Identifiability and Distinguishability of Fundamental Parameters in Catalytic Methanation

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Methods are presented to determine structural identifiability and distinguishability of parametric models. Results are applied to transient isotope tracing of methanation over a nickel catalyst. More meaningful information is obtained in this way about fundamental parameters than is possible by empirical curve-fitting.

SCOPE

A large proportion of industrial reactions involves heterogeneous catalysis systems. In the study of such systems kinetic equations are often developed by means of the so-called Langmuir-Hinshelwood-Hougen-Watson (LHHW) method. This method assumes that the Langmuir theory of adsorption and the law of mass action apply to the individual steps of a reaction mechanism, that a single rate-controlling step exists with the other steps at equilibrium. Such assumptions have led to reservations in acceptance of the intrinsic significance of the parameters obtained and in the applicability of the equations developed to a wider range of process conditions.

With transient isotope tracing, the parameters to be directly estimated are the concentrations of intermediates and the rates of elementary steps. These parameters may be functions of the temperature and gas phase composition. However, the exact functional relationships required to estimate them from overall kinetic data are generally not well established. Since these concentrations and rates are estimated in the present treatment without relying on the above mentioned assumptions (needed by the LHHW method), we propose to call them fundamental parameters.

The technique employed is similar to compartmental modeling, which has often been employed in the biosciences. Each of the terminal species and chemisorbed intermediates is assumed to occupy a well-mixed compartment and the transfer of isotope is described by material balances on each compartment. The parameters to be obtained appear as constants in a set of first-order differential equations and can be estimated using readily available computer routines.

In order to establish the extent to which parameters obtained are unique, it is necessary to consider problems of identifiability and distinguishability. This paper discusses how this can be accomplished with special reference to experimental studies in which transfer of ^{13}C was used to study the kinetics of catalytic methanation of mixtures of carbon monoxide and hydrogen (synthesis gas).

CONCLUSIONS AND SIGNIFICANCE

Even if a model is not uniquely identifiable, some computer routines (gradient methods for example) may be able to find parameter values. It is therefore desirable to consider whether other sets of parameters can

equally well correlate given experimental data. For a suitable model we show how such a set can be used to generate all other possible sets consistent with the given model structure. These parameters can then be examined from the standpoint of other information available on the basis of physical or theoretical knowledge of the system. If ambiguity still exists, it may be possible to alter the nature of tracer input or the tracer species employed to eliminate it.

In practical systems there may exist more than a single plausible model. It is shown how such additional models can be studied structurally to determine whether they are distinguishable from an initial model that correlates the data. In addition, methods are discussed whereby one can employ the parameters from the initial "generating" model to calculate all the possible parameters corresponding to models with the same external behavior. In turn these parameters can be examined from the standpoint of physical and chemical consistency.

The techniques discussed are in the context of transient isotopic tracing, although they can also be employed in LHHW modeling if desired. One of the values of their use in transient tracing is that it may be possible to resolve problems of rate-controlling steps at the outset, thus simplifying the problem of further construction of overall rate equations. This work should be useful to engineers concerned with the development of rate equations for the design or optimization of chemical process reactors. It should also furnish guidance in catalyst formulation by directing attention to reaction steps that constitute bottlenecks in obtaining improved conversion and selectivity.

Introduction

In this paper linear time-invariant state-space models are considered, although more complicated models are possible in transient tracing (Walter, 1982). It is supposed that a variable $x(t)$ belonging to IR^n describes the state of the system being modeled, that a variable $\boldsymbol{u}(t)$ belonging to IR^m, piecewise continuous, is permitted to act on the system at each instant (this is the input), and that a variable $y(t)$ belonging to IR^p corresponds to observations on the system (this is the output).

The corresponding state-space model can be written as:

$$\begin{aligned} \dot{x}(t) &= \boldsymbol{A}\, x(t) + \boldsymbol{B} u(t) \\ y(t) &= \boldsymbol{C}\, x(t) \end{aligned} \tag{1}$$

where the matrices $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{C}$ are real and independent of time (stationarity).

Roughly speaking a model is then identifiable if one can determine the numerical value of each element of these matrices from available information. Often, as is the case in the following examples, it is only possible to observe the points of entry and exit, so that the system behaves like a black box. However, if suitable instrumentation is available observations could also be conducted at intermediate points. They would then be included in the output vector y.

The first papers dealing with identifiability appeared in econometrics (Koopmans et al., 1950; Fisher, 1959, 1961), and dealt with models described by algebraic equations. For dynamic models described by ordinary differential equations, Berman and Schoenfeld (1956) addressed the problem of generating all the models having the same behavior, without explicitly using the term identifiability. Ho and Whalen (1963) and Fisher (1965) considered the identifiability of state-space models in the special (and rather restrictive) case where all the state variables are accessible to measurement. Bellman and Åström (1970) gave the first clear-cut definition of structural identifiability of dynamic models and triggered interest for this notion among people involved in mathematical modeling of biological systems. Many papers have been published since then, mostly in mathematical biosciences. For a more complete bibliography see Walter (1982) or Godfrey and DiStefano (1985).

In chemical kinetics the matrices $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{C}$ depend on the specific conditions and catalyst involved and a hypothesis concerning a mechanism yields family of models $\boldsymbol{M}(\boldsymbol{\theta}) = [\boldsymbol{A}(\boldsymbol{\theta}), \boldsymbol{B}(\boldsymbol{\theta}), \boldsymbol{C}(\boldsymbol{\theta})]$ parameterized by the constants $\boldsymbol{\theta} = (\theta_1, \ldots, \boldsymbol{\theta})^T$. Thus for identification one may seek the best possible values of $\theta_1, \ldots \boldsymbol{\theta}$, parameters for a model. If these values are unique, the model is said to be identifiable. More precisely, a model $\boldsymbol{M}(\boldsymbol{\theta})$ is structurally globally identifiable (SGI) if and only if, for all values of its parameter vector $\boldsymbol{\theta}$ (except possibly for some very special values), there exists an input function $\boldsymbol{u}$ such that the relation

$$y(t, \boldsymbol{\theta}', \mathbf{u}) = y(t, \boldsymbol{\theta}, \mathbf{u}) \text{ for all } t > 0 \tag{2}$$

implies that $\boldsymbol{\theta}' = \boldsymbol{\theta}$.

Note that structural global identifiability is a property of the model itself that is assessed independently of any measurements.

Local structural identifiability is a weaker condition than the former. A model $\boldsymbol{M}(\boldsymbol{\theta})$ is structurally locally identifiable (SLI) if and only if, under the same assumptions, Eq. 2 implies that $\boldsymbol{\theta}'$ belongs to a denumerable set. For practical applications this set should be finite and small.

From a practical standpoint, for any reasonable input (a step function, for example) there is therefore only one unique parameter vector that corresponds to a given output behavior for a SGI model. On the other hand, for a SLI model, there exists a number of parameter vectors corresponding to exactly the same output behavior.

Quite often it happens that entirely different choices of model structures are possible. The second question that it is necessary to pose is: Can one differentiate between two models by means of their input-output behavior (distinguishability)? If this is not the case one would have to abandon hope of knowing which corresponds to the "real" mechanism of the chemical reaction studied, unless other information was available.

A model $\hat{M}(\hat{\theta})$ is structurally distinguishable (SD) from another model $M(\theta)$, if and only if, for all values of the parameter vector θ (except possibly for some very special values), there exists an input function u such that the equation

$$\hat{y}(t, \hat{\theta}, u) = y(t, \theta, u) \text{ for all } t \geq 0 \qquad (3)$$

admits no solution for $\hat{\theta}$.

Note that $\hat{y}$ and y in Eq. 3 refer to the output of models $\hat{M}$ and M respectively.

The problem is here more complicated than in the case of identifiability studies. It is necessary first to test the distinguishability of M from $\hat{M}$ and then of $\hat{M}$ from M. When M is SD from $\hat{M}$ and $\hat{M}$ is SD from M, M and $\hat{M}$ are said to be SD. If such is the case, the two models cannot have the same output behavior.

These properties and algorithms have been considered in the case of structurally global identifiability and distinguishability for several systems by Happel et al. (1986). In the present paper, we wish to extend the treatment to the case where only local identifiability exists. In order to take advantage of the results of structural studies when modeling real data, we need to obtain from appropriate experiments at least one numerical estimate for the parameter vector θ. The methods described will then make it possible to generate all the other numerical parameter sets that will correspond to a model correlating the data in exactly the same way. To illustrate how this can be done, we shall consider tracer data obtained for the methanation of mixtures of carbon monoxide and hydrogen.

Studies illustrating identifiability and distinguishability

The production of methane by hydrogenation of carbon monoxide is of interest because it is a route for the production of pipeline gas from coal. The reaction proceeds for the most part by the overall equation $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$.

One method for studying the mechanism consists in the introduction of ^{13}CO into the reacting system as a step function in which ^{13}CO replaces unmarked CO, so that the reaction remains at steady state. One follows by mass spectrometry the evolution in time of the proportion of marked atoms in the carbon monoxide and methane leaving the system. The usual formalism for describing experiments using tracers is that of compartmental models. The following examples illustrate the usefulness of structural identifiability/distinguishability studies in conjunction with actual data analysis.

Example 1

The model envisaged to describe the evolution of marked carbon during the production of methane coming from carbon monoxide is presented in Figure 1. Compartments 1 and 2 correspond respectively to active and inactive carbon adsorbed on the catalyst. Compartment 3 combines the different hydrocarbon adsorbed species (CHl, CH_2l, CH_3l). Compartment 4 is associated with methane in the gas phase.

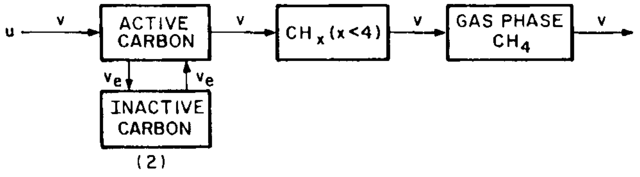

Figure 1. Compartmental model for ^{13}C tracing, structure 1.

The following equations describe the evolution of the proportions x_i of marked carbon atoms in the different compartments i ($i = 1, \ldots, 4$), deduced by material balances on each compartment:

$$\begin{aligned} C_1\dot{x}_1 &= -(v + v_e)x_1 + v_e x_2 + vu \\ C_2\dot{x}_2 &= -v_e x_2 + v_e x_1 \\ C_3\dot{x}_3 &= -v x_3 + v x_1 \\ C_4\dot{x}_4 &= -v x_4 + v x_3 \end{aligned} \qquad (4)$$

The reactor being at steady state, C_1, C_2, C_3, and v_e are constant for any given experimental condition and can thus be considered as parameters to be estimated. C_4 and v, which are also constants, can be directly measured, just as in usual kinetic experiments. The study of the effect of temperature, pressure, and gas phase composition on these parameters can be the subject of additional research in which a series of experiments is conducted at various constant temperatures, pressures, and gas phase compositions.

From Eq. 4, it is apparent that the rates of tracer transfer are linear with respect to the tracer concentrations. The tracer quantities accessible to measurement in this experiment are the input $u(t)$ and the output $y(t) = x_4(t)$, both measured for $t \in (t_1, t_2)$.

The method employed for testing structural properties that is convenient for these systems is based on first obtaining the transfer function (Walter, 1982; Happel et al., 1986). For all models (A, B, C) the transfer function $H(s) = C(sI\text{-}A)^{-1}B$ contains all the information regarding input-output behavior. In the case of a model structure $[A(\theta), B(\theta), C(\theta)]$ coefficients of the normalized transfer function depend on the parameters θ and correspond to identifiable parameter groupings. We will call $\psi(\theta)$ the vector formed from all of these groupings.

For the model in Figure 1, the transfer function can be obtained by taking the Laplace transform of the associated differential equation at zero initial condition and writing down the ratio of the Laplace transform of the output to the Laplace transform of the input. This can be done by hand or more readily by a program written in an algebraic manipulation language such as REDUCE, (Hearn, 1983):

$$H_2(s) = \frac{1}{1 + \frac{C_4}{v}s} \times \frac{1 + \left(\frac{C_2}{v_3} + \frac{C_2}{v}\right)s}{\left[\begin{aligned} &1 + s\left(\frac{C_2}{v_e} + \frac{C_1}{v} + \frac{C_2}{v} + \frac{C_3}{v}\right) \\ &+ s^2\left(\frac{C_1C_2}{vv_e} + \frac{C_2C_3}{v_e v} + \frac{C_1C_3}{vv} + \frac{C_2C_3}{vv}\right) \\ &+ s^3\left(\frac{C_1C_2C_3}{vv_e v}\right) \end{aligned}\right]} \qquad (5)$$

The first factor in Eq. 5 contains no parameters, so consideration can be limited to the second factor, which in order to simplify the notation, can be written with θ defined as

$$\theta_1 = \frac{C_1}{v}$$

$$\theta_2 = \frac{C_2}{v}$$

$$\theta_3 = \frac{C_3}{v}$$

$$\theta_4 = \frac{C_2}{v_e} \qquad (6)$$

Since v is known there exists a one-to-one correspondence between the newly defined θ and the original parameters C_1, C_2, C_3, v_e, and we can deduce the identifiability of the original parameters from that of θ. Thus one has

$$\frac{1 + \theta_4 s}{\left[\begin{array}{r} 1 + s(\theta_1 + \theta_2 + \theta_3 + \theta_4) \\ + s^2(\theta_1\theta_3 + \theta_1\theta_4 + \theta_2\theta_3 + \theta_3\theta_4) \\ + s^3(\theta_1\theta_3\theta_4) \end{array}\right]} \qquad (7)$$

From Eq. 7, a vector $\psi_1(\theta)$ of identifiable parameter groupings can be derived

$$\psi_1(\theta) = \begin{bmatrix} \theta_4 \\ \theta_1 + \theta_2 + \theta_3 + \theta_4 \\ \theta_1\theta_3 + \theta_1\theta_4 + \theta_2\theta_3 + \theta_3\theta_4 \\ \theta_1\theta_3\theta_4 \end{bmatrix} \qquad (8)$$

To test for global identifiability it is necessary to show that for almost all θ,

$$\psi_1(\theta') = \psi_1(\theta) \quad \text{implies that } \theta' = \theta \qquad (10)$$

This is equivalent to determining whether the following set of equations derived directly from Eq. 8 can lead to a unique solution of the parameters θ' in terms of θ.

$$\begin{gathered} \theta'_4 = \theta_4 \\ \theta'_1 + \theta'_2 + \theta'_3 + \theta'_4 = \theta_1 + \theta_2 + \theta_3 + \theta_4 \\ \theta'_1\theta'_3 + \theta'_1\theta'_4 + \theta'_2\theta'_3 + \theta'_3\theta'_4 = \theta_1\theta_3 + \theta_1\theta_4 + \theta_2\theta_3 + \theta_3\theta_4 \\ \theta'_1\theta'_3\theta'_4 = \theta_1\theta_3\theta_4 \end{gathered} \qquad (11)$$

This is a system of polynomial equations that can be solved using the REDUCE routine for algebraic manipulation. It can also be solved by hand. By elimination of θ'_2, θ'_3, and θ'_4 one obtains from Eq. 11

$$(\theta'_3)^3 - (\theta'_3)^2(\theta_1 + \theta_2 + \theta_3 + \theta_4) + \theta'_3(\theta_1\theta_3 + \theta_1\theta_4 + \theta_2\theta_3 + \theta_3\theta_4) - \theta_1\theta_3\theta_4 = 0 \qquad (12)$$

Since Eq. 12 has the trivial solution $\theta'_3 = \theta_3$, the lefthand side of the equation can be factored to obtain

$$(\theta'_3 - \theta_3)[\theta'^2_3 - \theta'_3(\theta_1 + \theta_2 + \theta_4) + \theta_1\theta_4] \qquad (13)$$

so that there are three possible values for θ'_3 as follows:

$$\theta'_3 = \theta_3$$

$$\theta'_3 = \frac{\theta_1 + \theta_2 + \theta_4 + \sqrt{\Delta_1}}{2}$$

$$\theta'_3 = \frac{\theta_1 + \theta_2 + \theta_4 - \sqrt{\Delta_1}}{2} \qquad (14)$$

with $\Delta_1 = (\theta_1 + \theta_2 + \theta_4)^2 - 4\theta_1\theta_4$, which means that the model described by Eq. 4 is not SGI. From Eq. 11, it is now possible to calculate the values of θ'_1 and θ'_2 associated with each possible value of θ'_3:

$$\theta'_1 = \frac{\theta_1\theta_3}{\theta'_3} \qquad (15)$$

$$\theta'_2 = \theta_1 + \theta_2 + \theta_3 - \theta'_3 - \frac{\theta_1\theta_3}{\theta'_3} \qquad (16)$$

Thus, the model described by Eq. 4 is SLI. From any numerical set of parameters, it is possible to compute two additional sets of parameters from the above equations. The three possible values of the original parameters are then readily calculated using Eq. 6. Note that $\theta'_4 = \theta_4 = C_2/v_e$.

As an illustration of the method, the data corresponding to the ^{13}CO step-up run no. 011680 in Table 2 of the paper by Otarod et al. (1983) were employed in conjunction with the previous equations to generate the three values for the four parameters in the model described by Eq. 4. The parameter vector for the generating model is not the same as originally presented, but corresponds to an improved fit of the data. One of the parameter vectors generated was rejected because it gave negative values of C_2 and v_e. The remaining parameter set corresponded to physically acceptable values. Table 1 presents the parameter sets corresponding to the generating model (column 1) and the acceptable generated model (column 2). Note that the parameters are listed with a number of significant digits that corresponds to the accuracy of the computer, which is larger than can be supported by the experimental data. In this table surface concentrations are given in mL/g catalyst STP and the exchange velocity in mL/g · min as in the original paper.

Another matter to be considered, using the same system, is whether other models could be constructed to fit the data

Table 1. Possible Values for Model Structure 1 Parameter Estimates

	Set	
Parameters	1	2
C_1, active carbon	1.630000	0.2620114
C_2, inactive carbon	5.338000	5.849728
C_3, absorbed CH_x	0.1640000	1.020261
v_e, exchange vel.	0.1770000	0.1939681

$v = 0.33$ mL/g · min

equally well, i.e., the problem of distinguishability. This problem is addressed in the following example for one given alternative structure. Others could have been considered as well.

Example 2

The same reaction of methanation with the same ^{13}C data is employed to test the applicability of a different model, given by Figure 2. In this model the compartments designate the same species as previously but it is assumed that the inactive carbon instead of exchanging with the active form can itself slowly react to produce the hydrocarbon intermediates.

The state equations for this model are

$$\begin{aligned} C_1\dot{x}_1 &= -vx_1 + vu \\ C_2\dot{x}_2 &= -v_1x_2 + v_1x_1 \\ C_3\dot{x}_3 &= -vx_3 + (v - v_1)x_1 + v_1x_2 \\ C_4\dot{x}_4 &= -vx_4 + vx_3 \end{aligned} \tag{17}$$

Here the parameters to be estimated are C_1, C_2, C_3, and v_1. As in the case of identifiability it is first necessary to obtain the normalized transfer function for this model, which we designate by the subscript 2.

Following the same procedure as previously, we have

$$H_2(s) = \frac{1}{1 + \frac{C_4}{v}s} \times \frac{1 + \left(\frac{C_2}{v_3} - \frac{C_2}{v}\right)s}{\left[\begin{aligned} &1 + s\left(\frac{C_1}{v} + \frac{C_2}{v_1} + \frac{C_3}{v}\right) \\ &+ s^2\left(\frac{C_1C_2}{vv_1} + \frac{C_1C_3}{vv} + \frac{C_2C_3}{v_1v}\right) \\ &+ s^3\left(\frac{C_1C_2C_3}{vv_1v}\right) \end{aligned}\right]} \tag{18}$$

and defining $\hat{\theta}$ as

$$\begin{aligned} \hat{\theta}_1 &= \frac{C_1}{v} \\ \hat{\theta}_2 &= \frac{C_2}{v} \\ \hat{\theta}_3 &= \frac{C_3}{v} \\ \hat{\theta}_4 &= \frac{C_2}{v_1} \end{aligned} \tag{19}$$

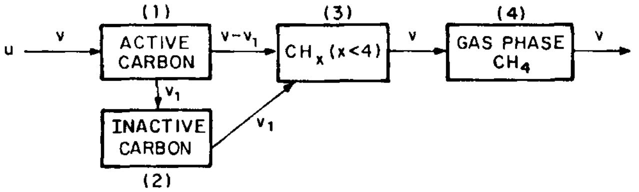

Figure 2. Compartmental model for ^{13}C tracing, structure 2.

we write the second factor of Eq. 18 as

$$\frac{1 + (\hat{\theta}_4 - \hat{\theta}_2)\,s}{1 + s(\hat{\theta}_1 + \hat{\theta}_3 + \hat{\theta}_4) + s^2\,(\hat{\theta}_1\hat{\theta}_3 + \hat{\theta}_1\hat{\theta}_4 + \hat{\theta}_3\hat{\theta}_4) + s^3\,(\hat{\theta}_1\hat{\theta}_3\hat{\theta}_4)} \tag{20}$$

As before, from this vector of the identifiable parameter groupings, $\psi_2(\hat{\theta})$ can be written

$$\psi_1(\hat{\theta}) = \begin{bmatrix} \hat{\theta}_4 - \hat{\theta}_2 \\ \hat{\theta}_1 + \hat{\theta}_3 + \hat{\theta}_4 \\ \hat{\theta}_1\hat{\theta}_3 + \hat{\theta}_1\hat{\theta}_4 + \hat{\theta}_3\hat{\theta}_4 \\ \hat{\theta}_1\hat{\theta}_3\hat{\theta}_4 \end{bmatrix} \tag{21}$$

We showed in example 1 that model 1 was structurally locally identifiable and that a set of three possible solutions existed. Now in this example we wish to know whether it is possible to compute parameter vectors for model 2 that would yield the same model output as obtained with model 1, and thus correlate the experimental data in exactly the same way. If so, it would prove that model 2 is indistinguishable from model 1. This is equivalent to obtaining a solution for $\hat{\theta}$ based on a set of equations derived from Eqs. 8 and 21 as follows:

$$\begin{aligned} \hat{\theta}_4 - \hat{\theta}_2 &= \theta_4 \\ \hat{\theta}_1 + \hat{\theta}_3 + \hat{\theta}_4 &= \theta_1 + \theta_2 + \theta_3 + \theta_4 \\ \hat{\theta}_1\hat{\theta}_3 + \hat{\theta}_1\hat{\theta}_4 + \hat{\theta}_3\hat{\theta}_4 &= \theta_1\theta_3 + \theta_1\theta_4 + \theta_2\theta_3 + \theta_3\theta_4 \\ \hat{\theta}_1\hat{\theta}_3\hat{\theta}_4 &= \theta_1\theta_3\theta_4 \end{aligned} \tag{22}$$

Using the REDUCE algebraic manipulation routine, the following solution is obtained for $\hat{\theta}$:

$$\begin{aligned} \hat{\theta}_1 &= \frac{\theta_1 + \theta_2 + \theta_4 - \sqrt{(\theta_1 + \theta_2 + \theta_4)^2 - 4\theta_1\theta_4}}{2} \\ \hat{\theta}_2 &= \theta_3 - \theta_4 \\ \hat{\theta}_3 &= \frac{\theta_1 + \theta_2 + \theta_4 + \sqrt{(\theta_1 + \theta_2 + \theta_4)^2 - 4\theta_1\theta_4}}{2} \\ \hat{\theta}_4 &= \theta_3 \end{aligned} \tag{23}$$

This solution can be checked by substitution of values from Eq. 23 into Eq. 22.

Thus model 2 cannot be distinguished from model 1, and using any specified local solution θ for model 1, we can compute a set of parameters $\hat{\theta}$ for model 2. We have similarly tested the distinguishability of model 1 from model 2. The test shows that model 1 is structurally indistinguishable from model 2, so that model 1 and model 2 are structurally indistinguishable. This means that if we happened to have initiated the search with model 2, we would have arrived at the same conclusion concerning the set of possible models.

In addition, we must now study the identifiability of model 2 in order to determine whether it can furnish more than the single set of parameters generated by Eq. 23 from those in model 1. This is accomplished by following the same procedure as in example 1, but using the transfer function corresponding to Eq. 18 instead of Eq. 5. It is found that there are six possible parameter sets that can be written as follows:

$$\begin{array}{lll}
1)\ \hat{\theta}'_1 = \hat{\theta}_1 & 2)\ \hat{\theta}'_1 = \hat{\theta}_3 & 3)\ \hat{\theta}'_1 = \hat{\theta}_4 \\
\quad \hat{\theta}'_2 = \hat{\theta}_2 & \quad \hat{\theta}'_2 = \hat{\theta}_2 & \quad \hat{\theta}'_2 = \hat{\theta}_2 + \hat{\theta}_3 - \hat{\theta}_4 \\
\quad \hat{\theta}'_3 = \hat{\theta}_3 & \quad \hat{\theta}'_3 = \hat{\theta}_1 & \quad \hat{\theta}'_3 = \hat{\theta}_1 \\
\quad \hat{\theta}'_4 = \hat{\theta}_4 & \quad \hat{\theta}'_4 = \hat{\theta}_4 & \quad \hat{\theta}'_4 = \hat{\theta}_3 \\
\\
4)\ \hat{\theta}'_1 = \hat{\theta}_1 & 5)\ \hat{\theta}'_1 = \hat{\theta}_3 & 6)\ \hat{\theta}'_1 = \hat{\theta}_4 \\
\quad \hat{\theta}'_2 = \hat{\theta}_2 + \hat{\theta}_3 - \hat{\theta}_4 & \quad \hat{\theta}'_2 = \hat{\theta}_1 + \hat{\theta}_2 - \hat{\theta}_4 & \quad \hat{\theta}'_2 = \hat{\theta}_1 + \hat{\theta}_2 - \hat{\theta}_4 \\
\quad \hat{\theta}'_3 = \hat{\theta}_4 & \quad \hat{\theta}'_3 = \hat{\theta}_4 & \quad \hat{\theta}'_3 = \hat{\theta}_3 \\
\quad \hat{\theta}'_4 = \hat{\theta}_3 & \quad \hat{\theta}'_4 = \hat{\theta}_1 & \quad \hat{\theta}'_4 = \hat{\theta}_1
\end{array} \tag{24}$$

The same six possible sets of parameters could also have been obtained by writing down all the solutions for $\hat{\theta}$ of Eq. 22.

From any numerical set of parameters for model 1, it is now possible using Eq. 23 to compute a numerical set of parameters for model 2. The remaining five numerical sets of parameters for model 2 can then be computed from the first one using Eq. 24. We generated the six parameter vectors for model 2 that corresponded to the parameter vectors for model 1 given in Table 1. Four of them happened to be associated with negative values of C_2. The remaining two are given in Table 2.

Interpretation of Tables 1 and 2

From these two tables, we are left with four parameter sets for further consideration. In an earlier work with deuterium tracing (Happel et al., 1982), it was shown that the combined CH_x species were present at a higher concentration than that of the active carbon. On these grounds, it seems reasonable to rule out parameter set 1 in both Tables 1 and 2. It is worthwhile noting that C_3 takes the same value in both remaining sets and that the sum of C_1 and C_2 is also identical. The parameters in both sets have the same order of magnitude as those published by Otarod et al. (1983). They thus lead to the same qualitative conclusions. A new thought introduced in the present paper is that the data are consistent with the production of methane from "inactive" carbon. This question requires further investigation along the lines reported in the survey by Biloen and Sachtler (1981).

Discussion

Methods are presented for using the concepts of identifiability and distinguishability for the examination of models employed in transient isotope tracing studies of catalytic reaction mechanisms. The so-called compartmental models that can be employed in such studies involve sets of linear ordinary differential equations with constant coefficients. Such equations are widely employed in process control and in the biosciences, so that a considerable body of information has been developed which should find increasing application in chemical engineering. In this paper application to parameter estimation has been explored.

Usually the interpretation of tracer data requires the selection of a most likely model from among a number of possible candidates. The notion of identifiability can be employed at the outset to indicate whether it is indeed possible to obtain desired parameters uniquely. If the parameters cannot be uniquely obtained, it is shown that a given local solution can be employed to generate all the remaining local solutions for the parameters.

Then, without having a computer estimation of parameters, it is possible to study the distinguishability of any competing models. Furthermore, using the values for the set of parameters corresponding to the original fitted model, it is then possible to compute all the parameter sets for the given indistinguishable competing model. Note that since the interpretation is based on structural properties of the models independent of any specific data, it is not affected by the noisiness of the experimental data to be correlated. If the numerical model obtained by processing the data with any standard estimation procedure fits the data satisfactorily then all other models to be generated will fit the data in exactly the same way.

The results reported here can be applied to improve catalyst formulations, since they enable the limiting steps in a catalytic mechanism to be identified rather than only the overall reaction rate. In addition, if kinetic rate equations are to be developed using generally accepted methods such as the Langmuir-Hinchelwood-Hougen-Watson (LHHW) technique, a priori identification of rate-controlling steps should be effective in eliminating the necessity of determining them from the usual overall rate data. This would provide considerable simplification in the formulation of such rate expressions.

Results similar to those reported in this paper may often be difficult to obtain without the use of algebraic manipulation routines such as that presented by Walter and Lecourtier (1982) for the solution of sets of nonlinear algebraic equations. The subject is presently an active field of research on the part of mathematicians and computer specialists.

The sets of parameters resulting from a structural study can be examined in conjunction with other information developed for any given system. In the case of catalytic reactions, this will include detection of surface intermediates by a variety of spectroscopies, measurement of adsorption and desorption characteristics of species involved, auxiliary kinetic measurements, theoretical calculation of step velocities, as well as the employment of other tracers and different input-output regimes with the same tracer. As in the examples treated in this paper, such considerations can serve to narrow the choice of physically acceptable models.

Table 2. Possible Values for Model Structure 2 Parameter Estimates

Parameters	Set 1	Set 2
C_1, active carbon	1.020261	0.1640000
C_2, inactive carbon	5.947740	5.947740
C_3, absorbed CH_x	0.1640000	1.020261
v_1, rate of transfer to inactive carbon	0.1234441	0.1234441

$v = 0.33$ mL/g · min

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Notation

A = matrix associated with states
B = matrix associated with controls
C = observation matrix
C_1, C_2, C_3, C_4 = concentrations of species
$H_1(s), H_2(s)$ = transfer functions
I = identity matrix
$\mathrm{IR}^n, \mathrm{IR}^m, \mathrm{IR}^p$ = Euclidean spaces of dimension n, m, p
s = Laplace transform variable
t = time
u = vector of inputs
v = rate of methanation
v_e = rate of exchange between active and inactive carbon
v_l = rate of transfer to inactive carbon
x = state vector
$\dot{x} = dx/dt$
ψ = vector of identifiable parameter groupings
θ = parameter vector

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