

# Unified Modeling Technique for High-Viscosity, Melt-Phase, Condensation Polymer Reactors

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## SYNOPSIS

Mathematical models for chemical reaction and mass transfer occurring in the manufacture of high-viscosity condensation polymers are considered. A preliminary study indicates that several diverse models can be represented using a single formula based upon an effectiveness factor. The effectiveness factor is shown to depend upon a ratio of time scales of mixing and reaction. The formula giving the effectiveness factor in terms of the time scales ratio is shown to depend upon mixing assumptions only. Starting with a mixing-cell model, a new modeling framework is developed and shown to include the previous models as special cases. The framework is free of inherent mixing assumptions and can be applied to a wide variety of situations once the mixing characteristics are specified.

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## INTRODUCTION

Manufacture of condensation polymers in a melt-phase process often requires continuous removal of the condensation product from the reaction mass to drive the reaction to high conversion. At high conversion, the high viscosity of the melt decreases the rate of transport of the condensation product through the reaction mass and thereby reduces the overall reaction rate. A primary reactor design problem is to generate large amounts of surface area within the polymerization reactor to reduce the effective distance over which the condensation product must diffuse. A second problem is to ensure adequate mixing between the bulk of the reaction mass and the surface. This design challenge is currently met using a variety of equipment configurations. Examples of commercial polycondensation reactor designs include twin- and multiple-screw extruders, twin-shaft paddle mixers, and horizontal disc-ring reactors.

The interconnection between the mass transfer and chemical reaction problems poses a serious

challenge to modeling these reactors. The problem is aggravated by the fact that the mass transfer is a function of both diffusion and convection. A fundamental understanding of the melt-phase polycondensation process is required to enable improved methods for design, scale-up, and operation of commercial reactors. This need is magnified by current trends in commercial polymer product development that include manufacture of increasingly high-viscosity polymers, use of low-diffusivity condensation products, and development of more thermally sensitive polymer products.

Previous mathematical models describing the combined mass transfer and reaction occurring in polycondensation reactors have been developed from the penetration theory concept originally put forth by Higbie.<sup>1</sup> Secor<sup>2</sup> considered the case of diffusion and reaction in several different geometries but did not include the effects of convective mixing. Convective mixing was included in the model by Ravindranath and Mashelkar.<sup>3</sup> They first developed a general expression for an overall reaction rate based upon a linearized penetration theory model applicable for long exposure times in a semiinfinite film. Then, they used the resulting reaction rate expression in combination with an axial dispersion plug flow model to construct a reactor model. The model

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was validated for a disc-ring reactor by fitting it to experimental results using adjustable parameters for the dispersion coefficient and surface area.

Several authors have considered the analysis of reaction and diffusion occurring in wiped-film reactors. Ault and Mellichamp<sup>4,5</sup> developed a penetration theory model for a finite thickness film that is exposed to the overhead vapor space and periodically remixed. Mass transfer and reaction occurs during the exposure time. After remixing, the concentration is assumed to be uniform. They used a simplified kinetic model and assumed that the concentration of the condensation product was zero at the liquid surface. Amon and Denson<sup>6,7</sup> added a liquid reservoir in a model similar to the one developed by Ault and Mellichamp. In their approach, it is assumed that most of the material will be in the liquid pool and that a small fraction of the material from the pool is withdrawn by the blade to form the film. It was also assumed that the film mixes completely with the bulk pool when it returns. Gupta et al.<sup>8</sup> compared the model of Ault and Mellichamp<sup>4</sup> to that of Amon and Denson<sup>6</sup> and found that the two models gave nearly identical predictions. They also considered bifunctional monomers where the reactive end groups have different reactivities. Ravindranath and Mashelkar<sup>9</sup> included side reactions in a comprehensive model. They also considered periodic remixing of a finite film. More recently, a model has been developed by Steppan et al.<sup>10</sup> for thin film nylon 6,6 polymerizers. They used a mixing-film model similar to the model proposed by Ault and Mellichamp<sup>4,5</sup> but used a reaction scheme that includes some side reactions. Khanna and Kumar<sup>11,12</sup> considered the molecular weight distribution of a general class of step growth polymers reacting and diffusing in a film.

Similar geometries arising in other chemical systems have also been studied. When modeling gas uptake into water in rotating disc contactors, Ravetkar and Kale<sup>13</sup> and Yamani and Yoshida<sup>14</sup> assumed that the film mixed perfectly with the bulk liquid. Suga and Boongorsrang<sup>15</sup> recognized the importance of the limited mixing between the liquid film and the bulk liquid and developed a model based upon a boundary layer analysis of the submerged liquid near the disc. Vaidya and Pangarkar<sup>16,17</sup> extended this work for the case of non-Newtonian fluids and more general contacting patterns.

Motivation for the current work stems from the fact that all the previous studies rely on questionable assumptions regarding the flow patterns in the reactor or mixer under consideration. More specifically, characteristics of the mixing between a bulk pool and film or of the remixing of the film are ideal-

ized. This article addresses this issue by developing a modeling framework that enables consideration of a general class of mixing geometries and is free of the need for restrictive mixing assumptions.

## REPRESENTATION USING AN EFFECTIVENESS FACTOR

The starting point of the analysis is the realization that several seemingly different models can be represented by the single form

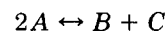
$$r_e = \eta r_k \quad (1)$$

where  $r_k$  is the overall rate of reaction predicted by the kinetic expression only,  $r_e$  is the overall rate of reaction including the effects of mass transfer limitations, and  $\eta$  is an effectiveness factor. The effectiveness factor is a function of a simple ratio only. The ratio is recognized as a generalized Thiele modulus (e.g., Smith<sup>18</sup>) that reflects both convective and diffusive mixing and is denoted by

$$R = t_m/t_r \quad (2)$$

where  $t_m$  is a time scale (characteristic time) of mixing and  $t_r$  is the time scale of reaction. The forms of  $r_k$  and  $t_r$  are essentially the same for every model. The forms of  $t_m$  and  $\eta$  vary among the different models depending upon their mixing assumptions. Equation (1) can be shown to hold for the models of Ravindranath and Mashelkar,<sup>3</sup> Ault and Mellichamp,<sup>4</sup> and three additional models included here to demonstrate the generality of this approach. Expressions for  $\eta$ ,  $t_m$ , and  $t_r$  for five different models are given in Table I.

The expressions in Table I are based upon the reaction mechanism



where  $A$  is a reactive end group on a polymer molecule,  $B$  is an internal repeat unit in a polymer molecule, and  $C$  is the volatile condensation by-product. The rate of formation of  $B$  or  $C$  is given by

$$r_k = k(C_A^2 - 4C_B C_C/K) \quad (3)$$

where  $k$  is the reaction rate constant,  $K$  is the equilibrium constant, and  $C_A$ ,  $C_B$ , and  $C_C$  are the concentrations of species  $A$ ,  $B$ , and  $C$ , respectively. The factor of 4 in eq. (3) reflects the bifunctionality of species  $B$  and  $C$ . Other variables used in Table I

**Table I** Expressions for  $\eta$ ,  $t_m$ , and  $t_r$ 

Model	$\eta$	$t_m$	$t_r$
1. Ravindranath and Mashelkar <sup>3</sup>	$1/R^{1/2}$	$(V/A)^2/D$	$K/(4C_B k)$
2. Ault and Mellichamp <sup>4</sup>	$1/(1 + 0.322R)$	$h^2/D$	$1/[4(C_A/2 + C_B)k]$
3. Film theory	$1/R$	$h^2/D$	$K/(4C_B k)$
4. Surface renewal—I	$[1 - \exp(-R)]/R$	$V/Q$	$K/(4C_B k)$
5. Surface renewal—II	$1/(1 + R)$	$V/Q$	$K/(4C_B k)$

include the reactor volume,  $V$ , and surface area,  $A$ , the volumetric flow rate to the surface,  $Q$ , the film thickness,  $h$ , and the diffusivity of species  $C$ ,  $D$ .

The expressions in Table I for the model of Ault and Mellichamp<sup>4</sup> correspond to a limiting case where the film is not periodically remixed. This form was generated by regressing numerical results from a more complicated model. Regression data included a wide range of reaction times and film thicknesses. The expressions in Table I for the model of Ravindranath and Mashelkar<sup>3</sup> also do not include the effects of convective mixing.

The first additional model in Table I is based upon a film theory model for mass transfer resistance. A bulk liquid phase is assumed to be well mixed and at reaction equilibrium. The condensation product diffuses from the bulk liquid phase across a thin film to the liquid surface, where the concentration takes the value in equilibrium with the vapor phase. The reaction rate is taken from the flux across the film times the surface area of the film divided by the volume of the film. Assuming a linear concentration profile in the film (neglecting reaction in the film) and using Fick's first law to express the flux gives

$$r_e = \frac{D}{h} \left[ \frac{C_{C,b} - C_C}{h} \right] \quad (4)$$

where  $C_{C,b}$  is the concentration of the condensation product in the bulk and  $C_C$  is the concentration in equilibrium with the vapor phase. Note that the surface area of the film divided by the volume of the film is the reciprocal of the film thickness. The bulk is in reaction equilibrium so

$$C_{C,b} = \frac{KC_A^2}{4C_B} \quad (5)$$

When eq. (5) is substituted into eq. (4), the result can be rearranged to the form given in Table I.

The second additional model is a surface renewal model. Fluid elements are periodically exposed to the liquid surface, where the concentration of con-

densation product immediately falls to the concentration in equilibrium with the vapor phase. The fluid elements then leave the surface and the polycondensation reaction begins to drive the concentration of the condensation product toward chemical equilibrium. Fluid elements are assumed to be isolated from each other. While it can be described as a surface renewal model, this model is not the same as the surface renewal model of Danckwerts,<sup>19</sup> which is more closely related to the penetration theory of Higbie.<sup>1</sup> The concentration in a fluid element is modeled by

$$\frac{dC_{C,b}}{dt} = k \left[ C_A^2 - \frac{4C_B C_{C,b}}{K} \right] \quad (6)$$

Here the subscript  $b$  is retained in  $C_{C,b}$  to indicate that the concentration is measured away from the liquid surface. Solving eq. (6) with the initial condition

$$C_{C,b} = C_C \quad \text{at } t = 0 \quad (7)$$

gives

$$C_{C,b} = \frac{kC_A^2}{4C_B} - \left[ \frac{kC_A^2}{4C_B} - C_C \right] \exp \left[ \frac{-4C_B kt}{K} \right] \quad (8)$$

The overall reaction rate is found by dividing the difference between the concentration of the condensation product in a fluid element just before exposure to the surface and just after exposure to the surface by the time expiring between renewal events. More precisely,  $C_C$  is subtracted from the rhs of eq. (8), the renewal time is substituted for  $t$ , and the result is divided by the renewal time. Taking the renewal time to be the total liquid volume divided by the liquid pumping rate gives the result in Table I identified as "surface renewal—I." The renewal time is assumed to be constant for all fluid elements.

This model is convenient and natural when considering a conventional continuous-stirred tank reactor where the liquid volume is known and the

pumping rate of the agitator can be estimated by correlation. Moreover, this model has practical significance for the case of prepolymer polycondensation reactors. These reactors typically operate at pressures low enough so that the static head in the liquid pool becomes large relative to the vapor pressure above the liquid. This allows the concentration of the condensation product in the lower part of the liquid pool to exceed the concentration in equilibrium with the vapor above the liquid. The liquid at the bottom of the reactor must be periodically brought to the top of the reactor, where condensation product can be removed by boiling and surface evaporation.

The third additional model is also a surface renewal model. In this case, the fluid elements are assumed to mix completely with the bulk liquid following the renewal event. The concentration of condensation product in the bulk phase (and hence the overall reaction rate) is found by equating the reaction rate expression in the bulk to the net convective transport rate for condensation product moving from the bulk to the surface.

$$r_e = \frac{Q}{V} (C_{C,b} - C_C) = k(C_A^2 - 4C_B C_{C,b}/K) \quad (9)$$

When  $C_{C,b}$  is eliminated from eq. (9) by equating the two expressions on the rhs, the form given in Table I labeled "surface renewal—II" is found. The assumed bulk mixing patterns in the two surface renewal models represent opposite extremes and can therefore be expected to bracket a range of intermediate mixing conditions.

The time scale of reaction is seen in Table I to be identical for each model except that of Ault and Mellichamp.<sup>4</sup> The significance of the deviation of the form used by Ault and Mellichamp<sup>4</sup> is diminished considerably by the facts that the expression is derived from regression results, the values of the term  $C_A/2$  are much smaller than values of the term  $C_B$ , and the value  $K = 1$  was used in the study. Given these mitigating details, it is apparent that the expression  $K/(4C_B k)$  is an appropriate measure of the time scale of reaction regardless of the mixing assumptions used in the model development.

Expressions for the time scale of mixing are seen to be of two distinct types depending upon whether transport of the condensation product is assumed to be limited by diffusion through a film or by mixing between the bulk liquid pool and the film. It should be stressed that this difference arises directly from mixing assumptions and does not necessarily reflect intrinsic details of the mixing characteristics. In a

more general model, the appropriate time scale of mixing should reflect both convective and diffusional mixing.

Differences between the various models appear in the functional dependence of the effectiveness factor,  $\eta$ , upon the time scales ratio,  $R$ . Each of the five models shows a distinct form for  $\eta(R)$ . However, as can be seen from Figure 1, the different expressions are qualitatively similar.

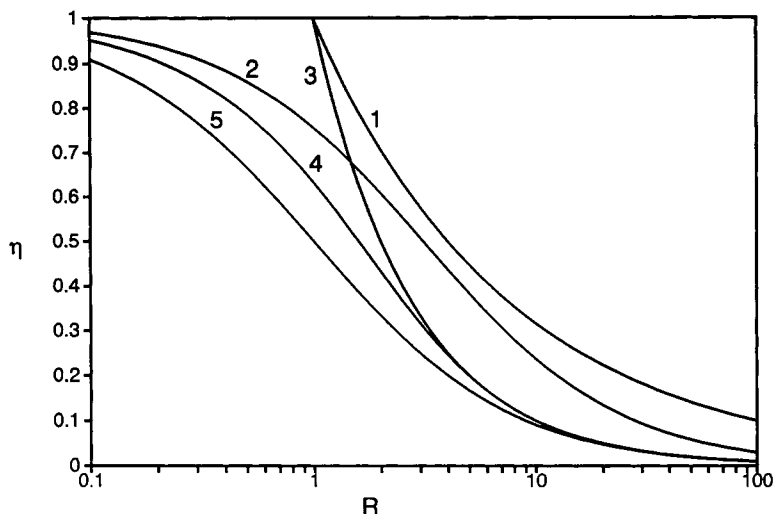
Consideration of the asymptotic behavior of the various curves in Figure 1 yields additional insight into the relationships between the models. As the ratio of time scales approaches 0, the reaction system becomes well mixed so that  $\eta$  should asymptotically approach 1. The film theory model and the model of Ravindranath and Mashelkar<sup>3</sup> do not show this behavior because they explicitly exclude convective mixing. The other models each show the appropriate behavior as  $R$  is decreased but vary in their rate of approach to the asymptotic limit. No *a priori* statements can be made concerning the asymptotic behavior at large values of  $R$ . Note, however, that three of the models converge to a single curve at high values of  $R$ .

While it is clear that this set of five examples does not represent an exhaustive search of all the possibilities, the similarities between the curves in Figure 1 suggest that a single expression with perhaps one additional adjustable parameter could be used as a general-purpose model. As a minimum conclusion, the fact that diverse models can be manipulated into a "standard" form suggests that this form is inherently correct regardless of the specific mixing assumptions used.

## GENERAL FRAMEWORK BASED UPON A MIXING-CELL STRUCTURE

It is clear from the range of physical situations modeled by the formulas given in Table I and Figure 1 that a comprehensive model must reflect both diffusive and convective resistances and include multiple transport resistances simultaneously. The analysis that follows achieves this goal using a stirred-tanks-in-series or mixing-cell formulation. The initial approach includes convective mixing processes only. The extension to diffusive resistances is discussed subsequently.

Consider a series of mixing cells or stirred tanks arranged in a linear fashion with cell 1 exposed to the overhead vapor space, cell  $i$  ( $1 < i < n$ ) connected to cell  $i - 1$  and cell  $i + 1$ , and cell  $n$  connected to cell  $n - 1$  only. This model is depicted schematically



**Figure 1** Dependence of the effectiveness factor,  $\eta$ , on the time scales ratio,  $R$ , for various models. Model identifiers correspond to those in Table I.

in Figure 2. Each cell exchanges material with its neighbors at a constant rate. The material balances

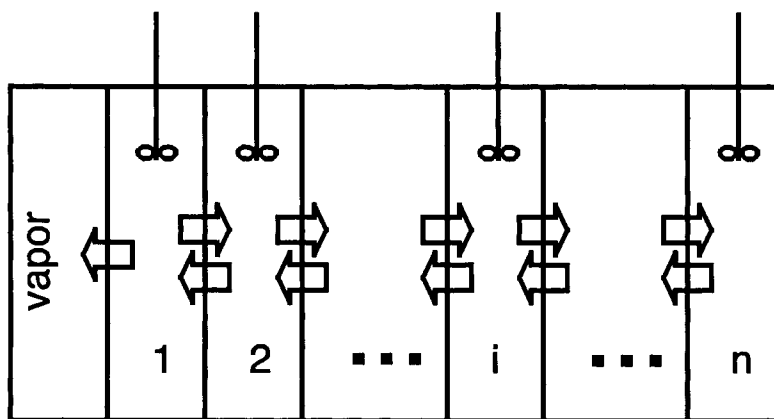
$$Q_1(C_{C,2} - C_{C,1}) + r_{k,1}V_1 - F = 0 \quad (10)$$

$$Q_{i-1}(C_{C,i-1} - C_{C,i}) + Q_i(C_{C,i+1} - C_{C,i}) + r_{k,i}V_i = 0 \\ i = 2, 3, 4, \dots, n - 1 \quad (11)$$

$$Q_{n-1}(C_{C,n-1} - C_{C,n}) + r_{k,n}V_n = 0 \quad (12)$$

can be written when generation of the condensation product by reaction is balanced by transport to the surface. In eqs. (10)–(12),  $Q_i$  is the intercell volumetric flow rate from cell  $i$  to cell  $i + 1$  and from cell  $i + 1$  to cell  $i$  and  $F$  is the molar flow rate of condensation product from cell 1 to the vapor space.

The other variables are as before with the new subscript referring to the mixing-cell identifier. Equations (10)–(12) represent an approximation that is valid for batch or continuous flow systems when the concentration of the condensation product is much lower than the concentration of the other two components. This condition is easily met in the final stages of polyethylene terephthalate melt polymerization due to its low equilibrium constant but may be a poorer approximation for systems with much higher equilibrium constants such as nylon 6,6. When the condition is not met, a concentration derivative term must be included in each equation for the case of a batch system and a reactor feed and product flow term appears in one of the equations for the case of a continuous flow system. The ap-



**Figure 2** Schematic representation of the mixing-cell model. Each cell is well-mixed. Condensation product is formed by reaction in each cell, transported between cells, and transported from cell 1 to the vapor space.

proximation can also be interpreted as a "pseudo-steady-state" hypothesis (e.g., Butt<sup>20</sup>), where the rate of formation of the condensation product is equal to its rate of removal by devolatilization.

After substituting eq. (3) into eqs. (10)–(12), they can be written as

$$-(Q_1 + 4C_B k V_1 / K) C_{C,1} + Q_1 C_{C,2} = -k C_A^2 V_1 + F \quad (13)$$

$$Q_{i-1} C_{C,i-1} - (Q_{i-1} + Q_i + 4C_B k V_i / K) C_{C,i} + Q_i C_{C,i+1} = -k C_A^2 V_i \quad i = 2, 3, \dots, n-1 \quad (14)$$

$$Q_{n-1} C_{C,n-1} - (Q_{n-1} + 4C_B k V_n / K) C_{C,n} = -k C_A^2 V_n \quad (15)$$

Note that the concentration of species A and B does not vary with the cell identifier (spatial position). This assumption is consistent with the linearized penetration theory model of Ravindranath and Mashelkar<sup>3</sup> but not with others such as that of Ravindranath and Mashelkar<sup>9</sup> and Steppan et al.<sup>10</sup> Once again, the impact of the assumption is small if values of  $C_A$  and  $C_B$  are large relative to the set  $\{C_{C,i}\}$ .

Equations (13)–(15) can be solved to yield an explicit expression for  $F$  and hence  $r_e$ .

$$r_e = \frac{F}{V_T} = f(C_A, C_B, C_{C,1}, k, K, \{V_i\}, \{Q_i\}) \quad (16)$$

Here,  $V_T$  denotes the total of all the cell volumes. All the concentrations  $\{C_{C,i}\}$  except  $C_{C,1}$ , which is

calculated from the vapor–liquid equilibrium relationship, have been eliminated from eq. (16). For the case  $n = 2$ , the solution can be written

$$r_e = \left[ \epsilon_1 + \epsilon_2 \left( \frac{1}{1 + \epsilon_2 R} \right) \right] r_k \quad (17)$$

where  $\epsilon_i$  is the fraction of the total liquid volume in cell  $i$ ,  $R$  is given in Table I under the surface renewal models with  $V$  identified as the total liquid volume, and  $r_k$  is given in eq. (3) with  $C_C$  replaced by  $C_{C,1}$ . Note that  $\eta$  can be considered to depend upon only two parameters because

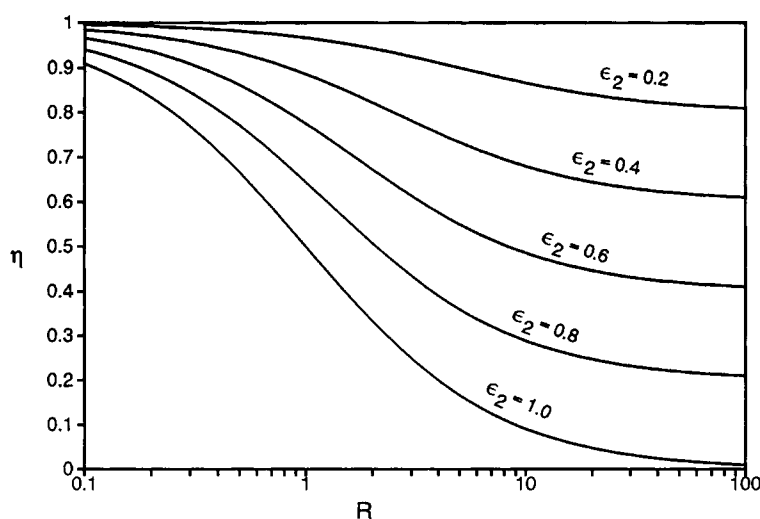
$$\epsilon_2 = 1 - \epsilon_1 \quad (18)$$

Numerical values of  $\eta$  as defined by eq. (17) are shown in Figure 3. The values are seen to span the range of models depicted in Figure 1 with limiting cases of a well-mixed model when  $\epsilon_2 = 0$  and the surface renewal—II model when  $\epsilon_2 = 1$ .

A recursive solution to eqs. (13)–(16) can be found when all the cell volumes are the same and all the intercell flow rates are the same. To maintain comparability between solutions with different numbers of cells, the intercell flow rates are scaled using the relation

$$Q_i = (n-1)Q \quad i = 1, 2, 3, \dots, n-1 \quad (19)$$

In this context,  $Q$  is interpreted as a reference flow rate or as simply the flow rate between cells when only two cells are present. Equation (19) implies



**Figure 3** Dependence of the effectiveness factor,  $\eta$ , upon the time scales ratio,  $R$ , for the general two-cell model. The third parameter is the volume fraction in cell 2.

that for a fixed concentration profile in the liquid the flow of condensation product toward the liquid surface will remain approximately constant as the number of mixing cells envisioned by the model increases. Expressions for  $\eta$  are found for various values of  $n$  by direct manipulation of eqs. (13)–(15). The first few expressions are

$$\eta = 1 \quad n = 1 \quad (20)$$

$$\eta = \frac{1}{2} \cdot \frac{2 + S}{1 + S} \quad n = 2 \quad (21)$$

$$\eta = \frac{1}{3} \cdot \frac{3 + 4S + S^2}{1 + 3S + S^2} \quad n = 3 \quad (22)$$

$$\eta = \frac{1}{4} \cdot \frac{4 + 10S + 6S^2 + S^3}{1 + 6S + 5S^2 + S^3} \quad n = 4 \quad (23)$$

where

$$S = \frac{R}{n(n - 1)} \quad (24)$$

In eq. (24),  $R$  is defined using eq. (2) and  $t_m$  is once again defined as the ratio between the total liquid volume,  $V$ , and the intercell flow rate,  $Q$  [as used in eq. (19)]. The complete set of solutions can be represented using the recursion formulas

$$\eta_n = \frac{A_n}{nB_n} \quad (25)$$

$$B_n = B_{n-1} + SA_{n-1} \quad (26)$$

$$A_n = B_n + A_{n-1} \quad (27)$$

$$A_1 = B_1 = 1 \quad (28)$$

where the subscript refers to the number of mixing cells in the model and  $A$  and  $B$  are polynomials in  $S$ .

Numerical values of  $\eta$  as defined by eqs. (25)–(28) are shown in Figure 4. Here again, the values are seen to cover a large part of the range of models depicted in Figure 1 with a limiting case of a well-mixed model when  $n = 1$ .

As  $n$  increases,  $\eta$  asymptotically approaches the solution to a penetration theory model that is a slightly modified form of the model presented by Ravindranath and Mashelkar.<sup>3</sup> If their semiinfinite film is replaced by a finite film, the problem under consideration becomes

$$D \frac{d^2 C_C}{dx^2} = -r_k \quad (29)$$

$$C_C = C_{C,1} \quad \text{at } x = 0 \quad (30)$$

$$\frac{dC}{dx} = 0 \quad \text{at } x = h \quad (31)$$

where  $x$  is the distance from the film surface,  $C_{C,1}$  is the concentration in equilibrium with the vapor phase, and the equation is written for long exposure times where the time variation becomes negligible. (Ravindranath and Mashelkar<sup>3</sup> approached the comparable result by solving the unsteady-state problem and finding the limiting behavior at large

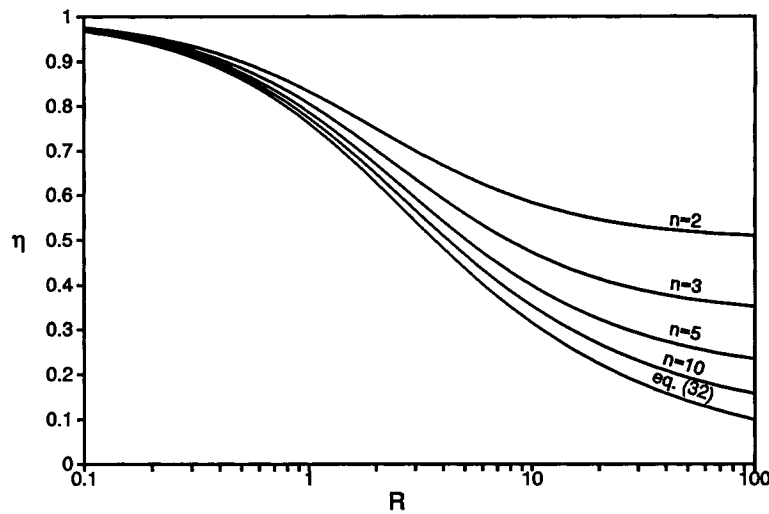


Figure 4 Dependence of the effectiveness factor,  $\eta$ , upon the time scales ratio,  $R$ , for the  $n$ -cell model. The third parameter is the number of cells.

times.) After eqs. (29)–(31) are solved, the result can be differentiated to yield the flow rate of condensation product across the liquid surface and hence the overall reaction rate. When viewed in the context of eq. (1), the resulting expression simplifies to

$$\eta = \frac{\tanh(R^{1/2})}{R^{1/2}} \quad (32)$$

where  $R$  is defined using

$$t_m = h^2/D \quad (33)$$

Equation (33) is identical to the form reported for the model of Ravindranath and Mashelkar,<sup>3</sup> shown in Table I, when the surface area,  $A$ , is the same as the cross section area perpendicular to the  $x$  direction.

The fact that the solution to the stirred-tanks-in-series model converges to the penetration theory model is not surprising; similar results have been noted elsewhere (e.g., Nauman and Buffham<sup>21</sup>). The relationship between the two models can be further strengthened by recognizing the similarity between convective flow in a series of mixing cells and diffusive flow in a series of stagnant films. This point is illustrated in Figure 5, where the condensation product concentration profile is plotted for a hypothetical mixing-cell model and layered-film model. The plot shows that a layered-film model with  $n$  films is equivalent to a mixing-cell model with  $n + 1$  cells. Furthermore, if the flow rate of condensation product through a given film is equated to

the flow rate through the corresponding mixing cell the result is

$$Q_i(C_{C,i+1} - C_{C,i}) = D_i A \frac{C_{C,i+1} - C_{C,i}}{h_i} \quad (34)$$

$i = 1, 2, 3, \dots, n - 1$

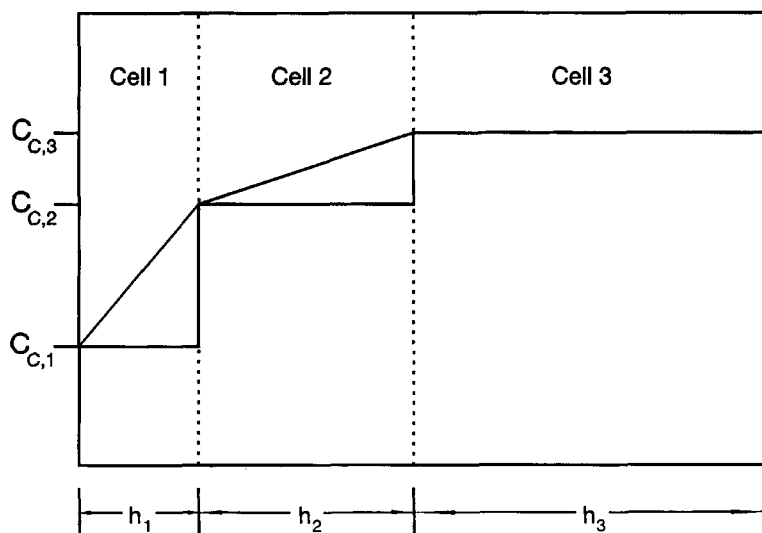
or

$$Q_i = D_i A / h_i \quad i = 1, 2, 3, \dots, n - 1 \quad (35)$$

Equations (34) and (35) are generalized to include dispersive mixing as well as diffusive mixing. A subscript has been added to  $D$  to emphasize the fact that it may represent a diffusion or dispersion coefficient and that the value may vary from cell to cell. Most importantly, eq. (35) indicates that the general modeling framework can be applied using any combination of diffusive flows, dispersive flows, or deterministic convective flows. One can envision a model using a diffusion coefficient for the stagnant film at the liquid surface (cell 1) followed by a series of cells with different dispersion coefficients reflecting different degrees of convective mixing.

## CONCLUDING REMARKS

Equations (13)–(15) have not been solved for the most general case. Instead, through two examples, a new modeling framework has been shown to be capable of modeling a wide range of mixing situations. The comparison between different model forms given in the preceding development does not



**Figure 5** Hypothetical concentration profile for the condensation product. The upper curve is for a layered-film model. The lower curve is for a mixing-cell model.



imply superiority of one form over another. What has been established is a modeling framework based upon a mixing cell structure that can reflect both diffusive and convective mixing processes, incorporates a wide range of previous models as special cases, can be constructed from mixing data directly, and does not resort to severe assumptions regarding the mixing characteristics.

Additional model refinements should wait until mixing data is available to determine the appropriate number of mixing cells to be used and values for intercell flow rates or dispersion coefficients. It will be most important to quantify the convection rate between liquid pools and surface films in reactor configurations of practical interest.

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## NOMENCLATURE

$A$	surface area ( $\text{m}^2$ )	$R$	time scales ratio or Thiele modulus (dimensionless)
$A_n$	polynomial in numerator of eq. (25)	$S$	modified time scales ratio (dimensionless)
$B_n$	polynomial in denominator of eq. (25)	$t_m$	time scale for mixing (s)
$C_A, C_B, C_C$	concentrations of reactive end group, polymer repeat unit, and condensation product ( $\text{kmol}/\text{m}^3$ )	$t_r$	time scale for reaction (s)
$C_{C,b}$	concentration of condensation product in the bulk or away from the liquid surface ( $\text{kmol}/\text{m}^3$ )	$V$	liquid volume ( $\text{m}^3$ )
$C_{C,i}$	concentration of condensation product in cell $i$ ( $\text{kmol}/\text{m}^3$ )	$V_i$	liquid volume in cell $i$ ( $\text{m}^3$ )
$D$	diffusivity of condensation product ( $\text{m}^2/\text{s}$ )	$V_T$	total liquid volume in all cells ( $\text{m}^3$ )
$D_i$	diffusion or dispersion coefficient for condensation product in cell $i$ ( $\text{m}^2/\text{s}$ )	$x$	distance away from surface (m)
$F$	molar flow rate of condensation product to vapor space ( $\text{kmol}/\text{s}$ )	$\epsilon_i$	liquid volume fraction in cell $i$ (dimensionless)
$h$	film or boundary layer thickness (m)	$\eta$	effectiveness factor (dimensionless)
$k$	reaction rate constant ( $\text{m}^3/\text{kmol}/\text{s}$ )		
$K$	reaction equilibrium constant (dimensionless)		
$n$	total number of mixing cells		
$Q$	volumetric flow rate ( $\text{m}^3/\text{s}$ )		
$Q_i$	volumetric flow rate between cell $i$ and $i + 1$ ( $\text{m}^3/\text{s}$ )		
$r_e$	actual overall reaction rate ( $\text{kmol}/\text{m}^3/\text{s}$ )		
$r_k$	kinetic reaction rate ( $\text{kmol}/\text{m}^3/\text{s}$ )		
$r_{k,i}$	kinetic reaction rate in cell $i$ ( $\text{kmol}/\text{m}^3/\text{s}$ )		

## REFERENCES

1. R. Higbie, *Trans. AIChE*, **31**, 365 (1935).
2. R. M. Secor, *AIChE J.*, **15**, 861 (1969).
3. K. Ravindranath and R. A. Mashelkar, *Polym. Eng. Sci.*, **22**, 628 (1982).
4. J. W. Ault and D. A. Mellichamp, *Chem. Eng. Sci.*, **27**, 1441 (1972).
5. J. W. Ault and D. A. Mellichamp, *Chem. Eng. Sci.*, **27**, 2233 (1972).
6. M. Amon and C. D. Denson, *Ind. Eng. Chem. Fund.*, **19**, 415 (1980).
7. M. Amon and C. D. Denson, *Ind. Eng. Chem. Fund.*, **22**, 268 (1983).
8. S. K. Gupta, A. Kumar, and A. K. Ghosh, *J. Appl. Polym. Sci.*, **28**, 1063 (1983).
9. K. Ravindranath and R. A. Mashelkar, *AIChE J.*, **30**, 415 (1984).
10. D. D. Steppan, M. F. Doherty, and M. F. Malone, *Ind. Eng. Chem. Res.*, **29**, 2012 (1990).
11. A. Khanna and A. Kumar, *Polym. Eng. Sci.*, **29**, 1774 (1989).
12. A. Kumar and A. Khanna, *J. Appl. Polym. Sci.*, **41**, 2077 (1990).
13. D. D. Ravetkar and D. D. Kale, *Chem. Eng. Sci.*, **36**, 399 (1981).
14. T. Yamane and F. Yoshida, *J. Chem. Eng. Jpn.*, **5**, 381 (1972).
15. K. Suga and A. Boongorsrang, *Chem. Eng. Sci.*, **39**, 767 (1984).
16. R. N. Vaidya and V. G. Pangarkar, *Chem. Eng. Comm.*, **39**, 337 (1985).
17. R. N. Vaidya and V. G. Pangarkar, *Water Res.*, **21**, 1499 (1987).
18. J. M. Smith, *Chemical Engineering Kinetics*, 3rd ed., McGraw-Hill, New York, 1981, p. 479.
19. P. V. Danckwerts, *Ind. Eng. Chem.*, **43**, 1460 (1951).
20. J. B. Butt, *Reaction Kinetics and Reactor Design*, Prentice Hall, Englewood Cliffs, NJ, 1980, p. 32.
21. E. B. Nauman and B. A. Buffham, *Mixing in Continuous Flow Systems*, Wiley, New York, 1983, p. 65.

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