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Observer Theory for Lumping Analysis of Monomolecular Reaction Systems

A new approach for the lumping analysis of reversible and/or irreversible monomolecular reaction systems (MRS) with constant or time-dependent rate coefficients in discrete and continuous mixtures is presented. The observer theory initiated by Luenberger is proposed and extended to obtain the necessary and sufficient conditions of exact and approximate lumping of such systems. Examples are given to illustrate the implications of lumping and to demonstrate the generality and promising aspects of the observer approach. It is shown that this theory is a unifying method for the lumping analysis of MRS. New insights on lumping analysis are discussed.

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SCOPE

Among those chemical reaction systems encountered in chemical processes, the monomolecular reaction system (MRS) is of particular interest to chemical engineers. This follows because many complex reactions such as isomerization and catalytic hydrodesulfurization can frequently be approximated by first- or pseudo first-order reactions. In the kinetic analysis of such reactions which usually contain a large number of distinct chemical species (discrete mixture) or a continuous distribution of components (continuous mixture), it is convenient and practical to lump the species together into kinetically equivalent groups and treat them as independent lumped components. A typical example of this lumping practice is the PONA analysis used in petroleum processing, in which all chemical species in the feedstock to the reformer are lumped into four groups, namely paraffins, olefins, naphthenes, and aromatics.

An important practical question in applying such lumping procedures is whether the kinetic behavior of the original complex reaction system can be satisfactorily represented by the simplified kinetic system described by the lumped components; in an opposite sense the following question may also be raised: if an appropriate lumped kinetic model is known, how can the kinetic parameters of the original system be evaluated from the available measurements of the lumped kinetic system? The latter question has been answered comprehensively by Wei and Prater (1962), Silvestri and Prater (1964), Riekert and Wei (1968), and Prater et al. (1967, 1968, and 1970) by introducing the concept of an experimentally measurable straight-line reaction path for the reversible MRS in a discrete mixture. The former question, however, has been discussed only briefly in the work of Wei and Kuo (1968) and Bailey (1972). Both considered the conditions for the exact and approximate lumping of the reversible MRS in discrete and continuous mixtures, respectively, although the conditions for the exact lumping of a specific class of irreversible MRS in a continuous mixture was also given (Bailey, 1972).

A number of important difficulties, however, prohibit the practical applications of these lumping techniques. All require a priori knowledge of the complete set of kinetic rate coefficients and such information is rarely available in practice. In addition, these results are not applicable for the general irreversible MRS, for the MRS with noisy experimental measurements, or for the MRS with time-dependent rate coefficients such as reactions

proceeding under nonisothermal conditions and catalyst deactivation. The development of a new technique to overcome such problems presents a serious challenge.

In the present work, a new approach for the lumping analysis of reversible and/or irreversible MRS with constant or time-dependent rate coefficients in discrete and continuous mixtures is developed. The proposed method utilizes the observer theory for the estimation of unmeasurable state variables in the framework of control theory as initiated by Luenberger (1964). A number of examples and remarks are presented to illustrate the applicability and implications of the present method. The possibility of using this new approach to overcome the difficulties in previous work is demonstrated.

CONCLUSIONS AND SIGNIFICANCE

The present work demonstrates a new general approach for the lumping analysis of reversible and/or irreversible MRS with constant or time-dependent rate coefficients in discrete and continuous mixtures. Specifically, the development of observer theory initiated by Luenberger (1964) for control problems is proposed and extended to obtain the necessary and sufficient conditions of exact and approximate lumping of such systems. In addition to reproducing in a simple fashion most of the essential results obtained by previous authors (Wei and Kuo, 1968; Bailey, 1972), a number of examples including the reversible MRS and the irreversible catalytic cracking by direct fission in continuous mixtures, transient MRS coupled with diffusion with time-dependent rate coefficients in a discrete mixture are given to illustrate the implications of lumping and to indicate new insights between theory and experiments. The applicability of the present approach to the general MRS with reversible and/or irreversible reactions, with possibly unknown rate coefficients and with noisy experimental measurements are discussed. As developed, the observer theory is shown to be a unifying method for the lumping analysis of MRS which incorporates much of previous work as special cases, and allows rather different visualization of the behavior of such systems. It also successfully demonstrates a new application of modern control theory to practical chemical engineering problems.

DISCRETE AND CONTINUOUS MONOMOLECULAR REACTION MIXTURES

Wei and Prater (1962) have treated comprehensively the closed, isothermal MRS of an n-component discrete mixture described kinetically by a linear, vector differential equation

$$\frac{da}{dt} = -Ka(t) \qquad a(0) = a_0 \tag{1}$$

where a is an n-vector of concentration and K is a monomolecular reaction rate matrix. The concept of lumping was used to obtain the lumped kinetic model with the experimentally measurable straight line reaction path (SLRP) for evaluating the kinetic parameters of the original kinetic system. Aris and Gavalas (1966) have suggested that if the number of components is very large, the reacting components can be reasonably characterized by a continuous distribution variable r, for example, the carbon number of component hydrocarbons in a catalytic cracking process. Thus, if we consider $x(t, r)$ to be the component concentration at time t with continuous distribution variable r between r and $r + dr$, the continuous analogue to (1) for component concentration distribution in the MRS can be described kinetically by the linear, differential-integral equation

$$\frac{dx(t,r)}{dt} = -\int_{\alpha}^{\beta} K(u,r)x(t,u)\,du \triangleq -Kx(t,r) \qquad x(0,r) = x_0(r) \tag{2}$$

Here, $r, u \epsilon [\alpha, \beta]$ are continuous variables to characterize the mixture, $K(u, r)$ is the kinetic rate coefficient kernel, and $x_0(r)$ is the initial component concentration distribution. In the present work, we will develop a technique for specifying (a) whether a given lumped kinetic model is kinetically equivalent to the original kinetic model (1) or (2), and (b) how the kinetic parameters of the original kinetic system can be evaluated from the available measurements of the lumped kinetic system.

Comparing the kinetic models of the MRS in discrete and continuous mixtures, (1) and (2), we note two important properties. First, if we allow $x(t, r)$ to be a linear combination of Dirac delta functions, (1) is then a special form of (2). Secondly, it is known in the theory of linear operators that relative to a given coordinate basis, the linear integral kinetic kernel $K(u, r)$ determines a unique, kinetic rate coefficient matrix K, and conversely, each kinetic rate coefficient matrix generates a unique, linear integral kernel. Such close relationships suggest the possibility of finding an unified approach for lumping analysis of the MRS in both discrete and continuous mixtures.

OBSERVER THEORY

An observer for a given linear system, for example, a system described by (1) or (2), is an auxiliary linear model whose outputs can be used to approximate the unknown state vector of the original system. It is driven by the same inputs as the given system and its dynamical behavior is identical with that of the given system it observes. Since its first presentation by Luenberger (1964), the observer theory has been extended by several researchers to include time-varying systems, discrete systems, stochastic systems, and nonlinear systems. For an excellent introduction to observer theory and an account of its present status, two recent review papers are available (Luenberger, 1971; Tse and Athans, 1971). For our purpose, the simple observer theory for a free, linear dynamic system due to Luenberger (1964) is sufficient for the lumping analysis of MRS.

In its simplest form we consider observing a free system S_1 with its available outputs used as inputs to drive another system S_2. The second system is the observer of the first system since its state will tend to track a linear transformation of the state of the first system. Using the notation of Wei and Kuo (1968) the following theorem may be stated:

> "Theorem 1 (Luenberger, 1964): Let S_1 be an n-component MRS in a discrete mixture, $da/dt = -Ka(t)$, which drives another $\hat{n}$th order ($\hat{n} \leqq n$) lumped kinetic model, S_2, $d\hat{a}(t)/dt = -\hat{K}\hat{a}(t) - Ea(t)$. Suppose there is a nonsingular, linear lumping transformation M satisfying $MK - \hat{K}M = E$. If $\hat{a}(0) = Ma(0)$, then $\hat{a}(t) = Ma(t)$ for all $t \geqq 0$. Or more generally, $\hat{a}(t) - Ma(t) = e^{-\hat{K}t}[\hat{a}(0) - Ma(0)] = e(t)$."

It should be noted that the two systems S_1 and S_2 need not have the same dimension n and Theorem 1 is valid whether S_1 and S_2 are reversible and/or irreversible reaction systems.

It will be shown that this observer theorem essentially gives simply the previous results obtained by Wei and Kuo (1968) for lumping analysis of the MRS in a discrete mixture. To grasp the reasoning and implications behind the observer approach and to demonstrate its generality for lumping analysis of the MRS, we first extend the observer theory to a class of systems described by a linear, differential-integral equation, for example, (2). We summarize our results in Table 1 to display the parallelism of lumping analysis in discrete and continuous mixtures in the framework of the observer approach. For later discussions, results in Table 1 for a discrete mixture will be referred to by "d" and for continuous mixture by "c"; for example (9d) is $\hat{a}(t) = Ma(t)$.

We note that if (a) E is a null matrix or (b) Ea is a zero vector, (4d) reduces to

$$\frac{d\hat{a}(t)}{dt} = -\hat{K}\hat{a}(t) \qquad \hat{a}(0) \text{ unknown} \tag{10}$$

A kinetic system whose lumped component concentration, $\hat{a}(t)$, satisfies (10) is called *lumpable*. One inherent difficulty associated with the design of an observer for a linear dynamic system is that the initial condition $\hat{a}(0)$ is usually unknown. This is essentially the feature of the experimental method of Wei and Prater (1962) for a completely reversible MRS in a discrete mixture. It is necessary to determine one highly curved reaction path and then perform additional experiments to locate by successive approximation the correct initial condition for the SLRP. By this successive approximation for satisfying $\hat{a}(0) = Ma(0)$, an exactly lumped kinetic model, (7d) can be achieved. For the case of a completely reversible MRS in a discrete mixture, it has been shown that K is diagonalizable and M can be chosen as the characteristic vector matrix X. Thus, the condition (8d) gives

$$\hat{K} = MKM^{-1} = XKX^{-1} \tag{11}$$

The experimental implications of such result in terms of SLRP are well-known.

When the error matrix of lumping E is not a null matrix, (5d) will have a unique solution for M when matrices K and $\hat{K}$ have no common eigenvalues (Luenberger, 1964). Otherwise, the nonunique solution of (5d) allows for degrees of freedom in choosing M and E. For a certain choice of M, it has been shown by Balakrishnan (1966) that if $\hat{n} < n$, there exists an $\hat{n}$-vector obtained by the projection of a onto the linear subspace spanned by the $\hat{n}$ linearly independent column vectors chosen from the observability criterion matrix for linear dynamic system. Hence, the lumping matrix M takes the form of the orthogonal projection matrix such that the error matrix of lumping E satisfies the projection property $Ea = 0$. A similar observation was obtained later by Wei and Kuo (1968) who noted that the lumped component concentration space is spanned by the row vector of the matrix MA, where A is the diagonal equilibrium composition matrix. Thus, applying the orthogonal projection property to obtain the approximately lumped kinetic model, (10), is to restrict the possible lumped kinetic models (observers) to a specific class whose kinetic behavior is experimentally measurable.

Many of the above discussions for discrete mixture are also applicable to a continuous mixture. Instead of pursuing this in detail, we present a few examples to illustrate its implications.

EXAMPLES

Example 1. Reversible MRS in Continuous Mixture

The continuous analog to the kinetic model for a reversible MRS in a discrete mixture

$$\frac{da_i(t)}{dt} = -a_i(t)\sum_j k_{ij} + \sum_j k_{ji}a_j(t) \tag{12}$$

can be written as

$$\begin{aligned}\frac{dx(t,r)}{dt} &= -x(t,r)\left[\int_\alpha^\beta k(r,u)du\right] + \int_\alpha^\beta k(u,r)x(t,u)du \\ &= \int_\alpha^\beta \left[-\delta(u-r)\int_\alpha^\beta k(r,u)du + k(u,r)\right]x(t,u)du \\ &\triangleq \int_\alpha^\beta K(r,u)x(t,u)du \end{aligned} \tag{13}$$

Aris and Gavalas (1966) have shown that if the normalized kinetic kernel $K(r,u)/\int_\alpha^\beta K(r,u)du$ is Lebesgue square-integrable for $r, u \epsilon [\alpha, \beta]$, the kinetic system, (13), has at least one equilibrium concentration distribution. Furthermore, if the conditions of microscopic reversibility, conservation of mass, and non-negative concentration distribution are all satisfied, the equilibrium concentration distribution is unique and stable. This property suggests that we may assume $K(r,u)$ to be a Hilbert-Schmidt kernel satisfying $\int |K(r,u)|^2 drdu < \infty$ for $r, u \epsilon [\alpha, \beta]$. Noting the fact that a Hilbert-Schmidt kernel generates a completely continuous operator which can be approximated in norm by a separable operator generated by a separable kernel (Stakgold, 1967), we write

$$K(r,u) = \sum_{i=1}^{N} p_i(r)q_i(u) \tag{14}$$

where p_i, q_i are both Lebesgue square-integrable for $r, u \epsilon [\alpha, \beta]$. Since it is customary to characterize the reaction product of a MRS in a continuous mixture by lumping according to carbon number or molecular weight and to approximate each grouped species with the same rate coefficient distribution (Fabuss et al., 1962), the separable kernel approximation is convenient and practical. Thus, we assume the lumping operator $M(r)$ and the kinetic kernel $K(r, u)$ to be

$$M(r) = [U(r-r_0) - U(r-r_1) \,|\, U(r-r_1) - U(r-r_2) \,|\, \ldots \,|\, U(r-r_{N-1}) - U(r-r_N)]^T \quad (15)$$

$$K(r,u) = \sum_{i=1}^{N} [U(r-r_{i-1}) - U(r-r_i)]q_i(u) \quad (16)$$

where $r_0 = \alpha < r_1 < r_2 \ldots < r_{i-1} < r_i < r_{i+1} \ldots < r_N = \beta$ for $r \epsilon [\alpha, \beta]$, $U(r - r_0)$ is the unit step function and T denotes the transpose of a matrix. Introducing such approximations to the results in Table 1, we get the following theorem for the Wei-Prater reaction system in a continuous mixture:

> "Theorem 2: The completely reversible MRS in a continuous mixture described kinetically by (13), with its kinetic kernel in the form of (16), is exactly lumpable by the nonsingular, linear lumping operator $M(r)$ defined by (15). The resulting lumped kinetic model is given by (7c) where the elements of the corresponding lumped kinetic matrix $\hat{K}$ are given by
>
> $$(\hat{k})_{ij} = \begin{cases} \int_{r_{i-1}}^{r_i} q_i(u)du & i + j \\ -\int_{\alpha}^{r_{i-1}} q_i(u)du - \int_{r_i}^{\beta} q_i(u)du & i = j\text{''} \end{cases} \quad (17)$$

Example 2. Irreversible, Catalytic Cracking by Direct Fission

Consider the irreversible, catalytic cracking of a mixture of paraffins (C_rH_{2r+2}) by direct fission (Aris and Gavalas, 1966; Fabuss, et al., 1962).

$$C_rH_{2r+2} \rightarrow C_{r'}H_{2r'+2} + C_{(r-r')}H_{2(r-r')} \quad (18)$$

The rate of reaction is given by

$$\begin{aligned} \frac{dx(t,r)}{dt} &= -x(t,r)k(r) + \int_r^{\beta} k(r')\nu(r,r')x(t,r')dr' \\ &= \int_{\alpha}^{\beta} [-\delta(r-r')k(r') \\ &\quad + U(r-r')k(r')\nu(r,r')]x(t,r')dr' \\ &\triangleq \int_{\alpha}^{\beta} K(r,r')x(t,r')dr' \end{aligned} \quad (19)$$

where $\nu(r, r')$ is the fractional conversion of cracking reaction from C_rH_{2r+2} to $C_{r'}H_{2r'+2}$. Fabuss et al. (1962) have shown experimentally that it is possible to lump the cracking products into two groups according to the carbon number r, the gaseous product with $r < 5$ and the cracked liquid with $r \geqq 5$, and to correlate the kinetic rate coefficient distribution by the linear form suggested by Voge and Good (1949):

$$k(r) = (2.3r - 15.6) \times 10^{-6} \quad (20)$$

In terms of our lumping analysis, the lumping operator (15) is

$$M(r) = \begin{bmatrix} U(r) - U(r-5) \\ U(r-5) \end{bmatrix} \quad (21)$$

and the condition for exact lumping (8c) yields

$$\hat{K} = \begin{bmatrix} \hat{k}_{11} & \hat{k}_{12} \\ \hat{k}_{21} & \hat{k}_{22} \end{bmatrix} = \left[\begin{array}{c:c} -k(r_a) + \int_0^r a_k(r_a)\nu(r,r_a)dr & \int_0^{r_a} k(r_b)\nu(r,r_b)dr \\ \hdashline 0 & -k(r_b) + \int_5^{r_b} k(r_b)\nu(r,r_b)dr \end{array}\right] \quad (22)$$

where $r_a \epsilon [0, 5]$ and $r_b \epsilon [5, \beta]$ are carbon numbers. Since $\hat{K}$ is not a diagonal matrix, exact lumping is not necessarily valid. For the special case when $\hat{k}_{11} = 0$, (7c) yields a set of upcoupled lumped kinetic equations

$$\begin{aligned} \frac{d^2\hat{x}_1}{dt^2} &= \hat{k}_{12}\,\hat{k}_{22}\,\hat{x}_1 \\ \frac{d\hat{x}_2}{dt} &= -\hat{k}_{22}\,\hat{x}_2 \end{aligned} \quad (23)$$

However, the kinetic behavior described by these uncoupled equations is no longer monomolecular. Furthermore, $\hat{k}_{11} = 0$ implies that the fractional conversion $\nu(r, r_a)$ is fixed by the kinetic rate coefficient distribution $k(r_a)$ for every $r_a \epsilon [0, 5]$. It can be true only in exceptional circumstances when one can control the conversion of the reaction. This confirms the previous experimental observation (Fabuss et al., 1962) that an exactly lumped kinetic system in a continuous mixture is difficult to find in practice.

The above analysis also holds for cracking by direct fission of mixtures of paraffins and olefins, since as Aris and Gavalas (1966) have shown, the differential-integral equations describing their kinetic behaviors are uncoupled in the form of (19).

FURTHER DEVELOPMENTS

The observer approach given by Theorem 1 and Table 1 can be extended to a MRS with time-dependent rate coefficients such as reactions proceeding under nonisothermal conditions and catalyst deactivation. Here, we consider the MRS described kinetically by

$$\begin{aligned} \frac{da(t)}{dt} &= -K(t)a(t) \\ a(0) &= a_0 \end{aligned} \quad (24)$$

and a possible lumped kinetic model (observer)

$$\begin{aligned} \frac{d\hat{a}(t)}{dt} &= -\hat{K}(t)\,\hat{a}(t) - E(t)a(t) \\ \hat{a}(0) &\text{ unknown} \end{aligned} \quad (25)$$

It can be shown easily by direct substitution that if there is a nonsingular, linear lumping matrix $M(t)$ satisfying

$$M(t)K(t) - \hat{K}(t)M(t) - \dot{M}(t) = E(t) \quad (26)$$

then

$$\hat{a}(t) = M(t)a(t) + e(t) \tag{27}$$

Here $e(t)$ is a concentration error vector due to the unknown initial condition $\hat{a}(0)$ which satisfies the properties

$$\frac{de(t)}{dt} = -\hat{K}(t)e(t) \tag{28}$$

and

$$\lim_{t\to\infty} e(t) = 0 \tag{29}$$

Thus, (25) can be considered as an approximately lumped kinetic model for the kinetic system (24). In the special case when $E(t)$ is a null matrix for all $t > 0$, (25) and (26) can be combined to give a class of specific observers

$$\begin{aligned}\frac{d\hat{a}(t)}{dt} &= -\hat{K}(t)\hat{a}(t)\\ &= -[M(t)K(t) - \dot{M}(t)]M^{-1}(t)\,\hat{a}(t) \qquad (30)\\ &\hat{a}(0) \text{ unknown}\end{aligned}$$

which serves as a promising candidate for the exactly lumped kinetic model for the MRS with time-dependent rate coefficients, (25). We note from the theory of Lyapunov transformation of a linear dynamic system (Zadeh and Desoer, 1963) that there may exist a constant lumped kinetic matrix $\hat{K}$ satisfying

$$\hat{K} = [M(t)K(t) - \dot{M}(t)]M^{-1}(t) \tag{31}$$

Thus, it is sometimes possible to model a kinetic system with time-dependent rate coefficients by a kinetically equivalent time-invariant MRS given by (8d). For example, when the time dependence of $K(t)$ is contained in a scalar coefficient $p(t)$ with a diagonalizable constant matrix factor K_0,

$$K(t) = p(t)K_0 \tag{32}$$

(31) can be satisfied. This case was previously studied by Wei and Prater (1962) and Riekert and Wei (1968). The present observer approach, however, gives more general results concerning approximate and exact lumping for such systems. The extension of such results to continuous reaction mixtures is straightforward.

The above analysis can also be used to obtain new insights to the lumping of a class of distributed reaction systems, for example, the transient MRS coupled with diffusion. Consider an isothermal MRS coupled with diffusion in a catalyst particle with interior V and boundary ∂V. The transient behavior of the component concentration vector $a(r, t)$ at any spatial position $r \epsilon V$ satisfies

$$\begin{aligned}&\frac{\partial}{\partial t}a(r,t) = D(t)\nabla^2 a(r,t) - K(t)a(t) && r\epsilon V\\ &\text{with I.C.} \quad a(r,0) = a_0(r) && r\epsilon V \quad (33)\\ &\text{B.C.} \quad a(r,t) = a_e(t) && r\epsilon \partial V\end{aligned}$$

Here the effective diffusivity matrix D and rate coefficient matrix K may be time-dependent due to catalyst deactivation and time-varying diffusing medium. Wei and Kuo (1968) have studied the lumping of steady state MRS

TABLE 1. APPROXIMATE AND EXACT LUMPING

	Discrete mixture		Continuous mixture
1. Kinetic model	$\begin{cases}\dfrac{da}{dt} = -Ka(t)\\ a(0) = a_0\end{cases}$	(3)	$\begin{cases}\dfrac{dx(t,r)}{dt} = -\displaystyle\int_\alpha^\beta K(u,r)\,x(t,u)\,du\\ x(0,r) = x_0(r)\end{cases}$
2. Observer: approximately lumped kinetic model	$\begin{cases}\dfrac{d\hat{a}}{dt} = -\hat{K}\hat{a}(t) - Ea(t)\\ \hat{a}(0) \text{ unknown}\end{cases}$	(4)	$\begin{cases}\dfrac{d\hat{x}(t)}{dt} = -\hat{K}(t)\,\hat{x}(t) - \displaystyle\int_\alpha^\beta E(r)\,x(t,r)dr\\ \hat{x}(0) \text{ unknown}\end{cases}$
(a) condition	$MK - \hat{K}M = E$	(5)	$\displaystyle\int_\alpha^\beta \left[\int_\alpha^\beta M(u)\,K(u,r)du - \hat{K}(t)\,M(r)\right]x(t,r)dr = \int_\alpha^\beta E(r)\,x(t,r)dr$
(b) relationship	$\hat{a}(t) = Ma(t) + e(t)$	(6)	$\hat{x}(t) = \displaystyle\int_\alpha^\beta M(r)\,x(t,r)dr + e(t)$
3. Specific observer: exactly lumped kinetic model	$\begin{cases}\dfrac{d\hat{a}(t)}{dt} = -\hat{K}\hat{a}(t)\\ \hat{a}(0) = Ma(0)\end{cases}$	(7)	$\begin{cases}\dfrac{d\hat{x}(t)}{dt} = -\hat{K}(t)\,\hat{x}(t)\\ \hat{x}(0) = \displaystyle\int_\alpha^\beta M(r)\,x_0(r)dr\end{cases}$
(a) condition	$MK = \hat{K}M$	(8)	$\displaystyle\int_\alpha^\beta \left[\int_\alpha^\beta M(u)\,K(u,r)du\right]x(t,r)dr = \int_\alpha^\beta \hat{K}(t)\,M(r)\,x(t,r)dr$
(b) relationship	$\hat{a}(t) = Ma(t)$	(9)	$\hat{x}(t) = \displaystyle\int_\alpha^\beta M(r)\,x(t,r)dr$

coupled with diffusion when both D and K are constant matrices, and observed that the exact lumping implies the diffusivities of species that are lumped together must be equal. By using the separation of variables and expanding $a(r, t)$ in the eigenfunctions of the Laplace operator that are appropriate to the configuration of the catalyst particle, the transient equation (33) can be transformed into a set of ordinary differential equations for the time-dependent coefficients in the eigenfunction expansion $T_i(t)$

$$\frac{dT_i(t)}{dt} = -[\lambda_i D(t) + K(t)]T_i(t) \qquad (34)$$

where i is the eigenfunction index and λ_i the corresponding eigenvalues. Comparing (24) and (34), we note that if $D(t)$ and $K(t)$ are products of a scalar time function with a diagonalizable constant matrix factor of the form $D(t) = p(t)D_0$ and $K(t) = q(t)K_0$, then it is possible to get a kinetically equivalent time-invariant lumped kinetic model in the form of (7d). However, this is valid only in exceptional cases. Since even if D and K are both constant matrices, they can be simultaneously diagonalized only if they have a complete set of common eigenvectors and therefore commute, that is, with $DK = KD$. Such strongly restrictive conditions for exact lumping of transient MRS coupled with diffusion cannot be satisfied in most cases.

CONCLUDING REMARKS

To emphasize the generality of the present approach for kinetic analysis by lumping in MRS, we discuss a few related publications and demonstrate the promising aspects of this observer approach.

It is worthwhile to comment briefly on the connections between the present work and those of Wei and Kuo (1968) and Bailey (1972). The latter paper is a most interesting extension of the former, with both considering the conditions and implications of the approximate and exact lumping of reversible MRS, in discrete and continuous mixtures, respectively. Using a completely different and much simpler approach, the present work has reproduced many of the essential results of these authors, and has also demonstrated the generality of the observer approach for the lumping of reversible and/or irreversible MRS with constant or time-dependent rate coefficients in both discrete and continuous mixtures. The latter is evident as there are no specific assumptions incorporated in the general results stated in Theorem 1 and Table 1. These results have also indicated additional insights between theory and experiment. For example, the initial conditions for the approximately and exactly lumped kinetic models together with experimental implication in terms of the SLRP in the method of Wei and Prater (1962) have been stated. Thus the observer theory seems to be a unifying method for the lumping analysis of MRS which incorporates much of the previous work as special cases.

Prater et al. (1967, 1968, and 1970) have shown that a general system of first-order reactions can be expressed in terms of reversible subsystems interconnected by irreversible steps. They have considered the approximate lumping of such systems by applying the projection properties of the concentration vector to each reversible subsystem. The conditions for approximate lumping they obtained can be reproduced simply by the observer theory. However, there are considerable advantages of the observer approach for kinetic analysis by lumping, since as we have shown it is applicable whether the MRS is reversible and/or irreversible, with constant or time-dependent rate coefficients, in discrete or continuous reaction mixtures. In addition, recent results on designing the minimal order subobservers and composite observers (Fortmann and Williamson, 1972; Luenberger, 1971) can be conveniently used to obtain the lumped kinetic models for each reversible subsystem and the whole system with a minimum number of lumped components.

The observer approach can also apply to the kinetic analysis of MRS with noisy measurement by lumping. Recently, Lombardo and Hall (1971) have noted the difficulties in locating exactly the initial conditions of the lumped kinetic systems (SLRP) and the experimental errors in measuring concentration in the method of Wei and Prater (1962). They assume the experimental measurements are subjected to errors with zero mean and equal variance and then choose the initial conditions for the SLRP by minimizing the least-square error. Knowing the role of the observer theory in the lumping analysis, we can easily relax this assumption of errors with zero mean and equal variance, as the design of observer with arbitrary initial condition statistics, for example, with nonzero mean and arbitrary variance, is available (Aoki, 1967; Luenberger, 1971; Tse and Athans, 1971). A similar investigation of lumping according to rate coefficient k in continuous mixtures by Hutchinson and Luss (1970) has used certain convex inequalities to obtain the upper and lower bounds on the behavior of the lumped concentration distribution from the knowledge of the first and second moments of the initial concentration distribution $x(0, k)$. Due to the special forms of the inequalities used, they cannot obtain general bounds concerning the behavior of the lumped component concentration $\hat{x}(t)$ if the lumping operator $M(k)$ in (6c) is not in the form of Dirac delta functions. The observer approach, however, provides an explicit way of estimating the error in component concentration by approximate lumping, for example, the continuous analog to (28) and (29) in the discrete mixture. Detailed discussions are available in the literature (Luenberger, 1964, 1971; Tse and Athans, 1971).

Finally, we mention the most promising aspect of the observer approach for kinetic analysis by lumping. As is also pointed out by Hutchinson and Luss (1970), the lumping analysis of Wei and Kuo (1968) requires a priori knowledge of all kinetic constants, that is, the matrix K, and such information is rarely available. This disadvantage, however, does not affect the generality of the observer approach. For example, Aoki (1967) has developed a class of specific observers (lumped kinetic models) when some of the elements of the matrix K in (1) are unknown under the assumption that there exist some matrices P and Q such that either PK and/or KQ are null matrices. The latter constraint is essentially satisfied by noting that the principle of mass conservation requires $1^T K = 0^T$ or $K1 = 0$ for a reversible MRS or a reversible subsystem in a general MRS. Furthermore, a systematic procedure for choosing the proper lumping matrix M to minimize some error criterion in this case is also available in this work. The possibility of using the observer approach for optimal lumping of MRS is thus encouraging.

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NOTATION

a = n-vector of component composition in a discrete reaction mixture

a_e = n-vector of component composition on ∂V in a discrete reaction mixture
a_i = ith element of the vector a
a_0 = n-vector of initial component composition in a discrete reaction mixture
$a_0(r)$ = initial component composition distribution function for species in a continuous reaction mixture
$a(r, t)$ = n-vector of component composition in a catalyst particle at any spatial position $r \epsilon V$ and time t
$\hat{a}$ = $\hat{n}$-vector of lumped composition in a discrete reaction mixture
A = diagonal equilibrium component composition matrix for a reversible, discrete monomolecular reaction system
A_i = ith reacting species in the original discrete or continuous reaction mixture
$\hat{A}_i$ = ith reacting species in the lumped discrete or continuous reaction mixture
D = effective diffusivity matrix
$e(t)$ = $\hat{n}$-vector of component composition error due to the unknown $\hat{a}(0)$
E = error matrix in a discrete reaction mixture, defined in Table 1
$E(r)$ = error function in a continuous reaction mixture, defined in Table 1
$k(r, u)$ = distribution function of reaction rate coefficient in a discrete reaction mixture
k_{ij} = reaction rate coefficient for reaction $A_j \rightarrow A_i$
$\hat{k}_{ij}$ = lumped reaction rate coefficient for reaction $\hat{A}_j \rightarrow \hat{A}_i$
K = kinetic rate coefficient matrix in a discrete reaction mixture
$K(r, u)$ = kinetic rate coefficient kernel in a continuous reaction mixture
K_0 = constant diagonalizable matrix factor of K, defined in (32)
$\hat{K}$ = lumped kinetic rate coefficient matrix in a discrete reaction mixture
M = lumping matrix in a discrete reaction mixture
$M(r)$ = lumping function in a continuous reaction mixture
$\dot{M}(t)$ = time derivative of the lumping matrix M
n = number of elements in the vector a
$\hat{n}$ = number of elements in the vector $\hat{a}$
$p(t)$ = scalar factor for K, defined in (32)
$p_i(r)$ = term appearing in $K(r, u)$, defined in (14)
$q_i(u)$ = term appearing in $K(r, u)$, defined in (14)
r = continuous distribution variable for molecular species, reactions in a continuous reaction mixture
r' = continuous distribution variable for molecular species, reactions in a continuous reaction mixture
t = time
$T_i(t)$ = ith time-dependent coefficient in the eigenfunction expansion of the Laplace operator, defined in (33) and (34)
u = continuous distribution variable for molecular species, reactions in a continuous reaction mixture
$U(r - r_i)$ = unit step function
V = interior of a catalyst particle
∂V = boundary of V
$x(t, r)$ = component composition distribution function in a continuous reaction mixture
$x_0(r)$ = initial component composition distribution function in a continuous reaction mixture
$\hat{x}(t)$ = lumped component composition distribution function in a continuous reaction mixture
x_i = ith eigenvector matrix of matrix K
X = eigenvector matrix of matrix K, defined as $(x_1, x_2, \ldots x_n)$
α = lower bound of the continuous distribution variable r or u
β = upper bound of the continuous distribution variable r or u
$\delta(u - r)$ = Dirac delta function
λ_i = ith eigenvalue of the matrix K
$\nu(r, r')$ = fractional conversion of cracking reaction of paraffin, (18)
1 = column vector with 1 as its elements $(1, 1, \ldots 1)$
0 = null vector or null matrix
$\triangleq$ = defined as
$(\cdot)^T$ = quantity $(\cdot)$ transposed

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