Using the Power-Law Rate Expression for Assessment of Rate Data and Detection of Infeasible Mechanisms for Reversible Reactions

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A procedure for analysis of experimental data and model discrimination in regression of rate data of reversible, heterogeneous reactions which uses the power-law rate expression is described. The numerical values of the power-law parameters are calculated first by regression of the experimental data. These parameters are used to assess whether the quality of the experimental data is sufficient to render the following mechanistic model discrimination process conclusive. The parameter values of the power-law rate expression are also used for initial screening of the mechanism-based rate expressions, to discard infeasible models. The use of the proposed procedure is demonstrated using two examples from the literature.

A. Introduction

The design of a catalytic reactor involves the need for a correlation relating the reaction rates and partial pressures of the various reactants and products, for the particular type of catalyst. The most widely used rate expressions are those based on the extended Langmuir−Hinschelwood theory, which are often referred to as Hougen and Watson (1947) rate expressions (LHHW). The selection of the most appropriate rate expression is a lengthy process, involving postulation of reaction mechanisms, isothermal regression for discarding obviously inappropriate mechanisms, nonisothermal regression, and the use of physicochemical criteria for selecting the most appropriate one from among competing mechanisms. Kittrell (1970), Froment (1975), and Froment and Bischoff (1990) discuss in detail the various steps of the model discrimination process and present extensive literature review of the subject. The physicochemical aspects employed are discussed by Boudart and Djéga-Marriadassou (1984) and by Boudart (1986).

The effort associated with model discrimination can be substantially reduced if inappropriate rate expressions are discarded at a very early stage. It is even more important to detect at an early stage of model discrimination data which is not precise enough or otherwise insufficient for determining the correct rate mechanism. Imprecision of the available data is often mentioned as a cause for inaccurate parameter values (Froment and Bischoff, 1990). It can even prevent discrimination between several proposed models (Churchill, 1992).

In this paper, a method is presented for using the numerical values of the power-law rate expression parameters for discarding some or all the inappropriate mechanism-based rate expressions. It is shown that this simple model can also be used to detect linear dependency among the concentrations of the reactants and products and rate data which is not precise enough.

B. Relationship between Power-Law and Mechanism-Based Rate Expressions

Let us consider a rather general form of a mechanism-based rate expression for a reversible reaction:

$$r = \frac{k(HT)}{\left[1 + \sum_{n=1}^{N} K_i x_i^{m_i}\right]^n} \tag{1}$$

where HT is the rate expression for the homogeneous reaction, $x_i (i=1,N)$ are the partial pressures of the reactants and products, and k and $K_i (i=1,N)$ are the parameters of the rate expression. These parameters are calculated by regression of experimental data, and they must all be positive for a feasible mechanism. A typical rate expression for a simple homogeneous reaction such as $A + B \rightleftharpoons C + D$ can be $HT = x_1 x_2 - x_3 x_4/K$, where x_1, x_2, x_3, and x_4 are the partial pressures of A, B, C, and D respectively. The form of HT and the associated equilibrium constant K are usually known a priori from thermodynamic considerations.

A corresponding power-law rate expression can be written in the following form:

$$r = k'(HT) \prod_{i=1}^{N} x_i^{a_i} \tag{2}$$

where k' and $a_i (i=1,N)$ are the parameters to be calculated based on experimental data.

Let us consider the expression for $k(HT)/r$ in the LHHW rate expression (eq 1) versus the expression for $k'(HT)/r$ in the power law rate expression (eq 2). Expanding the expression in the denominator of eq 1 shows that the lowest power of x_i (denoted $\alpha_{i,\min}$) is zero, while the highest power (denoted $\alpha_{i,\max}$) is nm_i. In eq 2, x_i appears in a single power: a_i.

Brauner and Shacham (1996) have shown that when eq 1 represents a feasible rate expression for the particular set of rate data, the inverse of the power of x_i, $-a_i$, will be between the minimum (zero) and maximum $(m_i n)$ powers defined by eq 1. Thus, in order for eq 1 to be a feasible rate expression, the following inequalities must be satisfied for all the N components involved in the reaction:

$$\alpha_{i,\min} = 0 \leq -a_i \leq nm_i = \alpha_{i,\max} \qquad i = 1,2, ..., N \tag{3}$$

The parameters "a_i" of the power law rate expression

are usually calculated by regression of experimental data and are therefore subject to uncertainty. The uncertainty is usually indicated by confidence intervals (say 95% confidence intervals). Thus the values of the parameters a_i are in the interval:

$$\tilde{a}_i - \epsilon_i < a_i < \tilde{a}_i + \epsilon_i \qquad (4)$$

where $\tilde{a}_i$ is the estimated value of a_i and ϵ_i is the confidence interval.

Any value of a_i inside the interval indicated by eq 4 is to be considered while applying inequality 3. A special case to be considered is when $|\tilde{a}_i| < \epsilon_i$. In such a case the value $a_i = 0$ is inside the confidence interval; thus, in the statistical sense, such a value is as good as any other value inside this interval. Setting $a_i = 0$ means that x_i can possibly be removed from both eq 2 and the denominator of eq 1.

It should be emphasized that regression of different sets of data, covering different partial pressure regions for the various components involved in the reaction, will yield different a_i values. However, inequalities 3 must hold for all of these regions.

Inequality 3 can be used in order to discard infeasible mechanism-based rate expressions. The parameters of the power-law expression can be obtained by performing a single linear or nonlinear regression. The values of, $\alpha_{i,\max}$ and $\alpha_{i,\min}$ can be found for the different postulated rate expressions by inspection. If a postulated rate expression violates any of the inequalities 3, it can be removed from further consideration. If it satisfies these inequalities, it will have to be further analyzed.

C. Assessing the Quality and Precision of the Data

There are two common reasons for a parameter (a_i) being not significantly different from zero. The first is that the rate is not affected by the particular variable (x_i in this case) besides the HT term. Another reason can be that x_i is linearly dependent on the other independent variable(s) as a result of improper experimental design.

Plots of x_i vs x_j can reveal a linear dependence among presumed independent variables. Experimental data which is aligned along a straight line in any of such plots indicate a linear dependence among the corresponding independent variables. Such data are insufficient for any further study, and more properly designed experiments will have to be carried out to obtain an appropriate set of data. Some rate data reported in the literature include linearly dependent partial pressures, as demonstrated by Shacham and Brauner (1995).

If no linear dependence among the independent variables is detected, then a_i being not significantly different from zero implies that there is no statistical justification to keep all the variables in the power-law rate expression (eq 2). One or more of the independent variables can be removed until all the remaining parameters are significantly different from zero. The quality of the correlations (the original one with all the variables included and the one including only variables with parameters significantly different from zero) can be compared using residual plots.

In formulating eqs 1 and 2 it was assumed that the reaction is reversible. While this fact is known a priori, often the contribution of the reverse reaction is too small to be noticeable because of "noise" due to experimental error in the measured rate data.

The significance of the information included in a given set of experimental data regarding the reverse reaction can be assessed by correlating the data with a power-law rate expression. First, the parameters of the rate expression are calculated using the equilibrium K obtained from thermodynamics. For instance, considering a reversible reaction A + B $\leftrightharpoons$ C + D with known power-law parameter values, (eq 2) can be rewritten as:

$$\frac{r}{K'x_1^{a_1} x_2^{a_2} x_3^{a_3} x_4^{a_4}} - x_1 x_2 = -\frac{1}{K}x_3 x_4 \qquad (5)$$

Plotting the left-hand side (LHS) of eq 5 versus $x_3 x_4$ should give a straight line with a slope of $-1/K$. If the contribution of the reverse reaction is not significantly above that of the experimental errors noise level, this plot will result in randomly located points not indicating any clear trend.

Another option is to carry out nonlinear regression on eq 2 when the equilibrium K is used as one of the parameters for minimization. If the reverse reaction is significant, the optimal value of K must closely fit the value predicted from thermodynamic principles. Otherwise, either this procedure will yield an absurd value for K or no clear minimum will be found.

In the following two sections, two examples will be presented to demonstrate the use of the power-law rate expression parameters for assessing the quality of the experimental data and for preliminary screening of the mechanism-based rate expressions. The numerical calculations in these examples were carried out using the nonlinear regression option of the POLYMATH program (Shacham and Cutlip, 1994).

D. Example 1: Water−Gas Shift Reaction

For the first example, data from Podolski and Kim (1974) is used. They investigated the water−gas shift reaction over an iron oxide-based catalyst. The experiments were carried out at temperatures of 360, 381, and 404 °C and near atmospheric pressure.

The homogeneous rate expression for this reaction is:

$$HT = P_{CO}P_{H_2O} - P_{CO_2}P_{H_2}/K \qquad (6)$$

The following equilibrium K values, reported by Podolski and Kim (1974), were used: $K = 18.07$ at 360 °C; $K = 14.29$ at 381 °C; and $K = 11.22$ at 404 °C. The power-law rate expression that is used for model discrimination studies reads:

$$r = K'P_{CO}{}^{a}P_{H_2O}{}^{b}P_{CO_2}{}^{c}P_{H_2}{}^{d}(HT) \qquad (7)$$

The parameters, including 95% confidence intervals, obtained for the data at 360 °C, using the nonlinear regression option in POLYMATH (numbers are rounded to four significant digits) are $K' = (2.1 \pm 0.8017) \times 10^{-3}$, $a = -0.067\,12 \pm 0.1975$, $b = -1.0186 \pm 0.1129$, $c = -0.1193 \pm 0.054\,61$, $d = -0.052\,39 \pm 0.052\,06$, and $S^2 = 5.0 \times 10^{-9}$. S^2 is the sum of squares of errors over n_p data points defined as:

$$S^2 = \sum_{i=1}^{n_p}(r_{i,\text{obs}} - r_{i,\text{calc}})^2 \qquad (8)$$

Figure 1 presents the residual plot of error = $r_{\text{obs}} - r_{\text{calc}}$ versus r, for the data at 360 °C represented by eq 7. It can be seen that the error is randomly distributed
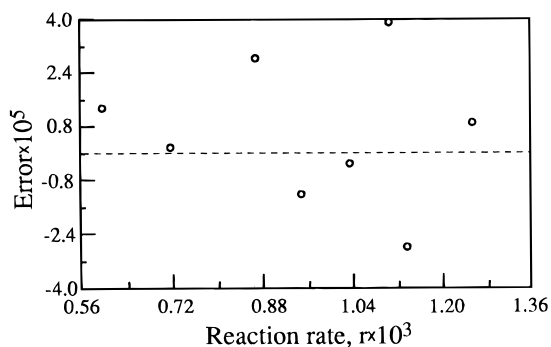
Figure 1. Residual plot for Podolski and Kim's (1974) rate data at 360 °C represented by five-parameter power-law rate expression (error $r_{obs} - r_{calc}$).
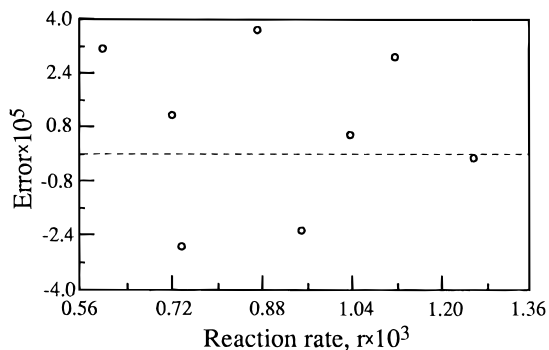
Figure 2. Residual plot for Podolski and Kim's (1974) rate data at 360 °C represented by a four-parameter power-law rate expression.

and it is smaller by 2 orders of magnitude than the rate values. Thus, the five parameter power-law rate expression gives a good representation of the data. However, reviewing the numerical results presented earlier reveals that the parameter a is not significantly different from zero. Plotting the independent variables against each other does not indicate a linear dependency among them. Thus, a probable cause for a being not significantly different from zero is that the P_{CO} terms in eq 7 have no effect on the rate and can be removed from the correlation. The results obtained after removing P_{CO} are $K' = (2.32 \pm 0.509) \times 10^{-3}$, $b = -1.0 \pm 0.0904$, $c = -0.1208 \pm 0.05$, $d = -0.054\,17 \pm 0.047\,55$, and $S^2 = 6.104 \times 10^{-9}$. In this case, all the parameters are significantly different from zero. The residual plot for the four parameter power-law rate expression is presented in Figure 2. It can be seen that this representation is definitely not worse than using the five parameter rate expression.

In order to check the significance of the reverse reaction, eqs 6 and 7 can be combined and rearranged to yield:

$$\frac{rP_{H_2O}^{-b}P_{CO_2}^{-c}P_{H_2}^{-d}}{k} - P_{CO}P_{H_2O} = -\frac{1}{K}P_{CO_2}P_{H_2} \quad (9)$$

The plot of $Y \equiv$ LHS (eq 9) vs $X \equiv P_{CO_2}P_{H_2}$ shown in Figure 3 reveals that the experimental points are located more or less randomly. They certainly do not lie along a straight line with a slope of $-1/K$, implying that the reversibility of the reaction is not reflected by the experimental data.

The calculations of the power-law rate expression parameters, S^2, and the test for significance of the reverse reaction were carried out for the other temperatures of 381 and 404 °C. The reverse reaction was
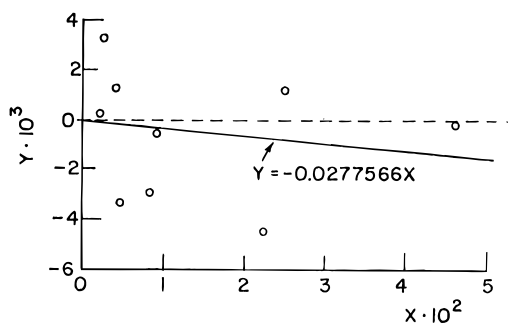
Figure 3. Plot of the reverse reaction contribution to the rate vs $P_{CO_2}P_{H_2}$ for example 1.

Table 1. Power-Law Rate Expression Parameters and Sum of Squares of Errors for the Water−Gas Shift Reaction[a]

	temp (°C)		
param	360	381	404
K	$(2.32 \pm 0.51) \times 10^{-3}$	$(3.91 \pm 1.41) \times 10^{-3}$	$(6.42 \pm 2.30) \times 10^{-3}$
a	*	*	-0.314 ± 0.209
b	-1.0 ± 0.091	-1.07 ± 0.143	-1.027 ± 0.073
c	-0.12 ± 0.05	-0.182 ± 0.123	-0.135 ± 0.101
d	-0.054 ± 0.048	*	*
S^2	6.18×10^{-9}	4.85×10^{-8}	2.59×10^{-8}

[a] Asterisks indicate values not significantly different from zero.

again found insignificant at 381 °C but significant at 404 °C. The rest of the results are summarized in Table 1. It can be seen that at 381 °C the powers of both P_{CO} and P_{H_2} are not significantly different from zero, while at 404 °C only the power of P_{H_2} is not significantly different from zero.

The facts that the reverse reaction is insignificant at two out of the three temperatures and that there is inconsistency in the significant variables at the different temperatures suggest that the data is not accurate enough to allow successful discrimination between mechanism-based rate expressions.

Podolski and Kim's (1974) results confirm this conclusion. They compared several mechanism-based rate expressions using these data. The results were inconclusive. They noted, for example, that: "The parameters in each model are relatively poorly estimated from the data, and in the case of the Langmuir−Hinschelwood model, the enthalpy and entropy of absorption of water are opposite in sign to what is normally expected." They could not identify the cause for these difficulties, but the above analysis shows that the data are not accurate enough to successfully discriminate between competing models.

E. Example 2: Methane−Steam Reaction

For this example, data and models from Quanch and Rouleau (1975) will be used. They investigated the kinetics of the methane-steam reaction over nickel catalyst in a continuous stirred tank reactor. The experiments were carried out at temperatures of 350, 375, 400, 425, and 450 °C. The homogeneous rate expression for this reaction is:

$$HT = P_{CH_4}P_{H_2O}^2 - \frac{P_{CO_2}P_{H_2}^4}{K} \quad (10)$$

The equilibrium constant K used here is the same value used by Quanch and Rouleau; $K = 4.587 \times 10^{-5}$ at 350
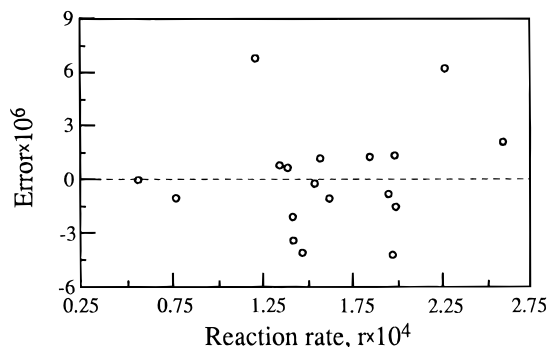
Figure 4. Residual plot for the rate data at 350 °C of Quanch and Rouleau (1975) represented by a two parameter power-law rate expression.

Figure 5. Plot of the reverse reaction contribution to the rate vs $P_{CO_2}P_{H_2}^4$ for example 2.

°C. (This value is not reported in their paper but can be calculated from their results.)

The following form of the power-law rate expression is used:

$$r = k'P_{CH_4}{}^aP_{H_2O}{}^bP_{CO_2}{}^cP_{H_2}{}^d(HT) \qquad (11)$$

The parameter values obtained (including 95% confidence intervals) at 350 °C are: $k' = 0.003\ 696 \pm 0.000\ 553\ 2$; $a = -0.8789 \pm 0.023\ 49$; $b = 0.058\ 28 \pm 0.089\ 81$; $c = 0.0041 \pm 0.0144$; $d = -0.000\ 188\ 2 \pm 0.0329$, and $S^2 = 8.124 \times 10^{-11}$. The residual plot (not shown) indicates a good fit between the experimental rate data and its five-parameter power-law rate expression representation.

However, inspection of the power-law rate expression parameter values reveals that three of them, b, c, and d are not significantly different from zero. For all of these parameters the confidence interval is larger than the value itself; consequently the value of zero is included inside the confidence interval. This suggests the possibility of removing P_{H_2O}, P_{CO_2}, and P_{H_2} and from the correlation. Using the simplified form of the rate expression, the following parameter values are obtained: $k' = 0.003\ 369 \pm 0.000\ 208\ 8$, $a = -0.8785 \pm 0.021\ 67$, and $S^2 = 1.024 \times 10^{-10}$.

The residual plot for this case is shown in Figure 4. It can be seen that the error is randomly distributed and the error is smaller by 2 orders of magnitude than the rate value. Thus, the two-parameter power-law rate expression represents the data well.

We can now assess the significance of the reverse reaction. Combining eqs 10 and 11, and rearranging yields:

$$\frac{rP_{CH_4}{}^{-a}}{k'} - P_{CH_4}P_{H_2O}{}^2 = -\frac{1}{K}P_{CO_2}P_{H_2}{}^4 \qquad (12)$$

The plot in Figure 5 yields a straight line with a slope ($= -1/K$) of $-21\ 882.2$, yielding $K = 4.57 \times 10^{-5}$. This value is almost exactly the same as that obtained from thermodynamic considerations. Thus, the contribution of the reverse reaction to the rate value is indeed significant.

The same procedure was repeated with the data at four additional temperatures. In all cases it is found that the powers of P_{H_2O}, P_{CO_2}, and P_{H_2} are not significantly different from zero; thus, these variables can be removed from the correlation. Furthermore, the reverse reaction in all cases is found to be significant. The parameter values of the power-law rate expression,
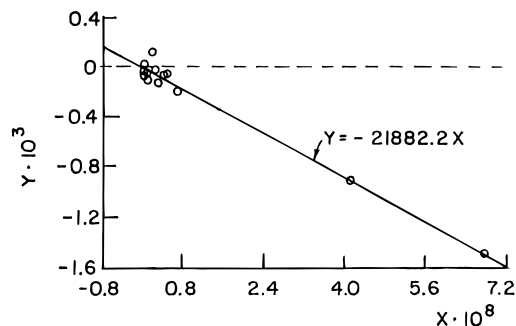
Table 2. Equilibrium Constant K, Two-Parameter Power-Law Expression Parameters, and Sum of Squares of Errors for the Methane−Steam Reaction

temp (°C)	equilibrium K^a	k'	a	S^2
350	4.587×10^{-5}	0.00337 ± 0.0002	-0.878 ± 0.012	1.02×10^{-10}
375	0.000178	0.00791 ± 0.00036	-0.828 ± 0.018	3.85×10^{-10}
400	0.0006208	0.0321 ± 0.011	-0.628 ± 0.115	1.24×10^{-7}
425	0.00214	0.052 ± 0.011	-0.599 ± 0.07	4.72×10^{-8}
450	0.00637	0.191 ± 0.038	-0.375 ± 0.067	2.13×10^{-8}

[a] Calculated from the data and results of Quanch and Rouleau (1975).

Table 3. LHHW Rate Expression Parameters and Sum of Squares of Errors for the Methane−Steam Reaction

temp (°C)	k	K_{CH_4}	S^2
350	$0.00276 \pm 7.59 \times 10^{-5}$	114.93 ± 22.63	9.24×10^{-11}
375	$0.00608 \pm 2.78 \times 10^{-5}$	71.65 ± 4.57	8.92×10^{-11}
400	0.0165 ± 0.00269	38.53 ± 18.67	1.2×10^{-7}
425	0.0359 ± 0.00518	22.07 ± 6.208	4.09×10^{-8}
450	0.0858 ± 0.0216	10.73 ± 4.25	3.41×10^{-8}

S^2 and the equilibrium constant K obtained, are summarized in Table 2.

The conclusion that can be reached at this stage is that the data is precise enough to justify further analysis of model discrimination among mechanism-based models (eq 1). On the basis of the power-law model, the partial pressures of H_2O, CO_2, and H_2 can be removed from the denominator of such rate expressions.

The results of Quanch and Rouleau (1975) confirm these conclusions. They have considered 40 different rate expressions, and the one they found the most appropriate, after carrying out all the necessary steps of model discrimination, is the following:

$$r = \frac{kK_{CH_4}(HT)}{1 + K_{CH_4}P_{CH_4}} \qquad (13)$$

In this equation $\alpha_{1,min} = 0$ and $\alpha_{1,max} = 1$. On the basis of the values of parameter a in Table 2, this rate model satisfies inequality (3) at all temperatures; thus, it would have been considered acceptable in view of the power-law-based screening method.

The parameters of the mechanism-based rate expression (eq 13) and the S^2 values at the various temperatures as calculated using POLYMATH are summarized in Table 3. They are essentially the same as those obtained by Quanch and Rouleau (1975). It can be seen that the proposed procedure predicts correctly the right mechanism-based rate expression. The fit between experimental and calculated rate values, as measured by the sum of squares of errors, is slightly better

(compared to Table 2) in all but one temperature when using the LHHW rate expression.

F. Summary and Conclusions

The study demonstrates the benefits of using the power-law model for assessing the quality of experimental data and for the initial screening of postulated LHHW models in regression of rate data of reversible, heterogeneous reactions.

Using this method, the parameters of a particular power-law rate expression are calculated first by regression of the experimental data. If some of the parameter values are not significantly different from zero, the data are examined for possible linear dependency among the independent variables or existence of superfluous variables in the rate expression. The bounds set on the values of the power-law parameters allow elimination of infeasible LHHW mechanisms in the early stages of the model discrimination process. The power-law rate expression is also used to assess the significance of the reverse reaction, as insignificance of the reverse reaction often indicates imprecision of the data.

The use of the proposed method was demonstrated using two examples from the literature. The preliminary investigation using the power-law rate expression parameters led, in one case, to a conclusion that the data are not precise enough to allow model discrimination. In the second example, the power-law parameter values clearly indicate the requirements for a feasible LHHW rate expression. In both cases, the results of a detailed discrimination procedure verify the results of the initial screening. Additionally, more detailed demonstrations of the proposed screening procedure for irreversible reactions are presented in Brauner and Shacham (1996).

Thus, the proposed procedure may reduce considerably the effort required for model discrimination by allowing identification of inappropriate data and elimination of infeasible mechanisms at a very early stage of the model discrimination process.

Literature Cited

Boudart, M. Classical Catalytic Kinetics: A Placebo or the Real Thing. *Ind. Eng. Chem. Fundam.* **1986**, *25* (4), 656−658.

Boudart, M.; Djéga-Marriadassou, G. *Kinetics of Heterogeneous Catalytic Reactions*; Princeton University Press: Princeton, NJ, 1984.

Brauner, N.; Shacham, M. Using Power-Law Rate Expression Parameters for Discrimination among Mechanistic Models in Rate Data Regression. *Chem. Eng. Commun.* **1996**, in press.

Churchill, S. W. The Role of Analysis in the Rate Processes. *Ind. Eng. Chem. Res.* **1992**, *31*, 643−658.

Froment, G. F. Model Discrimination and Parameter Estimation in Heterogeneous Catalysis. *AIChE J.* **1975**, *21* (6), 1041−1057.

Froment, G. F.; Bischoff, K. B. *Chemical Reactor Analysis and Design*, 2nd ed.; John Wiley: New York, 1990.

Hougen, O. A.; Watson, K. M. *Chemical Process Principles*, *Part Three*; John Wiley: New York, 1947.

Kittrell, J. R. Mathematical Modeling of Chemical Reactions. *Adv. Chem. Eng.* **1970**, *8*, 97−183.

Podolski, W. F.; Kim Y. G. Modeling the Water−Gas Shift Reaction. *Ind. Eng. Chem. Process Des. Dev.* **1974**, *13* (4), 415−421.

Quanch, Q. P.; Rouleau, D. Kinetics of the Methane−Steam Reaction over Nickel Catalyst in a Continuous Stirred Tank Reactor. *J. Appl. Chem. Biotechnol.* **1975**, *25*, 445−459.

Shacham, M.; Brauner, N. Correlation and Overcorrelation of Heterogeneous Reaction Rate Data. *Chem. Eng. Ed.* **1995**, *29* (1), 22−25.

Shacham, M.; Cutlip, M. B. *Polymath 3.0 Users Manual*; CACHE Corp.: Austin, TX, 1994.