Lumping Nonlinear Kinetics in a CSTR

The model of uniform nonlinear kinetics recently developed for the continuous description of a multicomponent mixture reacting in a batch or plug flow reactor (Astarita, 1989) is applied to the analysis of a continuous stirred tank reactor (CSTR). It is shown that most of the equations can be solved in general, independently of the specific kinetic mechanism. Some specific mechanisms are discussed. The difference between the behavior in a plug flow reactor (PFR) and a CSTR turns out to be quite dissimilar from what one would expect by considering the single-component case.

Gianni Astarita
Chemical Engineering Department
University of Naples
Naples, Italy

Abhash Nigam
Chemical Engineering Department
University of Delaware
Newark, DE 19716

Introduction

When dealing with mixtures containing a large number of components, it is often useful to choose a continuous description (de Donder, 1931; Aris and Gavalas, 1966). One then is interested in determining the "lumped" concentration, i.e., the integral of the concentration distribution function. There have been several recent papers dealing with the continuous description of the lumping of nonlinear kinetics (Aris, 1989; Astarita, 1989; Astarita and Ocone, 1988; Chou and Ho, 1988, 1989; Ho and Aris, 1987); the continuous description of the lumping of linear kinetics dates back to 1968 (Aris). These papers deal with the case of a batch reactor, and of course the same results apply also to a plug flow reactor (PFR). In this paper, we address the question of lumping nonlinear kinetics in a continuous stirred tank reactor (CSTR).

Consider a CSTR reactor with an average residence time T'. Let x be the (dimensionless) reactant label; we will use y instead of x when the label is regarded as a dummy one. Let the feed stream concentration distribution be $C^*G(x)$, i.e., $C^*G(x)dx$ is the concentration of species with labels between x and $x + dx$ in the feed; $G(x)$ is normalized so that its integral is unity, and C^* is the lumped concentration in the feed. Let the concentration distribution in the CSTR and in the exit stream be $C^*g(x)$. The overall (or lumped) concentration in the exit stream, C, is given by:

$$C/C^* = U = \int_0^\infty g(y)\,dy; \quad 0 \le U \le 1 \tag{1}$$

As for the kinetics of the reaction, we consider the case termed uniform by Astarita and Ocone (1988). Let $k^*h(x)$ be the frequency factor for component x: by requiring the integral of $h(x)G(x)$ to be unity, k^* is identified with the average value of the frequency factor in the feed. Let $r(x)$ be the rate of consumption of reactant x per unit volume in the CSTR environment. The uniform kinetics model assigns the following constitutive equation for $r(x)$:

$$r(x) = k^*h(x)C^*g(x)A \tag{2}$$

The factor A in Eq. 2 is the term which allows for nonlinear kinetics, since it depends on the whole spectrum of weighted concentrations. Let $K'(x)$ be the weighting factor of component x, and let $K(x) = C^*K'(x)$ be the corresponding dimensionless weighting factor. Then the nonlinearity factor is given by the following equation:

$$A = F\left[\int_0^\infty K(y)g(y)\,dy\right] \tag{3}$$

$F[]$ is some function describing the kinetics which would be identically equal to unity in the case of linear kinetics. Different nonlinear kinetics can be described by assigning appropriate forms to the $F[]$ function. The "uniformity" comes in because the weighting factor distribution $K(\cdot)$ depends only on y and not on x, so that the value of $F[]$ is the same for all components in the mixture.

Let $T = k^*T'$ be the dimensionless residence time in the CSTR. The mass balance for component x over the CSTR reads:

$$g(x) = G(x)/[1 + ATh(x)] \tag{4}$$

Substituting this into Eq. 3 yields:

$$F\left[\int_0^\infty \frac{K(y)G(y)}{1 + ATh(y)}\,dy\right] = A \tag{5}$$

which is an implicit equation for the constant A which can be solved in general, even if only numerically often. Once A has been obtained from the solution of Eq. 5, Eq. 4 gives the required concentration distribution in the CSTR, and Eq. 1 can be used to calculate the lumped concentration in the exit stream.

The case where the kinetics are linear is recovered trivially. Equation 3 degenerates to $A = 1$, and Eq. 4 gives $g(x)$ explicitly:

$$g(x) = G(x)/[1 + Th(x)] \tag{6}$$

Solution Technique Independent of Kinetics

In this section, the solution technique is developed to the extent that it can be done without assigning any specific form to the kinetic function $F[]$. One first needs to assign the distributions $G(x)$, $K(x)$, and $h(x)$. Without significant loss of generality, one can, by appropriate rescaling, set $h(x)$ to be x. This is legitimate provided there are no two reactants having exactly the same value of k. We choose the following forms for $G(x)$ and $K(x)$:

$$G(x) = \alpha^{\alpha} x^{\alpha-1} \exp(-\alpha x)/\Gamma(\alpha); \quad \alpha \geq 1 \tag{7}$$

$$K(x) = K^* \Gamma(\alpha) \alpha^{\beta} x^{\beta}/\Gamma(\alpha + \beta), \quad \alpha + \beta > 0 \tag{8}$$

The distributions represented by Eqs. 7–8 have been called α, β, Γ distributions by Aris (1989). They are such that the overall concentration in the feed and the average value of h (but not of K) are normalized to be unity:

$$\int_0^\infty G(x)\,dx = 1; \quad \int_0^\infty K(x)G(x)\,dx = K^*$$
$$\int_0^\infty h(x)G(x)\,dx = \int_0^\infty xG(x)\,dx = 1 \tag{9}$$

Let $Q = AT$. Substitution of Eqs. 4 and 7 into Eq. 1 gives the lumped concentration in the exit stream in terms of Q:

$$U = \int_0^\infty \frac{\alpha^{\alpha} x^{\alpha-1} \exp(-\alpha x)}{\Gamma(\alpha)(1 + Qx)}\,dx \tag{10}$$

Equation 10 can always be solved numerically. When α is an integer, the solution can be obtained explicitly. It is best expressed in terms of the following two functions, which are useful also in the subsequent analysis (I is a nonnegative integer):

$$f(\alpha, Q, I) = \sum_{i=1}^{I} (-1)^{i-1} \frac{\alpha^i}{I(I-1)\ldots(I-i+1)Q^i} \tag{11}$$

$$H(\alpha, Q, I) = -(-1)^I \alpha^{I+1} e^{\alpha/Q} Q^{-(1+I)} Ei(-\alpha/Q)/I! \tag{12}$$

where $Ei()$ is the exponential integral function.

The lumped concentration in the exit stream is given by:

$$U = f(\alpha, Q, \alpha - 1) + H(\alpha, Q, \alpha - 1) \tag{13}$$

Equation 10 can easily be solved numerically for any value of α. Before presenting some such solutions, it is useful to look at asymptotic behaviors. First, consider the limit where the dimensionless time T approaches zero (very low conversions). The Taylor series expansion truncated at the second order gives:

$$U = 1 - Q + (\alpha + 1)Q^2/\alpha\ldots \tag{14}$$

Conversely, one may look for an expansion in terms of powers of $1/Q$ to be used for very large residence times and conversions approaching 100%. This is possible for $\alpha > 1$, and one obtains the following leading term:

$$U = \frac{1}{Q}\int_0^\infty \frac{G(y)}{y}\,dy = \frac{\alpha}{(\alpha - 1)Q} \tag{15}$$

It should be borne in mind that, for very small residence times, one is not so much interested in the value of U (which is bound to be close to unity), but in the *conversion* $1 - U$. Conversely, for large residence times one is not so much interested in the value of the conversion (which is bound to be close to unity), but in the value of the *residue* U. It is therefore convenient to define the quantity μ as follows:

$$\mu = U/(1 - U) \tag{16}$$

The quantity μ approaches the inverse of the conversion at low conversions and the residue at low residues. Equations 14 and 15 now yield directly the two asymptotic behaviors of μ vs. Q:

$$Q \ll 1, \quad \mu = 1/Q \tag{17}$$

$$Q \gg 1, \quad \mu = \alpha/(\alpha - 1)Q \tag{18}$$

In the single-component case ($\alpha = \infty$), the two asymptotes coincide, and one simply has $\mu = 1/Q$ for all values of Q. As α decreases, the two asymptotes become quite distant from each other, and the transition is extremely smooth. Figure 1 gives the $\mu(Q)$ curve for $\alpha = 2$ and for $\alpha = 1.1$. The case where $\alpha = 1$ gives the result:

$$U = H(1, Q, 0) \tag{19}$$

As Q approaches ∞, the righthand side of Eq. 19 approaches $(\ln Q)/Q$, i.e., the slope in a log-log plot of U vs. Q never becomes -1, as it does for all other values of α. Physically, this result is not surprising, since the case $\alpha = 1$ has a unique property: it is the only one for which there is a finite concentration of components with vanishingly small frequency factors in the feed stream.

Plots such as in Figure 1 give the complete solution for the case of first-order kinetics, where $A = 1$, and hence Q is simply the dimensionless residence time T. Incidentally, the results above show that, for an initially exponential concentration distribution ($\alpha = 1$), the dimensionless concentration U in the exit stream for linear kinetics approaches $\ln T/T$ for very large dimensionless residence times. The single-component case is also recovered correctly, since for α approaching ∞ one obtains $U = 1/(1 + T)$ as required.

We now come to the solution of Eq. 5. Let K be the argument of the $F[]$ function:

$$K = \int_0^\infty \frac{Py^{\Omega} e^{-\alpha y}}{1 + Qy}\,dy \tag{20}$$

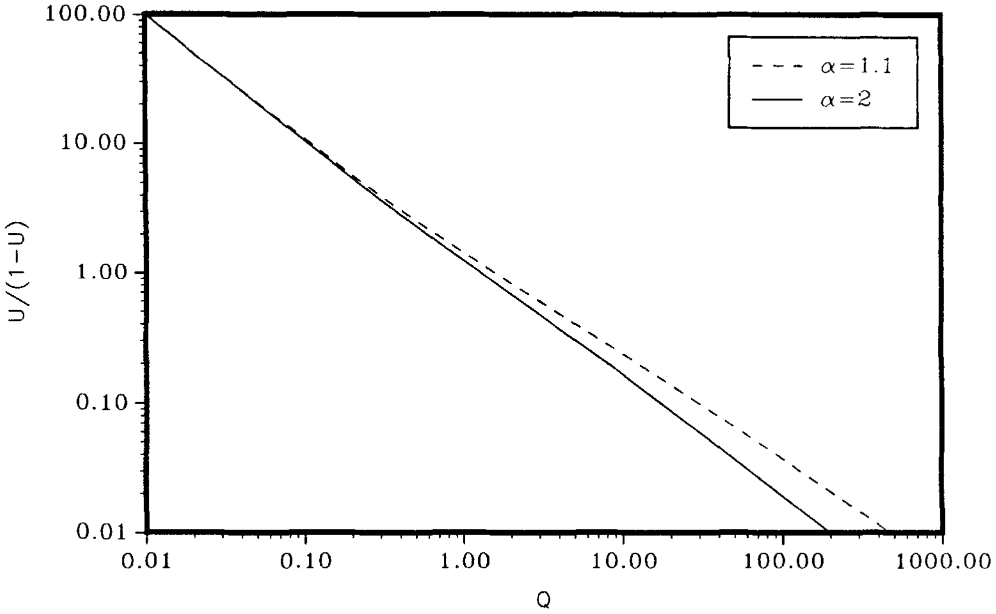

Figure 1. μ vs. Q curve for $\alpha = 2$ and $\alpha = 1.1$.

where

$$\Omega = \alpha + \beta - 1 > -1; \quad P = K^* \alpha^{\alpha+\beta}/\Gamma(\alpha + \beta) \tag{21}$$

We first restrict attention to the case where Ω is positive. The value of K/K^* can be obtained formally if Ω is integer:

$$K/K^* = f(\alpha, Q, \Omega) + H(\alpha, Q, \Omega) \tag{22}$$

For small values of the residence time, one obtains:

$$K = K^* - QK^*(\alpha + \beta)/\alpha + \ldots \tag{23}$$

In this case the leading term, K^*, is what one is mainly interested in, and hence one does not need to introduce a quantity analogous to μ. If Eq. 23 is substituted into Eq. 3, the result is substituted into Eq. 14, and only terms up to second order in T are retained, one obtains:

$$U = 1 - F(K^*)T + T^2[(\alpha + 1)F^2(K^*)/\alpha + (\alpha + \beta)K^*F(K^*)F'(K^*)/\alpha] + \ldots \tag{24}$$

Equation 24 deserves some detailed comments. First of all, if the expansion is truncated at the first-order term, one gets the same result, $U = 1 - F(K^*)T$, as for a PFR: to within first order in the residence time, the CSTR behaves just as a PFR, as one expects it to do. Differences, however, appear at the second-order term, which in the CSTR is twice as large as in the PFR. The single-component case is of course recovered correctly, since when α approaches ∞ the coefficients $(\alpha + 1)/\alpha$ and $(\alpha + \beta)/\alpha$ both approach unity.

The low T expansion holds for arbitrary values of Ω. The situation is different for the converse case of large Q values, where an expansion in terms of powers of $1/Q$ is possible only if $\Omega > 0$. The leading term is:

$$K = K^*\alpha/Q\Omega \tag{25}$$

Equations 23 and 25 suggest to plot K/K^* vs. the quantity Y defined as follows:

$$Y = \Omega Q/\alpha \tag{26}$$

When α approaches ∞, i.e., in the single-component case, the equation for K/K^* is trivially:

$$K/K^* = C = 1/(1 + Q) = 1/(1 + Y) \tag{27}$$

Curves for some combinations of values of α and β are given in Figure 2. For Ω values in excess of unity, the curves are very close to each other, and Eq. 27 is an approximate equation which can be used with some confidence in the estimation of K as a function of Q.

Now focus attention on the case of very large residence times, large enough for the asymptotic expansions being truncated at the leading term. Since all reactions considered in this paper are irreversible, at very large residence times the concentrations of all species become vanishingly small, and hence the quantity A approaches $F[0]$. The question which arises is of course whether $F[0]$ is or is not finite, and this is briefly discussed in the following.

If one accepts the thermodynamic analysis (with the concomitant assumptions) of Astarita and Ocone (1988), which regards the reactions as truly irreversible, then indeed $F[0]$ is finite, and by renormalization of the value of k^* one can indeed take $F[0]$ to be unity. This sets k^*x as the first-order rate constant in the neighborhood of equilibrium for component x. This, however, excludes from consideration kinetics which are intrinsically nth order, for which one would have $F[K] = K^{n-1}$, so that, except for the linear case $n = 1$, $F[0]$ would approach either 0 or ∞ depending on whether n is larger or smaller than one. Astarita and Ocone (1988), however, have presented an argument to show that an nth-order irreversible reaction is not a realistic situation unless $n = 1$. If one sets $F[0]$ to unity, thus excluding nth-order kinetics from consideration, the following equations hold for a

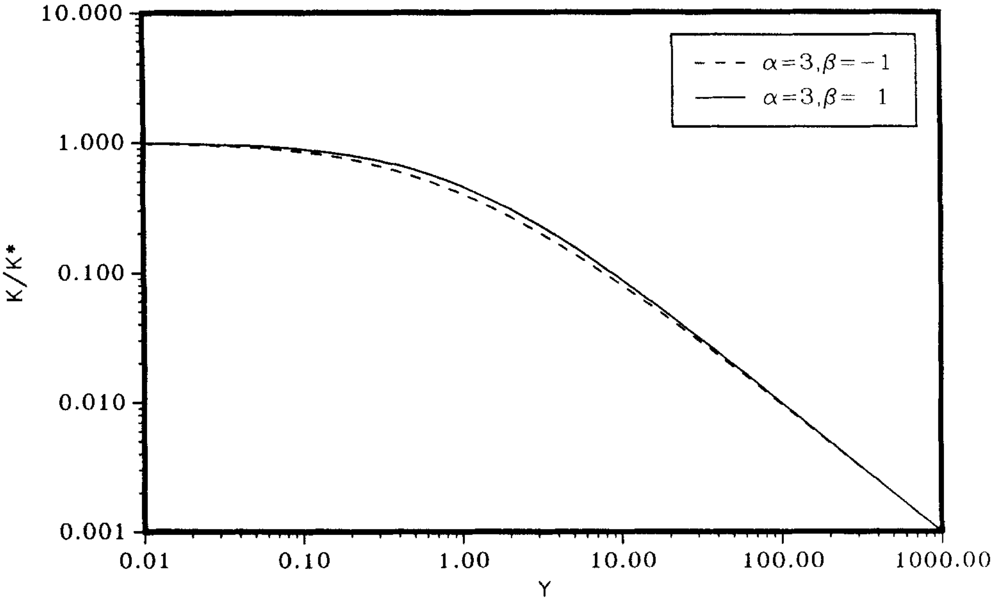

Figure 2. K/K^* vs. Y for several values of the parameters.

CSTR with very large residence times:

$$UT = \alpha/(\alpha - 1); \quad \alpha > 1 \tag{28}$$

$$UT = \ln T; \quad \alpha = 1 \tag{29}$$

Specific Kinetic Schemes

In principle, the procedure to follow in order to obtain the solution for any given kinetic form consists of the following steps.

1. The values of α, β, K^*, and T are data of the problem when the unknown is the total conversion $1 - U$. Thus one can plot K/K^* as a function of Q; the curve is guaranteed to be a monotonous one. It is convenient in fact to plot Q vs. K/K^*, as in the right half of Figure 3.

2. The appropriate $\mu(Q)$ curve is read from a plot of the type given in Figure 1 and is plotted as Q vs. μ as in the left half of Figure 3. (Note that the μ axis points leftwards.)

3. Once $F[]$ has been assigned (i.e., the kinetic form is given), one plots on the right side the curve $TF(K)$ vs. K/K^*. In Figure 3, we have chosen A to be $1/(1 + K)$, which corresponds to Langmuir isotherm kinetics. The intersection of this curve with the other one (if it exists) determines the value of Q, and now μ can be read from the left-side curve, as shown by the two lines with arrows.

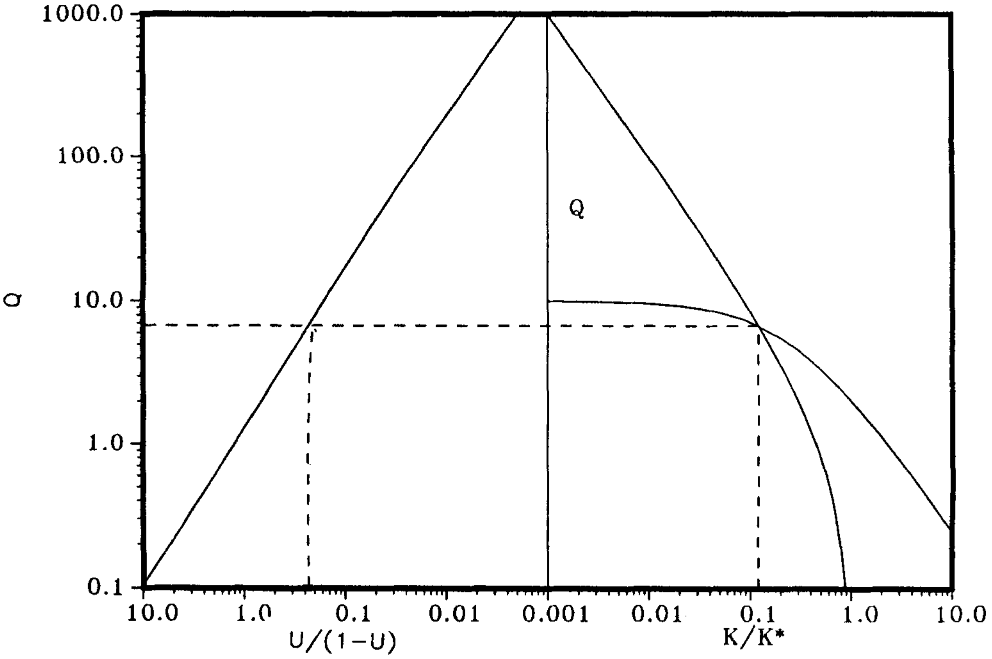

Figure 3. Graphical solution of the problem.

Should the unknown be the design variable, i.e., the value of T, the first two steps would be the same. One would now read Q from the left side plot, and K/K^* from the right side one. Since $Q = TF[K]$, this yields the desired value of T. Note that this second procedure is guaranteed to yield a value of T, provided $F[]$ is defined for all nonnegative values of K less or equal to K^*. The first procedure is not guaranteed to give an intersection for those cases where there are no reactants with vanishingly small frequency factor, and the intrinsic kinetics are such that a finite exhaustion time exists; then any time larger than the exhaustion time of the most refractory component is uselessly large and no intersection will be found.

We now move to the consideration of two specific kinetic schemes, which we believe are realistic ones. The first one is that of Langmuir Isotherm Kinetics (LIK), for which $F[K] = 1/(1 + K)$. We examine a special case in the following, by assigning the parameters $\alpha = 2$, $\beta = 9$, and $K^* = 5$. These are admittedly rather extreme values, but they have been chosen in order to point out vividly the sort of behavior which can be predicted for mixtures. Figure 4 is a conversion plot of U vs. T for four cases: the mixture CSTR and PFR, and, for comparison, the single-component ($\alpha = \infty$) CSTR and PFR. Several striking features are worth noting. First, the difference in behavior between a CSTR and a PFR is much more marked for a mixture than it is for a single component. At a conversion level of 60% ($U = 0.4$), for the single-component case the CSTR needs a residence time only 15% larger than the PFR; in the mixture case, the CSTR needs more than twice the residence time of the PFR. The PFR mixture case clearly shows the apparent negative-order behavior predicted by Astarita (1989) for the case where β and K^* are large: the curvature is markedly negative up to conversions of about 70%. Of course, all curves begin with the same slope of $-F[K^*] = -1/6$.

The LIK is a realistic kinetic scheme, and it yields a finite value of $F[0]$. For all kinetic schemes enjoying this property, at very large residence times the intrinsic kinetics become linear, and Eqs. 28 and 29 can be used. We believe that every realistic kinetic scheme would reduce to linear behavior at very large residence times (i.e., when conditions approach equilibrium).

In the LIK case, the apparent intrinsic order of reaction is less than unity. We now consider a converse case, that of a system of irreversible dimerization reactions governed by mass action kinetics. First, consider the discrete case, where the rate of consumption of component I would be written as:

$$r_I = -dc_I/dt = \Sigma_J k_{IJ} c_I c_J \tag{30}$$

The matrix k_{IJ} is necessarily symmetrical, since $k_{IJ} c_I c_J$ represents the rate of the reaction which consumes both the I and J components. If Eq. 30 is to be cast in a form which can be generalized to Eq. 2, one needs to write:

$$k_{IJ} = k_I K_J = k_{JI} = k_J K_I \tag{31}$$

This shows that the weighting factors K_J must be directly proportional to the kinetic constants k_J, or, in the formalism considered here, β must be unity. With this, the continuous mixture kinetic description reduces to:

$$F[K] = K; \quad \beta = 1; \quad K^* = 1 \tag{32}$$

The last one of 32 is a normalization which is possible because of the monomial nature of $F[]$; this is related to the dimensional degeneracy of nth-order kinetics, which was discussed by Astarita and Ocone (1988).

The intrinsic order of reaction is of course $n = 2$; and hence in the case of a PFR, the apparent overall order of reaction N has a value of $(2\alpha + 2)/\alpha$, as calculated from the equation given by Astarita (1989). This implies that the apparent overall order of reaction in a PFR may vary between a maximum of 4 and a minimum of 2. Conversion plots of U vs. T for the case considered, with $\alpha = 2$, are plotted in Figure 5. Both the CSTR and the PFR

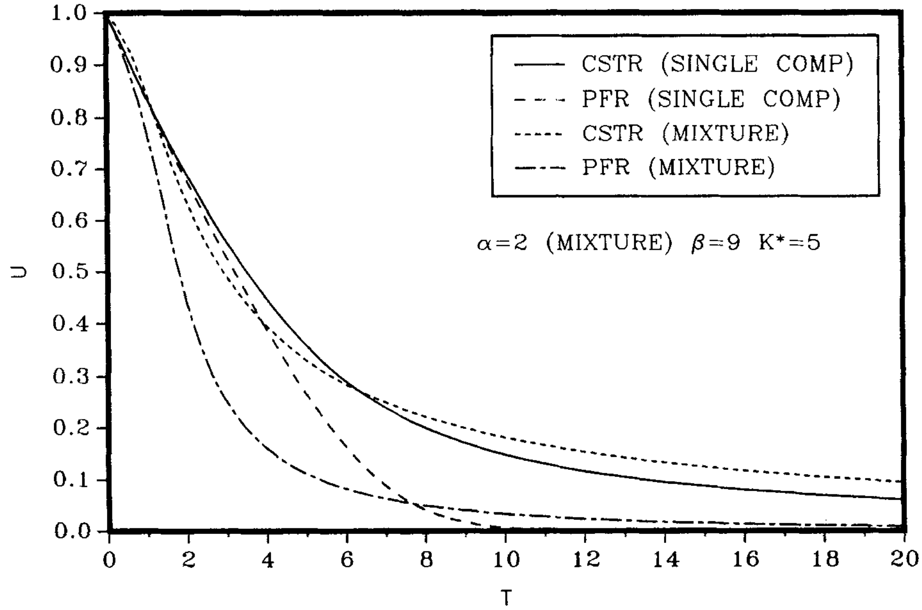

Figure 4. Conversion plot for LIK kinetics, $\beta = 9$, $K^* = 5$.
The mixture curves are for $\alpha = 2$.

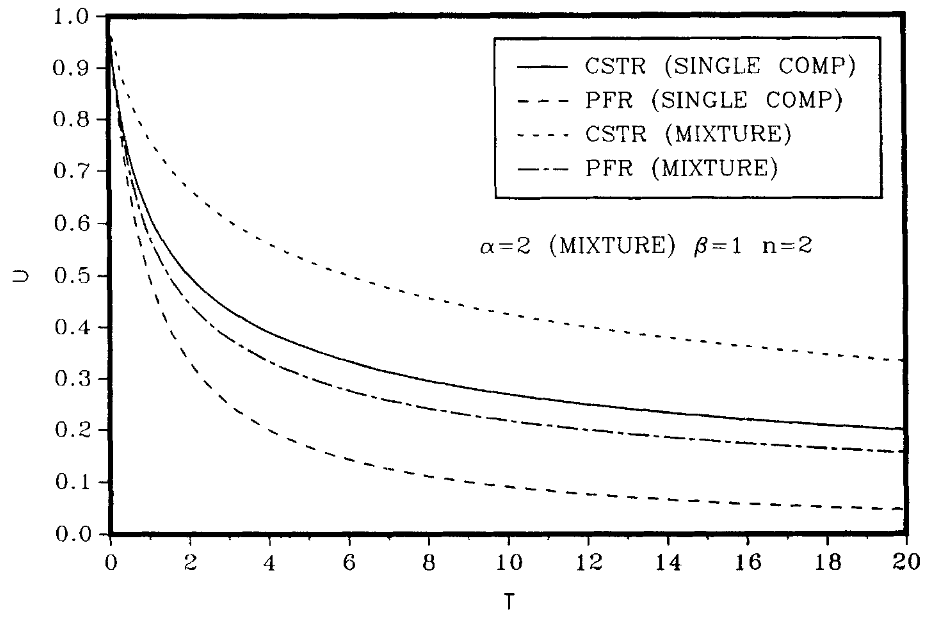

Figure 5. Conversion plot for dimerization kinetics.
The mixture curves are for $\alpha = 2$.

are significantly less efficient for the mixture than they would be for the single component; mixture conversions larger than about 70% would require exceedingly large residence times in the CSTR. Again, one concludes that for both the PFR and the CSTR the mixture behavior is very significantly different from that of a single component. This is not surprising, since the simple-minded analysis of the case where there are only two components (or only two 'lumps') would easily conduce to the same conclusion.

Acknowledgment

We are indebted to Prof. R. Aris for constructive comments on the first draft of this paper. We are also indebted to the Editor of the *Journal* for addressing our attention to the deceivingly simple point made in the very last sentence.

Notation

A = value of $F[\,]$ function
C = lumped concentration in exit stream, kmol/m^3
C^* = dimensional lumped concentration in feed, kmol/m^3
$Ei()$ = exponential integral function
$f()$ = function defined in Eq. 12
$F[\,]$ = nonlinearity function
$g()$ = concentration distribution function in exit stream
$G()$ = concentration distribution function in feed
$h()$ = dimensionless frequency fator distribution
$H()$ = function defined in Eq. 13
I = a nonnegative integer
i = dummy summation index in Eq. 12
k^* = average value of $k'()$, s^{-1}
k_{IJ} = kinetic constant for I-J dimerization, m^3/kmol·s
k_I = frequency factor for I component, s^{-1}
$K()$ = weighing factor distribution function
$K'()$ = dimensional weighting factor distribution, m^3/kmol
K = average value of $K()$ in the exit stream
K^* = average value of K in the feed
K_J = weighting factor for J component, m^3/kmol
n = intrinsic order of reaction
N = overall order of reaction in a PFR
P = defined in Eq. 17
$Q = AT$
$r()$ = reaction rate distribution function, kmol/m^3
T = dimensionless residence time in CSTR
T' = dimensional residence time in the CSTR, s
U = dimensionless lumped concentration in CSTR, $= C/C^*$
x = component label
y = dummy component label
$Y = \Omega Q/\alpha$
α = parameter of gamma distribution
β = parameter for $K()$ distribution
$\Gamma()$ = gamma function
$\mu = U/(1 - U)$
θ = ratio of CSTR to PFR residence time
$\Omega = \alpha + \beta - 1$

Literature Cited

Aris, R., "On Reactions in Continuous Mixtures," *AIChE J.*, **35**, 539 (1989).

———, "Prolegomena to the Rational Analysis of Chemical Reactions: II. some addenda," *Arch. Ratl. Mech. Anal.*, **27**, 356 (1968).

Aris, R., and G. Astarita, "On Aliases of Differential Equations," *Rend. Acc. Lincei*, in press (1989).

Aris, R., and G. R. Gavalas, "On the Theory of Reactions in Continuous Mixtures," *Phil. Trans. Royal Soc. London*, **A-260**, 351 (1966).

Astarita, G., "Lumping Nonlinear Kinetics: Apparent Overall Order of Reaction," *AIChE J*, **35**, 529 (1989).

Astarita, G., and R. Ocone, "Lumping Nonlinear Kinetics," *AIChE J.*, **34**, 1299 (1988).

Chou, M. Y., and T. C. Ho, "Continuum Theory for Lumping Nonlinear Reactions," *AIChE J*, **34**, 1519 (1988).

Chou, M. Y., and T. C. Ho, "Lumping Coupled Nonlinear Reactions in Continuous Mixtures," *AIChE J*, in press (1989).

De Donder, Th., "L'Affinite' Deuxieme partie," Guathiers Villers, Paris (1931).

Ho, T. C., and R. Aris, "On Apparent Second-Order Kinetics," *AIChE J*, **33**, 1050 (1987).

Manuscript received Apr. 18, 1989, and revision received Sept. 18, 1989.