

The Mathematical Modeling of Heterogeneous Catalytic Processes

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Abstract. The basic strategies in the mathematical modeling of heterogeneous catalytic processes are reviewed. A novel approach together with a general computational scheme are presented for modeling any heterogeneous catalytic reaction. The proposed mathematical approach permits dynamic simulation of process performance as a function of all major operating variables, including time, and provisions are made to include interactions between catalyst deactivation and catalyst selectivity. Furthermore, necessary conditions are formulated that permit internal consistency checks. The principles and approach outlined are expected to be helpful in developing new mathematical process models and in improving the general validity and predictive capabilities of existing process correlations/models.

Introduction

To aid in the design and operation of commercial heterogeneous catalytic reactors, a number of mathematical models have been developed. Mathematical models of heterogeneous catalytic reactions are concerned principally with two areas of catalyst performance prediction: 1) selectivity and 2) activity and stability. To predict selectivity, *i.e.* yield structure, as a function of operating conditions and feed composition, kinetic models have been built that are designed to simulate the actual reactions.

Kinetic models that attempt to simulate the actually observed yield structures have been developed and published for hydrocracking [1–5], for catalytic cracking [6–9], for naphtha reforming [10–12], and hydrotreating [13–16], as well as for steam methane reforming [17] [18].

To accommodate for slight differences in catalyst manufacture and/or catalyst pretreatment, which in turn effect differences in selectivity, catalyst activity factors (relative catalyst functional activities) have been introduced. Depending upon the general validity of the modeling approach, adjustments of these activity factors only may be required to adapt a kinetic model from a given catalyst to another, if the two catalyst systems do not differ significantly.

Mathematical simulation of catalyst activity and stability is usually accomplished *via* a catalyst-deactivation model. Here again, slight differences in catalyst manufacture and/or pretreatment may be accommodated by adjustment of appropriate activity factors. Furthermore, changing from a given catalyst system to another may also be accomplished by appropriate adjustments in the catalyst activity factors,

if the two catalyst systems do not differ significantly. Here again, catalyst deactivation models have been proposed for catalytic cracking [6] [7] [9] [19], naphtha reforming [10–12], hydrotreating [23–25], and steam methane reforming [20]. Aside from the above mentioned, somewhat reaction-specific deactivation models/mechanisms, more general catalyst deactivation phenomena and mechanisms have been discussed and reviewed quite frequently [21] [22]. Furthermore, the influence of diffusion and mass-transfer limitations on the reaction kinetics is now quite well understood [26–29].

In most instances, separate routes have been followed to develop the kinetic and the deactivation models. As a consequence, interactions between the two types of models are confined to specific aspects of the process at hand, and they have to be approximate by some simplifying assumptions. The strategy of this approach is generally dictated by the extreme complexity of the task, as well as the need to develop useful correlations in as short a time as possible.

Note that the underlying reason for the complexity is due to the fact that 'so-called' kinetic separability is only possible for a few special cases [30–32], *i.e.*

$r_{ii} = a$ (past history)₁ · r_{oi} (present conditions)

r_{ii} = Rate at present conditions for species *i* after experiencing processing sequence [1]

a (past history)₁ = Activity after experiencing processing sequence [1]

r_{oi} (present conditions) = Rate for species *i* at activity = 1.0 and present conditions

Furthermore, it has been pointed out that the assumption of surface homogeneity is not sufficient to guarantee separability [31] [32]. Thus, there is a need to develop a formalism and associated calculation scheme that provide a sound basis for an integrated yield structure/deactivation model package.

Mathematical Modeling

In the following, the fundamental principles are presented for development of a single mathematical model that predicts both yields and catalyst deactivation. The interaction between catalyst deactivation and catalyst selectivity is also reflected in this model.

Yield-structure models for heterogeneous catalytic reactions may be represented by the following equation:

$$\frac{d\vec{S}}{d\tau} = M[\vec{C}, \vec{A}\vec{c}(\bar{t})] R[k_{ij}(T)] I(\vec{S}) \vec{S} \quad (1)$$

$$\tau = 1/WHSV$$

$WHSV$ = Weight hourly space velocity
 \vec{S} = Species vector, includes heteroatom species

M = Matrix function of conditions and activities

R = Matrix of rate constants, k_{ij}

T = Temperature

\vec{C} = Conditions (P, T, H₂/Oil, *etc.*)

$\vec{A}\vec{c}(\bar{t})$ = Activity vector (average across reactor) at time \bar{t}

\bar{t} = $(t_i + t_{i+1}) / 2$ = Average elapsed time for which $S_i(\bar{t})$ is calculated

t_i = Time after *i* changes in conditions and/or feed have been made

t_{i+1} = Time after *i* + 1 changes in conditions and/or feed have been made

$I(\vec{S})$ = Matrix of inhibition effects

$\vec{S}_0 = \vec{F}$ = Feed vector

$\vec{S}_i(\bar{t})$ = Product composition at reactor exit ($WHSV = 1/\tau$) and time \bar{t}

Note that the components of the activity vector $\vec{A}\vec{c}(\bar{t})$ should reflect physically meaningful phenomena such as surface coverage, pore blockage, extent of poisoning, level of coke formation, *etc.*, and, in turn, these entities affect certain types and/or entire classes of reaction rate constants. In mathematical terms:

$$k_{ij}^e(\vec{C}) = k_{ij} \cdot (\vec{C}) \cdot A_{cm}$$

$k_{ij}^e(\vec{C})$ = Effective rate constant, adjusted for conditions and deactivation

$k_{ij}(\vec{C})$ = Rate constant (adjusted for conditions)

A_{cm} = Component *m* of activity vector

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To illustrate the chosen formalism, well-known examples of commercial processes may aid in its understanding. In hydrocracking for instance, certain types of catalyst deactivation phenomena are thought of as being related to 'soft coke' that brings about 'semi-irreversible' deactivation, whereas others are believed to be due to 'hard coke' that is responsible for irreversible deactivation. In the case of 'soft coke' deactivation, catalytic activity can be restored after catalyst exposure to high hydrogen partial pressure at elevated temperature, *i.e.* hydrogen stripping. However, catalytic activity cannot be restored by hydrogen stripping, when deactivation is due to 'hard coke'. Note that recent experimental evidence by Barbier [22] has confirmed the existence of two types of coke in catalytic reforming.

To further clarify the meaning of the activity vector, let us consider hydrotreating operations of distillate fractions, *i.e.* materials typically in the boiling range of 300–650°F. Depending upon requirements, the given operation might be conducted to result in a product target level of: *a)* aromatics, *b)* sulfur, *c)* nitrogen or, *d)* a given hydrogen uptake. Clearly then, a mathematical model capable to describe successive operations of types *a)* through *d)* requires a knowledge of how the relevant functions (respective activities) under consideration change as a function of these types of operations and time.

In analogy to the above examples, a 'complete' naphtha reforming model should be capable of describing successive operations involving, for instance: *a)* target aromatics production, *b)* target hydrogen production, *c)* operation at constant 'average bed temperature'.

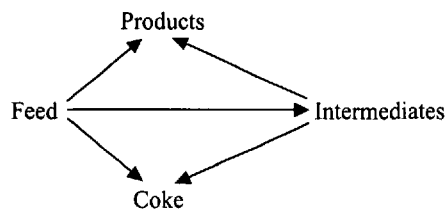
A catalyst deactivation model may be formulated as follows:

$$\vec{A}\vec{c}(\bar{t}) = \vec{A}\vec{c}(t_i, t_{i+1}, \vec{C}, \vec{S}_{av}(\bar{t}), \text{KS}) \quad (2)$$

$$\vec{S}_{av}(\bar{t}) = \frac{\vec{S}_o(\bar{t}) + \vec{S}_i(\bar{t})}{2}$$

= Average concentration across reactor at \bar{t}

KS = Kinetic scheme of deactivation:



Owing to the rather complex deactivation relationships involved, most components in the deactivation vector $\vec{A}\vec{c}$ cannot be evaluated explicitly, and thus must be determined *via* iterative algorithms. This situation is principally due to the adiabaticity of reactor (or at least sections of a reactor) operation which affects: *a)* reaction rate constants (*via Arrhenius* relationships) and, hence, the species vector, and *b)* adsorption/desorption equilibria. Since

both of these phenomena interact with each other, it is easily understood that iterative algorithms are required.

The simultaneous solution of *Eqns. 1* and *2* provides information on both selectivity and deactivation of the catalyst, if the mathematical representations involved in the two sets of equations reflect actual catalyst behavior. As indicated, *Eqns. 1* and *2* are dependent on the catalyst activity vector, $\vec{A}\vec{c}(\bar{t})$. This vector has to be exactly the same for both equations, since the catalyst experiences changes in both selectivity and activity simultaneously and yet the catalyst 'does not know' which set of equations is being solved. Thus, the criterion for simultaneous solution of the two equations depends on finding the steady-state value for the activity vector, $\vec{A}\vec{c}_{ss}$, that satisfies both equations. This value may be found by an algorithm as outlined below.

To initiate the calculation for a fresh catalyst, a starting value for $\vec{A}\vec{c} = \vec{A}\vec{c}_o$ is assumed, and then *Eqn. 1* is solved. The average concentrations, $\vec{S}_{av}(\bar{t})$, are then substituted into *Eqn. 2* and the system solved for $\vec{A}\vec{c}$, whereby the solution $\vec{A}\vec{c}_{o1}$ is found.

If, for each component *k*,

$$|\vec{A}\vec{c}_{ok}| - |\vec{A}\vec{c}_{o1k}| \leq |\vec{\epsilon}_k| \quad (3)$$

$\vec{\epsilon}$ = Convergence tolerance

Then $\vec{A}\vec{c}_{ss}(\bar{t})$ is found. If *Eqn. 3* is not satisfied, the solution of *Eqn. 2* is substituted for $\vec{A}\vec{c}$ in *Eqn. 1* and the computation repeated, until a steady state value for $\vec{A}\vec{c}$ is found that satisfies both equations.

For a partially deactivated catalyst, *i.e.*, a catalyst that has been in service for some time, the same basic computational scheme is applied. However, instead of guessing the initial value for activity (due to small difference in catalyst manufacturing and pretreatment) as was required for a fresh catalyst, the steady-state value of the activity vector for the preceding time increment is substituted into *Eqn. 1* and the system of equations solved, until the appropriate steady state value of the activity is found.

It is emphasized again that the two systems of equations have to converge to one and only steady-state value for the activity vector. If no solution is found, *i.e.*, divergence occurs, which means that the functional relationships in either one or both of the two sets of equations do not reflect actual catalyst behavior. Convergence to a unique solution for $\vec{A}\vec{c}_{ss}(\bar{t})$ is a necessary condition that has to be satisfied, and it may be used as one criterion to determine the validity of the functional relationships built into the model. Additional (sufficiency) criteria are, of course, agreement between experimental and predicted performance data for a wide variety of conditions and feed compositions.

It is noted that, for the proposed modeling approach and computational scheme, any other physically meaningful condition or constraint may be imposed on the system. Such a condition or constraint re-

quires an additional degree of freedom so that the overall system can attain a solution while satisfying the constraint. This additional degree of freedom may be added by allowing to vary at least one component of the vector of the operating conditions. Thus, the system of *Eqns. 1* and *2* may be solved for a constraint of the following form:

$$|P_g(\vec{S}_t)| - |P_r(\vec{S}_t)| \leq \epsilon_c \quad (4)$$

$P_g(\vec{S}_t)$ obtained at conditions \vec{C}_t and time \bar{t}
 $P_r(\vec{S}_t)$ set at conditions \vec{C}_t ; (\vec{C}_t is not known)

\vec{C}_t = Vector of assumed operating conditions

\vec{C}_r = Vector of required operating conditions

$P_g(\vec{S}_t)$ = Average calculated property of the reaction product at time \bar{t}

$P_r(\vec{S}_t)$ = Required average value of the property of the reaction product at time \bar{t}

ϵ_c = Convergence tolerance for constraint.

It may be noted that the time increment $\Delta t = t_{i+1} - t_i$ can be chosen as small as desired. Thus, the properties $P_g(\vec{S}_t)$ and $P_r(\vec{S}_t)$ can be calculated for any point in time.

To best illustrate what the constraint, *Eqn. 4*, may mean in practice, some examples of commercial processes are cited. In first-stage hydrocracking (also called pretreatment), the hydrogen uptake may be restricted to a set value whereby adjustment of either space velocity, or more frequently, temperature is permitted. More common in first-stage hydrocracking is operation to obtain a target nitrogen level in the product by varying operating temperature. In second-stage hydrocracking (*i.e.* molecular-weight reduction), the most frequent mode of operation is so-called recycle to extinction operation. In this mode, the amount of recycle feed to the reactor is held constant and all of the fresh feed is converted into products. Operation at these condition and catalyst deactivation are compensated for by an increase in operating temperature.

In catalytic cracking, operation at a set conversion is carried out by varying temperature, space velocity or catalyst circulation rate. Operation of the catalytic reformer may be carried out to obtain a target aromatics (*i.e.* octane number) value in the product by varying temperature or space velocity.

To satisfy constraint (*Eqn. 4*) in the proposed model, an additional algorithm has to be developed that adjusts the particular component or components of the operating vector. The computational scheme for such an algorithm determines first the steady-state value of the activity vector for any arbitrary value of the vector of the operating conditions. The property that has to attain a required value is then determined, and this value is substituted in *Eqn. 4*.

If *Eqn. 4* is satisfied, the operating conditions are found that satisfy the constraint. If this is not the case, the particular component of the operating vector is adjusted. In

most instances, not only the direction of the adjustment is known, but also its approximate order of magnitude, since detailed processing studies allow estimation of this adjustment based upon the differences of the required and actual properties. After adjusting the vector of the operating conditions, Eqns. 1 and 2 are solved, until the new steady-state value of the activity vector is found; the desired property again determined and checked against its required value. If the new value for the property satisfies Eqn. 4, the calculation is terminated. If this is not the case, the vector of the operating condition is again adjusted. Linear interpolation can now be used to determine this adjustment, since two previous values of the desired property together with the values of the appropriate vectors of the operating conditions are known. The computational scheme is now continued. That is, the steady-state value of the activity vector is determined, the value of the property calculated and checked against the required value. If an additional adjustment in the vector of the operating conditions should be necessary, interpolation is carried out between those two values of the property, and associated vectors of operating conditions, that are closest to the required property. The algorithm is eventually terminated when the constraint Eqn. 4 is satisfied.

It is pointed out that the principles of the proposed model for heterogeneous catalytic reactions have been discussed for the specific situation where the components of

the steady-state activity vector are assumed to be composed of average values over the entire reactor. The more general case, where the components of this vector as well as the product vector \bar{S}_i , vary considerably as a function of catalyst bed length, is treated in a similar manner.

Instead of determining average values of the steady state activity vector and the product vector across the entire bed, the values of these vectors may be calculated in a similar manner across finite increments of the catalyst bed.

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Determination of Heats of Reaction under Refluxing Conditions

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Abstract. The accuracy of thermal measurements under reflux conditions strongly depends on the experimental conditions. The temperature difference $T_j - T_R$ imposed on the system and the temperature of the reactor lid and reflux equipment play an important role. The optimization of these parameters and their use in the evaluation of different chemical model reactions is shown.

1. Introduction

In industrial processes, some reactions are advantageously run under reflux conditions, because the boiling point is the highest reaction temperature available at

atmospheric pressure. In this way, the highest reaction rate can be achieved in a conventional reactor, increasing the productivity and profitability of an industrial unit. Moreover, using a condenser, the heat removal can be increased consider-

ably compared to the heat exchange across the reactor wall. This is due to two reasons:

- The heat exchange area of a reactor is limited, while the condenser can be dimensioned independently of the tank geometry.
- The overall heat-transfer coefficient of a condenser is higher than that of a reactor wall, where heat transfer is due to forced convection.

However, such a process is not free of risks. In case of a cooling failure and with inflammable solvents, an explosive cloud may form, or, due to loss of control of the reaction, the boiling rate can dramatically

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