Design of Homogeneous Biphasic Catalytic Processes

Divya J. Singh and Ketan D. Samant
Dept. of Chemical Engineering, University of Massachusetts, Amherst, MA 01003

Ka M. Ng
Dept. of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, P.R.C.

A systematic procedure for the design of homogeneous catalytic processes with special emphasis on biphasic reactions was developed. First, the reaction kinetics were determined, and then a generic stirred cell model for biphasic homogeneous catalytic reactions was used to elucidate the interplay of reaction and mass transfer and the impact of phase equilibria. The optimal range of reactor conditions, as captured by the Damköhler numbers, was then related to reactor attributes. Process alternatives for catalyst recovery and recycle were considered.

Introduction

Homogeneous catalysis is responsible for a large segment of the chemical process industries with products ranging from potential chlorofluorocarbon (CFC) replacements, basic chemicals such as acetic acid and butyraldehyde, monomers such as vinyl chloride and terephthalic acid, polymers such as polyesters to pharmaceuticals such as Naproxen. Well-designed homogeneous catalytic processes can offer significant advantages such as high yields and high selectivities to the desired products. Biphasic homogeneous catalysis offers the additional advantage of easy catalyst recovery and recycle, and has been commercialized for propylene hydroformylation (Cornils et al., 1985). Since then, other processes employing homogeneous catalysis have been modified to biphasic catalysis (Cornils and Herrmann, 1998), along with its widespread acceptance in industry.

There is a vast literature pertaining to various aspects of homogeneous catalysis, including several excellent reviews (Parshall and Ittel, 1992; Cornils and Herrmann, 1996). Gas-liquid reactions have been extensively studied in reaction engineering literature (Levenspiel, 1972; Doraiswamy and Sharma, 1984). There have been efforts to specifically model homogeneous catalytic systems using conventional reaction engineering techniques (Chaudhari, 1984). In addition, there are numerous patents for specific reaction systems such as hydroformylation (for example, Cornils et al., 1985). However, little has been done on the design of these processes from a process systems engineering perspective. This is a serious omission because a systematic approach can lead to a more economical process with reduced development time and effort. In fact, there has been little effort to even model such reaction systems (Wachsen et al., 1998). To fill this gap, we present a design procedure that considers the entire system, with emphasis on biphasic reactions. Specifically, models, and heuristics are used to synthesize the reactor, as well as the overall plant that includes the catalyst recovery system, in a systematic manner.

Over the past several years, we have been developing systematic design methods for a variety of reaction systems. These include extractive reaction processes (Samant and Ng, 1998a,b,c), liquid-phase agitated reactors (Samant and Ng, 1999), multiphase reactions (Kelkar and Ng, 1998, 2000), and phase transfer catalytic systems (Samant et al., 2001). Although each reaction system has its unique features, we can identify a common underlying strategy that can be described as follows:

- *Identification of the Underlying Phenomena*. As the first step, the systematic methods identify the key underlying phenomena that need to be considered for the given reaction system.
- *Development of Tools and Learning Models to Understand these Phenomena.* In many cases, these underlying phenomena and their interactions are not well understood. In such

---

Correspondence concerning this article should be addressed to K. M. Ng.
Current address for D. J. Singh: OFS Fitel, 50 Hall Rd., Sturbridge, MA 01566.
Current address for K. D. Samant: CWB Technology, 20311 Valley Blvd., Suite C, Walnut, CA 91789.

cases, the systematic methods provide tools and learning models to generate this understanding.

- *Organization of Existing Knowledge.* In some cases, the reaction systems are fairly well understood. However, this knowledge exists in an unstructured form either as experimental studies, heuristics, or as models that are far too complex to be used for systematic design. Here, the systematic methods organize this information in a meaningful fashion.
- *Use of this Understanding.* Once the phenomena are identified and understood, this understanding serves as the basis to reach the desired objective by way of a systematic procedure.

Design Procedure for Homogeneous Catalytic Processes

We now present a generic design procedure for homogeneous catalytic processes with emphasis on biphasic catalysis. The procedure takes into account complex kinetics, phase equilibria, mass transfer, and catalyst recovery and recycle.

Step 1: determination of reaction kinetics

Any new process development starts with the determination of the basic reaction chemistry. This relies on laboratory experiments usually performed by the chemist. There are a number of techniques for analyzing the experimental data to estimate kinetic parameters and discriminate between potential kinetic models (Hostrup and Balakrishna, 2001). We assume that this step has been completed and that the reaction mechanism and kinetic parameters are available.

For homogeneous catalytic processes, the basic reaction chemistry is often complicated and involves a large number of reaction intermediates. While we can numerically incorporate the whole mechanism into a reactor model, it is easier to reduce the kinetic network to facilitate the determination of the effect of the dominant reactions on system performance. A number of tools are available for reducing the reaction kinetics, for example, the systematic rules summarized in Table 1 developed by Chern and Helfferich (1990). These rules are applicable to reaction kinetic networks of arbitrary topology.

Step 2: identification of optimal range of reactor conditions

After the determination of reaction kinetics, the reduced reaction mechanism, and information about the components and phase equilibria, we study the reactor performance. The generic stirred cell model enables the determination of the

Table 1. Rules for the Reduction of Multistep Reaction Networks

- Linear simple segments $X_j \leftrightarrow X_{j+1} \leftrightarrow \cdots \leftrightarrow X_k$ with an arbitrary number of steps can be reduced to a pseudo single step $X_j \leftrightarrow X_k$ with rate contribution

$$r_{j\leftrightarrow k} = \Lambda_{jk}[X_j] - \Lambda_{kj}[X_k]$$

where the segment coefficients Λ can be expressed in terms of the pseudo first-order reaction rate coefficients λ as

$$\Lambda_{jk} = \prod_{i=j}^{k-1} \lambda_{i,i+1}/D_{jk} \quad \Lambda_{kj} = \prod_{i=j}^{k-1} \lambda_{i+1,i}/D_{jk}$$

and $D_{jk} = \sum_{i=j+1}^{k} \left(\prod_{m=j+1}^{i-1} \lambda_{m,m-1} \prod_{m=j}^{k-1} \lambda_{m,m+1} \right) \quad (k > j)$

- A looped simple segment between nodes X_j and X_m, such as

$$X_j \leftrightarrow \cdots \leftrightarrow X_k \leftrightarrow \cdots \leftrightarrow X_l \leftrightarrow \cdots \leftrightarrow X_m$$

$$\searrow \ldots \nearrow$$

can be reduced to a pseudo single step $X_j \leftrightarrow X_m$ with collective coefficients Γ_{jm} and Γ_{mj} and rate contribution

$$r_{j\leftrightarrow m} = \Gamma_{jm}[X_j] - \Gamma_{mj}[X_m]$$

where $\Gamma_{jm} = \Lambda_{jk} L_{kl} \Lambda_{lm} / (L_{kl}\Lambda_{lm} + \Lambda_{kj}\Lambda_{lm} + \Lambda_{kj}L_{lk})$

$\Gamma_{mj} = \Lambda_{kj} L_{lk} \Lambda_{ml} / (L_{kl}\Lambda_{lm} + \Lambda_{kj}\Lambda_{lm} + \Lambda_{kj}L_{lk})$

and where the loop coefficients L_{kl} and L_{lk} are the sums of the Λ coefficients of the respective parallel pathways connecting X_k and X_l.

- The rate law of the formation of any product P_j is composed of additive contributions from all $P_i \leftrightarrow P_j$ $(i \neq j)$, each expressing the net rate at which P_j is formed from (or, if negative, reverts to) the respective P_i.
- Each contribution $P_i \leftrightarrow P_j$ consists of a factor $(\Pi_{ij}[P_i] - \Pi_{ji}[P_j])$, a factor determinant $\boldsymbol{M}_{ij}$, and a factor $1/\det \boldsymbol{M}$. Here, Π_{ij} is the product of all the forward Λ coefficients (or Γ coefficients) on the path from P_i to P_j and $\prod_{ji}$ is the product of all the reverse Λ coefficients on that path.
- The matrix $\boldsymbol{M}$ is a matrix of order n, with elements S_i $(i = 1, 2, \ldots, n)$ along its diagonal, elements Λ_{km} in row k and column m for all X_k and X_m directly connected to with one another, and elements of zero in all other positions. $\boldsymbol{M}_{ij} = \boldsymbol{M}_{ij}$ is a matrix similarly compiled, but with mth rows and columns omitted, where m are the indices of all intermediates on the path from P_i to P_j and S_i is the sum of the Λ coefficients of the reduced steps $X_i \rightarrow J$, where J represents the immediate neighbors of X_i in the network (intermediates or end members)
- In networks containing loops with branches, the contributions of both parallel pathways to an affected rate $P_i \leftrightarrow P_j$ are additive.

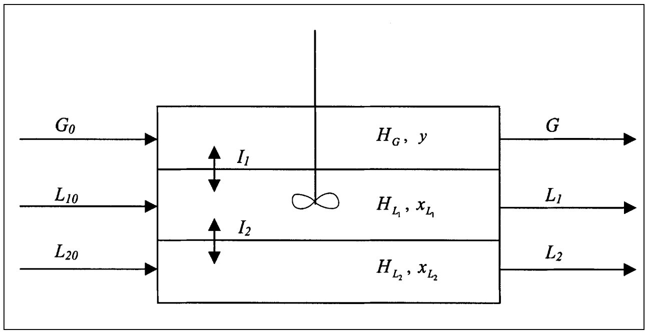

Figure 1. Stirred cell model.

effect of kinetics and mass transfer and helps in the identification of the optimal range of reactor conditions that maximize the performance objective, which may be yield, conversion, or selectivity of a product. Since the stirred cell model is an integral part of our procedure, we discuss the model in detail below.

Determining the Effect of Kinetics and Mass Transfer. Consider a three-phase open system, consisting of a gas phase and two liquid phases. "G" denotes the dispersed gas phase, "L_1" denotes the organic phase containing the products and the reactants, and "L_2" denotes the aqueous catalyst phase. We assume that the reaction takes place only in the bulk of the aqueous catalyst phase. This assumption is reasonable if the reaction is not too fast with respect to mixing and mass transfer (Samant and Ng, 1999). The gas phase, the organic phase and the aqueous catalyst phase have n_G, n_{L_1}, and n_{L_2} components, respectively, and n_m components are miscible in both the liquid phases. The present model takes the organic phase as the bulk liquid phase, and the aqueous catalyst phase as the dispersed liquid phase (Figure 1). It is assumed that the direct gas-phase mass transfer takes place only to the bulk liquid phase (in this case the organic phase). Thus, we have to consider two interfaces: the gas-phase-organic phase interface (I_1) and the organic phase-aqueous phase interface (I_2). Except for a dispersed phase having a very high volume fraction, this assumption is expected to be correct for most cases because coalescence of a liquid droplet and a gas bubble is highly unlikely. Let us look at the mass transfer and phase equilibria.

Mass Transfer and Phase Equilibria. Consider the mass transfer at the gas-phase-organic liquid phase interface. The component fluxes at the interface are given by

$$N_i^{I_1L_1} = k_i^{I_1L_1} c_{TL_1}\left(x_i^{I_1L_1} - x_i^{L_1}\right) + x_i^{I_1L_1} N_T^{I_1L_1} \qquad i = 1, 2, \ldots, n_G \quad (1)$$

$$N_i^{I_1G} = k_i^{I_1G} c_{TG}\left(y_i - y_i^{I_1}\right) + y_i^{I_1} N_T^{I_1G} \quad (2)$$

Here, the flux terms are positive for transfer from gas to liquid. The description of mass transfer given by Eqs. 1 and 2 is not complete, as these equations are not closed. We need to know $N_T^{I_1L_1}$ and $N_T^{I_1G}$ to evaluate $N_i^{I_1L_1}$ and $N_i^{I_1G}$ and vice versa. This closure is resolved here by using the continuity of molar fluxes at the interface. At the interface, the continuity of fluxes implies

$$N_i^{I_1L_1} = N_i^{I_1G} = N_i^{I_1} \qquad N_T^{I_1L_1} = N_T^{I_1G} = N_T^{I_1} \qquad i = 1, 2, \ldots, n_G \quad (3)$$

From Eqs. 1, 2, and 3, we can write the total flux at I_1 as

$$N_T^{I_1} = \frac{k_i^{I_1L_1} c_{TL_1}\left(x_i^{I_1L_1} - x_i^{L_1}\right) - k_i^{I_1G} c_{TG}\left(y_i - y_i^{I_1}\right)}{\left(y_i^{I_1} - x_i^{I_1L_1}\right)} \qquad i = 1, 2, \ldots, n_G \quad (4)$$

The component fluxes at I_1 are given by

$$N_i^{I_1} = \left(\frac{y_i^{I_1}}{y_i^{I_1} - x_i^{I_1L_1}}\right) k_i^{I_1L_1} c_{TL_1}\left(x_i^{I_1L_1} - x_i^{L_1}\right) - \left(\frac{x_i^{I_1L_1}}{y_i^{I_1} - x_i^{I_1L_1}}\right) k_i^{I_1G} c_{TG}\left(y_i - y_i^{I_1}\right) \qquad i = 1, 2, \ldots, n_G \quad (5)$$

Similarly for the organic phase-aqueous phase interface, the total and component fluxes are given by

$$N_T^{I_2} = \frac{k_i^{I_2L_2} c_{TL_2}\left(x_i^{I_2L_2} - x_i^{L_2}\right) - k_i^{I_2L_1} c_{TL_1}\left(x_i^{L_1} - x_i^{I_2L_1}\right)}{\left(x_i^{I_2L_1} - x_i^{I_2L_2}\right)} \qquad i = 1, 2, \ldots, n_m \quad (6)$$

$$N_i^{I_2} = \left(\frac{x_i^{I_2L_1}}{x_i^{I_2L_1} - x_i^{I_2L_2}}\right) k_i^{I_2L_2} c_{TL_2}\left(x_i^{I_2L_2} - x_i^{L_2}\right) - \left(\frac{x_i^{I_2L_2}}{x_i^{I_2L_1} - x_i^{I_2L_2}}\right) k_i^{I_2L_1} c_{TL_1}\left(x_i^{L_1} - x_i^{I_2L_1}\right) \qquad i = 1, 2, \ldots, n_m \quad (7)$$

Here, the flux is positive for transfer from the organic to the aqueous phase. Note that in this case the equations are written for n_m components miscible in both liquid phases. The subscript i refers to these n_m components. For the organic phase components insoluble in the aqueous phase, the flux is zero at the interface I_2

$$N_i^{I_2} = k_i^{I_2L_1} c_{TL_1}\left(x_i^{L_1} - x_i^{I_2L_1}\right) + x_i^{I_2L_1} N_T^{I_2} = 0 \qquad i = n_m + 1, \ldots, n_{L_1} \quad (8a)$$

Similarly, for the aqueous phase components insoluble in the organic phase, the flux is zero at I_2

$$N_i^{I_2} = k_i^{I_2L_2} c_{TL_2}\left(x_i^{I_2L_2} - x_i^{L_2}\right) + x_i^{I_2L_2} N_T^{I_2} = 0 \qquad i = n_m + 1, \ldots, n_{L_2} \quad (8b)$$

For the nonvolatile components in the organic liquid phase, the flux is zero at I_1

$$N_i^{I_1} = k_i^{I_1L_1} c_{TL_2}\left(x_i^{I_1L_1} - x_i^{L_1}\right) + x_i^{I_1L_1} N_T^{I_1} = 0$$

$$i = n_G + 1, \ldots, n_{L_1} \qquad (9)$$

The condition of phase equilibrium at the gas phase-organic liquid phase interface is given by

$$x_i^{I_1L_1} = H_i y_i^{I_1} \qquad i = 1, 2, \ldots, n_G \qquad (10)$$

For phase equilibrium at the liquid-liquid interface, we have an activity-based model. We define the distribution coefficient as the ratio of the activity of the component in the organic phase to that in the aqueous phase. Hence, we have

$$\gamma_i^{L_2} x_i^{I_2L_2} = \gamma_i^{L_1} x_i^{I_2L_1} \qquad (11a)$$

$$m_i = \frac{\gamma_i^{L_1}}{\gamma_i^{L_2}} \qquad i = 1, 2, \ldots, n_m \qquad (11b)$$

Equations 1 to 11 completely describe the mass transfer and phase equilibrium at the two interfaces.

Conservation Equations. The gas-phase overall and component material balance equations for the open gas-liquid-liquid system can be written as

$$G = G_o - a_T^{I_1} N_T^{I_1} \qquad (12)$$

$$G y_i = G_0 y_{i0} - a_T^{I_1} N_i^{I_1} \qquad i = 1, 2, \ldots, n_G \qquad (13)$$

Here, $a_T^{I_1}$ is the total interfacial area for interface I_1. The organic liquid phase overall and component material balance equations can be written as

$$L_1 = L_{10} + a_T^{I_1} N_T^{I_1} - a_T^{I_2} N_T^{I_2} \qquad (14)$$

$$L_1 x_i^{L_1} = L_{10} x_{i0}^{L_1} + Z_i a_T^{I_1} N_i^{I_1} - Y_i a_T^{I_2} N_i^{I_2}$$

$$i = 1, 2, \ldots, n_{L_1} \qquad (15)$$

Note that $Y_i = 0$ for components immiscible in L_2 and 1 for components miscible in both L_1 and L_2. $Z_i = 1$ for gas-phase components and 0 for the rest. The aqueous catalyst phase overall and component material balance equations can be

Table 2. Conservation Equations for the Three Phases

Gas Phase

$$\frac{G}{G_0 + L_{10} + L_{20}} = \frac{G}{G_0 + L_{10} + L_{20}} - \frac{Da_{mi}^{I_1L_1}(x_i^{I_1L_1} - x_i^{L_1}) - Da_{mi}^{I_1G}(y_i - y_i^{I_1})}{(y_i^{I_1} - x_i^{I_1L_1})} \qquad (21)$$

$$\frac{G}{G_0 + L_{10} + L_{20}} y_i = \frac{G_0}{G_0 + L_{10} + L_{20}} y_{i0} - \frac{y_i^{I_1}}{y_i^{I_1} - x_i^{I_1L_1}} Da_{mi}^{I_1L_1}(x_i^{I_1L_1} - x_i^{L_1})$$
$$+ \frac{x_i^{I_1L_1}}{y_i^{I_1} - x_i^{I_1L_1}} Da_{mi}^{I_1G}(y_i - y_i^{I_1}) \quad i = 1, 2, \ldots, n_G \qquad (22)$$

Liquid Phase 1

$$\frac{L_1}{G_0 + L_{10} + L_{20}} = \frac{L_{10}}{G_0 + L_{10} + L_{20}} + \frac{Da_{mi}^{I_1L_1}(x_i^{I_1L_1} - x_i^{L_1}) - Da_{mi}^{I_1G}(y_i - y_i^{I_1})}{(y_i^{I_1} - x_i^{I_1L_1})}$$
$$- \frac{Da_{mi}^{I_2L_2}(x_i^{I_2L_2} - x_i^{L_2}) - Da_{mi}^{I_2L_1}(x_i^{L_1} - x_i^{I_2L_1})}{(x_i^{I_2L_1} - x_i^{I_2L_2})} \qquad (23)$$

$$\frac{L_1}{G_0 + L_{10} + L_{20}} x_i^{L_1} = \frac{L_{10}}{G_0 + L_{10} + L_{20}} x_{i0}^{L_1} +$$
$$Z_i \frac{y_i^{I_1}}{y_i^{I_1} - x_i^{I_1L_1}} Da_{mi}^{I_1L_1}(x_i^{I_1L_1} - x_i^{L_1}) - Z_i \frac{x_i^{I_1L_1}}{y_i^{I_1} - x_i^{I_1L_1}} Da_{mi}^{I_1G}(y_i - y_i^{I_1})$$
$$- Y_i \frac{x_i^{I_2L_1}}{x_i^{I_2L_1} - x_i^{I_2L_2}} Da_{mi}^{I_2L_2}(x_i^{I_2L_2} - x_i^{L_2})$$
$$+ Y_i \frac{x_i^{I_2L_2}}{x_i^{I_2L_1} - x_i^{I_2L_2}} Da_{mi}^{I_2L_1}(x^{L_1} - x_i^{I_2L_1})$$
$$i = 1, 2, \ldots, n_{L_1} \qquad (24)$$

Liquid Phase 2

$$\frac{L_2}{G_0 + L_{10} + L_{20}} = \frac{L_{20}}{G_0 + L_{10} L_{20}} + \frac{Da_{mi}^{I_2L_2}(x_i^{I_2L_2} - x_i^{L_2}) - Da_{mi}^{I_2L_1}(x_i^{L_1} - x_i^{I_2L_1})}{(x_i^{I_2L_1} - x_i^{I_2L_2})} + k_f^{-1} Da_r^{L_2} \Sigma r_i \qquad (25)$$

$$\frac{L_2}{G_0 + L_{10} + L_{20}} x_i^{L_2} = \frac{L_{20}}{G_0 + L_{10} + L_{20}} x_{i0}^{L_2} + Y_i \frac{x_i^{I_2L_1}}{x_i^{I_2L_1} - x_i^{I_2L_2}} Da_{mi}^{I_2L_2}(x_i^{I_2L_2} - x_i^{L_2}) -$$
$$Y_i \frac{x_i^{I_2L_2}}{x_i^{I_2L_1} - x_i^{I_2L_2}} Da_{mi}^{I_2L_1}(x_i^{L_1} - x_i^{I_2L_1})$$
$$+ k_f^{-1} Da_r^{L_2} r_i \quad i = 1, 2, \ldots, n_{L_2} \qquad (26)$$

written as

$$L_2 = L_{20} + a_T^{I_2} N_T^{I_2} + H_{L_2} \Sigma r_i \tag{16}$$

$$L_2 x_i^{L_2} = L_{20} x_{i0}^{L_2} + Y_i a_T^{I_2} N_i^{I_2} + H_{L_2} r_i \qquad i = 1, 2, \ldots, n_{L_2} \tag{17}$$

We can nondimensionalize the above equations using the following dimensionless groups

$$Da_{mi}^{I_1 G} = \frac{H_G/(G_0 + L_{10} + L_{20})}{H_G/a_T^{I_1} k_i^{I_1 G} c_{TG}} \tag{18}$$

$$Da_{mi}^{I_1 L_1} = \frac{H_{L_1}/(G_0 + L_{10} + L_{20})}{H_{L_1}/a_T^{I_1} k_i^{I_1 L_1} c_{TL_1}} \tag{19}$$

We can define similar mass-transfer Damköhler numbers ($Da_{mi}^{I_2 L_1}$, $Da_{mi}^{I_2 L_2}$) for the second interface. Since the reaction takes place only in the aqueous catalyst phase, we define Damköhler number for reaction in the aqueous phase as

$$Da_r^{L_2} = \frac{H_{L_2}/(G_0 + L_{10} + L_{20})}{1/k_f} \tag{20}$$

The Damköhler numbers for mass transfer represent the ratio of the characteristic residence time of a phase to the characteristic time for mass transfer at the respective interface. The Damköhler number for reaction is similarly the ratio of the characteristic residence time of the aqueous phase where the reaction takes place to the characteristic time for reaction.

Using the Eqs. 1–7, developed for the fluxes at the two interfaces in the previous section and the dimensionless numbers defined by Eqs. 18–20 and, nondimensionalizing the conservation Eqs. 12–17, we get the final form of conservation equations (Table 2).

In the overall material balance equations the total fluxes at the two interfaces ($N_T^{I_1}$ and $N_T^{I_2}$) are evaluated at a particular component index using the nondimensionalized forms of Eqs. 4 and 6. We can equivalently use any other component index. Hence, for a particular choice of a component index, we have additional equations given by

$$\frac{Da_{mi}^{I_1 L_1}\left(x_i^{I_1 L_1} - x_i^{L_1}\right) - Da_{mi}^{I_1 G}\left(y_i - y_i^{I_1}\right)}{\left(y_i^{I_1} - x_i^{I_1 L_1}\right)} = \frac{Da_{mj}^{I_1 L_1}\left(x_j^{I_1 L_1} - x_j^{L_1}\right) - Da_{mj}^{I_1 G}\left(y_j - y_j^{I_1}\right)}{\left(y_j^{I_1} - x_j^{I_1 L_1}\right)}$$

$$i \in (1, 2, \ldots, n_G - 1) \quad j = 1, 2, \ldots, n_G - 1 \quad j \neq i \tag{27}$$

$$\frac{Da_{mi}^{I_2 L_2}\left(x_i^{I_2 L_2} - x_i^{L_2}\right) - Da_{mi}^{I_2 L_1}\left(x_i^{L_1} - x_i^{I_2 L_1}\right)}{\left(x_i^{I_2 L_1} - x_i^{I_2 L_2}\right)} = \frac{Da_{mj}^{I_2 L_2}\left(x_j^{I_2 L_2} - x_j^{L_2}\right) - Da_{mj}^{I_2 L_1}\left(x_j^{L_1} - x_j^{I_2 L_1}\right)}{\left(x_j^{I_2 L_1} - x_j^{I_2 L_2}\right)}$$

$$i \in (1, 2, \ldots, n_m - 1) \quad j = 1, 2, \ldots, n_m - 1 \quad j \neq i \tag{28}$$

In addition, mole fractions of the inlet and outlet streams and the mole fractions at the interfaces add to unity

$$\sum_{i=1}^{n_G} y_{i0} = \sum_{i=1}^{n_G} y_i^{I_1} = \sum_{i=1}^{n_G} y_i = \sum_{i=1}^{n_{L_1}} x_{i0}^{L_1} = \sum_{i=1}^{n_{L_1}} x_i^{I_1 L_1} = \sum_{i=1}^{n_{L_1}} x_i^{I_2 L_1} = \sum_{i=1}^{n_{L_1}} x_i^{L_1} = \sum_{i=1}^{n_{L_2}} x_{i0}^{L_2} = \sum_{i=1}^{n_{L_2}} x_i^{I_2 L_2} = \sum_{i=1}^{n_{L_2}} x_i^{L_2} = 1.0 \tag{29}$$

This completes the general mathematical model for an open gas-liquid-liquid system. In these equations the effects of reaction kinetics and mass transfer are parameterized by the dimensionless Damköhler numbers for reaction and mass transfer.

Degrees of Freedom. The material balance equations (Eqs. 20–26) represent a set of ($n_G + n_{L_1} + n_{L_2}$) equations. In addition, we have ($n_G + n_m$) equations from the two sets of phase equilibrium relations (Eqs. 10 and 11), ($n_G + n_m - 4$) constraints given by Eqs. 27 and 28, and 10 equations given by Eq. 29. Equations 8 and 9 give $[(n_{L_1} + n_{L_2} - 2n_m) + (n_{L_1} - n_G)]$ zero component flux constraints. Hence, the model equations form a set of ($2n_G + 3n_{L_1} + 2n_{L_2} + 6$) equations, which contain the following ($3n_G + 4n_{L_1} + 3n_{L_2} + 6$) variables: G_0, L_{10}, L_{20}, G, L_1, L_2, y_{i0}, $y_i^{I_1}$, y_i, $x_{i0}^{L_1}$, $x_i^{I_1 L_1}$, $x_i^{I_2 L_1}$, $x_i^{L_1}$, $x_{i0}^{L_2}$, $x_i^{I_2 L_2}$, and $x_i^{L_2}$. Therefore, we have ($n_G + n_{L_1} + n_{L_2}$) degrees of freedom that are completely specified by fixing the feed compositions y_{i0} ($i = 1, 2, \ldots, n_G - 1$), $x_{i0}^{L_1}$ ($i = 1, 2, \ldots, n_{L_1} - 1$), $x_{i0}^{L_2}$ ($i = 1, 2, \ldots, n_{L_2} - 1$), G_0, L_{10}, and L_{20}.

There are two possible liquid-liquid phase configurations: Aqueous in Organic and Organic in Aqueous. The model equations have been derived in detail for the first case. For organic in aqueous, the equations are exactly analogous except that in this case the aqueous phase is in direct contact with the gaseous phase and organic phase. Therefore, for organic in aqueous, the two interfaces are $G - L_2$ (I_1) and $L_2 - L_1$ (I_2) and the mass-transfer Damköhler numbers are given as $Da_{mi}^{I_1 G}$, $Da_{mi}^{I_1 L_2}$, $Da_{mi}^{I_2 L_2}$, and $Da_{mi}^{I_2 L_1}$. The conservation equations for the aqueous phase have additional terms for the mass transfer across I_1 and the conservation equations for the organic phase only have the terms for mass transfer across I_2.

This completes the discussion of the stirred cell model. Examples considered later illustrate the salient features of the model and its utility in the identification of the optimal range of reactor conditions.

Step 3: identification of reactor attributes

We now outline a qualitative procedure for synthesizing a biphasic reactor after the identification of the optimal reactor conditions. Some of the important factors that affect reactor performance are:

- Choice of dispersed phase and continuous phase.
- Mean droplet size of dispersed phase.
- Residence time or reactor size.

These factors can be chosen based on the model developed for biphasic reactions. The liquid-liquid mass transfer and reaction Damköhler numbers can be rewritten as (Samant and Ng, 1998b)

$$Da_{mi}^{I_2L_2} = \tau_{L_2} a_s^{I_2L_2} k_{mi}^{I_2L_2} \tag{30}$$

$$Da_r^{L_2} = \tau_{L_2} k_f \tag{31}$$

For clarity of discussion, we have assumed that the mass-transfer coefficients for all the components are equal ($k_{mi}^{I_2L_2} = k_m^{I_2L_2}$). We also have

$$\frac{Da_r^{L_2}}{Da_m^{I_2L_2}} = \frac{1}{a_s^{I_2L_2}} \frac{k_f}{k_m^{I_2L_2}} \tag{32}$$

Equation 32 is independent of the residence time of the reactive aqueous phase and, hence, can be used to choose the mean droplet size of the dispersed phase. In Step 2, the values of the Damköhler for achieving the desirable performance have been determined. For a specified value of $k_f/k_m^{I_2L_2}$ for a given reaction mixture, the specific surface area of the reactive phase $a_s^{I_2L_2}$ can be selected to achieve the desirable value of $Da_r^{L_2}/Da_m^{I_2L_2}$. $Da_m^{I_2L_2}$ or $Da_r^{L_2}$ (Eq. 30 or 31) can then be used to fix the residence time. For example, if we want a low value of the ratio $Da_r^{L_2}/Da_m^{I_2L_2}$ and it is given that $k_f/k_m^{I_2L_2}$ is high, then based on Eq. 32, $a_s^{I_2L_2}$ should be high. This means that the droplet size should be small and the reactive phase should be dispersed. Furthermore, if the desired $Da_m^{I_2L_2}$ is low then according to Eq. 29, τ_{L_2} should be decreased.

The mass-transfer Damköhler numbers at the gas-liquid interface can also be rewritten as

$$Da_m^{I_1L_2} = \tau_{L_2} a_s^{I_1L_2} k_m^{I_1L_2} \text{ organic in aqueous phase configuration} \tag{33}$$

$$Da_m^{I_1L_1} = \tau_{L_1} a_s^{I_1L_1} k_m^{I_1L_1} \text{ aqueous in organic phase configuration} \tag{34}$$

Once the liquid-liquid phase attributes and the residence time have been fixed on the basis of Eqs. 30, 31, and 32, we can look at the gas-liquid interface and achieve the desired operating range for the gas-liquid mass-transfer Damköhler numbers by controlling $a_s^{I_1L_i}$. In this case the gaseous phase is always the dispersed phase, and $a_s^{I_1L_i}$ increases with decreasing mean bubble size for the dispersed gas phase. Typical $a_s^{I_1L_i}$ values are available for various gas-liquid interface generating devices (Kelkar and Ng, 1998).

Step 4: catalyst recovery and recycle

Homogeneous catalysis almost always involves the use of organometallic complexes of metals such as rhodium, platinum, cobalt, and palladium as catalysts. Both economic and environmental constraints make the recovery and recycle of the homogeneous catalyst a key issue for successful commercial operation. There is a need for a systematic classification of various alternatives and a generic procedure for choosing the right catalyst recovery and recycle method.

Classification. We have classified the various catalyst recovery and recycle methods drawn from the patent literature and various publications (Cornils and Herrmann, 1996, 1998). Figures 2–5 show the generic flowsheets that have been developed for these cases. We consider three generic classes of flowsheets based on thermal operation, liquid-liquid equilibrium (LLE), and chemical addition.

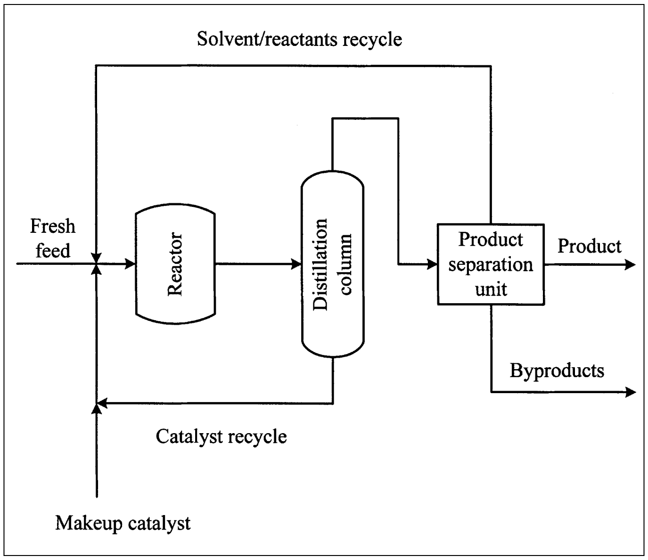

Figure 2. Type I flowsheet.

Type I flowsheet (Figure 2) is based on thermal operation. This is the most common means of catalyst recovery and recycle. The reactor outlet stream is sent to the flasher or the distillation column(s) where the catalyst and a fraction of the solvent are separated and recycled. The catalyst is usually obtained from the bottom of the column(s), as it is the least volatile species. The stream from the catalyst recovery section is then sent to the product separation unit that usually consists of a series of distillation columns and separates the product(s) and solvent/unconverted reactants to be recycled. Qualitatively, the requirements for the successful operation of a Type I flowsheet are:

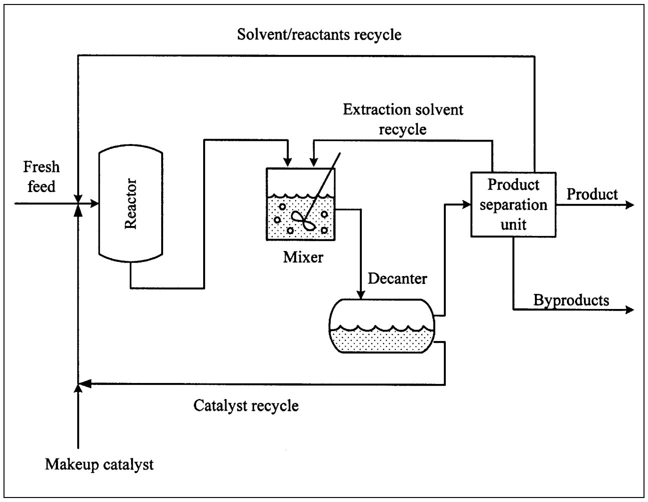

Figure 3. Type II(a) flowsheet.

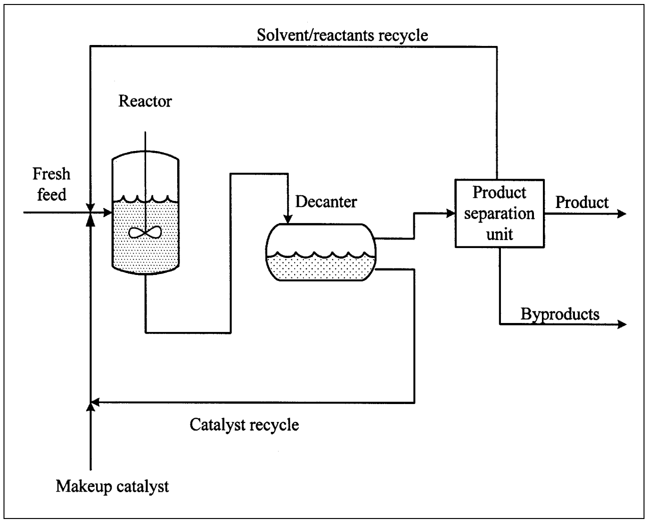

Figure 4. Type II(b) flowsheet.

- Exposure to repeated thermal stress does not deactivate the catalyst significantly.
- No significant amounts of high boiling byproducts and impurities accumulate in the system and cause excessive deposits.
- None of the components are heat sensitive.

We may state three relevant heuristics for this case. First, consider adding additives to stabilize the catalyst if it is heat sensitive. An example is the use of iodide salts in acetic acid production by carbonylation of methanol to prevent the rhodium catalyst from precipitating out (Smith et al., 1992). Second, consider taking a side stream, removing its impurities by any suitable chemical or physical means, and recycling it to prevent the buildup of impurities in the system. Third, consider using a flasher if there is a relatively large difference in the volatility of the products/reactants and solvent/catalyst. A boiling reactor where the reaction and thermal separation take place simultaneously can also be considered a Type I flowsheet.

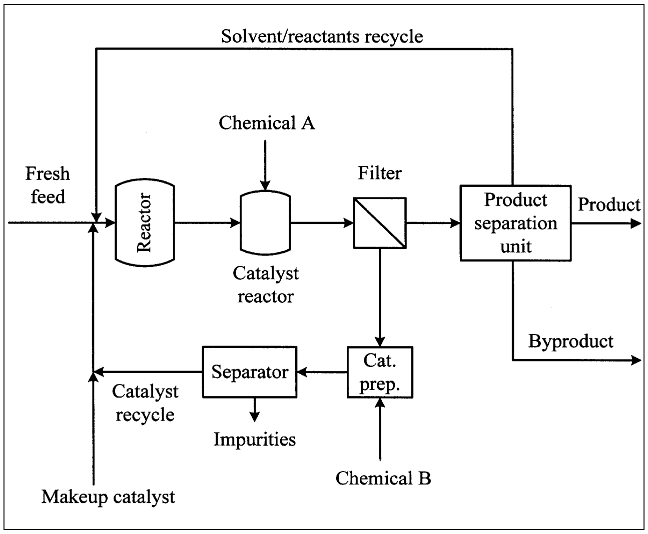

Figure 5. Type III flowsheet.

The Type II flowsheet is based on LLE and may be further classified into Type II (a) flowsheet (Figure 3) based on extraction and the Type II(b) flowsheet (Figure 4) based on biphasic reactor operation. The key difference between extraction and biphasic reactor operation is that in the former case the LLE is external to the reactor, which has a single-phase operation, whereas in the latter case LLE is *in-situ*. Let us consider the Type II(a) flowsheet first. The reactor outlet stream is sent to the mixer-settler where the extraction solvent is mixed and the product is extracted. The extract is sent to the product separation unit to recover the product, and the raffinate containing the catalyst, solvent, and unconverted reactants is recycled. This method is useful when any of the components are heat sensitive, and there is excessive accumulation of catalyst poisons, high boiling byproducts, and other impurities in the system. Obviously the key issue in this case is the selection of a suitable extraction solvent, which selectively extracts the products and byproducts with high efficiency. This method has significant advantages over the Type I flowsheet:

- The catalyst can be separated out without heating and, hence, thermal deactivation is avoided.
- Accumulation of high boiling byproducts and impurities is avoided as extraction equilibrium is achieved for all components and thermal degradation of various components is avoided.

The Type II(b) flowsheet combines the above advantages with a short catalyst recovery and recycle and, hence, considerable process simplification. The key to biphasic operation is the development of suitable polar catalysts. The reactor is fed with the aqueous catalyst and reactants. The reactant operation is biphasic with the catalyst in the aqueous phase and the product(s) in the organic phase. After the reaction, the aqueous catalyst is separated from the organic product phase by simple decantation and is recycled as is. The product stream may be further processed as required. An extension to this method is the use of a suitable nonaqueous polar solvent for catalyst retention. We can also consider adding surfactants, co-solvents, and phase transfer agents for improving the miscibility of reactants and the catalyst phase and, thus, increasing the conversion. Such a flowsheet may also lead to increased selectivity for a given reaction scheme. For example consider a series-parallel scheme as follows

$$\mathbf{A + B \Rightarrow C}$$

$$\mathbf{B + C \Rightarrow D}$$

In this case, C is the desired product and D is the undesired byproduct. We can get a higher selectivity if we remove product C as soon as it is formed so that the second reaction is minimized. This is possible if we operate under biphasic conditions and use an appropriate organic solvent in which the miscibility of C is relatively high.

Finally, we have the Type III flowsheet (Figure 5) based on catalyst recovery and recycle by chemical addition. This is a relatively common method for catalysts that are thermally sensitive. The reactor outlet stream is reacted with a suitable chemical "A"so that the catalyst species precipitates out. The

Table 3. Heuristics for Catalyst Recovery and Recycle Method Selection

- Use a biphasic system [Type II(b)] if suitable catalyst solvent system is available.
- Consider adding a co-solvent or a surfactant for improving the miscibility of the reactants in the aqueous phase for a Type II(b) flow sheet.
- Consider using a Type I flowsheet if:
  (a) Catalyst does not deactivate significantly
  (b) No significant accumulation of impurities
  (c) Product, byproducts, and solvent are not heat sensitive
- Consider adding additives to stabilize catalyst for Type I.
- Consider processing a side stream and recycling it for Type I.
- For Type I, use a flasher if the volatility difference is large.
- If the relative volatility of the solvent and product(s) is less than 1.1, then Type I flow sheet may not be economical (Douglas, 1988).
- For a Type II flowsheet, the distribution coefficient of the catalyst in the extractor [for Type II(a)] or the biphasic reactor [for Type II(b)] should be sufficiently large. If this condition is not satisfied, then a Type II is not feasible due to excess catalyst loss.
- Use a Type II(a) flowsheet if phase split occurs with a change in temperature.
- Use a Type III if Type I and II are not feasible.

precipitated catalyst is then separated by filtration and then re-dissolved using either the solvent or a suitable reagent "B". The impurities are separated in the separator unit and the catalyst is recycled. The chemicals actually used will depend on the process chemistry. This method introduces additional compounds into the system and, hence, is not preferable if suitable Type I or Type II alternatives are available.

Table 3 gives a summary of heuristics for the catalyst recovery and recycle method selection. The most important parameter in this case is obviously the fractional catalyst recovery of the flowsheet. For a Type II flowsheet, this depends on the distribution of the catalyst in the extractor [for Type II(a)] or in the biphasic reactor [for a Type II(b)]. A number of variations and combinations of the basic flowsheets are possible depending on specific needs and design. For example, a relatively new Union Carbide hydroformylation process (Haggin, 1995) consists of both an extractor and a separation column. Instead of extracting the product as in a Type II(a) flowsheet, the catalyst itself is extracted using water and then the catalyst is concentrated, dried, and recycled using a separation column and a vaporizer. In general the catalyst recovery and recycle is a strong function of process chemistry and economics. However, the heuristics in Table 3 serve as a starting point for screening different catalyst recovery and recycle methods after which a detailed analysis and design can be carried out.

Examples

The first example is a single step reaction that examines the dominant mechanisms and the effect of various model parameters. The next example considers series-parallel schemes and illustrates the identification of optimal reactor conditions and the reactor attributes. Since homogeneous catalytic processes generally involve complex reaction networks with multiple reactions, the final example is a complex network and takes into account all the design steps including network reduction and catalyst recovery and recycle. The re-

Table 4. Parameter Values and Specifications for the Examples Considered

Thermodynamic Parameters		Relative Input Molar Flows
Distribution Coefficients	*Base case 1*	*Aqueous in Organic*
	Henry(A) = 0.04 (a/o)	$G_1 = 0.2$
md(A) = 0.5	0.01 (o/a)	$L_1 = 0.5$
md(B) = 0.2		$L_2 = 0.3$
md(C) = 0.02		
md(D) = 0.02	*Base case 2*	*Organic in Aqueous*
md(E) = 0.04	Henry(A) = 0.04 (a/o)	$G = 0.2$
	4×10^{-4} (o/a)	$L_1 = 0.3$
		$L_2 = 0.5$

Kinetic Parameters (s^{-1})	Input Concentrations (Mole Fractions)			
		Gas phase	*Organic phase*	*Aqueous phase*
$k_f = 0.02$ (Simple irreversible reaction)	A	0.6	0.0	0.0
$k_{f_1} = 0.02$ (Series parallel schemes)	B	—	0.3	0.0
$k_{f_2} = 0.005$	C	—	0.0	0.0
$k_{f_1} = 0.01$ (Complex reaction scheme)	D	—	0.0	0.0
$k_{f_2} = 0.5 \quad k_{f_3} = 0.02 \quad k_d = 1.0$	E	—	0.0	0.0
	S	—	0.7	0.0
	W	—	0.0	1.0
	I	0.4	0.0	0.0

actions are fictitious, but the data used are close to those for typical systems.

Example 1: single step irreversible reaction

Consider a single step of reversible reaction with a total of seven components. The chemical reaction takes place only in the aqueous phase

$$\mathbf{A} + \mathbf{B} \Rightarrow \mathbf{C}$$

We assume that the catalyst with relatively low and constant concentration is confined to the aqueous phase. Hence, it is not separately represented as a component in the aqueous phase. The following components are present in the respective phases:

- Gas-phase components: A (reactant gas), I (Inert gas, negligible solubility in the liquid phase).
- Liquid phase 1 (Organic Phase) components: A, B (nonvolatile liquid phase reactant), C (nonvolatile product), S (nonvolatile organic solvent).
- Liquid phase 2 (Aqueous catalyst phase) components: A, B, C, W (water).

Table 4 shows the various model parameter values and specifications used for this example, as well as the data for the other two examples where additional products D and E are present in the two liquid phases. For this example, the conversion is defined on the basis of the amount of liquid reactant B consumed.

Mass Transfer vs. Reaction. The rates of mass transfer and reaction relative to each other are crucial in determining whether the process lies in a reaction controlled or mass-transfer controlled regime. Figure 6 shows conversion vs. the ratio of Damköhler number for reaction and the aqueous phase Damköhler number for mass transfer ($Da_r^{L_2}/Da_{mi}^{I_2L_2}$) for aqueous dispersed in organic phase configuration. The ratio is the conventional second Damköhler number or Hatta number for the aqueous phase. High values of $Da_r^{L_2}/Da_{mi}^{I_2L_2}$ represent the mass transfer controlled regime, in which the reaction is much faster relative to mass transfer across the liquid-liquid interface. Low values of $Da_r^{L_2}/Da_{mi}^{I_2L_2}$ represent the reaction controlled regime where the reaction is much slower relative to mass transfer across the liquid-liquid interface.

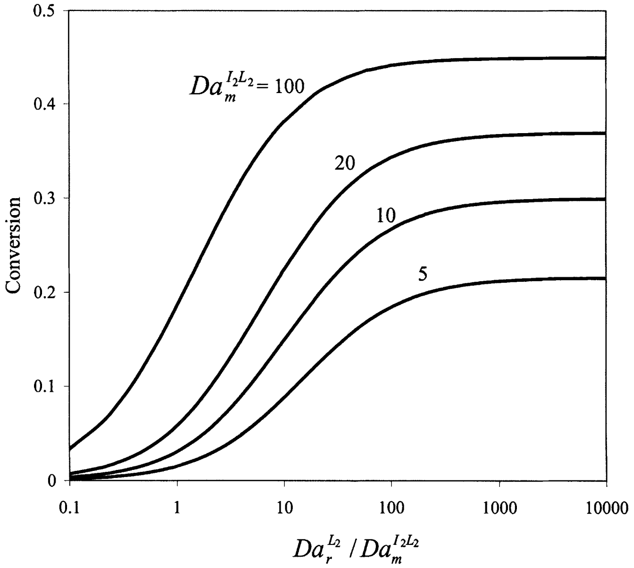

Figure 6. Conversion vs. aqueous phase Hatta number for Example 1.

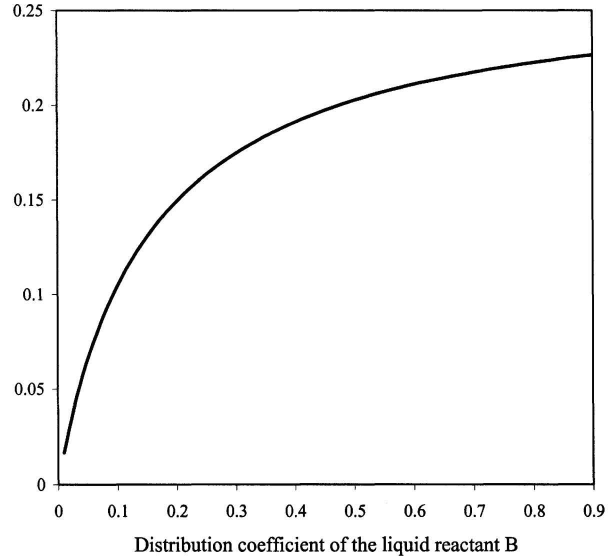

Figure 7. Variation of the conversion with the distribution coefficient of the liquid reactant B for Example 1.

Figure 6 also gives the variation of conversion with $Da_{mi}^{I_2L_2}$. The conversion increases with increasing $Da_{mi}^{I_2L_2}$ as the aqueous phase mass-transfer resistance decreases and, hence, the liquid reactant B can get transferred at a higher rate to the aqueous phase and the conversion increases. Let us state some other observations for which the plots are not included in this article. The conversion also increases with increasing $Da_{mi}^{I_2L_1}$ and $Da_{mi}^{I_1L_1}$, but is less sensitive to $Da_{mi}^{I_2L_1}$ and $Da_{mi}^{I_1L_1}$ as no reaction takes place in the organic phase. The variation with the gas-phase Damköhler number $Da_{mi}^{I_1G}$ at the first interface is negligible. This is consistent with a physically realistic situation where the mass transfer at a gas-liquid interface is limited by only the liquid side resistance.

Effect of Liquid-Liquid Phase Equilibrium. Figure 7 shows the variation of conversion with the distribution coefficient of the liquid reactant B for the aqueous in organic phase configuration. The conversion obviously increases as the distribution coefficient increases because more reactant is then available in the aqueous phase. However, we see that after a point the increase tapers off. This is due to the fact that the gaseous reactant (A) becomes limiting as the concentration of the liquid reactant (B) increases. In general the reactants need to have a minimum solubility in the aqueous phase for a significant conversion. Hence, in some cases we may even need to use a co-solvent to increase the solubility of the reactants in the aqueous phase to achieve significant conversion.

Comparison of the Two Liquid-Liquid Phase Configurations Based on the Model. Using the stirred cell model, we can compare the two-phase configurations (Aqueous in Organic and

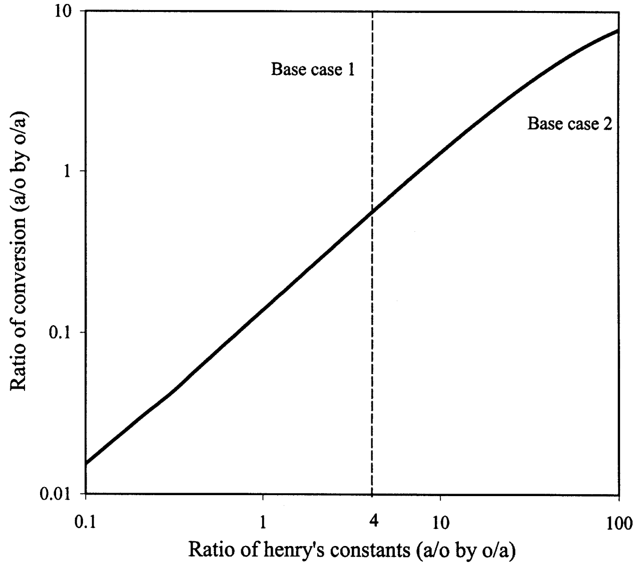

Figure 8. Ratio of conversion vs. ratio of Henry's constants (aqueous in organic/organic in aqueous) for Example 1.

Organic in Aqueous) and select the one that gives better performance. We adopt a shorthand convention for the two-phase configurations. Aqueous in organic is denoted as a/o and organic in aqueous as o/a. Figure 8 shows the ratio of conversion vs. ratio of Henry's constants (a/o by o/a) for a simple irreversible reaction. Let us consider two specific base cases. The first represents a relatively low ratio (a/o by o/a) of Henry's constant (~ 4) and the second represents a high ratio (~ 100). For base case 1, the conversion for o/a is higher than a/o as a higher concentration of the reactant gas is available for o/a, and o/a is the preferred phase configuration. On the other hand, for base case 2, a/o gives better conversion as the solubility of the gaseous reactant A in water is very low in this case.

The reactor attributes for this example have been determined and are summarized in Table 5. The table also lists the optimal range of reactor conditions ($Da_r^{L_2}/Da_{mi}^{I_2L_2}$, $Da_m^{I_2L_2}$, and $Da_m^{I_1L_x}$) for maximizing the performance objective-conversion.

Example 2: simple series parallel schemes

Let us consider two series-parallel schemes with two gas-phase components (A, I) and a total of seven components (A, B, C, D, I, S and W)

$$\underline{\text{Scheme 1.}}\quad \mathbf{A+B \Rightarrow C}$$

$$\mathbf{B+C \Rightarrow D}$$

$$\underline{\text{Scheme 2.}}\quad \mathbf{A+B \Rightarrow C}$$

$$\mathbf{A+C \Rightarrow D}$$

The reactions take place in the presence of aqueous catalyst. As before, we assume that the catalyst's relatively low and constant concentration is confined to the aqueous phase. Hence, it is not separately represented as a component in the aqueous phase. The model parameter values and specifications are given in Table 4. The distribution of the various components in the three phases is the same as in the first example. We define conversion on the basis of the amount of liquid reactant B consumed. Selectivity is defined as the ratio of C produced by B consumed and the yield as the ratio of C produced by B introduced.

Selectivity, Conversion and Yield. We first consider aqueous in organic phase configuration. Figure 9 shows the dependency of selectivity, conversion, and yield on the ratio of aqueous phase Damköhler numbers ($Da_r^{L_2}/Da_{mi}^{I_2L_2}$) for Scheme 1. The conversion increases with increasing $Da_r^{L_2}/Da_{mi}^{I_2L_2}$ and the selectivity shows a steady decline. There is a tradeoff between selectivity and conversion. In fact the yield goes through a maximum at a particular value of the ratio $Da_r^{L_2}/Da_{mi}^{I_2L_2}$. Thus, if we want to maximize the yield, we should operate around this value. This tradeoff is due to

Table 5. Reactor Attributes for Given Examples

Example 1. Single Step Irreversible Reaction (Base Case 1)

Performance Objectives	$\frac{Da_r^{L_2}}{Da_m^{I_2L_2}}$	$Da_m^{I_2L_2}$	$Da_m^{I_1L_X}$	$a_s^{I_1L_X}$	$k_f/k_m^{I_2L_2}$	$a_s^{I_2I_2}$	Reactor Attributes
High conversion	High	High	High	High	Low	Low	• Disperse organic phase • Use large mean droplet size • Use large reactor • Use small mean bubble size
					High	Highest possible	• Disperse organic phase • Use mean droplet size that gives highest possible $a_s^{I_2L_2}$ • Use small mean bubble size

Example 2. Series Parallel Scheme 1/Example 3 (Base Case 2)

Performance Objective	$\frac{Da_r^{L_2}}{Da_m^{I_2L_2}}$	$Da_m^{I_2L_2}$	$Da_m^{I_1L_X}$	$a_s^{I_1L_X}$	$k_f/k_m^{I_2L_2}$	$a_s^{I_1L_2}$	Reactor Attributes
High yield/ High product distribution	Low	High	High	High	Low/High	High	• Disperse aqueous phase • Use small mean droplet size • Use small mean bubble size • Increase reactor size if necessary

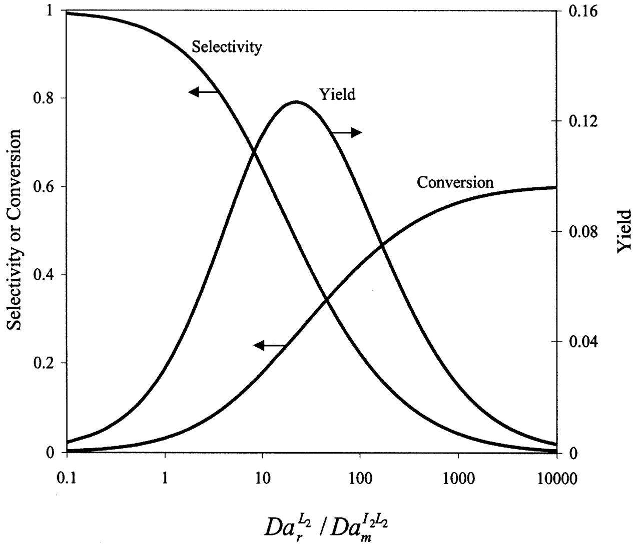

Figure 9. Selectivity, conversion, and yield vs. aqueous phase Hatta number for series-parallel scheme 1.

the fact that, if the reaction rates are faster (that is, $Da_r^{L_2}$ increases), more C is produced initially, but, for high $Da_r^{L_2}/Da_{mi}^{I_2L_2}$, the second reaction leads to an even faster depletion of C as more D is produced. Hence, the yield goes through a maximum. Figure 10 shows the effect of the distribution coefficients of the products on the yield of the primary product C for Scheme 1. We see that the yield decreases significantly if the distribution coefficient of the primary product C is greater than the distribution coefficient of the byproduct D. This is because in such a case more C is available in the aqueous phase for the second reaction, which gives more D. Hence, we prefer to operate with an organic solvent with a small distribution coefficient ratio.

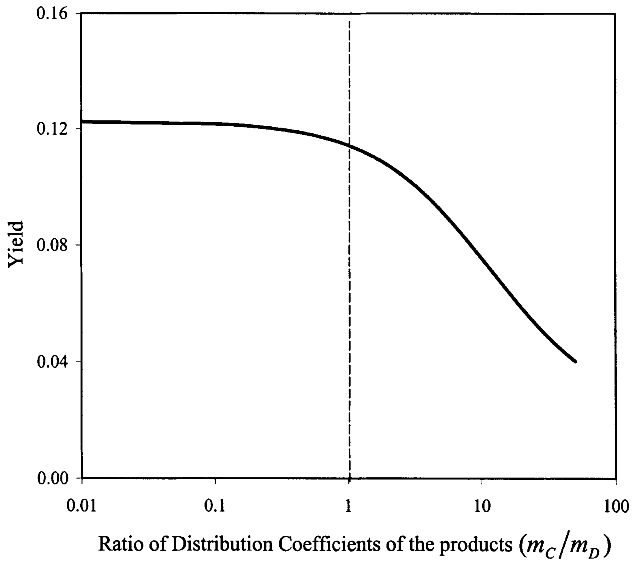

Figure 10. Effect of the distribution of the products on the yield of the primary product C for series-parallel scheme 1.

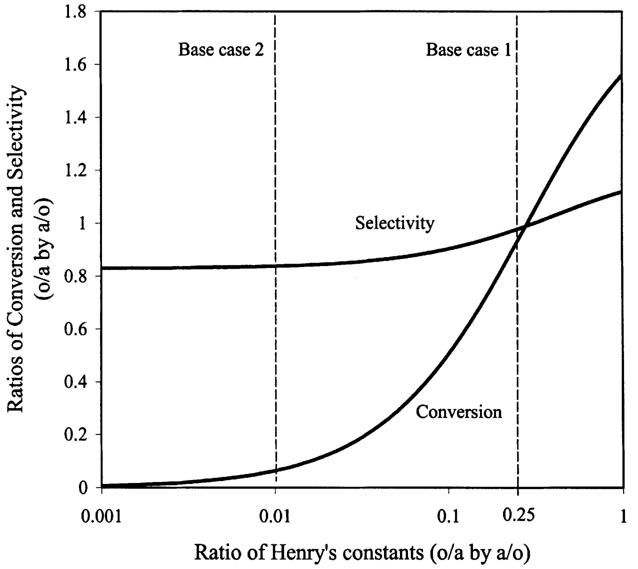

Figure 11. Ratios of conversion and selectivity vs. ratio of Henry's constants (organic in aqueous/aqueous in organic) for series-parallel scheme 1.

Identification of Reactor Attributes. Figure 11 shows the ratio of conversion and selectivity (Organic in Aqueous/Aqueous in Organic) vs. ratio of Henry's constants for Scheme 1. For both base cases, the Aqueous in Organic configuration gives better conversion and selectivity as compared to the Organic in Aqueous configuration. Increasing the relative solubility of the gas in the aqueous phase reduces the difference between the two-phase configurations as the amount of dissolved gaseous reactant is higher and is, therefore, less limiting. We can conclude that a/o would be preferred if we want to maximize conversion, selectivity, and, hence, the yield. Figure 12 shows the dependence of conversion and selectivity on the Henry's constant for series-parallel scheme 2. The o/a configuration gives a higher conversion, but lower selectivity, and, hence, there is a trade-off between selectivity and conversion. After determining the desired phase configuration, we determine other reactor attributes based on the qualitative procedure. Table 5 summarizes the reactor attributes we obtain for series parallel scheme 1. The table also lists the optimal range of reactor conditions ($Da_r^{L_2}/Da_{mi}^{I_2L_2}$, $Da_m^{I_2L_2}$ and $Da_m^{I_1L_x}$) for maximizing selectivity.

Example 3: complex reaction

The final example demonstrates the complete design procedure by considering all the four steps. Consider the following reaction scheme

$$A \xleftrightarrow{\text{cat}} X_1 \xleftrightarrow{B} X_2 \xleftrightarrow[\text{cat}]{} X_3 \longrightarrow C \xrightarrow{B} D \xrightarrow{B} E$$

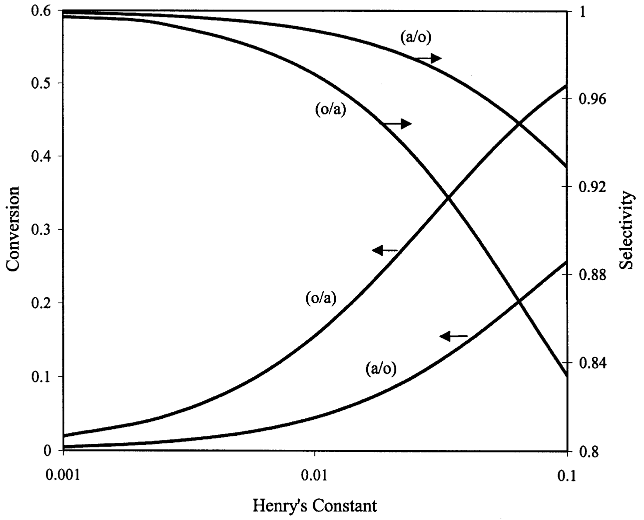

Figure 12. Comparison of conversion and selectivity of the two-phase configurations for series-parallel scheme 2.

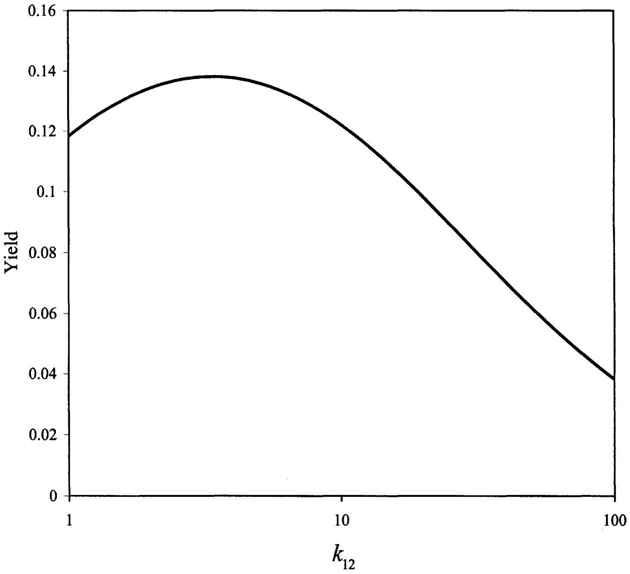

Figure 13. Variation of the yield with reaction rate constant k_{12} for Example 3.

Here the co-reactants are shown above the reaction arrows and the co-products below the arrows. This is a typical mechanism for a homogeneous catalytic reaction. The first step is the formation of a complex between a substrate (A) and the catalyst. The second reactant (B) then adds to this complex after which the catalyst separates and we get the intermediate (X_3), which rearranges to give the intermediate product C. C reacts with B to give the desired product D which further reacts to give the undesired byproduct E. If we can eliminate the intermediates (X_i), then the reaction scheme may be simplified to a three-step scheme

$$\mathbf{A+B \Rightarrow C}$$

$$\mathbf{B+C \Rightarrow D}$$

$$\mathbf{B+D \Rightarrow E}$$

As before, the reaction takes place in the presence of the aqueous catalyst. We assume that the catalyst with relatively low and constant concentration is confined to the aqueous phase. The model parameters values and specifications are given in Table 4. We define conversion on the basis of the amount of the liquid reactant B consumed. Product distribution is defined as the ratio of D produced by E produced. Since the desired product is D, we would prefer a high product distribution.

Step 1: Determination of Reaction Kinetics. We can use the first rule in Table 1 to reduce the underlined segment of the complete reaction scheme into a pseudo single step

$$\mathbf{A+B \Rightarrow C}$$

We use for reducing our linear segment. The same notation as Table 1 is used. Thus, we have

$$\Lambda_{AC} = \lambda_{01}\lambda_{12}\lambda_{23}\lambda_{34}/D_{AC} \tag{35a}$$

$$D_{AC} = \lambda_{12}\lambda_{23}\lambda_{34} + \lambda_{10}\lambda_{23}\lambda_{34} + \lambda_{10}\lambda_{21}\lambda_{34} + \lambda_{10}\lambda_{21}\lambda_{32} \tag{35b}$$

Here, the subscript indexes represent the various species ($j = 0$ for A to $k = 4$ for C). After replacement of the pseudo first-order reaction rate coefficients (λ_{ij}) and a rearrangement of the overall expression, we get the rate of production of C as

$$r_C = \frac{k_{12}k_a[A][B]}{1+k_{12}k_d[B]} \tag{36}$$

We can easily study the complete reaction scheme by using the reduced Eq. 36 which gives the rate of formation of C. Figure 13 shows the impact of k_{12} on the yield of the desired product D. There is an initial increase in the yield after which it goes through a maximum and starts decreasing. Thus, in this case increasing the rate constant of the second reaction (say by increasing the temperature) will not necessarily give a better performance. For this particular case, the optimum value of k_{12} is approximately equal to 2.

Step 2: Identification of Optimal Range of Reactor Conditions. Figure 14 shows the plots of product distribution, conversion, and yield with the ratio of aqueous phase Damköhler numbers ($Da_r^{L_2}/Da_{mi}^{I_2L_2}$) for aqueous in organic phase configuration. The conversion increases with increasing $Da_r^{L_2}/Da_{mi}^{I_2L_2}$ and the product distribution shows a decrease. There is a tradeoff between the product distribution and the conversion, and this is evident from the fact that the yield goes through a maximum. Thus, if our performance objective is product distribution, then $Da_r^{L_2}/Da_{mi}^{I_2L_2}$ should be low. Further analysis shows that high Damköhler numbers ($Da_m^{I_2L_2}$ and $Da_m^{I_2L_X}$) lead to higher product distribution. This identifies the reactor conditions for the given performance objective.

Step 3: Identification of Reactor Attributes. We also compare the two-phase configurations for this example (Figures 15 and

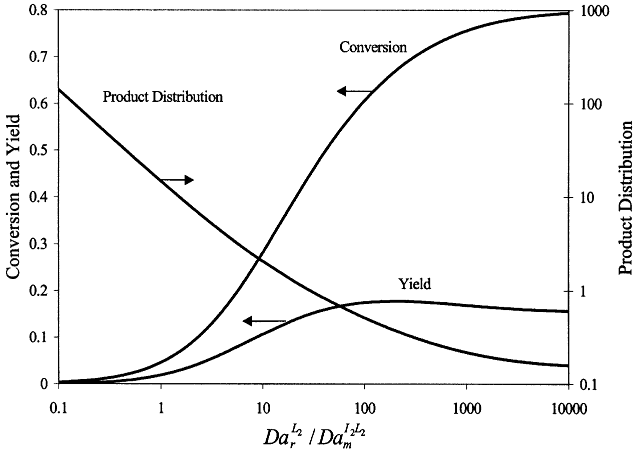

Figure 14. Product distribution, conversion and yield vs. aqueous phase Hatta number for Example 3.

16). The o/a configuration gives a significantly better performance. Next, we identify other reactor attributes. As $Da_r^{L_2}/Da_{mi}^{I_2L_2}$ should be low, from Eq. 32, $a_s^{I_2L_2}$ should be high. This implies that small droplet size should be used. For this case, high Damköhler numbers ($Da_m^{I_2L_2}$ and $Da_m^{I_2L_X}$) are preferred. However, since $a_s^{I_2L_2}$ is already high, from Eq. 30, we can increase the reactor size (that is residence time), if necessary. In addition, small bubble size should be used as this leads to high $Da_m^{I_2L_X}$.

Step 4: Catalyst Recovery and Recycle. Let us look at the alternatives if the given system has the following thermal properties:

- Relative thermal volatilities of the products (C, D and E) vs. the solvent are 2.0, 1.5 and 2.5.
- Boiling point of the organic solvent is 120°C.
- E degrades and deposits at around 130°C.

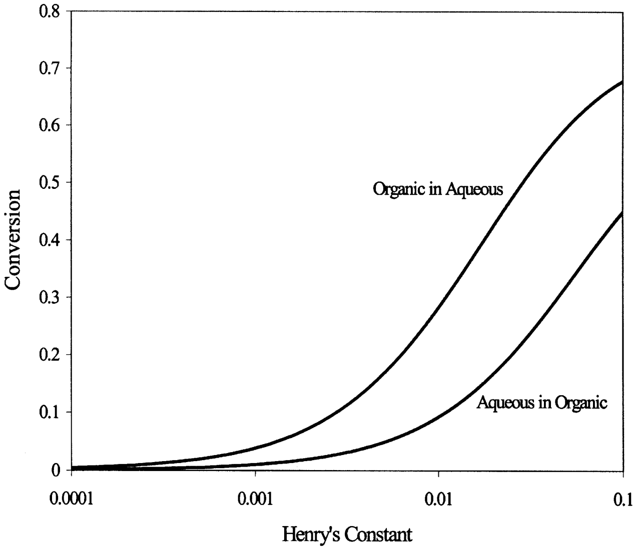

Figure 15. Comparison of conversion of the two-phase configurations for Example 3.

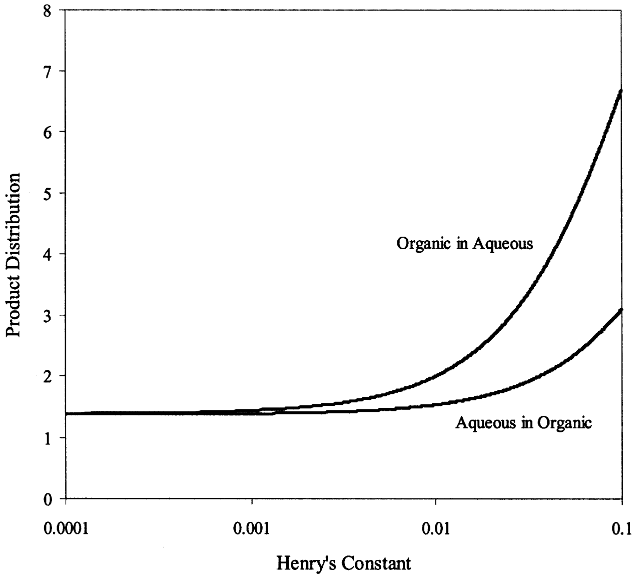

Figure 16. Comparison of product distribution of the two-phase configurations for Example 3.

Thus, the thermal separation of the products and the solvent (Type I flowsheet) is relatively easy, but since the secondary product E degrades and causes deposits at a temperature comparable to the boiling point of the solvent, a vacuum column is necessary. Next, consider the feasibility of a Type II flowsheet which mainly depends on the distribution of the catalyst in the extractor [Type II(a)] or the biphasic reactor [Type II(b)]. Thus, if the economic constraints demand a 99% recovery, the distribution coefficient of the catalyst should be very high. If this condition is not satisfied, a Type III flowsheet based on chemical addition might be necessary. A detailed analysis can be readily worked out when the process chemistry is specified.

Conclusions

Biphasic homogeneous catalysis can play an important role in both bulk and fine chemical synthesis. A generic procedure as summarized in Figure 17 is developed for the design of such homogeneous catalytic processes. The first step is determination and reduction of the reaction kinetics. Next, the identification of optimal reactor conditions, using the stirred cell model we have formulated, is made. This provides important information about the range of Damköhler numbers that give optimum performance. Using the model, we can also compare and select the phase configuration that gives the best performance. Utilizing the qualitative procedure outlined, other reactor attributes are selected. The selection of the proper catalyst recovery and recycle method is an important issue. While only the analysis of biphasic reactions is presented, various catalyst recovery and recycle methods are reviewed and heuristics for their selection are provided.

This study represents our continuing effort to study reaction system synthesis from a multiscale perspective (Lerou and Ng, 1996). Further work on studying multiphase systems,

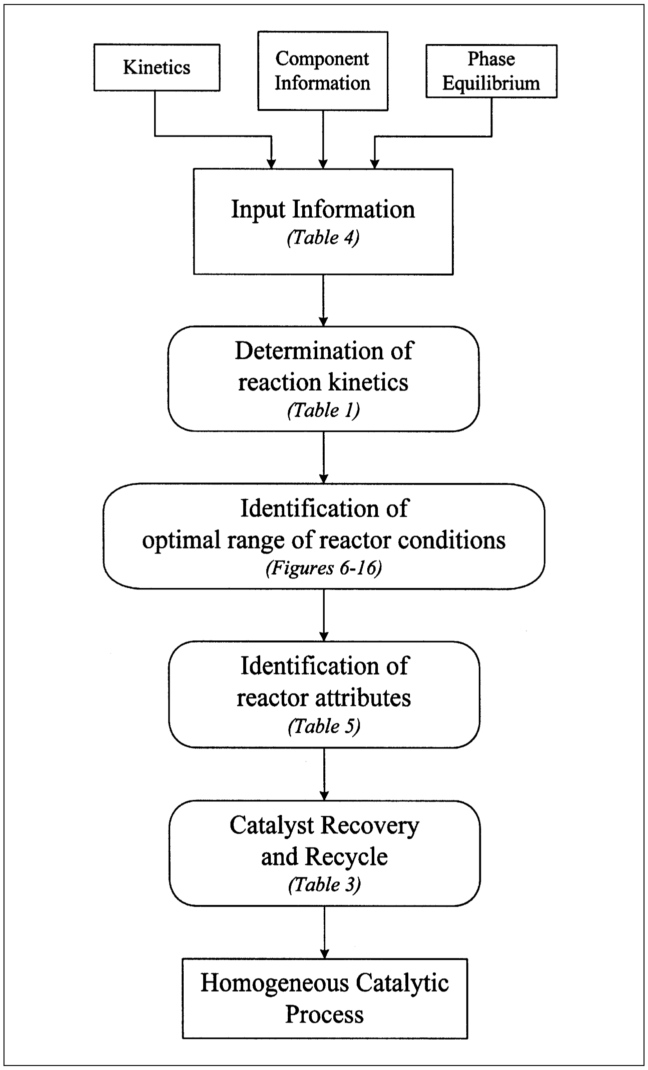

Figure 17. Systematic procedure for the development of homogeneous catalytic processes.

which combine both homogeneous catalysis and phase transfer catalysis, is underway.

Acknowledgments

We express our appreciation to the National Science Foundation, Grant No. CTS-9807101 and NETI for support of this research.

Notation

a_s = specific interfacial area for mass transfer, m^2/m^3
a_T = total interfacial area for mass transfer, m^2
A, B, C, D, I, S, W = generic chemical species
c_{TX} = total molar concentration of phase X, mol/m^3
$Da_{mi}^{I_iX}$ = Damköhler numbers for mass transfer for phase X at interface I_i
$Da_r^{L_2}$ = Damköhler number for reaction in the aqueous reactive phase
G_0, G = input and output molar flow rates of gaseous phase, mol/s
H_i = Henry's constant of component i
H_X = molar holdup of phase X, mol
k_f = forward reaction rate constant for the reference reaction, L/s
k_m = mass transfer coefficients across the respective interfaces, m/s
L_{0X}, L_X = input and output molar flow rates of the liquid phases, mol/s
md = distribution coefficient
n = number of components
n_m = number of components miscible in both the liquid phases
N_i = molar flux of component i, $mol/m^2 \cdot s$
N_T = total molar flux, $mol/m^2 \cdot s$
x_i = mole fraction of component i in the liquid phase
y_i = mole fraction of component i in the gaseous phase
Y, Z = binary integer parameters
γ_i = activity coefficient of component i
τ_X = residence time of phase X

Subscripts and superscripts

i, j = indices
G = gaseous phase
I_1 = interface between gaseous and bulk liquid phase
I_2 = liquid-liquid interface
L_1 = organic liquid phase
L_2 = aqueous liquid phase
X = phase index

Literature Cited

Chaudhari, R. V., "Kinetic Modeling of Homogeneously Catalyzed Gas-Liquid Reactions," *Frontiers in Chem. Eng.: Proc. Int. Chem. React. Eng. Conf.*, New Delhi, Vol. 1, L. K. Doraiswamy, ed., Wiley, New York, 291 (1984).

Chern, J., and F. G. Helfferich, "Effective Kinetic Modeling of Multistep Homogeneous Reactions," *AIChE J.*, **36**, 1200 (1990).

Cornils, B., J. Hibbel, B. Lieder, J. Much, V. Schmidt, E. Wiebus, and W. Konkol, "Process for the Preparation of Aldehydes," U.S. Patent No. 4,523,036 (1985).

Cornils, B., and W. A. Herrmann, *Homogeneous Catalysis with Organometallic Compounds*, VCH, Germany (1996).

Cornils, B., and W. A. Herrmann, *Aqueous-Phase Organometallic Catalysis*, VCH, Germany (1998).

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

Douglas, J. M., *Conceptual Design of Chemical Processes*, McGraw-Hill, New York (1988).

Haggin, J., "New Hydroformylation Process Developed," *Chem. & Eng. News*, 25 (Apr. 17, 1995).

Helfferich, F. G., "Systematic Approach to Elucidation of Multistep Reaction Networks," *J. Phys. Chem.*, **93**, 6676 (1989).

Hostrup, M., and S. Balakrishna, "Systematic Methodologies for Chemical Reaction Analysis," in ESCAPE-11, R. Gani and S. B. Jorgensen, eds., Elsevier, Amsterdam (2001).

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, "Screening Multiphase Reactors for Nonisothermal Multiple Reactions," *AIChE J.*, **46**, 389 (2000).

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

Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed., Wiley, New York (1972).

Parshall, G. W., and S. D. Ittel, *Homogeneous Catalysis*, 2nd ed., Wiley-Interscience, New York (1992).

Sahgal, A., H. M. La, and W. Hayduk, "Solubility of Ethylene in Several Polar and Non-Polar Solvents," *Can. J. of Chem. Eng.*, **56**, 354 (1978).

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 Scale-up," *AIChE J.*, **45**, 2371 (1999).

Samant, K. D., D. J. Singh, and K. M. Ng, "Design of Liquid-Liquid Phase Transfer Catalytic Processes," *AIChE J.*, **47**, 1832 (2001).

Smith, B. L., G. P. Torrence, A. Aguilo, and J. S. Alder, "Methanol Carbonylation Process," U.S. Patent No. 5,144,068 (Sept. 1, 1992).

Wachsen, O., K. Himmler, and B. Cornils, "Aqueous Biphasic Catalysis: Where the Reaction Takes Place," *Catalysis Today*, **42**, 373 (1998).

Manuscript received Aug. 7, 2001, and revision received Mar. 8, 2002.