Aggregate Behavior and Lumped Kinetics of Many Reactions in Backmixed and Plug-Flow Reactors

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The long-time behavior of a reaction mixture containing infinitely many species in isothermal continuous stirred tank reactors (CSTRs) is analyzed and contrasted with that in a plug-flow reactor (PFR). The reaction kinetics considered are irreversible first-order, irreversible coupled pseudo first-order, and reversible first-order. Asymptotic lumped kinetics for the mixture as a whole are developed as a function of feed properties and reactor type. Such lumped kinetics in many cases are of the power law form, with the exponent for a CSTR being lower than that for a PFR. Conditions under which non-power-law kinetics arise are given. Due to the wide spread of reactor residence times, the mixture in CSTRs admits a much richer variety of asymptotic possibilities than in the PFR. The results uncover some behavioral differences and relationships between CSTRs and a PFR for converting complex mixtures such as petroleum distillates or coal liquids.

Introduction

Perhaps the two most obvious distinguishing features of petroleum refining, when compared with chemicals manufacturing, are that the number of reactions is astronomically large and that the feedstock properties are constantly changing. As a result, refiners are primarily interested in the aggregate, rather than the individual, behavior of a large number of reactions. They very much would like to be able to predict how this aggregate behavior changes as feedstocks vary—preferably with minimum information on feedstock properties. Process designers want to know how different reactor types affect the aggregate behavior. And it is essential for catalyst developers to have a consistent catalyst ranking system that takes feedstock properties into account. These considerations motivated the present study.

Specifically, the purpose of this work was twofold: to discuss the aggregate behavior and lumped kinetics of a continuum of independent or interacting reactions in continuous stirred-tank reactors (CSTRs), and to compare and contrast the performances of CSTRs and a plug-flow reactor (PFR) for processing such reaction mixtures.

To set the stage for the discussion to follow, it is helpful to give a perspective on the problem to be addressed here. Let $c(t)$ be the concentration of the individual reactant and $C(t)$ be the total concentration of all reactants at time t. The aim is to predict the dependence of $C(t)$ on feedstock properties and reactor type for given underlying kinetics $r(c)$. It is also of interest to know if an overall lumped kinetics $R(C)$ can be found for the mixture as a whole. To do so, it is necessary to have complete information on the feed composition and reactivity spectra *a priori* (Aris, 1968), that is, to be working with a mixture that has been fully characterized. Unfortunately, hydrocarbon mixtures (e.g., petroleum feedstocks) can seldom be fully characterized. Therefore, the question then is whether or not one can say something about C and/or $R(C)$ based on minimum feed information, that is, for a mixture that has only partially been characterized. To answer the question, so far at least two approaches have been pursued. One is to find $C(t)$ and $R(C)$ in some asymptotic regime of practical interest, say, at high conversions (Krambeck, 1984). The other is to develop bounds on $C(t)$ (Hutchinson and Luss, 1970).

The present work deals mainly with partially characterized mixtures based on the continuous mixture theory advanced by Aris and Gavalas (1966) and Aris (1968). The theory treats the mixture as a continuum because of the large number of reactants present in the mixture. Recent contributions in this area can be found in Sapre and Krambeck (1991) and Astarita and Sandler (1991). Ho and White (1995) have addressed the validity of the continuum theory in the high-conversion regime, both experimentally and theoretically.

The present article consists of three parts. The first examines the long-time (or high-conversion) asymptotic behavior of irreversible first-order reactions in isothermal CSTRs, the performance of which is compared and contrasted with that of a PFR. The asymptotic results are used to develop a semiempirical model of and bounds on $C(t)$. Also, the effects of pore diffusion are discussed. The second part shows that the long-time behavior of uniformly coupled nonlinear reactions (Astarita and Ocone, 1988; Aris, 1989) in CSTRs is much more complex than that in the PFR. Special cases include bimolecular power law and Langmuir–Hinshelwood kinetics. The third part addresses the near-equilibrium behaviors of lumped reversible first-order reactions in a CSTR and PFR. It is shown that with equilibrium constraints, both reactors exhibit a much wider variety of asymptotic behaviors than in the irreversible case. Specifically, the PFR admits 13 possibilities, whereas the CSTR admits as many as 21 possibilities. The results uncover some structural differences between the two reactor systems. For instance, the near-equilibrium behavior of the mixture in the PFR can be governed by species of *intermediate* reactivities. This is not the case in a CSTR. For all $r(c)$ considered, $R(C)$ for long times can be found asymptotically and in many cases takes a power-law form. The order for a PFR is always higher than that for a CSTR, consistent with experimental results. Conditions are established for the occurrence of non-power-law kinetics whose forms are also given. Some key findings of this work are summarized in the Conclusion section. The Appendix gives some mathematical details.

First-Order Irreversible Reactions

Problem formulation

The reactants in a continuous mixture are labeled by a dimensionless real variable x in the interval, say, $[0, \infty)$. Suppose that the mixture contains a total of Q different types of reactants, each disappearing at a first-order rate. We first consider a series of N equal-volume, isothermal, constant-density CSTRs, each with an average holding time of t/N. Let $\hat{c}_N(x;t)$ be the concentration of reactant x with rate constant $k(x)$ leaving the Nth CSTR, then

$$\hat{c}_N(x;t) = \frac{c_f(x)}{[1+k(x)t/N]^N}, \tag{1}$$

where $c_f(x)$ is the concentration of reactant x in the feed. Evidently, $\hat{c}_N$ decays asymptotically as $1/t^N$ as $t \to \infty$. The total concentration of the reactants $C_N(t)$ is (Chou and Ho, 1988)

$$C_N(t) = \int_0^\infty \hat{c}_N(x;t) D(x) dx, \tag{2}$$

in which $D(x)dx$ is the total number of reactant types with x between x and $x+dx$.

The system in question is scaled as follows:

$$c_f(x) = c_0 f(x), \qquad \hat{c}_N(x;t) = c_0 c_N(x;t), \qquad k(x) = \hat{k}s(x),$$
$$D(x) = Qg(x), \qquad \tau = \hat{k}t, \qquad U_N = C_N(t)/C(0), \tag{3}$$

where U_N and τ are the dimensionless total concentration and holding time, respectively. Without loss of generality, we let $s(x) = x$. Thus, the reactant with $x = 0$ is unconvertible. A reactant with a small x is refractory; the closer its x value is to zero, the more refractory is the reactant.

The following normalization conditions can be imposed (Ho et al., 1990):

$$\int_0^\infty g(x) dx = \int_0^\infty f(x) g(x) dx = 1. \tag{4}$$

The total concentration U_N at the exit of the Nth CSTR after time τ reads

$$U_N(\tau) = \int_0^\infty \frac{f(x)g(x)}{(1+x\tau/N)^N} dx. \tag{5}$$

The performance of a single CSTR for converting a specific class of fully characterized mixtures has been discussed by Astarita and Nigam (1989). Our interest here is mainly in the long-time behavior of an *arbitrary* partially characterized mixture. Intuitively, one may expect that the most refractory species play the dominant role in the high-conversion regime. It is thus useful to know the behaviors of $f(x)$ and $g(x)$ near $x = 0$. Following Ho and Aris (1987), we assume that $g(x)$ and $f(x)$ can each be expanded as

$$\left.\begin{aligned} g(x) &\sim x^{\mu}(g_0 + g_1 x + \cdots) \sim g_0 x^{\mu} \\ f(x) &\sim x^{\nu}(f_0 + f_1 x + \cdots) \sim f_0 x^{\nu} \end{aligned}\right\} \quad \text{as} \quad x \to 0, \tag{6}$$

where $f_0 \nleq 0$, $g_0 \nleq 0$, $\nu \geq 0$, and $1 + \mu > 0$. When $\mu \leq 0$, the feed has a finite number of reactant types whose x values are arbitrarily close to zero. When the feed contains a finite amount of unconvertible species, $\mu = \nu = 0$. It will be shown that the asymptotic behavior of U_N depends on the feed parameter γ defined as

$$0 < \gamma \equiv \mu + \nu + 1. \tag{7}$$

This parameter characterizes the number of refractory reactant types and their concentrations. A large γ, say due to a large μ, means that the number of refractory reactants is small [$g(x)$ is concave upward], so the feed is reactive. A small γ signifies a refractory feed. For instance, $\gamma = 1$ may mean that the feed has a nonzero amount of unconvertibles ($\mu = \nu = 0$) or a finite number of reactants whose reactivities are arbitrarily close to zero (for example, $\mu = -0.5$, $\nu = 0.5$). While the focus here is on the most refractory part of the feed, the long-time behavior of the mixture is *not* always governed by the most refractory species, as will be seen.

The foregoing development also forms the basis for subsequent discussions on reversible first-order reactions and uniformly coupled reactions. A characteristic common to all these kinetics is that the individual concentration $c_N(x;\tau)$ is linear in its feed concentration $f(x)$. As a result, $f(x)$ and $g(x)$ always appear as the product $f(x)g(x)$ in the lumping integral (Eq. 5). For notational simplicity, let

$$h(x) \equiv f(x)g(x) \qquad \text{and} \qquad h_0 = f_0 g_0. \tag{8}$$

That is, the behavior of this type of system is completely defined by $h(x)$. Such is not the case with kinetics of arbitrary nonlinearity, however. An analogy in this respect may be made with the characterization of reactor performance by residence time distribution.

In general, $h(x)$ can be assumed to approach zero rapidly as $x \to \infty$. And as discussed, $h(x) \sim h_0 x^{\gamma-1}$ near $x = 0$. Suppose that $\gamma > 1$ and $h(x)$ is monomodal, then as γ increases, the peak gets sharper and sharper because $h(x)$ becomes smoother and smoother for small x [$h(x)$ can be differentiated many times at $x = 0$]. As an example, consider the case where $h(x)$ is represented by the gamma distribution

$$h(x) = \frac{\gamma^\gamma x^{\gamma-1} e^{-\gamma x}}{\Gamma(\gamma)}, \tag{9}$$

where Γ is the gamma function. With only one parameter, this distribution can describe a wide variety of feeds. As Figure 1 shows, when $\gamma > 1$, the distribution is monomodal and $\gamma = 1$ corresponds to an exponential distribution. A large γ means not only an easy but also a relatively homogeneous feed. In fact, in the limit $\gamma \to \infty$, the feed has only one component. A linear combination of two gamma distributions gives a bimodal distribution.

Asymptotic behavior

Since in many refining processes one wants to achieve the highest permissible conversion, predicting the behavior of U_N as $\tau \to \infty$ is of considerable interest. To do so amounts to the asymptotic evaluation of the lumping integral, Eq. 5. Because Ho et al. (1990) have treated a similar problem of this kind, we omit the details of the derivation and simply give the final results in terms of the leading-order term of the asymptotic expansion. Three cases can be distinguished.

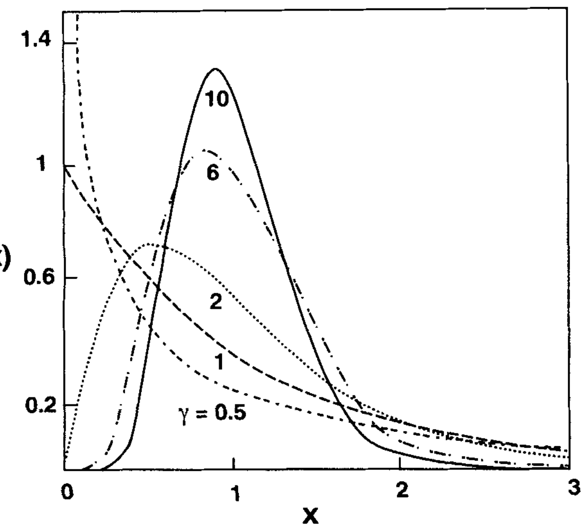

Figure 1. Gamma distribution $h(x)$ (Eq. 9) for different γ values.

Case A. $\gamma > N$

$$U_N(\tau) \sim \frac{N^N I_N}{\tau^N} \qquad \tau \to \infty, \tag{10}$$

where I_N is a constant given by

$$I_N \equiv \int_0^\infty x^{-N} h(x)\,dx. \tag{11}$$

As can be seen, the long-time behavior of the mixture is governed by *all* species, not just by the refractory species. Moreover, the behavior is qualitatively similar to that of the constituent reactants [that is, $0(1/\tau)^N$ as $\tau \to \infty$]. Here we are dealing with mixtures comprising primarily fast-reacting species (γ large). For each reactant type, there is an exponential distribution of residence times among all the molecules of that reactant. Even after a long time, U_N is affected by fast-reacting species because there are lots of such molecules whose residence times can be very long.

Case B. $0 < \gamma < N$

$$\begin{aligned} U_N(\tau) &\sim N^\gamma h_0 B(\gamma, N-\gamma)\left(\frac{1}{\tau}\right)^\gamma \\ &= \frac{N^\gamma h_0 \Gamma(\gamma)\Gamma(N-\gamma)}{\Gamma(N)}\left(\frac{1}{\tau}\right)^\gamma \end{aligned} \qquad \tau \to \infty, \tag{12}$$

where B is the beta function. Unlike the $\gamma > N$ case, here U_N at large τ is governed by the most refractory reactants, even though some molecules of a small amount of highly reactive reactants have very long residence times.

Case C. $\gamma = N$

$$U_N(\tau) \sim N^N h_0 \ln \tau/\tau^N \qquad \tau \to \infty. \tag{13}$$

This represents the transition from case A to case B, or vice versa. In rough terms, the decay of U_N at large τ, while governed by the refractory species, is accelerated by the reactive species.

The above results provide an instructive contrast to the PFR case for which Ho and Aris (1987) have shown that

$$U_p(\tau) \sim h_0 \Gamma(\gamma)/\tau^\gamma \qquad \tau \to \infty. \tag{14}$$

The subscript p denotes the PFR. Here the long-time behavior is *always* dominated by the refractory species. Despite this distinction, one notices that Eq. 14 has the same functional form as Eq. 12. This is not surprising since for any γ, no matter how large, one can always increase N so that $N > \gamma$, and the resulting CSTR cascade behaves qualitatively as a PFR.

The CSTR results may further be interpreted physically as follows. As shown above, U_N has different asymptotic forms in three regions of the N-γ plane. When either of the two parameters N and γ is fixed, the other plays a pivotal role in determining the behavior of U_N. This is due to the interplay of the wide spreads of reactor residence times, reactant reactivities, and concentrations. In a CSTR, the residence times of the molecules of each reactant type are distributed exponentially. While all reactants are slowed down compared to those in a PFR, the fast-reacting ones are hampered more than the slow-reacting ones (Wei, 1966). So the disparities among the species become smaller, that is, the mixture appears more homogeneous. An already homogeneous feed (cf. Figure 1 for high γ) will become even more homogeneous. In fact, when $\gamma > N$ the feed is "homogenized" to such an extent that the mixture decays in a manner qualitatively similar to that of a single reactant $[0(1/\tau)^N]$. The same feed, processed in the PFR at high conversions, behaves differently from a single reactant: the lump decays as $0(1/\tau)^\gamma$, while each constituent reactant decays exponentially. It is worth mentioning that although the present PFR has a unique asymptotic behavior, the introduction of reversibility into the reaction leads to a variety of possible asymptotic behaviors, as will be seen.

To get some feel for the accuracy of the asymptotic theory, let us first consider the following feed ($\gamma = 1$)

$$h(x) = \exp(-x). \tag{15}$$

For a single CSTR, the exact and asymptotic expressions for U_1 are

$$U_1 = \exp(1/\tau)E_1(1/\tau)/\tau \sim \ln\tau/\tau \quad \text{as} \quad \tau \to \infty, \tag{16}$$

where E_1 is the exponential integral. As shown in Figure 2, the asymptotic result (dotted line) compares well with the exact calculation (solid line) at high total fractional conversions χ (defined as $\chi = 1 - U_N$). When the same feed is run in a series of two CSTRs, then

$$U_2(\tau) = \frac{2}{\tau}\left[1 - \frac{2}{\tau}e^{2/\tau}E_1(2/\tau)\right] \sim \frac{2}{\tau} \quad \text{as} \quad \tau \to \infty. \tag{17}$$

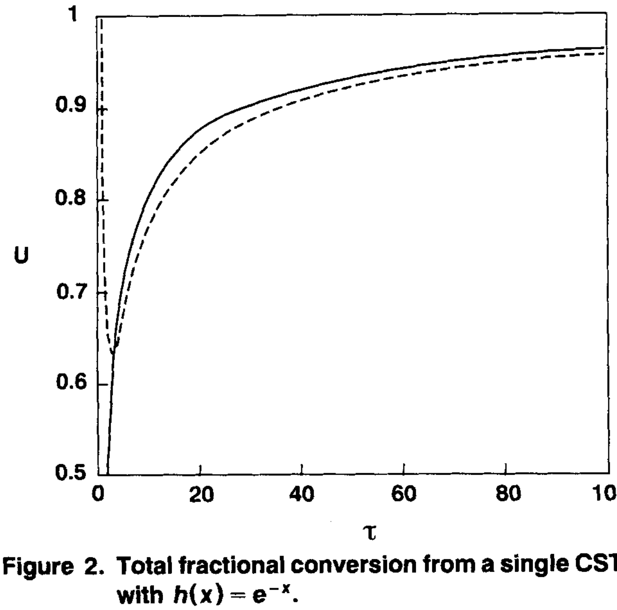

Figure 2. Total fractional conversion from a single CSTR with $h(x) = e^{-x}$.

"——" exact calculation; "- - -" asymptotic result.

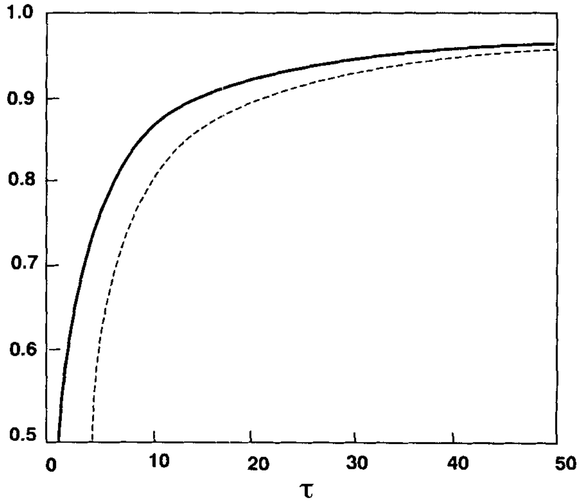

Figure 3. Total fractional conversion from two CSTRs in series with $h(x) = e^{-x}$.

"——" exact calculation; "- - -" asymptotic result.

Figure 3 compares the asymptotic and exact results. As expected, the extent of conversion is higher with two CSTRs. Now consider a tougher feed with

$$h(x) = \left(\frac{2}{3\pi}\right)^{1/2} x^{-1/2}e^{-2x/3}. \tag{18}$$

If a single CSTR is used, this feed gives

$$U_1(\tau) = \left(\frac{2\pi}{3\tau}\right)^{1/2} e^{2/(3\tau)}\operatorname{erfc}\left[\left(\frac{2}{3\tau}\right)^{1/2}\right], \tag{19}$$

where erfc is the complementary error function. The leading term, given by Eq. 12, has the form $U_1 \sim [2\pi/(3\tau)]^{1/2}$. The comparison in Figure 4 shows that this tougher feed needs a much larger CSTR than the previous case (cf. Figure 2).

Comparison of reactor sizes

To compare the sizes of a PFR and N CSTRs for converting the mixture considered in the preceding section, we define a residence time ratio S_N at a constant χ as

$$S_N = \left(\frac{\tau_N}{\tau_P}\right)_{\text{constant } \chi}, \tag{20}$$

where τ_N and τ_P are the total holding time for N CSTRs and the residence time for the PFR, respectively. The difference in sizes between the two reactor systems is especially pronounced at high conversions. As $\chi \to 1$, S_N for each fixed N takes one of the following asymptotic forms:

$$\gamma > N, \qquad S_N \sim \frac{N I_N^{1/N}}{[h_0\Gamma(\gamma)]^{1/\gamma}}\left(\frac{1}{1-\chi}\right)^{(\gamma-N)/(\gamma N)} \tag{21}$$

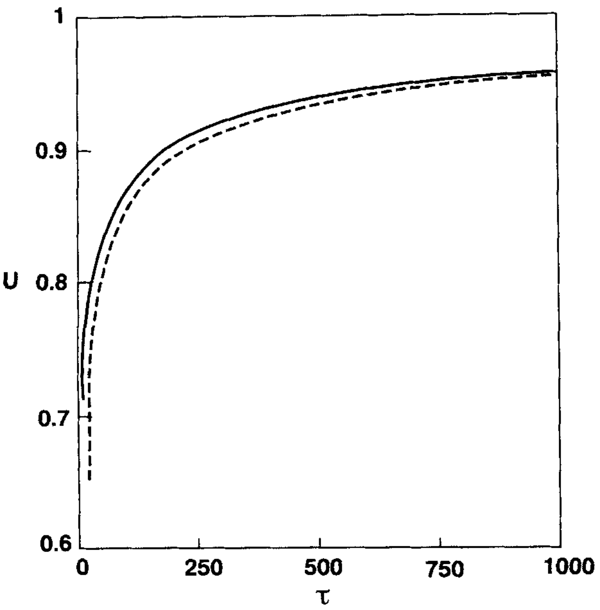

Figure 4. Total fractional conversion from a single CSTR with $h(x) = [2/(3\pi)]^{1/2}x^{-1/2}e^{-2x/3}$.

"——" exact calculation; "– – –" asymptotic result.

$$\gamma = N, \qquad S_N \sim \gamma\left[\frac{1}{\gamma\Gamma(\gamma)}\right]^{1/\gamma} |\ln(1-\chi)|^{1/\gamma} \tag{22}$$

$$\gamma < N, \qquad S_N \sim N\left[\frac{\Gamma(N-\gamma)}{\Gamma(N)}\right]^{1/\gamma}. \tag{23}$$

In all cases, $S_N > 1$ for any finite N. Note that when $\gamma < N$, S_N approaches a constant as $\chi \to 1$.

The ratio S_N should be compared with that for a single reaction. The latter, denoted by S'_N, is given by

$$S'_N = \frac{1}{|\ln(1-\chi)|}\left[\left(\frac{1}{1-\chi}\right)^{1/N} - 1\right]. \tag{24}$$

Take $h(x) = \exp(-x)$ and $N = 1$ as an example. The PFR gives $U_p = 1/(1+\tau)$, with $U_p \sim 1/\tau$ at large τ. Here S_1 can be calculated exactly. Figure 5 compares the asymptotic S_1 (both τ_1 and τ_p were calculated from the leading-order terms) with the exact S_1 at high conversions. Also shown in Figure 5 is S'_1 for the single-reaction case. At high conversions, S_1 is less sensitive to conversion than S'_1.

Lumped kinetics

With the analysis restricted to a single CSTR, here we want to show that asymptotic lumped kinetics, denoted by $R_\infty(U_1)$, can be obtained at high conversions. There are two possibilities, as discussed below.

$\gamma \not\gtrless 1$. In this case, U_1 can be represented by the general power law

$$U_1 \sim \delta/\tau^l \qquad \tau \to \infty, \tag{25}$$

where $\delta = h_0\Gamma(\gamma)\Gamma(1-\gamma)$ and $l = \gamma$ when $\gamma < 1$, and $\delta = I_1$ and $l = 1$ when $\gamma > 1$. Equation 25 indicates the existence of an asymptotic lumped kinetics of the power-law form

$$R_\infty(U_1) \sim \delta^{-1/l}U_1^{1/l} \qquad U_1 \to 0. \tag{26}$$

To show this, let us examine the asymptotic behavior of true power-law kinetics in a CSTR. Denoting the kinetics as $R(U_1) = \hat{K}U_1^M$ with $M > 0$, one can write the mass balance equation for all τ as

$$1 - U_1 = \tau R(U_1) = \tau\hat{K}U_1^M, \tag{27}$$

which cannot be solved for U_1 explicitly for arbitrary M. However, the asymptotic behavior of U_1 at large τ can be obtained by the following perturbation expansion:

$$U_1 \sim \left(\frac{1}{\tau}\right)^{1/M} Z_0 + \left(\frac{1}{\tau}\right)^{2/M} Z_1 + \cdots, \tag{28}$$

where Z_0 and Z_1 are both of order unity. The zeroth-order term obviously corresponds to complete consumption of the feed in the CSTR. Substituting Eq. 28 into Eq. 27 and equating coefficients of like power of $(1/\tau)^{1/M}$, one finds that $Z_0 = (1/\hat{K})^{1/M}$ and $Z_1 = -(1/\hat{K})^{2/M}/M$. Thus the Mth-order kinetics with rate constant $\hat{K}$ produces, to leading order,

$$U_1 \sim \frac{(1/\hat{K})^{1/M}}{\tau^{1/M}} \qquad \tau \to \infty, \tag{29}$$

which in fact is in the form of Eq. 25, thus establishing Eq. 26 with

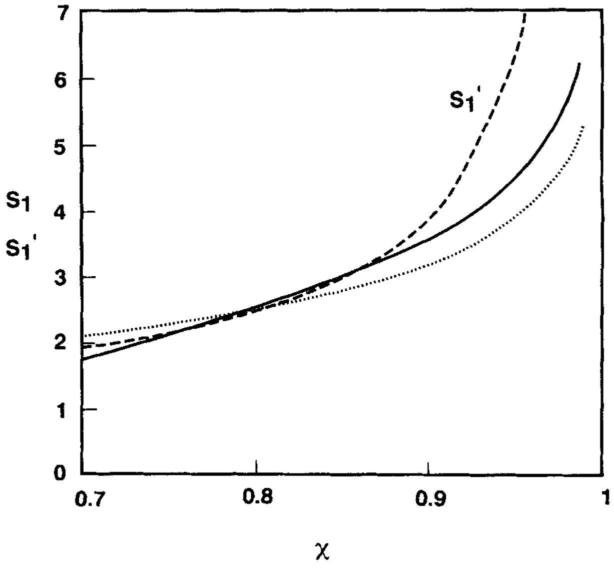

Figure 5. Ratios of CSTR and PFR reactor sizes for a mixture with $h(x) = e^{-x}$ and for a single reaction.

"——" exact S_1 for mixture; "· · · ·" asymptotic S_1 for mixture; "– – –" exact S'_1 for a single reaction.

$$M = 1/l \qquad \hat{K} = \delta^{-1/l}. \tag{30}$$

One also sees that the lumped kinetic parameters M and $\hat{K}$ assume two sets of values, depending on γ. For feeds with $\gamma > 1$,

$$M = 1 \quad \text{and} \quad \hat{K} = 1/I_1, \tag{31}$$

indicating that the asymptotic lumped order is the same as the underlying order. For feeds of $\gamma < 1$, we have

$$M = 1/\gamma \quad \text{and} \quad \hat{K} = [h_0 \Gamma(\gamma) \Gamma(1-\gamma)]^{-1/\gamma}. \tag{32}$$

Here $M > 1$; that is, the lumped order is higher than the underlying reaction order.

Equation 32 should be compared with that for the PFR. It can be shown from Eq. 14 that (Ho and Aris, 1987)

$$R_\infty(U_p) \sim \gamma [h_0 \Gamma(\gamma)]^{-1/\gamma} U_p^{(1+1/\gamma)} \qquad \text{for all } \gamma. \tag{33}$$

Equations 32 and 33 say that with the same feed information, the long-time performance of the CSTR can be predicted from the data obtained from the PFR, and vice versa.

It is of practical interest to know when the system attains the asymptotic regime. From Eqs. 28, 30 and 32, this occurs when

$$\tau \gg I_1 \qquad \gamma > 1 \tag{34}$$

$$\tau \gg [h_0 \gamma \Gamma(\gamma) \Gamma(1-\gamma)]^{1/\gamma} \qquad \gamma < 1. \tag{35}$$

For comparison, the corresponding waiting time in the PFR case is (Ho, 1991)

$$\tau \gg \gamma h_1 / h_0, \tag{36}$$

where $h_1 = f_0 g_1 + f_1 g_0$.

$\gamma = 1$. Here $U \sim h_0 \ln \tau/\tau$ for large τ, which implies that (Ho et al., 1990)

$$\tau \sim h_0 |\ln U_1| / U_1. \tag{37}$$

One can then show via a perturbation analysis that the long-time overall asymptotic kinetics, to leading order, is

$$R_\infty(U_1) \sim \left(\frac{1}{h_0}\right) \frac{U_1}{|\ln U_1|}. \tag{38}$$

Although no reaction order can be found in this case, one may define an instantaneous asymptotic order as $M(\tau) = d \ln R_\infty / d \ln U_1$. Then at high conversions

$$M(\tau) = 1 + 1/|\ln U_1|. \tag{39}$$

For instance, at a total conversion of 90% ($U_1 = 0.1$), the instantaneous order is 1.43. Note that M is a weak decreasing function of conversion, consistent with Gray's (1994) analysis of gas oil hydrodesulfurization data using a discrete model. In a study of hydrodemetallization, van Dongen et al. (1980) considered the feed $h(x) = \exp(-x)$ (that is, $U_1 \sim \ln \tau/\tau$ at high conversions). They showed that if $U_1(\tau)$ is empirically fitted by a power law, the overall order, over the 0 to 80% conversion range, is 1.5. The same feed gave an overall order of 2 when run in a PFR.

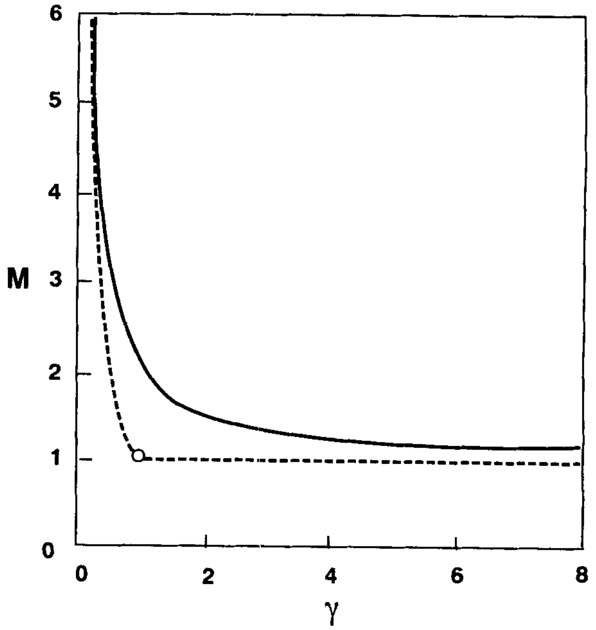

Figure 6. Order of asymptotic kinetics M as a function of γ.

"——" PFR; "- - -" a single CSTR. No M can be found when $\gamma = 1$ for CSTR, denoted by ○.

As a summary of the preceding results, Figure 6 shows the asymptotic order M as a function of γ for both PFR and CSTR. Evidently, for any finite γ, M for a PFR is *always* higher than that for a CSTR. This has been observed experimentally (van Dongen et al., 1980; Gray, 1994). As mentioned, the difference between the lumped orders for the two reactors is one when $\gamma < 1$. In the CSTR case, M does not exist for $\gamma = 1$ (denoted by the open circle) and $M = 1$ whenever $\gamma > 1$. Finally, we comment that although the asymptotic kinetics are developed for long times, they are very useful for modeling the mixture's behavior by power-law kinetics. This aspect has been discussed by Ho et al. (1990).

One-parameter model

Here we construct a one-parameter model valid for *all* τ by combining the large and small τ asymptotes for the case $\gamma \neq N$. The utility and limitation of the model can be found in Ho (1991) and will not be discussed here. It suffices to say that for practical applications the model represents a compromise between exactness and practicality. What the model offers is an approximate expression for U_N, denoted by U_q, that takes the form

$$U_q(\tau) = \frac{1}{(1 + \tau^{ql}/\delta^q)^{1/q}} \qquad q > 0, \tag{40}$$

Table 1. Comparison Between U, U_q, U_q' for $N=2$ and $h(x)=e^{-x}$

τ	U	U_q	U_q'
0.0	1.0	1.0	1.0
0.1	0.9126	0.8813	0.9208
0.3	0.7871	0.7589	0.8163
0.5	0.6985	0.6773	0.7390
0.8	0.6029	0.5900	0.6510
1.0	0.5547	0.5455	0.6045
2.0	0.4036	0.4036	0.4499
3.0	0.3218	0.3244	0.3609
5.0	0.2323	0.2359	0.2604
7.0	0.1834	0.1867	0.2044
10	0.1403	0.1429	0.1550
15	0.1015	0.1034	0.1108
20	0.0799	0.0812	0.0864
25	0.0659	0.0669	0.0708
30	0.0562	0.0570	0.0600
50	0.0355	0.0359	0.0373
70	0.0260	0.0263	0.0271

where q is the model parameter. As can be seen, for any q, $U_q \to 1$ when $\tau \to 0$, and $U_q(\tau) \sim \delta/\tau^l$ ($l=N$ if $\gamma > N$, and $l=\gamma$ if $\gamma < N$) when $\tau \to \infty$. The parameter q can be determined from a *single* experiment performed at $\tau = \hat{\tau}$ where

$$\hat{\tau} = \delta^{1/l}. \tag{41}$$

The rationale behind this is that at $\tau=\hat{\tau}$, the deviation of U_q from the asymptotes is greatest (Churchill and Usagi, 1972). Once $U_N(\hat{\tau})$ is known, q is determined by

$$q = -\ln 2/\ln U_N(\hat{\tau}). \tag{42}$$

If $\hat{\tau}$ is unknown, q can be estimated from U_N at an intermediate conversion, as illustrated in the following example.

Consider the example $N=2$ and $h(x)=e^{-x}$. Then $U_2(\tau)$ is given by Eq. 17. Therefore $l=1$ and $\delta=2$, which gives $\hat{\tau}=2$. Hence $q = -\ln 2/\ln U_2(2) = -0.693/\ln 0.4037 = 0.764$. A sensitivity test was done using $q=0.868$ (corresponding to $U_2=0.45$ instead of 0.4037). Table 1 compares the exact and approximate results (U_q and U_q' correspond to $q=0.764$ and 0.868, respectively). Although U_q' is less accurate than U_q, it is quite satisfactory for many practical purposes. As will be shown next, Eq. 40 can be used to develop an upper bound on $U_N(\tau)$, as in the PFR case (Ho, 1991).

Upper and lower bounds

As noted early, one rarely has complete information on the feed. A useful approach then is to develop bounds on the behavior of the mixture—based on minimum information. In this section we first construct a set of upper and lower bounds on $U_N(\tau)$ in terms of the moments of $h(x)$. Following the development of Hutchinson and Luss (1970) for a PFR, we use Jensen's inequality (Gradshteyn and Ryzhik, 1980), which says that for a convex function $\rho(\omega)$

$$\frac{\int_0^\infty \rho[\omega(x)]p(x)dx}{\int_0^\infty p(x)dx} \geq \rho\left(\frac{\int_0^\infty \omega(x)p(x)dx}{\int_0^\infty p(x)dx}\right), \tag{43}$$

where $p(x) \geq 0$. The mth moment of $h(x)$ is defined as

$$M_m = \int_0^\infty x^m h(x)dx. \tag{44}$$

Let $\rho = 1/(1+\omega)^N$, $\omega = x\tau/N$, and $p(x)=h(x)$. It follows that

$$U_N(\tau) \geq \frac{1}{(1+M_1\tau/N)^N} \equiv U_l, \tag{45}$$

where the first moment M_1 represents an average rate constant and can be obtained from measuring the initial decay rate of $U_N(\tau)$ since $M_1 = -dU_N/d\tau$ at $\tau=0$. Physically, U_l is the concentration of a single pseudospecies exiting a series of N CSTRs. This pseudospecies decays at a first-order rate with rate constant M_1. Evidently, use of the average rate constant leads to an overestimate of the decay rate of the mixture (a numerical example will be given later).

To find an upper bound, we let $p(x)=xh(x)$, and $\rho(\omega) = 1/(1+\omega)^{N+1}$. Use of Eq. 43 yields

$$\frac{dU_N}{d\tau} \leq \frac{-M_1}{[1+M_2\tau/(NM_1)]^{N+1}} \tag{46}$$

where the second moment M_2 can be obtained from measuring $d^2U_N/d\tau^2$ at $\tau=0$. Integrating Eq. 46 gives the upper bound

$$U_N(\tau) \leq \left(1-\frac{M_1^2}{M_2}\right) + \frac{M_1^2}{M_2}\left(\frac{NM_1}{NM_1+M_2\tau}\right)^N \equiv U_u. \tag{47}$$

As expected, as $N \to \infty$, both the upper and lower bounds reduce to those for the PFR. The gap between the bounds increases monotonically with time and eventually reaches $(1 - M_1^2/M_2)$. These bounds become rather conservative at large τ because they are based on information at early times. Hutchinson and Luss (1970) obtained tighter bounds for the PFR when more information on $h(x)$ was given.

To complement these bounds, one can obtain a relatively tight upper bound based on late-time information, as discussed by Ho (1991) for the PFR. The upper bound, denoted by U_u', is simply obtained by letting $q=1/l$ in Eq. 40; that is,

$$U_N \leq \frac{1}{(1+\tau/\delta^{1/l})^l} \equiv U_u' \tag{48}$$

U_u' may be viewed as the concentration of a single pseudospecies exiting a series of l CSTRs. That $U_N \leq U_u'$ is no surprise, since $l \leq N$ and the decay rate of this species is governed by the most refractory portion of the feed.

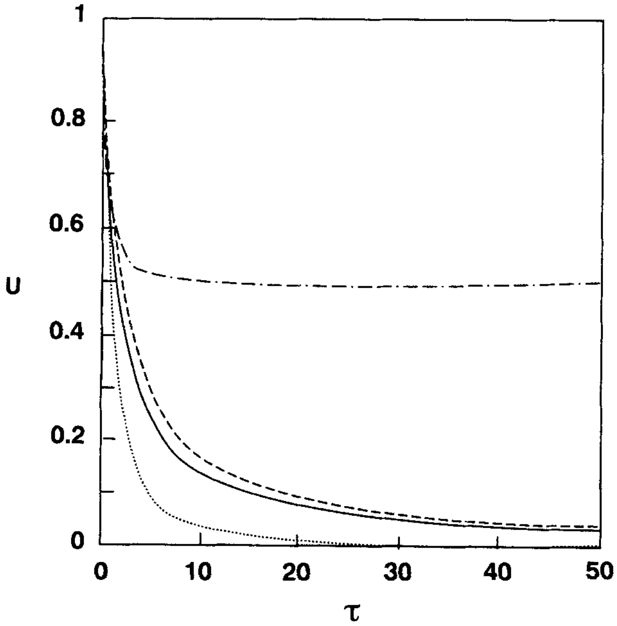

Figure 7. Comparison of various bounds with exact calculation for $h(x) = e^{-x}$ and $N = 2$.

"——" exact calculation; "- - -" U_u'; "· · · ·" U_ℓ; "-·-·-" U_u.

Take $N = 2$ and $h(x) = e^{-x}$ as an example. Then $M_1 = 1$, $M_2 = 2$, $\delta = 2$, and $l = 1$. The expression for U_2 is given by Eq. 17. Figure 7 compares various bounds with the exact behavior; at very early times, U_l and U_u are quite good. Finally, we mention that the approach of finding bounds on the mixture's behavior has been used for studying the pore diffusion effect (Golikeri and Luss, 1971; Ho et al., 1995).

Pore diffusion effect

When a single species undergoes an nth-order reaction, it is known that a severe pore diffusion limitation causes a shift in the reaction order—from n to $(n+1)/2$. The only exception is when $n = 1$, for which the order remains unchanged. One may wonder if this means that the overall order of a continuum of first-order reactions remains intact when all reactions are severely diffusion limited. This question is addressed here. For simplicity of exposition, we assume all reactants have the same diffusivity and consider a single CSTR. We want to find out in what way a given feed behaves differently when run with small vs. large particles of the same catalyst.

Let the characteristic size (volume-to-surface ratio) of the catalyst particles be L. Under strong diffusion limitation, the individual effectiveness factor $\eta(x)$ approaches the reciprocal of the generalized Thiele modulus Φ

$$\eta(x) \sim \frac{1}{L[k(x)/\hat{D}]^{1/2}} = \frac{1}{\Phi x^{1/2}}, \tag{49}$$

where $\hat{D}$ is the diffusivity and $\Phi = L(\hat{k}/\hat{D})^{1/2}$ ($\Phi \gg 1$). Consider a single CSTR charged with large catalyst particles. Let U_{1d} be the total concentration under diffusion-controlled condition (denoted by the subscript d). Then

$$U_{1d}(\tau) \sim \int_0^\infty \frac{h(x)dx}{(1+\tau\sqrt{x}/\Phi)}. \tag{50}$$

Here U_{1d} is the integral of all reactant concentrations in the bulk fluid phase. It can be shown that in the high-conversion regime ($\tau \to \infty$)

$$U_{1d} \sim \begin{cases} \dfrac{\Phi}{\tau}\displaystyle\int_0^\infty x^{-1/2}h(x)\,dx & \gamma > 1/2 \\ 2h_0\Phi(\ln\tau/\tau) & \gamma = 1/2 \\ 2h_0\Phi^{2\gamma}B(2\gamma, 1-2\gamma)\left(\dfrac{1}{\tau}\right)^{2\gamma} & \gamma < 1/2. \end{cases} \tag{51}$$

This result can be rationalized as follows. The effect of diffusion is to slow down all reactions; the effect is stronger with faster reactions than with slower ones. The mixture in the CSTR becomes more homogeneous than in the absence of diffusion limitation. As a result, the region of "single-reactant" behavior [$U = O(1/\tau)$ as $\tau \to \infty$] is widened.

From this development, one sees that the asymptotic order of the lumped kinetics under strong diffusion limitation is $M_d = 1$ when $\gamma > 1/2$ and $M_d = 1/(2\gamma)$ when $\gamma < 1/2$. It follows that the relationship between M and M_d is

$$\begin{aligned} &\gamma > 1, && M_d = M = 1 \\ &1/2 < \gamma < 1, && M_d = \gamma M = 1 \\ &0 < \gamma < 1/2, && M_d = M/2 = 2/\gamma. \end{aligned} \tag{52}$$

Thus, diffusion intrusion lowers the asymptotic order of the lumped kinetics for feeds with $\gamma < 1$. For feeds of $\gamma > 1$ (relatively homogeneous), the asymptotic order is unity, whether or not the reactions are diffusion controlled. This behavior is similar to that of a single first-order reaction.

The preceding result should be compared with that for the PFR. Let U_{pd} be the total concentration under severe diffusion limitation, then

$$U_{pd} \sim \int_0^\infty h(x)e^{-\Phi\tau\sqrt{x}}dx. \tag{53}$$

As shown by Ho et al. (1994),

$$U_{pd}(\tau) \sim 2h_0\left(\frac{1}{\Phi}\right)^{2\gamma}\Gamma(2\gamma)/\tau^{2\gamma} \qquad \tau \to \infty, \tag{54}$$

This says that $M_d = 1 + 1/(2\gamma)$ for any finite γ. From Eq. 33 it follows that

$$M_d = (M+1)/2, \qquad M > 1, \tag{55}$$

which is the same relationship for a single reactant. Hence, as far as the asymptotic order is concerned, the mixture in a PFR at high conversions under strong diffusion limitation can be treated as a single reactant. This statement, in general, cannot be applied to the CSTR (Eq. 52).

Uniformly Coupled Reactions

Returning to the diffusion-free situation, we now consider more complex systems in which the reactants *interact* with each other. We use the kinetics proposed by Astarita and Ocone (1988)

$$r(c) = -xc(x;\tau)F(\xi), \tag{56}$$

where F is a continuous function of τ through its argument ξ, which is an integral over all reactants; that is,

$$\xi(\tau) = \int_0^\infty w(x)c(x;\tau)g(x)\,dx. \tag{57}$$

What is meant by "uniform coupling" is that F is independent of x. This assumption, although quite strong, greatly simplifies the analysis and provides at least qualitative insight into the behavior of more realistic interacting systems. When $F(\xi) = 1/(1+\xi)^n$ (n is assumed to be constant for all species), $w(x)$ is the adsorption constant for species x in a Langmuir–Hinshelwood (L–H) mechanism. The $n = 1$ case is sometimes referred to as the Eley–Rideal mechanism. If $F(\xi) = \xi^{n-1}$, one speaks of biomolecular power law kinetics. One can argue that the mechanistically important situation is when $n > 1$. A special case is when $n = 2$ and $w(x) = x$, corresponding to a class of mass-action bimolecular kinetics for which each of the bimolecular rate constants is separable; that is, it is the product of two rate constants. Li and Ho (1991), Ho et al. (1995), and White et al. (1994) have examined the discrete analog of this system and extended the analysis to more general bimolecular systems.

Here $U_N(\tau)$ takes the form

$$U_N(\tau) = \int_0^\infty \frac{h(x)\,dx}{(1+\tau x\upsilon/N)^N}, \tag{58}$$

where $\upsilon(\tau)$, a wrapped time, can be found by solving the following equation

$$\upsilon(\tau) = F[\xi(\tau)], \tag{59}$$

in which

$$\xi(\tau) = \int_0^\infty \frac{w(x)h(x)\,dx}{(1+\tau x\upsilon/N)^N}. \tag{60}$$

Incidentally, we mention that in the PFR case $\upsilon(\tau)$ is found by solving an integro-differential equation.

Astarita and Nigam (1989) treated a problem similar to the one posed here. Their attention was focused on a specific class of fully characterized feeds. Our interest is in the long-time behavior of $U_N(\tau)$ for partially characterized feeds. Let υ_∞ and ξ_∞ be the leading terms in the expansion of $\upsilon(\tau)$ and $\xi(\tau)$,

$$\upsilon(\tau) \sim \upsilon_\infty(\tau) \quad \text{and} \quad \xi(\tau) \sim \xi_\infty(\tau) \quad \text{as} \quad \tau \to \infty. \tag{61}$$

Then

$$\upsilon_\infty(\tau) = F[\xi_\infty(\tau)] \tag{62}$$

and

$$U_N(\tau) \sim \int_0^\infty \frac{h(x)\,dx}{(1+\tau x\upsilon_\infty/N)^N} \quad \text{as} \quad \tau \to \infty. \tag{63}$$

To find υ_∞, we first need to know ξ_∞. The behavior of $w(x)$ near $x = 0$ is also assumed to be expressible as

$$w(x) = x^\zeta(w_0 + w_1 x + \cdots) \sim w_0 x^\zeta, \tag{64}$$

where $w_0 \ngtrless 0$. To ensure integrability, we impose $\gamma + \zeta > 0$. A negative ζ means that the most refractory species has the highest w.

Based on the results shown in the preceding section, it is not difficult to see that $\xi_\infty(\tau)$ has the following forms, depending on the magnitude of $\gamma + \zeta$ compared to N. Specifically,

(1) If $\gamma + \zeta > N$, then

$$\xi_\infty(\tau) = \frac{N^N J_N}{(\tau\upsilon_\infty)^N} \equiv \phi_1(\tau,\upsilon_\infty;N), \tag{65}$$

where

$$J_N \equiv \int_0^\infty x^{-N} w(x)h(x)\,dx. \tag{66}$$

(2) If $\gamma + \zeta < N$, then

$$\xi_\infty(\tau) = \frac{N^{\gamma+\zeta}\theta_N}{(\tau\upsilon_\infty)^{\gamma+\zeta}} \equiv \phi_2(\tau,\upsilon_\infty;N), \tag{67}$$

where $\theta_N \equiv h_0 w_0 B(\gamma+\zeta,\ N-\gamma-\zeta)$.

(3) If $\gamma + \zeta = N$, then

$$\xi_\infty(\tau) = \frac{w_0 h_0 N^N}{(\tau\upsilon_\infty)^N} \ln(\tau\upsilon_\infty) \equiv \phi_3(\tau,\upsilon_\infty;N). \tag{68}$$

Hence, for a given functional form of F, υ_∞ can be calculated by solving Eq. 62. In the same vein as before, the leading behavior of U_N at large τ can be obtained as follows:

$$\gamma > N, \qquad U_N(\tau) \sim \frac{I_N}{(\tau\upsilon_\infty)^N} \equiv \psi_1(\tau,\upsilon_\infty;N) \tag{69}$$

$$\gamma < N, \qquad U_N(\tau) \sim \frac{N^\gamma h_0}{(\tau\upsilon_\infty)^\gamma} B(\gamma, N-\gamma) \equiv \psi_2 \tag{70}$$

$$\gamma = N, \qquad U_N(\tau) \sim \frac{N^N h_0}{(\tau\upsilon_\infty)^N} \ln(\tau\upsilon_\infty) \equiv \psi_3. \tag{71}$$

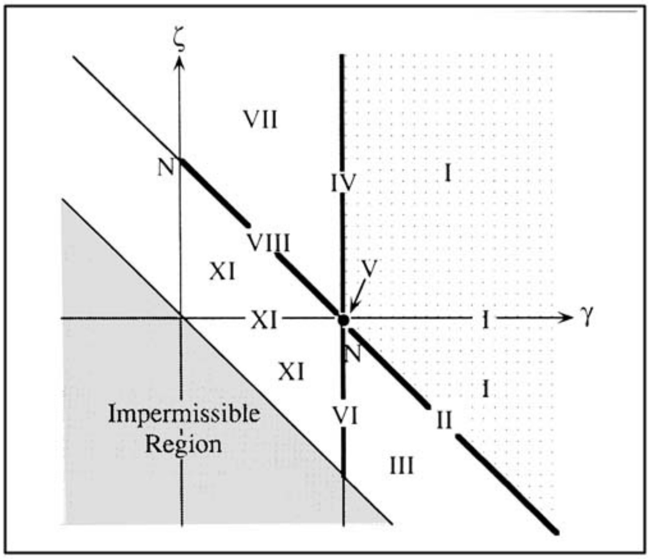

Figure 8. Different asymptotic regimes for U_N for uniformly coupled kinetics (cf. Table 2).

Thus, the long-time behavior of U_N depends on the relative magnitude of the parameters γ, ζ, and N. As Figure 8 shows, nine regions in the parameter domain can be distinguished; in each region U_N assumes a distinct asymptotic form. These are summarized in Table 2. Here a characteristic feature is that finding U_N requires solving the auxiliary equations, Eqs. 65, 67 and 68.

Special cases with a single CSTR

Bimolecular power-law kinetics: $F(\xi) = \xi^{n-1}$. The asymptotic forms of U_1 and the corresponding asymptotic power-law kinetic parameters (M and $\hat{K}$) for some special cases are given as follows.

(a) $\gamma > 1$ and $\gamma + \zeta > 1$,

$$U_1(\tau) \sim I_1 J_1^{(1-n)/n} (1/\tau)^{1/n}, \tag{72}$$

which implies

$$M = n, \qquad \hat{K} = [I_1 J_1^{(1-n)/n}]^{-n}. \tag{73}$$

Table 2. Asymptotic Behavior of U_N for Uniformly Coupled Reactions

Region No.	Condition	U_N as $\tau \to \infty$	Equation for υ_∞
I	$\gamma > N,\ \gamma + \zeta > N$	ψ_1	$\upsilon_\infty = F(\phi_1)$
II	$\gamma > N,\ \gamma + \zeta = N$	ψ_1	$\upsilon_\infty = F(\phi_3)$
III	$\gamma > N,\ \gamma + \zeta < N$	ψ_1	$\upsilon_\infty = F(\phi_2)$
IV	$\gamma = N,\ \gamma + \zeta > N$	ψ_3	$\upsilon_\infty = F(\phi_1)$
V	$\gamma = N,\ \gamma + \zeta = N$	ψ_3	$\upsilon_\infty = F(\phi_3)$
VI	$\gamma = N,\ \gamma + \zeta < N$	ψ_3	$\upsilon_\infty = F(\phi_2)$
VII	$\gamma < N,\ \gamma + \zeta > N$	ψ_2	$\upsilon_\infty = F(\phi_1)$
VIII	$\gamma < N,\ \gamma + \zeta = N$	ψ_2	$\upsilon_\infty = F(\phi_3)$
XI	$\gamma < N,\ \gamma + \zeta < N$	ψ_2	$\upsilon_\infty = F(\phi_2)$

Note: $\gamma + \zeta > 0$, $\gamma > 0$; the functions ψ_i and ϕ_i ($i = 1, 2, 3$) are defined in the text.

In the case of bimolecular reactions of the mass-action type, $U_1(\tau) \sim I_1/\sqrt{\tau}$, implying $M = 2$.

(b) $\gamma > 1$ and $\gamma + \zeta < 1$,

$$U_1(\tau) \sim I_1 \theta_1^{(1-n)/\sigma} (1/\tau)^{1/\sigma}, \tag{74}$$

where $\sigma \equiv 1 + (n-1)(\gamma + \zeta) > 0$. Then

$$M = \sigma, \qquad \hat{K} = [I_1 \theta_1^{(1-n)/\sigma}]^{-\sigma} \tag{75}$$

Here $M < n$ if $n > 1$. Astarita (1989) found for a feed given by Eq. 9 that the order of lumped kinetics in a PFR can be less than that of the underlying kinetics.

(c) $\gamma = 1$, $\gamma + \zeta > 1$, and $\zeta > 0$,

$$U_1(\tau) \sim h_0 J_1^{(1-n)/n} \ln \tau / \tau^{1/n}. \tag{76}$$

A subcase is the mass-action kinetics for which $U_1(\tau) \sim (h_0/2) \ln \tau / \sqrt{\tau}$. Equation 76 implies the following asymptotic kinetics

$$R_\infty(U_1) \sim J_1^{n-1} (n h_0)^{-n} \left[\frac{U_1}{|\ln U_1|} \right]^n \tag{77}$$

(d) $\gamma = 1$, $\gamma + \zeta < 1$, and $\zeta < 0$,

$$U_1(\tau) \sim (h_0/\sigma) \theta_1^{(1-n)/\sigma} \ln \tau / \tau^{1/\sigma}. \tag{78}$$

In a manner similar to the previous case, here $R_\infty \sim [U_1/|\ln U_1|]^\sigma$.

(e) $0 < \gamma < 1$ and $\gamma + \zeta > 1$,

$$U_1(\tau) \sim \frac{h_0 B(\gamma, 1-\gamma)}{J_1^{\gamma(n-1)/n}} \left(\frac{1}{\tau} \right)^{\gamma/n}. \tag{79}$$

Hence,

$$M = n/\gamma > n, \quad \hat{K} = [h_0 B(\gamma, 1-\gamma) J_1^{\gamma(1-n)/n}]^{-n/\gamma}. \tag{80}$$

In particular, for the mass-action kinetics, $U_1(\tau) \sim h_0 B(\gamma, 1 - \gamma)(1/\tau)^{\gamma/2}$.

(f) $\gamma < 1$ and $\gamma + \zeta < 1$,

$$U(\tau) \sim h_0 B(\gamma, 1-\gamma) \theta_1^{\gamma(1-n)/\sigma} \left(\frac{1}{\tau} \right)^{\gamma/\sigma} \tag{81}$$

The asymptotic order becomes

$$M = \sigma/\gamma. \tag{82}$$

It follows that

$$M \ge n \qquad \text{when} \quad n \ge (\gamma + \zeta - 1)/\zeta. \tag{83}$$

For comparison, the relationship between M and n in the PFR case is (Ho, 1991)

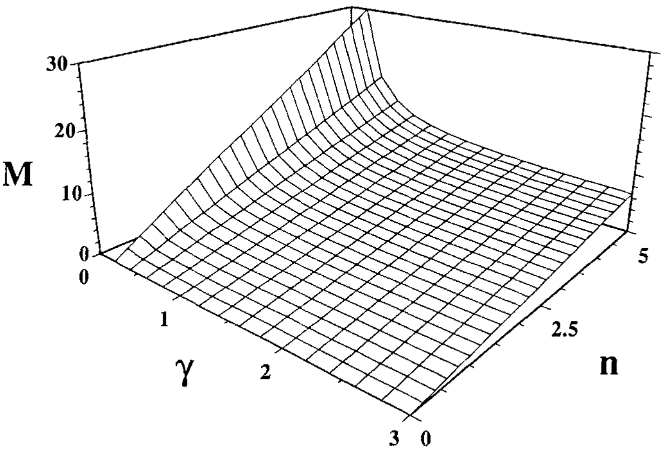

Figure 9. Asymptotic kinetic order *M* as a function of *n* and γ for a PFR; biomolecular power law kinetics with $\zeta = 1$.

$$M = 1 + \sigma/\gamma = [n(\gamma + \zeta) + 1 - \zeta]/\gamma \qquad (84)$$

for all $\gamma > 0$ and $\gamma + \zeta > 0$. Figure 9 shows M as a function of n and γ for $\zeta = 1$.

Langmuir-Hinshelwood Kinetics: $F(\xi) = 1/(1+\xi)$. Intuitively, one may expect that as time increases competitive adsorption becomes increasingly unimportant, so $U_1(\tau)$ should degenerate to the first-order case. This means that as $\tau \to \infty$, $\upsilon_\infty \to 1$. Indeed, when $\upsilon_\infty = F(\phi_1) = 1/(1+\phi_1)$, one readily sees that $\upsilon_\infty \to 1$ as $\tau \to \infty$. When $\upsilon_\infty = F(\phi_2)$, we have

$$\upsilon_\infty + \frac{\theta_1}{\tau^{\gamma+\zeta}\upsilon_\infty^{\gamma+\zeta-1}} = 1, \qquad (85)$$

where $0 < \gamma + \zeta < 1$. It can be shown via a perturbation expansion that

$$\upsilon_\infty \sim 1 - \frac{\theta_1}{\tau^{\gamma+\zeta}} + O\left[\frac{1}{\tau^{2(\gamma+\zeta)}}\right] \to 1 \qquad \text{as} \quad \tau \to \infty. \qquad (86)$$

In the same vein as previously, when $\upsilon_\infty = F(\phi_3)$, υ_∞ is determined by

$$\upsilon_\infty + h_0 w_0 \ln(\tau\upsilon_\infty)/\tau = 1 \qquad (87)$$

whose asymptotic solution is

$$\upsilon_\infty \sim 1 + h_0 w_0 \ln\tau/\tau + o(\ln\tau/\tau) \to 1 \qquad \text{as} \quad \tau \to \infty, \qquad (88)$$

where $o(\ln\tau/\tau)$ are terms that vanish faster than $\ln\tau/\tau$ as $\tau \to \infty$.

Summarizing, for the L-H kinetics $F(\xi) = 1/(1+\xi)$, the nine regions collapse to the three-region case for first-order kinetics. For a PFR, the asymptotic kinetics also degenerate to the first-order case (Ho, 1991; Chou and Ho, 1989), with

$$M = 1 + 1/\gamma. \qquad (89)$$

We close this section by mentioning that the foregoing treatment can be extended to the bimolecular surface reactions represented by

$$r(x;\tau) = \frac{-xc(x;\tau)\int_0^\infty x'c(x';\tau)g(x')\,dx'}{\left[1 + \int_0^\infty w(x')c(x';\tau)g(x')\,dx'\right]^n} \qquad (90)$$

Reversible First-Order Reactions

Consider the following first-order reversible reactions

$$a(x;t) \rightleftarrows b(x;t). \qquad (91)$$

The concentrations of a and b in the feed are $c_f(x)$ and $\tilde{c}_f(x)$, respectively. For reversible reactions, it is nearly meaningless to distinguish reactants and products. However, for labeling purposes, $a(x;t)$ and $b(x;t)$ are considered reactants and products, respectively. An example of this type of system is the hydrogenation of aromatics in fuels and lubes refining (Wilson et al., 1985). The forward reactions are pseudo-first-order because hydrogen is present in large excess. The following analysis is restricted to a single CSTR, and subsequently, a treatment of the PFR case.

Let x and $K(x)$ be the forward reaction rate constant and equilibrium constant, respectively. Here the added complication is a spectrum of equilibrium constants. The reverse reaction rate constant can generally be expressed as $x/K(x)$. To proceed, a constitutive assumption regarding the relationship between K and x is needed.

Polanyi relation

For a homologous series of reactions, the rate constant x and equilibrium constant K can often be related by the Polanyi equation (Boudart and Djega-Mariadassou, 1984)

$$K(x) = x^{-\beta}/\alpha, \qquad \alpha > 0. \qquad (92)$$

Equations of this type are also referred to as the linear free-energy relationship. When $\beta < 0$, K and x change in the same direction. Usually, it appears that $\beta \leq -1$. When $\beta > 0$, K is a decreasing function of x. Both α and β are presumed to be the same for all species.

With Eq. 92, the reverse reaction rate constant is $\alpha x^{1+\beta}$. Hence, if $\beta = -1$, all species have the same reverse rate constant. When $\beta < -1$, the reverse reactions of species with small x are fast.

CSTR

Before treating the mixture, it is helpful to look at the single-reactant case.

Single reactant. The following discussion is general and the Polanyi relation is not needed. Like c_f, $\tilde{c}_f$ is scaled as $\tilde{c}_f = c_0\tilde{f}(x)$. With $\tilde{c}(x;\tau) = f(x) + \tilde{f}(x) - c(x;\tau)$, $c(x;\tau)$ for a single CSTR reads

$$c(x;\tau) = \frac{(f+\tilde{f})x\tau + Kf}{K+(1+K)x\tau}. \qquad (93)$$

So $c(x;\tau)$ approaches equilibrium at a rate of $O(1/\tau)$; specifically,

$$c(x;\tau) = \frac{f+\tilde{f}}{1+K} + \frac{Kf-\tilde{f}}{x(1+K)^2}\left(\frac{K}{\tau}\right) + O\left(\frac{1}{\tau}\right)^2, \qquad \tau \to \infty. \quad (94)$$

Obviously, the first term on the righthand side represents the equilibrium concentration. The equilibrium point can be approached from either side, depending on the sign of $Kf - \tilde{f}$. It can be shown that the reversible kinetics can be replaced by an equivalent irreversible first-order kinetics of the form $r(c) = k'(c - c_e)$ where $k' = x(1+1/K)$ and $c_e = (\tilde{f}+f)/(1+K)$, the equilibrium concentration. In other words, the mass balance equation can be written as

$$f(x) - c(x;\tau) = k'\tau[c(x;\tau) - c_e]. \qquad (95)$$

We will look at whether this type of equivalence can be carried over to the mixture case.

Continuous Mixture. Similar to Eq. 6, the leading behavior of $\tilde{f}(x)$ near $x = 0$ is $\tilde{f}_0 x^{\tilde{\nu}}$. Also, the function $\tilde{f}(x)$ is scaled as $\int \tilde{f}(x)g(x)\,dx = \lambda$ (cf. Eq. 4) where λ is the ratio of the total concentration of b to that of a; that is, $\lambda = \tilde{C}(0)/C(0)$. The total concentration U of all reactants (henceforth we drop the subscript one) can be calculated from the expression

$$U = \int_0^\infty \frac{x\tau h(x)\,dx}{K(x)+[1+K(x)]x\tau} + \int_0^\infty \frac{x\tau \tilde{h}(x)\,dx}{K(x)+[1+K(x)]x\tau} + \int_0^\infty \frac{h(x)K(x)\,dx}{K(x)+[1+K(x)]x\tau} \equiv G_1 + G_2 + G_3, \quad (96)$$

where $\tilde{h}(x) = \tilde{f}(x)g(x)$, with its leading behavior being $\tilde{h}(x) \sim \tilde{h}_0 x^{\tilde{\gamma}}$ as $x \to 0$ and $\tilde{\gamma} \equiv \mu + \tilde{\nu} + 1$. We next need to find the asymptotic forms of G_i ($i = 1$, 2, and 3). First, let us calculate the equilibrium concentration.

Equilibrium Concentration. G_1 and G_2 have the same functional form. As can be seen from the single-reactant case, the leading terms of G_1 and G_2 should be independent of τ. This indicates that the sum of the two leading terms represents the equilibrium concentration U_e and that we need to carry out the asymptotic expansion to the next higher-order term. To see this, we introduce the following notation:

$$G_i(\tau) \sim Q_i + W_i(\tau) \qquad i = 1, 2 \qquad (97)$$

$$\text{as } \tau \to \infty,$$

$$G_3(\tau) \sim V(\tau) \qquad (98)$$

where Q_i are the leading-order, time independent terms; W_i are the leading correction to the constant terms Q_i and are time dependent; and $V(\tau)$ is the leading-order term in the asymptotic expansion of $G_3(\tau)$. That $U_e = Q_1 + Q_2$ can be seen by finding the leading-order term of $G_1 + G_2$ in the limit $\tau \to \infty$. Substituting $K(x) = x^{-\beta}/\alpha$ and factoring out τ in the denominator of G_1 and G_2 gives

$$G_1 + G_2 = \int_0^\infty \frac{[h(x)+\tilde{h}(x)]x\,dx}{[x^{-\beta}/(\alpha\tau) + (x + x^{1-\beta}/\alpha]}$$

$$\sim \int_0^\infty \frac{[h(x)+\tilde{h}(x)]\,dx}{1+x^{-\beta}/\alpha} = Q_1 + Q_2 = U_e < \infty \qquad \tau \to \infty. \quad (99)$$

The term $x^{-\beta}/(\alpha\tau)$ can be legitimately dropped in the denominator because the resulting integral converges when $\gamma > 0$. Note that U_e is contributed by *all* species, as it should be. The expression for U_e is independent of reactor type and therefore can be applied to the PFR as well.

It remains to determine the time-dependent terms W_i and V for different β's and feed types.

Near-Equilibrium Behavior. Since W_1 and W_2 have the same functional form, only W_1 is evaluated here. The result can be applied to W_2 by replacing $h(x)$, h_0, and γ in W_1 by $\tilde{h}(x)$, $\tilde{h}_0$, and $\tilde{\gamma}$, respectively.

Evaluation of $W_i(\tau)$. For ease of computation we consider three different cases according to the sign of β. Omitting the details of the derivation, we will just state the results. A typical derivation for the case $\beta > 0$ is given in the Appendix.

Case I. $\beta > 0$

$$W_1(\tau) = \begin{cases} -\left(\frac{1}{\tau}\right)\int_0^\infty \frac{\alpha h(x)\,dx}{x^{1+\beta}(\alpha + x^{-\beta})^2}, & \gamma + \beta > 1 \\ -\alpha h_0 B(\gamma+\beta, 1-\gamma-\beta)\left(\frac{1}{\tau}\right)^{\gamma+\beta}, & \gamma + \beta < 1 \\ -\alpha h_0 \ln\tau/\tau, & \gamma + \beta = 1. \end{cases} \quad (100)$$

Case II. $\beta < 0$

$$W_1(\tau) = \begin{cases} -\left(\frac{1}{\tau}\right)\int_0^\infty \frac{\alpha h(x)\,dx}{x^{1+|\beta|}(1 + \alpha x^{-|\beta|})^2}, & \gamma + |\beta| > 1 \\ -\frac{h_0\alpha^{-z}}{1-|\beta|}B(z, 1-z)\left(\frac{1}{\tau}\right)^z, & \gamma + |\beta| < 1 \\ -h_0(\alpha\gamma)^{-1}\ln\tau/\tau, & \gamma + |\beta| = 1, \end{cases} \quad (101)$$

in which $z \equiv \gamma/(1-|\beta|)$ and $0 < z < 1$.

Case III. $\beta = 0$

$$W_1(\tau) = \begin{cases} -\left(\frac{1}{\tau}\right)\frac{\alpha}{(1+\alpha)^2}\int_0^\infty x^{-1}h(x)\,dx, & \gamma > 1 \\ -\alpha h_0(1+\alpha)^{-\gamma-1}B(\gamma, 1-\gamma)\left(\frac{1}{\tau}\right)^\gamma, & \gamma < 1 \\ -\alpha h_0(1+\alpha)^{-2}\ln\tau/\tau, & \gamma = 1. \end{cases} \quad (102)$$

Note that $W_1 = 0$ when $\alpha = 0$, as expected.

Evaluation of $V(\tau)$. Again we consider three possible cases based on the sign of β.

Case I. $\beta > 0$

$$V(\tau) = \begin{cases} \left(\dfrac{1}{\tau}\right)\displaystyle\int_0^\infty \frac{x^{-1}h(x)\,dx}{1+\alpha x^{\beta}}, & \gamma > 1 \\ h_0 B(\gamma, 1-\gamma)\left(\dfrac{1}{\tau}\right)^{\gamma}, & \gamma < 1 \\ h_0 \ln\tau/\tau, & \gamma = 1. \end{cases} \tag{103}$$

Case II. $\beta < 0$

$$V(\tau) = \begin{cases} \left(\dfrac{1}{\tau}\right)\displaystyle\int_0^\infty \frac{x^{-1}h(x)\,dx}{1+\alpha x^{-|\beta|}}, & \gamma + |\beta| > 1 \\ h_0 \alpha^{-z}(1-|\beta|)^{-1}B(z, 1-z)/\tau^{z}, & \gamma + |\beta| < 1 \\ (h_0/\gamma)\ln\tau/\tau, & \gamma + |\beta| = 1. \end{cases} \tag{104}$$

Note that when $\gamma + |\beta| \le 1$, $V(\tau) = -W_1(\tau)$.

Case III. $\beta = 0$

$$V(\tau) = \begin{cases} \left(\dfrac{1}{\tau}\right)\displaystyle\int_0^\infty \frac{x^{-1}h(x)\,dx}{1+\alpha}, & \gamma > 1 \\ h_0(1+\alpha)^{-\gamma}B(\gamma, 1-\gamma)\left(\dfrac{1}{\tau}\right)^{\gamma}, & \gamma < 1 \\ h_0(1+\alpha)^{-1}\ln\tau/\tau, & \gamma = 1. \end{cases} \tag{105}$$

Here in no case does $V(\tau) = -W_1(\tau)$. Also, V reduces to the irreversible case as $\alpha \to 0$, as expected.

Summary of results for CSTR

Having found G_1, G_2, and G_3 asymptotically, one can obtain the asymptotic form of U by picking the dominant term among W_1, W_2, and V in different regions of the parameter domain. The results, expressed in terms of $U - U_e$, are summarized in Tables 3–5 according to the sign of β. There are 21 possible cases. U_e is given by Eq. 99. As seen β, γ, and $\tilde{\gamma}$ play the pivotal role in determining the near-equilibrium behavior of U. Although U admits so many asymptotic behaviors, the underlying mathematical structure remains the same as in the irreversible case in that $(U_e - U)$ behaves either as $O(1/\tau)^l$ or as $O(\ln\tau/\tau)$ for large τ.

As an illustration, consider the following example of case *A′* in Table 4: $\beta = -1$, $\alpha = 1$, $h(x) = \exp(-x)$, and $\tilde{h}(x) = (2/3/\pi)^{1/2}x^{-1/2}\exp(-2x/3)$. Then $U_e = 1.2960$ and Eq. 97 can be integrated to give

$$U(\tau) = e^{1+1/\tau}E_1\left(\frac{1+\tau}{\tau}\right)\left(1+\frac{1}{\tau}\right) + \left(\frac{2\pi}{3}\right)^{1/2} \times \frac{\tau e^{2(\tau+1)/(3\tau)}}{\sqrt{\tau(\tau+1)}}\operatorname{erfc}\left\{\frac{1}{\tau}\left[\frac{2\tau(\tau+1)}{3}\right]^{1/2}\right\}. \tag{106}$$

Table 3. Asymptotic Behavior of $U(\tau) - U_e$ for First-Order Reversible Reactions in a CSTR: $\beta > 0$

Region	Condition	$U - U_e$ as $\tau \to \infty$
A	$\gamma > 1$, $\tilde{\gamma} > 1 - \beta$	$\left(\dfrac{1}{\tau}\right)\displaystyle\int_0^\infty \frac{[x^{-\beta}h(x) - \alpha\tilde{h}(x)]dx}{x(1+\alpha x^{\beta})(\alpha + x^{-\beta})}$
B	$\gamma > 1$, $\tilde{\gamma} = 1 - \beta$	$-\alpha\tilde{h}_0(\ln\tau/\tau)$
C	$\gamma = 1$, $\tilde{\gamma} > 1 - \beta$	$h_0(\ln\tau/\tau)$
D	$\gamma = 1$, $\tilde{\gamma} = 1 - \beta$	$(h_0 - \alpha\tilde{h}_0)(\ln\tau/\tau)$
E	$\gamma < \tilde{\gamma} + \beta < 1$	$h_0 B(\gamma, 1-\gamma)(1/\tau)^{\gamma}$
F	$\gamma = \tilde{\gamma} + \beta < 1$	$(h_0 - \alpha\tilde{h}_0)B(\gamma, 1-\gamma)(1/\tau)^{\gamma}$
G	$\gamma > \tilde{\gamma} + \beta$, $\tilde{\gamma} < 1 - \beta$	$-\alpha\tilde{h}_0 B(\tilde{\gamma} + \beta, 1 - \tilde{\gamma} - \beta)(1/\tau)^{\tilde{\gamma}+\beta}$

Table 4. Asymptotic Behavior of $U(\tau) - U_e$ for First-Order Reversible Reactions in a CSTR: $\beta < 0$

Region	Condition	$U - U_e$ as $\tau \to \infty$
A′	$\gamma > 1 - \lvert\beta\rvert$, $\tilde{\gamma} > 1 - \lvert\beta\rvert$	$\left(\dfrac{1}{\tau}\right)\displaystyle\int_0^\infty \frac{[x^{\lvert\beta\rvert}h(x) - \alpha\tilde{h}(x)]dx}{x(1+\alpha x^{-\lvert\beta\rvert})(\alpha + x^{\lvert\beta\rvert})}$
B′	$\gamma > 1 - \lvert\beta\rvert = \tilde{\gamma}$	$-\dfrac{\tilde{h}_0}{\alpha\gamma}\left(\dfrac{\ln\tau}{\tau}\right)$
C′	$\tilde{\gamma} > 1 - \lvert\beta\rvert = \gamma$	$\dfrac{h_0}{\gamma}\left(\dfrac{\alpha-1}{\alpha}\right)\left(\dfrac{\ln\tau}{\tau}\right)$ $(\alpha \neq 1)$ $-\left(\dfrac{1}{\tau}\right)\displaystyle\int_0^\infty \frac{\tilde{h}(x)dx}{x^{1+\lvert\beta\rvert}(1+x^{-\lvert\beta\rvert})^2}$ $(\alpha = 1)$
D′	$\gamma = 1 - \lvert\beta\rvert = \tilde{\gamma}$	$\left(\dfrac{\alpha h_0 - h_0 - \tilde{h}_0}{\alpha\gamma}\right)\dfrac{\ln\tau}{\tau}$
E′	$\gamma < 1 - \lvert\beta\rvert$, $\tilde{\gamma} > 1 - \lvert\beta\rvert$	$-\left(\dfrac{1}{\tau}\right)\displaystyle\int_0^\infty \frac{\alpha\tilde{h}(x)dx}{x^{1+\lvert\beta\rvert}(1+\alpha x^{-\lvert\beta\rvert})^2}$
F′	$\gamma < 1 - \lvert\beta\rvert = \tilde{\gamma}$	$-\dfrac{\tilde{h}_0}{\alpha\tilde{\gamma}}\left(\dfrac{\ln\tau}{\tau}\right)$
G′	$\tilde{\gamma} < 1 - \lvert\beta\rvert$	$-\dfrac{\tilde{h}_0\alpha^{-\tilde{z}}}{1-\lvert\beta\rvert}B(\tilde{z}, 1-\tilde{z})\left(\dfrac{1}{\tau}\right)^{\tilde{z}}$

$\tilde{z} \equiv \tilde{\gamma}/(1 - |\beta|)$

Table 5. Asymptotic Behavior of $U(\tau) - U_e$ for First-Order Reversible Reactions in a CSTR: $\beta = 0$

Region	Condition	$U - U_e$ as $\tau \to \infty$
A″	$\gamma > 1, \tilde{\gamma} > 1$	$(1+\alpha)^{-2}\left(\dfrac{1}{\tau}\right)\displaystyle\int_0^\infty x^{-1}(h - \alpha\tilde{h})dx$
B″	$\gamma > 1, \tilde{\gamma} = 1$	$-\alpha\tilde{h}_0(1+\alpha)^{-2}\left(\dfrac{\ln\tau}{\tau}\right)$
C″	$\gamma = 1, \tilde{\gamma} > 1$	$h_0(1+\alpha)^{-2}\left(\dfrac{\ln\tau}{\tau}\right)$
D″	$\gamma = \tilde{\gamma} = 1$	$(h_0 - \alpha\tilde{h}_0)(1+\alpha)^{-2}\left(\dfrac{\ln\tau}{\tau}\right)$
E″	$\gamma < 1, \tilde{\gamma} > \gamma$	$\dfrac{h_0}{(1+\alpha)^{\gamma+1}}B(\gamma, 1-\gamma)\left(\dfrac{1}{\tau}\right)^{\gamma}$
F″	$\gamma = \tilde{\gamma} < 1$	$\dfrac{h_0 - \alpha\tilde{h}_0}{(1+\alpha)^{\gamma+1}}B(\gamma, 1-\gamma)\left(\dfrac{1}{\tau}\right)^{\gamma}$
G″	$\tilde{\gamma} < 1, \tilde{\gamma} < \gamma$	$-\dfrac{\alpha\tilde{h}_0}{(1+\alpha)^{1+\tilde{\gamma}}}B(\tilde{\gamma}, 1-\tilde{\gamma})\left(\dfrac{1}{\tau}\right)^{\tilde{\gamma}}$

Table 6. Asymptotic Behavior of $U(\tau) - U_e$ for First-Order Reversible Reactions in a PFR

	Condition	$U \sim U_e$ as $\tau \to \infty$
$\beta > 0$	$\tilde{\gamma} > \gamma - \beta$	$h_0 \Gamma(\gamma)/\tau^{\gamma}$
	$\tilde{\gamma} = \gamma - \beta$	$(h_0 - \tilde{\alpha} h_0)\Gamma(\gamma)/\tau^{\gamma}$
	$\tilde{\gamma} < \gamma - \beta$	$-\alpha \tilde{h}_0 \Gamma(\tilde{\gamma} + \beta)/\tau^{\gamma + \beta}$
$\beta < 0$ and $\lvert\beta\rvert < 1$	$\tilde{\gamma} > \gamma + \lvert\beta\rvert$	$\frac{h_0}{1-\lvert\beta\rvert}\left(\frac{1}{\alpha}\right)^{(\gamma+1)/(1-\lvert\beta\rvert)} \Gamma\left(\frac{\gamma+\lvert\beta\rvert}{1-\lvert\beta\rvert}\right)\left(\frac{1}{\tau}\right)^{(\gamma+\lvert\beta\rvert)/(1-\lvert\beta\rvert)}$
	$\tilde{\gamma} = \gamma + \lvert\beta\rvert$	$\frac{\Gamma(\tilde{z})}{1-\lvert\beta\rvert}\left(\frac{1}{\alpha}\right)^{\tilde{z}+1}(h_0 - \alpha\tilde{h}_0)\left(\frac{1}{\tau}\right)^{\tilde{z}}$
	$\tilde{\gamma} < \gamma + \lvert\beta\rvert$	$-\frac{\tilde{h}_0}{1-\lvert\beta\rvert}\left(\frac{1}{\alpha}\right)^{\tilde{z}}\Gamma(\tilde{z})\left(\frac{1}{\tau}\right)^{\tilde{z}}$
$\beta < 0, \lvert\beta\rvert > 1$		$\frac{(2\pi)^{1/2}[H(\hat{x}) - \tilde{H}(\hat{x})]}{[\kappa''(\hat{x})\tau]^{1/2}} e^{-\kappa(\hat{x})\tau}$
$\beta = -1$	$\tilde{\gamma} > \gamma + 1$	$h_0 \Gamma(\gamma+1)\alpha^{-1} e^{-\alpha\tau}/\tau^{\gamma+1}$
	$\tilde{\gamma} = \gamma + 1$	$(h_0 - \alpha\tilde{h}_0)\alpha^{-1}\Gamma(\tilde{\gamma})e^{-\alpha\tau}/\tau^{\tilde{\gamma}}$
	$\tilde{\gamma} < \gamma + 1$	$-\tilde{h}_0 \Gamma(\tilde{\gamma}) e^{-\alpha\tau}(1/\tau)^{\tilde{\gamma}}$
$\beta = 0$	$\gamma < \tilde{\gamma}$	$[h_0 \Gamma(\gamma)/(1+\alpha)^{1+\gamma}](1/\tau)^{\gamma}$
	$\gamma = \tilde{\gamma}$	$[\Gamma(\gamma)(h_0 + \alpha\tilde{h}_0)/(1+\alpha)^{1+\gamma}](1/\tau)^{\gamma}$
	$\gamma > \tilde{\gamma}$	$-[\alpha\tilde{h}_0 \Gamma(\tilde{\gamma})/(1+\alpha)^{1+\tilde{\gamma}}](1/\tau)^{\tilde{\gamma}}$

$\tilde{z} \equiv \tilde{\gamma}/(1 - \lvert\beta\rvert)$. $H(\hat{x})$, $\tilde{H}(\hat{x})$, and $\kappa''(\hat{x})$ are given in the text.

From Table 4, the leading-order behavior of U has the form

$$U(\tau) \sim 1.2960 - \frac{0.3573}{\tau}. \tag{107}$$

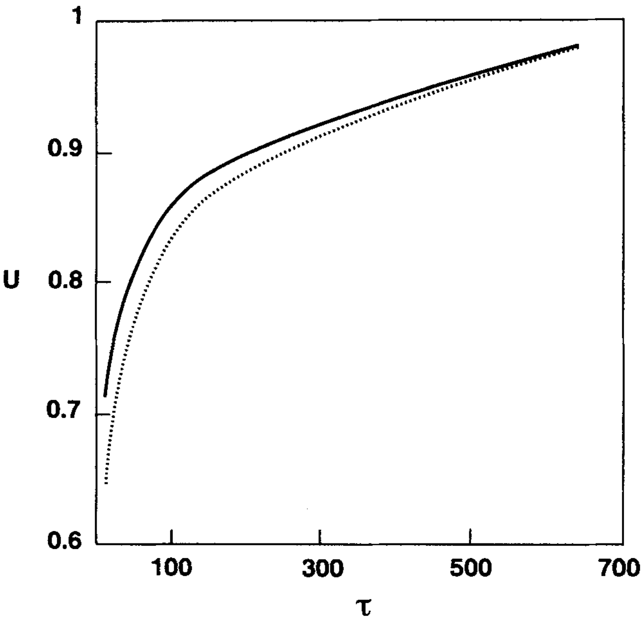

Figure 10. Comparison of exact and asymptotic $U(\tau)$ for a first-order reversible reaction mixture in a CSTR.

Case A′ in Table 4: $\beta = -1$; $\alpha = 1$; $h(x) = e^{-x}$; and $\tilde{h}(x) = (2/3\pi)^{1/2} x^{-1/2} \exp^{-2x/3}$; "——" exact calculation; "– – –" asymptotic result.

This asymptotic result is close to the exact calculation at large τ (Figure 10).

Lumped kinetics

As mentioned, in many cases $U - U_e \sim \delta/\tau^l$ at large τ. Here we want to show that this behavior asymptotically corresponds to an "irreversible" power law kinetics of the form $R_\infty \sim \hat{K}(U - U_e)^M$, with

$$M = 1/l \qquad \text{and} \qquad \hat{K} = (1 - U_e)/\delta^{1/l} \tag{108}$$

To this end, let us consider the following power-law kinetics in a CSTR

$$1 - U = \tau R(U) = \tau \hat{K}(U - U_e)^M. \tag{109}$$

Here, without loss of generality, we consider the case $U_e < U < 1$. The behavior of $U - U_e$ at large τ can be obtained by the same perturbation method used before. The result is

$$U - U_e \sim \frac{[(1 - U_e)/\hat{K}]^{1/M}}{\tau^{1/M}} \qquad \tau \to \infty, \tag{110}$$

from which Eq. 108 follows. From Tables 3–5, it can be seen that

$$M \geq 1 \tag{111}$$

and in some cases M is a function of β. The domain of validity for this asymptotic kinetics is

$$\tau \gg (1 - U_e)^{1-M}/(\hat{K}M^M). \tag{112}$$

When $U - U_e \sim \delta(\ln \tau/\tau)$, it can be shown that the equivalent irreversible kinetics takes the asymptotic form

$$R_\infty \sim \frac{U - U_e}{\delta |\ln (U - U_e)|}. \tag{113}$$

Plug-flow reactor

In the case of irreversible reactions, the mixture's asymptotic behavior is uniquely defined by Eq. 14. Here we show that the introduction of reversibility into the system changes the structure of the problem. Dropping the subscript p, we compute the total concentration of $a(x;\tau)$ as follows:

$$U = U_e + \int_0^\infty \frac{K(x)h(x)}{1+K(x)} e^{-\kappa(x)\tau} dx - \int_0^\infty \frac{\tilde{h}(x)}{1+K(x)} e^{-\kappa(x)\tau} dx \equiv U_e + L_1 - L_2, \tag{114}$$

where U_e is given by Eq. 99 and

$$\kappa(x) = x(1 + \alpha x^\beta), \tag{115}$$

Here, $\kappa(x)$ can be regarded as the effective rate constant for the reversible reaction involving species x. The behaviors of some special mixtures in the PFR have been examined by Chou and Ho (1988) and Aris (1991a). Here we wish to know the behavior of U near its equilibrium for an *arbitrary* feed. This amounts to asymptotic evaluation of the integrals L_1 and L_2, both of which are of the Laplace type (Bender and Orszag, 1978). The key to the asymptotic approximation of such integrals is a small region in the integration interval, due to the exponential term, that provides the dominant contribution to the integration.

Specifically, the overwhelming contribution to L_i ($i = 1, 2$) comes from a thin region near $x = \hat{x}$ where $\hat{x}$ is the point at which $\kappa(x)$ assumes its minimum value. It is easily verified that as long as $\beta \geq -1$, $\hat{x} = 0$ because $\kappa(x)$ increases monotonically. When $\beta < -1$, κ has a minimum within the interval $[0, \infty)$, with

$$\hat{x} = [\alpha(|\beta| - 1)]^{1/|\beta|} > 0 \tag{116}$$

and at this point

$$\kappa(\hat{x}) = |\beta| \alpha^{1/|\beta|} (|\beta| - 1)^{-1 + 1/|\beta|} > 0. \tag{117}$$

We now can proceed to evaluate the integrals L_i for all possible β. Five cases need to be considered.

Case I: $\beta > 0$. Here L_1 is dominated by the region near $x = 0$. Replacing $h(x)$ by its asymptotic form and noting that $\alpha x^\beta \ll 1$ leads to

$$L_1 \sim \int_0^\infty h_0 x^{\gamma - 1} e^{-x\tau} dx = \frac{h_o \Gamma(\gamma)}{\tau^\gamma}. \tag{118}$$

Similarly,

$$L_2 \sim \alpha \tilde{h}_0 \Gamma(\tilde{\gamma} + \beta) \left(\frac{1}{\tau} \right)^{\tilde{\gamma} + \beta} \tag{119}$$

As expected, the behavior of the mixture near equilibrium must be governed by the most refractory reactants because they happen to have the highest equilibrium constants.

Case II: $\beta = 0$. In this case all reactions have the same equilibrium constant. Again, as expected, the near-equilibrium behavior is governed by the most refractory species. The leading asymptotic forms of L_1 and L_2 are

$$L_1 \sim \frac{h_0 \Gamma(\gamma)}{(1+\alpha)^{1+\gamma}} \left(\frac{1}{\tau} \right)^\gamma \tag{120}$$

$$L_2 \sim \frac{\alpha \tilde{h}_0 \Gamma(\tilde{\gamma})}{(1+\alpha)^{1+\tilde{\gamma}}} \left(\frac{1}{\tau} \right)^{\tilde{\gamma}}. \tag{121}$$

Chou and Ho (1988) considered the special case $\gamma = \tilde{\gamma} = 1$.

Case III: $\beta < 0$ *and* $|\beta| < 1$. Here the higher the reactivity of the species, the higher the equilibrium constant. But the increase in K as x increases is not fast enough for the refractory species to lose their dominance. With $x = 0(1/\tau)$ being the dominant region, $x^{-|\beta|} \gg 1$ and $h(x)$ can be replaced by its asymptotic form. Asymptotically, L_1 then becomes

$$L_1 \sim \frac{h_0}{\alpha} \int_0^\infty x^{\gamma - 1 + |\beta|} e^{-\alpha\tau x^{1-|\beta|}} dx \qquad \text{as} \quad \tau \to \infty. \tag{122}$$

Let $y = \alpha x^{1-|\beta|}$, then

$$L_1 \sim \frac{h_0}{1-|\beta|} \left(\frac{1}{\alpha} \right)^{(\gamma+1)/(1-|\beta|)} \int_0^\infty y^{(\gamma - 1 + 2|\beta|)/(1-|\beta|)} e^{-\tau y} dy, \qquad \tau \to \infty$$

$$= \frac{h_0}{1-|\beta|} \left(\frac{1}{\alpha} \right)^{(\gamma+1)/(1-|\beta|)} \frac{\Gamma\left(\dfrac{\gamma + |\beta|}{1-|\beta|} \right)}{\tau^{(\gamma+|\beta|)/(1-|\beta|)}}. \tag{123}$$

Similarly, L_2's asymptotic form is

$$L_2 \sim \frac{\tilde{h}_0 \Gamma(\tilde{z})}{1-|\beta|} \left(\frac{1}{\alpha\tau} \right)^{\tilde{z}} \qquad \tau \to \infty, \tag{124}$$

where $\tilde{z} \equiv \tilde{\gamma}/(1-|\beta|)$.

In all three of the preceding cases, the mixture approaches equilibrium in a fashion $[O(1/\tau^j)]$ similar to that in the irreversible case. And its near equilibrium behavior is dominated by the most refractory species. This need not be true, as shown below. Case IV reveals a *new* structure: the asymptotic behavior is governed by species of *intermediate* reactivities. Case V represents the transition to the new structure.

Case IV: $\beta < 0$ *and* $|\beta| > 1$. Here $K(x)$ is such a strong increasing function of x that neither the refractory nor the reactive species wins. Instead, species with intermediate reactivities (hence intermediate equilibrium constants) become dominating. Both L_1 and L_2 are now dominated by an *inter-*

nal boundary layer near $x = \hat{x}$. We can approximate $\kappa(x)$ by its Taylor series about $x = \hat{x}$; that is,

$$\kappa(x) = \kappa(\hat{x}) + \frac{1}{2}\kappa''(\hat{x})(x - \hat{x})^2, \tag{125}$$

where κ'' is the second derivative of κ. It can be readily shown that

$$\kappa''(\hat{x}) = |\beta|[\alpha(|\beta| - 1)]^{-1/|\beta|}. \tag{126}$$

Let $H(\hat{x})$ and $\tilde{H}(\hat{x})$ be given by

$$H(\hat{x}) = \frac{K(\hat{x})h(\hat{x})}{1 + K(\hat{x})} = \frac{(|\beta| - 1)h(\hat{x})}{|\beta|} \tag{127}$$

$$\tilde{H}(\hat{x}) = \frac{\tilde{h}(\hat{x})}{1 + K(\hat{x})} = \frac{\tilde{h}(\hat{x})}{|\beta|}. \tag{128}$$

Then

$$\begin{aligned} L_1 &\sim \int_{\hat{x}-\epsilon}^{\hat{x}+\epsilon} H(\hat{x})\exp\left\{\left[\kappa(\hat{x}) + \frac{1}{2}\kappa''(\hat{x})(x - \hat{x})^2\right]\tau\right\}dx \\ &\sim H(\hat{x})\exp^{-\kappa(\hat{x})\tau}\int_{-\infty}^{\infty}\exp[\tau\kappa''(\hat{x})(x - \hat{x})^2/2]\,dx \\ &= \frac{(2\pi)^{1/2}H(\hat{x})e^{-\kappa(\hat{x})\tau}}{[\kappa''(\hat{x})\tau]^{1/2}} \quad \text{as} \quad \tau \to \infty. \end{aligned} \tag{129}$$

The error introduced by extending the integration limits to $-\infty$ and $+\infty$ is exponentially small. Likewise,

$$L_2 \sim \frac{(2\pi)^{1/2}\tilde{H}(\hat{x})e^{-\kappa(\hat{x})\tau}}{[\kappa''(\hat{x})\tau]^{1/2}} \quad \text{as} \quad \tau \to \infty. \tag{130}$$

It is seen that L_1 and L_2 are of the same order of magnitude.

Case V: $\beta = -1$. It can be shown that as $\tau \to \infty$,

$$L_1 \sim [h_0\Gamma(\gamma + 1)/\alpha]e^{-\alpha\tau}/\tau^{\gamma+1} \tag{131}$$

$$L_2 \sim h_0\Gamma(\tilde{\gamma})e^{-\alpha\tau}/\tau^{\tilde{\gamma}}. \tag{132}$$

In rough terms, the exponential terms signifies the onset of the effect due to species outside the boundary layer near $x = 0$, reminiscent of the logarithmic term in the CSTR case.

Summary of results for PFR

Having found the asymptotic expressions for L_1 and L_2 under all possible circumstances, we combine them to obtain the asymptotic forms of U in different regions of the parameter domain, as summarized in Table 6. Despite the existence of 13 possibilities, the qualitative behavior of the mixture near equilibrium is either in the power-law form $O(1/\tau)^l$ or in the form of $O(e^{-u\tau}/\tau^l)$. The latter represents a new structural feature when contrasted to the irreversible case. Here the near equilibrium behavior can be governed by species of intermediate reactivities. Such is not the case with the CSTR. Hence the kind of feed information needed for predicting the CSTR performance can be very different from that needed for the PFR.

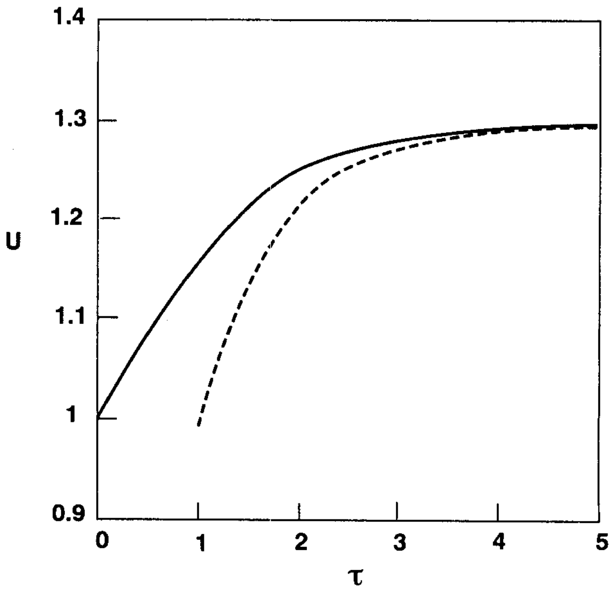

Figure 11. Comparison of exact and asymptotic $U(\tau)$ for a first-order reversible-reaction mixture in a PFR.

Case 10 in Table 6: $h(x) = e^{-x}$; $\tilde{h}(x) = (2/3/\pi)^{1/2}x^{-1/2}\exp^{-2x/3}$; $\alpha = 1$; and $\beta = -1$; "——" exact calculation; "- - -" asymptotic result.

Now consider an example of $\beta = -1$ and $\tilde{\gamma} < \gamma + 1$. Let $h(x) = \exp(-x)$, $\tilde{h}(x) = (2/3/\pi)^{1/2}x^{-1/2}\exp(-2x/3)$, and $\alpha = 1$. Then $U_e = 1.2960$ and the analytical expression for $U(\tau)$ for all τ is

$$\begin{aligned} U(\tau) = 1.2960 + \frac{e^{-\tau}}{1+\tau} - eE_1(1+\tau) \\ - \left(\frac{2\pi}{3}\right)^{1/2} e^{2/3}\operatorname{erfc}\left(\sqrt{\tau + 2/3}\right). \end{aligned} \tag{133}$$

The leading behavior for large τ, easily obtained from Table 6, is

$$U(\tau) \sim 1.2960 - \left(\frac{2}{3\tau}\right)^{1/2} e^{-\tau}. \tag{134}$$

The comparison between the asymptotic and exact results is shown in Figure 11.

Lumped kinetics

Here we show that the system can be treated as though the asymptotic lumped reactions were irreversible, as in the CSTR case.

Table 5 indicates that the asymptotic decay of $(U - U_e)$ takes the following general form: $U - U_e \sim \delta/\tau^l$ or $\sim \delta e^{-u\tau}/\tau^l$. In the former case, it is easy to show that R_∞ takes the following power law form:

$$R_\infty \sim l\delta^{-1/l}(U-U_e)^{1+1/l}. \tag{135}$$

Now the consider the case where

$$U-U_e \sim \delta e^{-u\tau}/\tau^l. \tag{136}$$

Let

$$\Omega = -\ln(U-U_e) \tag{137}$$

so $\Omega \to \infty$ as $\tau \to \infty$. Equation 136 implies that

$$\frac{\Omega}{\tau} = u + \frac{l(\ln\tau)}{\tau} - \frac{\ln\delta}{\tau} + o(1), \tag{138}$$

where $o(1)$ are terms that varnish as $\tau \to \infty$. We thus have

$$\frac{\Omega}{\tau} = u + o(1) \qquad \text{as} \quad \tau \to \infty. \tag{139}$$

Therefore,

$$\ln\tau = \ln\Omega - \ln u + o(1) \qquad \tau \to \infty. \tag{140}$$

Combining Eqs. 138 and 140 gives

$$u\tau = \Omega + \ln(u^l\delta) - \ln\Omega^l + o(1), \tag{141}$$

which says that

$$\tau \sim \frac{1}{u}\ln\left\{\frac{u^l\delta}{(U-U_e)|\ln(U-U_e)|^l}\right\} \qquad \tau \to \infty. \tag{142}$$

The asymptotic kinetics then becomes

$$R_\infty \sim \frac{u}{\ln\left\{\dfrac{u^l\delta}{(U-U_e)|\ln(U-U_e)|^l}\right\}} \qquad U \to U_e. \tag{143}$$

Conclusions

This article presents an asymptotic theory of the overall behaviors of a reaction mixture in CSTRs and a PFR. This mixture contains infinitely many species undergoing independent or interacting reactions, with kinetics that are either first-order (reversible or irreversible) or coupled pseudo first-order. For reversible reactions, the treatment is based on a Polanyi relation. The focus is on the behavior of the mixture and the asymptotic lumped kinetics at *high* conversion or *near* equilibrium. Some key findings, in qualitative terms, are summarized as follows.

(1) Asymptotic lumped kinetics depend as much on the feedstock properties as on reactor type. In many cases, the kinetics are of the power-law form. Conditions are established for the occurrence of non-power-law kinetics whose forms are also given.

(2) When the lumped kinetics are power law, the kinetic order is always higher for the PFR than for the CSTR.

(3) When the individual bimolecular kinetics are power law of order n ($n > 1$), the order of the lumped kinetics in a CSTR can be less than n, as is the case with a PFR.

(4) When the individual kinetics are of the Langmuir–Hinshelwood type, the lumped kinetics degenerate to that of first-order reactions, regardless of reactor type.

(5) As far as asymptotic order is concerned, the lumped kinetics of irreversible first-order reactions in a PFR under strong diffusion limitations behaves like the kinetics of a single reaction. This statement cannot be applied to the CSTR.

(6) With tough feeds, the behavior of the mixture in CSTRs is dominated by refractory species. With easy feeds, the behavior is determined by all species and is qualitatively similar to the single-reactant case.

(7) With irreversible reactions, the behavior of the mixture in a PFR is always governed by the most refractory fraction of the feed, regardless of the reactivity of the feed. With reversible reactions, the mixture's behavior in a PFR can be governed by species of intermediate reactivities. This is not the case with a CSTR.

(8) When the individual reactions are reversible first-order, the asymptotic lumped kinetics can be expressed in terms of an equivalent irreversible kinetics.

(9) With the same feed information, in some cases, the performance of the CSTR can be predicted from the PFR data and *vice versa*. Conditions under which such cannot be done are given.

Finally, we remark that the restriction on the reaction kinetics in this work should be relaxed in future studies. Also, other reactor types should be considered; some initial results have been reported by Aris (1991b).

Notation

c_e = equilibrium concentration in the single-reaction case
$C(0)$ = total concentration of reactants in feed
$c(x;t)$ = dimensionless reactant concentration
$f(x)$ = dimensionless reactant concentration in feed
$\tilde{f}(x)$ = feed concentration of $b(x;t)$
$g(x)$ = normalized $D(x)$ function, Eq. 3
$h(x)$ = defined as $h(x) \equiv f(x)g(x)$
$k(x)$ = rate constant for reactant x
$\hat{K}$ = power-law rate constant of lumped kinetics
M = lumped kinetic order without diffusion limitation
M_d = lumped kinetic order with diffusion limitation
n = order of biomolecular reaction, or exponent of adsorption
$r(c)$ = kinetics of underlying reactions
R = lumped kinetics
R_∞ = asymptotic lumped kinetics
U_e = dimensionless total equilibrium concentration
U_N = dimensionless total concentration in N CSTRs
U_p = dimensionless total concentration in PFR
τ = dimensionless reactor residence time

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Appendix: Typical Derivations of $W_1(\tau)$

In the text, the derivations of W_1 and V are omitted. Here an example is given to show the details of the derivation for Eq. 100.

We can obtain W_1 by subtracting the integrand of Q_1 from that of G_1 and integrating the resulting expression. This leads to

$$G_1 - Q_1 = \int_0^\infty \alpha h(x)\left[\frac{x^{1+\beta}}{x+\alpha x^{1+\beta}+1/\tau} - \frac{1}{\alpha + x^{-\beta}}\right]dx$$

$$= -\left(\frac{1}{\tau}\right)\int_0^\infty \frac{\alpha h(x) x^{\beta}\,dx}{(1+\alpha x^{\beta})(x+\alpha x^{1+\beta}+1/\tau)}. \tag{A1}$$

The next step is to find the leading-order term for the integral as $\tau \to \infty$. The sign of $\gamma + \beta - 1$ plays a pivotal role, as shown below.

If $\gamma + \beta > 1$, it is permissible to drop the $1/\tau$ term in the denominator, which gives

$$G_1 - Q_1 \sim W_1 = -\left(\frac{1}{\tau}\right)\int_0^\infty \frac{\alpha h(x)\,dx}{x^{1+\beta}(\alpha + x^{-\beta})^2}. \tag{A2}$$

Here W_1 is contributed by all species.

When $\gamma + \beta < 1$, the integral is dominated by the boundary layer near $x = 0$. Over this thin interval, $\alpha x^{1+\beta} \ll x$ and $x^{\beta} \ll 1$. Replacing $h(x)$ by its asymptotic form produces

$$G_1 - Q_1 = -\left(\frac{1}{\tau}\right)\int_0^\epsilon \frac{\alpha h_0 x^{\gamma+\beta-1}}{x+1/\tau}\,dx + O\left(\frac{1}{\tau}\right), \tag{A3}$$

where ϵ is a small number of $O(1/\tau)$. To enlarge the boundary-layer region, we let $y = \tau x$, which after some algebra gives

$$W_1(\tau) = -\alpha h_0 B(\gamma+\beta, 1-\gamma-\beta)\left(\frac{1}{\tau}\right)^{\gamma+\beta}, \qquad \gamma + \beta < 1. \tag{A4}$$

In deriving this expression, we have extended the upper limit of the integration to infinity with a small error.

The case $\gamma + \beta = 1$ can be treated by following the procedures outlined in Ho et al. (1990).

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