constant, s^{-1}
k_L = overall gas-liquid mass-transfer coefficient, m/s
k_S = solid-liquid mass-transfer coefficient, m/s
$L_i^f(j)$ = concentration of species i in the liquid film, mol/m^3
m_G, m_L, m_P = number of gas and liquid-phase reactants, and liquid-phase products, respectively
P = reactor performance index (selectivity, conversion, total cost)
Q = heat load generated during reaction, or removed by heat transfer
s_j, s_j^T = vector of sensitivity coefficients (Eq. 6)
$s_i^G(j)$, $s_i^L(j)$, $s_i^f(j)$ = sensitivity of the concentration of the ith species with respect to a reactor parameter in the jth cell in the gas phase, bulk liquid and the liquid film, respectively
T', T'' = first and second differentials of T with respect to z
V = volume of a single tank in the network, m^3
X = dimensionless distance in the liquid film
z = axial direction
$\epsilon_S, \epsilon_L, \epsilon_G$ = solid, liquid and gas phase holdup in the reactor
$\Phi_i(j)$ = kinetic rate expression for the consumption of the ith species
ν_{ik} = stoichiometric coefficient for species i in the kth reaction
$\Theta_k(j)$ = rate of the kth reaction in the jth cell in the network, $mol/m^3 \cdot s$
ρ = density, kg/m^3
τ_G, τ_G = residence time of the gas and liquid phase, s
$\Psi(\alpha_j)$ = sensitivity coefficient of the performance index to the parameter α_j
$\overline{\Psi}(\alpha_j)$ = normalized performance index sensitivity coefficient

Subscripts and superscripts

f = pertaining to the liquid film
G = gas phase
i = pertaining to species i
L = liquid phase

Literature Cited

Achenie, L. K. E., and L. T. Biegler, "Superstructure Based Approach to Chemical Reactor Network Synthesis," *Computers Chem. Eng.*, **14**, 23 (1990).

Akita, K., and F. Yoshida, "Gas Holdups and Volumetric Mass Transfer Coefficients in Bubble Columns," *Ind. Eng. Chem. Process Des. Dev.*, **12**, 76 (1973).

Balakotaiah, V., and D. Luss, "Effect of Flow Direction on Conversion in Isothermal Radial Flow Fixed-Bed Reactors," *AIChE J.*, **27**, 442 (1981).

Baldyga, J., J. R. Bourne, and S. J. Hearn, "Interaction between Chemical Reactions and Mixing on Various Scales," *Chem. Eng. Sci.*, **52**, 457 (1997).

Brian, P. L. T., and M. C. Beaverstock, "Gas Absorption Accompanied by a Two Step Chemical Reaction," *Chem. Eng. Sci.*, **20**, 47 (1966).

Charpentier, J. C., "Mass Transfer Rates in Gas-Liquid Absorbers and Reactors," *Adv. Chem. Eng.*, **11**, 2 (1981).

Charpentier, J. C., and M. Faviar, "Some Liquid Holdup Experimental Data in Trickle Bed Reactors for Foaming and Nonfoaming Hydrocarbons," *AIChE J.*, **21**, 1213 (1975).

Chitra, S. P., and R. Govind, "Synthesis of Optimal Serial Reactor Structures for Homogeneous Reactions. Part I: Isothermal Reactors," *AIChE J.*, **31**, 177 (1985a).

Chitra, S. P., and R. Govind, "Synthesis of Optimal Serial Reactor Structures for Homogeneous Reactions. Part II: Nonisothermal Reactors," *AIChE J.*, **31**, 185 (1985b).

Darde, T., N. Midoux, and J. C. Charpentier, "Contribution to the Analysis of the Selectivity in Gas-Liquid Reactions. Part I: Literature and Theory," *Chem. Eng. Comm.*, **22**, 221 (1983).

Dassori, C. G., "Three Phase Reactor Modeling with Significant Backmixing in the Liquid Phase Using a Modified Cell Model (MCM)," *Computers Chem. Eng.*, **22** Supp., S679 (1998).

Deans, H. A., and L. A. Lapidus, "A Computational Model for Predicting and Correlating the Behavior of Fixed Bed Reactors: 1. Derivation of the Model for Nonreactive Systems," *AIChE J.*, **6**, 656 (1960).

Dharwadkar, A., and N. D. Sylvester, "Liquid-Solid Mass Transfer in Trickle Beds," *AIChE J.*, **23**, 376 (1977).

Doraiswamy, L. K., and M. M. Sharma, *Heterogeneous Reactions*, Vol. 2, Wiley, New York (1984).

Gianetto, A., and P. L. Silveston, eds., *Multiphase Chemical Reactors*, Hemisphere, Washington, DC (1986).

Glasser, D., D. Hildebrandt, and C. Crowe, "A Geometric Approach to Steady Flow Reactors: The Attainable Region and Optimization in Concentration Space," *Ind. Eng. Chem. Res.*, **26**, 1803 (1987).

Guha, A. K., P. V. Shanbhag, K. K. Sirkar, D. A. Vaccari, and D. H. Trivedi, "Multiphase Ozonolysis of Organics in Wastewater by a Novel Membrane Reactor," *AIChE J.*, **41**, 1998 (1995).

Hanika, J., P. Vychodii, and V. Ruzicka, "A Cell Model of the Isothermal Trickle-Bed Reactor," *Coll. Czech. Chem. Comm.*, **43**, 2111 (1978).

Hildebrandt, D., and L. T. Biegler, "Synthesis of Chemical Reactor Networks," *Proc. Found. Computer-Aided Proc. Des.*, AIChE Symp. Ser., No. 304, **91**, 52 (1995).

Kale, D. D., R. V. Chaudhari, and P. A. Ramachandran, "Butynediol Synthesis—A Kinetic Study," *Ind. Eng. Chem. Proc. Des. Dev.*, **20**, 309 (1981).

Kelkar, V. V., and K. M. Ng, "Screening Procedure for Synthesizing Isothermal Multiphase Reactors," *AIChE J.*, **44**, 1563 (1998).

Kelkar, V. V., and K. M. Ng, "Design of Reactive Crystallization Systems Incorporating Kinetics and Mass Transfer Effects," *AIChE J.*, **45**, 69 (1999).

Khinast, J., D. Luss, T. M. Leib, and M. P. Harold, "Boiling-Slurry Reactor: Feasible Operation and Stability," *AIChE J.*, **44**, 1868 (1998).

Kondelik, P., "Optimization. Part II. Optimum Design of a Chemical Reactor," *Int. Chem. Eng.*, **22**, 709 (1982).

Krishna, R., and S. T. Sie, "Strategies for Multiphase Reactor Selection," *Chem. Eng. Sci.*, **49**, 4029 (1994).

Lerner, H., and V. A. Citarella, "Improve Alkylation Efficiency," *Hydrocarbon Processing*, **70**, 89 (Nov. 1991).

Lerou, J. J., and K. M. Ng, "Chemical Reaction Engineering: A Multiscale Approach to a Multiobjective Task," *Chem. Eng. Sci.*, **51**, 1595 (1996).

Lewis, W. K., and W. G. Whitman, "Principles of Gas Absorption," *Ind. Eng. Chem.*, **16**, 1215 (1924).

Mann, R., "Gas-Liquid Stirred Vessel Mixers," *Chem. Eng. Res. Des.*, **64**, 23 (1986).

Mehta, V. L., and A. Kokossis, "Development of a Novel Multiphase Reactor Using a Systematic Design Procedure," *Comput. Chem. Eng.*, **21** Suppl., S325 (1997).

Mehta, V. L., and A. Kokossis, "New Generation Tools for Multiphase Reaction Systems: A Validated and Systematic Methodology for Novelty and Design Automation," *Computers Chem. Eng.*, **22** Suppl., S119 (1998).

Mills, P. L., P. A. Ramachandran, and R. V. Chaudhari, ‘‘Multiphase Chemical Reactors for Fine Chemicals and Pharmaceuticals,’’ *Rev. Chem. Eng.*, **8**, 1 (1992).

Naik, S. D., and L. K. Doraiswamy, ‘‘Phase Transfer Catalysis: Chemistry and Engineering,’’ *AIChE J.*, **44**, 612 (1998).

Nienow, A. W., ‘‘Agitated Vessel Particle-Liquid Mass Transfer. A Comparison Between Theories and Data,’’ *Chem. Eng. J.*, **9**, 153 (1975).

Park, B., V. S. Ravi-Kumar, and T. T. Tsotsis, ‘‘Models and Simulation of Liquid-Phase Membrane Reactors,’’ *Ind. Eng. Chem. Res.*, **37**, 1276 (1998).

Rabitz, H., M. Kramer, and D. Dacol, ‘‘Sensitivity Analysis in Chemical Kinetics,’’ *Ann. Rev. of Phys. Chemistry*, **34**, 419 (1983).

Ramachandran, P. A., and R. V. Chaudhari, *Three Phase Catalytic Reactors*, Gordon and Breech, London (1983).

Ramachandran, P. A., and J. M. Smith, ‘‘Mixing Cell Method for Design of Trickle-Bed Reactors,’’ *Chem. Eng. J.*, **17**, 91 (1979).

Reiss, L. P., ‘‘Cocurrent Gas-Liquid Contacting in Packed Columns,’’ *Ind. Eng. Chem. Process Des. Dev.*, **6**, 486 (1967).

Samant, K. D., and K. M. Ng, ‘‘Synthesis of Extractive Reaction Processes,’’ *AIChE J.*, **44**, 1363 (1998a).

Samant, K. D., and K. M. Ng, ‘‘Effect of Kinetics and Mass Transfer on Design of Extractive Reaction Processes,’’ *AIChE J.*, **44**, 2212 (1998b).

Samant, K. D., and K. M. Ng, ‘‘Design of Multistage Extractive Reaction Processes,’’ *AIChE J.*, **44**, 2689 (1998c).

Samant, K. D., and K. M. Ng, ‘‘Development of Liquid Phase Agitated Reactors: Synthesis, Simulation and Scaleup,’’ *AIChE J.*, **45**, 2353 (1999).

Schembecker, G., T. Droge, U. Westhaus, and K. H. Simmrock, ‘‘A Heuristic-Numeric Consulting System for the Choice of Chemical Reactors,’’ *Proc. Found. Computer-Aided Proc. Des.*, AIChE Symp. Series, No. 304, **91**, 336 (1995).

Schweiger, C. A., and C. A. Floudas, ‘‘Optimization Framework for the Synthesis of Chemical Reactor Networks,’’ *Ind. Eng. Chem. Res.*, **38**, 744 (1999).

Sedriks, W., and C. N. Kenney, ‘‘Partial Wetting in Trickle Bed Reactors. The Reduction of Crotonaldehyde Over a Palladium Catalyst,’’ *Chem. Eng. Sci.*, **28**, 559 (1973).

Shah, Y. T., *Gas-Liquid-Solid Reactor Design*, McGraw Hill, New York (1979).

Shah, Y. T., ‘‘Design Parameters for Mechanically Agitated Reactors,’’ *Adv. Chem. Eng.*, **17**, 1 (1991).

Turpin, J. L., and R. L. Huntington, ‘‘Prediction of Pressure Drop for Two Phase, Two-Component Cocurrent Flow in Packed Beds,’’ *AIChE J.*, **13**, 1196 (1967).

van Swaaij, W. P. M., J. C. Charpentier, and J. Villermaux, ‘‘Residence Time Distribution in the Liquid Phase of a Trickle Flow in Packed Columns,’’ *Chem. Eng. Sci.*, **24**, 1083 (1969).

Villermaux, J., ‘‘Nomenclature and Symbols Recommended by the Working Party *Chemical Reaction Engineering*,’’ *Inst. Chem. Engr. Symp. Ser.*, No. 87 (ISCRE 8), 815 (1984).

Wen, C. Y., and L. T. Fan, *Models for Flow Systems and Chemical Reactors*, Marcel Dekker, New York (1975).

Westerterp, K. R., W. P. M. van Swaaij, and A. A. C. M. Beenackers, *Chemical Reactor Design and Operation*, Wiley, Chichester (1984).

Yagi, H., and F. Yoshida, ‘‘Gas Absorption by Newtonian and Non-Newtonian Fluids in Sparged Agitated Vessels,’’ *Ind. Eng. Chem. Process Des. Dev.*, **14**, 488 (1975).

Manuscript received Apr. 30, 1999, and revision received Oct. 18, 1999.