P = pressure, lb.$_f$/sq.ft.
Q = heat, B.t.u.
R = universal gas constant, B.t.u./(lb.-mole)(°R.) or equivalent
t = time, sec.
T = temperature, °R.
V = velocity, ft./sec.
W = work (excluding injection work), ft.lb.$_f$ or equivalent
z = elevation, ft.
ρ = density, lb.$_m$/cu.ft.

Subscripts

B = solid blocks
G = gas
L = liquid

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Discrimination Among Rival Hougen-Watson Models Through Intrinsic Parameters

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In attempting to describe rate data from a heterogeneous chemical reaction, the chemical engineer has frequently postulated a set of Hougen-Watson models (*1, 2*), taken rate data, and analyzed them to specify a "best" model and to estimate the rate parameters in this model. In so doing, the techniques suggested by Yang and Hougen (*3*) of making appropriate linear plots of the initial rate data are among the most widely used procedures (*4, 5*). Also, it is often necessary to test the ability of a model to fit high conversion data. This may be done by nonlinear least squares (*5*), by model building techniques at constant pressure (*6*), or by the use of nonintrinsic parameters (*7*). This communication presents an extension of an existing method (*8*) of preparing linear plots for high conversion data, which is entirely analogous to the method of initial rates. Hence, these plots provide a visual indication of the ability of a model to fit the high conversion data and thus allow a more complete test of a model than does the initial rate analysis alone; estimates of product adsorption constants are also obtained.

LINEAR ANALYSIS THROUGH INTRINSIC PARAMETERS

When any Hougen-Watson model is written in terms of fractional conversions instead of a partial pressures, two groupings of terms inherently arise within the denominator. These two groupings will be called the *intrinsic parameters* C_1 and C_2. It will first be shown how the linear initial rate analysis can be formalized through the specification of an intrinsic parameter C_1 and then how the high conversion analysis logically follows from a second intrinsic parameter C_2.

Consider for example, a single site model

$$r = \frac{kK_A\,(p_A - p_o p_W/K)}{(1 + K_A p_A + K_W p_W)} \tag{1}$$

When data are taken for the olefinic dehydration of a pure alcohol feed, Equation (1) may be rewritten in terms of fractional conversions:

$$r = \frac{k\,K_A\left(\frac{1-x}{1+x}\right)\pi}{\left[1 + K_A\left(\frac{1-x}{1+x}\right)\pi + K_W\left(\frac{x}{1+x}\right)\pi\right]} \tag{2}$$

In this formulation, the reaction is assumed to be essentially irreversible; the existence of product partial pressures in the numerator does not alter the method of analysis to be discussed here, however. Equation (2) may be written as

$$r = \frac{(1-x)\,\pi}{(C_1 + C_2 x)} \tag{3}$$

where

$$C_1 = \frac{1}{k\,K_A} + \frac{\pi}{k} \tag{4}$$

$$C_2 = \frac{1}{k\,K_A} + \frac{K_W - K_A}{k\,K_A}\,\pi \tag{5}$$

The C_1 parameter, then, is the collection of terms which is not multiplied by conversion, while C_2 is the collection which is multiplied by the conversion x.

The use of the parameter C_1 in Equation (3) has been discussed elsewhere (*3*), for Equation (3) can be utilized to estimate the parameter C_1 from zero conversion data ($C_1 = \pi/r_o$). Equation (4) requires that these observed values be linearly dependent upon total pressure if the model of Equation (2) is adequate. This constitutes a formalization of the conventional linear initial rate approach in terms of the intrinsic parameter C_1.

It can be seen from Equation (3) that rate data taken at zero conversion (initial rate data) can give little information concerning the magnitude and the pressure dependence of the parameter C_2. Equation (5) dictates that if values of the parameter C_2 can be estimated, they must be linearly dependent upon total pressure if the model of

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Equation (2) is adquate. This is analogous to the linear pressure dependence used with initial reaction rates and required by Equation (4). The exhibition of such a linear dependence of C_2, however, would ensure that the model fits the *high* conversion data (required to estimate C_2), in contrast to the test of the fit of the initial rate data provided by the parameter C_1. Furthermore, for a single reactant, the slopes and intercepts of the C_1 and C_2 plots will provide estimates of *all* of the rate and adsorption constants, not just those pertaining to the reactants as was available from the C_1 analysis.

The estimation of the parameter C_2 can be carried out in several ways. A rearrangement of Equation (3) yields

$$C_2 = \frac{(1-x)\,\pi}{x\,r} - \frac{\pi}{x\,r_o} \qquad (6)$$

Here, the several values of C_2 (corresponding to several conversion points) at each pressure level can be averaged, and this average can be plotted vs. total pressure. A second method is obtained by combining the continuity equation for a plug-flow reactor with Equation (3). The integration of this equation, for zero conversion in the reactor feed, yields

$$C_2\,[-x - \ln(1-x)] - C_1 \ln(1-x) = \pi\,(W/F) \qquad (7)$$

Utilizing estimates of C_1 from initial reaction rates, we can solve Equation (7) for C_2 at each conversion point, an average value of C_2 for each pressure can be obtained, and a plot of C_2 vs. pressure can be made.

The utilization of least squares allows a simultaneous estimation of C_1 and C_2. A linear least squares analysis using a dependent variable $\pi(W/F)$ in Equation (7) should not be used, however, due to severe violations of error distribution assumptions. On the other hand, if reaction rates are available at each conversion point, simultaneous estimates of C_1 and C_2 at each pressure level may be obtained through a nonlinear least squares analysis of the isobaric data using Equation (3). If conversion-space-time data are available, C_1 and C_2 may simultaneously be estimated from Equation (7). The use of this equation will necessitate the inclusion of an equation solving routine, perhaps based upon the Newton-Raphson method, with the nonlinear estimation routine so that the sum of squares of residual conversions may be minimized. Such a procedure of combining nonlinear estimation with other special purpose subroutines has also been discussed in another context (*9, 10*). In our case, however, this nonlinear least squares analysis requires the estimation of only two parameters, rather than the three to six parameters which often must be estimated for Hougen-Watson models. Such estimation may usually be accomplished relatively easily and precisely.

Two of the above three methods of calculating the parameter C_2 involve the calculation of C_2 at each conversion point. Since the defining equation of C_2, such as Equation (5), is independent of conversion, these calculated values of C_2 should be averaged at each pressure level and then plotted vs. total pressure. One manifestation of an inadequate model, on the other hand, is a definite correlation of the estimated parameter C_2 with the conversion level. Our experience has indicated that some care must be exercised in rejecting models based on such trends, however, because some dependency of C_2 upon conversion can arise from the use of inaccurate methods of data differentiation.

EXAMPLE

Johnson (*11*) studied the vapor phase dehydration of secondary butyl alcohol to the olefin over a commercial silica alumina cracking catalyst. Data were taken on the −28+35 Tyler mesh catalyst particles in an integral reactor, at temperatures of 400°, 450°, and 500°F. and from 1 to 11 atm. abs. pressure. Although the primary reaction product was butylene, side reactions forming cracked and polymerized olefin were also observed. Since the activity of the catalyst was not stable, all experimental observations were corrected to a standard activity level. The effectiveness factor for the catalyst used was estimated to be greater than 0.95, and calculations suggested that the external film gradient was negligible. A more complete description of the data and the reactor is presented elsewhere (*11*). The 500°F. data set, also presented else-

TABLE 1. THREE RIVAL MODELS FOR ALCOHOL DEHYDRATION

Model	Predicted parameter values	Observed parameter values
1. Single site, surface reaction controlled $r = \frac{k\,K_A p_A}{(1 + K_A p_A + K_W p_W)} = \frac{(1-x)\pi}{(C_1 + C_2 x)}$	$C_1 = \frac{1}{k\,K_A} + \frac{\pi}{k}$ $C_2 = \frac{1}{k\,K_A} + \frac{K_W - K_A}{k\,K_A}\pi$	$C_1 = \pi/r_o$ $C_2 = \frac{(1-x)\pi}{xr} - \frac{C_1}{x}$
2. Dual site, surface reaction controlled $r = \frac{k\,K_A p_A}{(1 + K_A p_A + K_{wo} p_W)^2} = \frac{(1-x^2)\pi}{(C_1 + C_2 x)^2}$	$C_1 = \frac{1}{\sqrt{k\,K_A}} + \frac{K_A}{\sqrt{k\,K_A}}\pi$ $C_2 = \frac{1}{\sqrt{k\,K_A}} + \frac{K_{wo} - K_A}{\sqrt{k\,K_A}}\pi$	$C_1 = \sqrt{\pi/r_o}$ $C_2 = \frac{1}{x}\sqrt{\frac{(1-x^2)\pi}{r}} - \frac{C_1}{x}$
3. Adsorption controlled $r = \frac{k\,p_A}{(1 + K_{wo} p_o p_W + K_W p_W)} = \frac{(1-x^2)\pi}{C_1 + C_2 x + C_3 x^2}$	$C_1 = \frac{1}{k}$ $C_2 = \frac{2}{k} + \frac{K_W}{k}\pi$ $C_3 + C_1 - C_2 = \frac{K_{wo}}{k}\pi^2$	$C_1 = \pi/r_o$ $C_2 = \pi\left(\frac{d^2 W/F}{d\,x^2}\right)_{x=0}$ $C_3 = \frac{(1-x^2)\pi}{r\,x^2} - \frac{C_2}{x} - \frac{C_1}{x^2}$

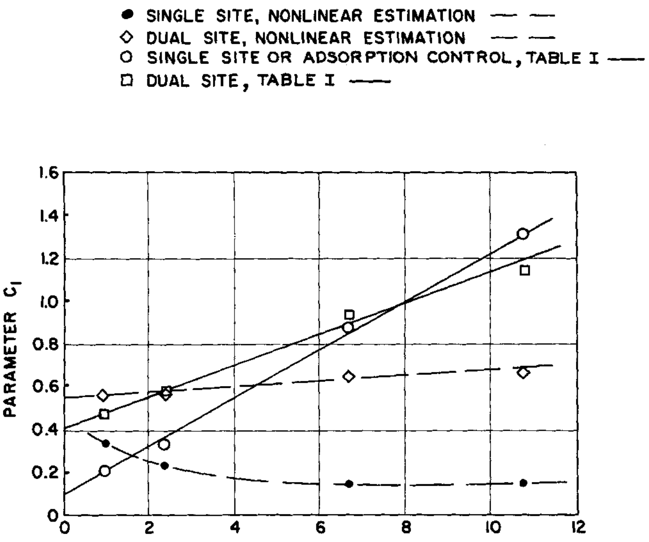

Fig. 1. Plot of parameter C_1 vs. total pressure.

where (7), was chosen for further study by the linear analysis using intrinsic parameters.

For data in which pressure is the primary variable, the various rival models are to be written as in Equation (3). If the initial partial pressure of the reactants is the primary variable, a slightly different formulation is required (6). For the alcohol dehydration data, three possible models are presented in Table 1. In this table K_{wo} denotes the sum of the olefin and water adsorption constants. Since only pure alcohol feed was used, stoichiometric requirements prevent the separate estimation of these two adsorption constants. Also, integrated forms of the rate equations analogous to Equation (7) may be written; for the dual site equation we have

$$\frac{1}{2}(C_1^2 + C_2^2)\ln\left(\frac{1+x}{1-x}\right) - C_1C_2\ln(1-x^2) - C_2^2\,x = \pi(W/F) \qquad (8)$$

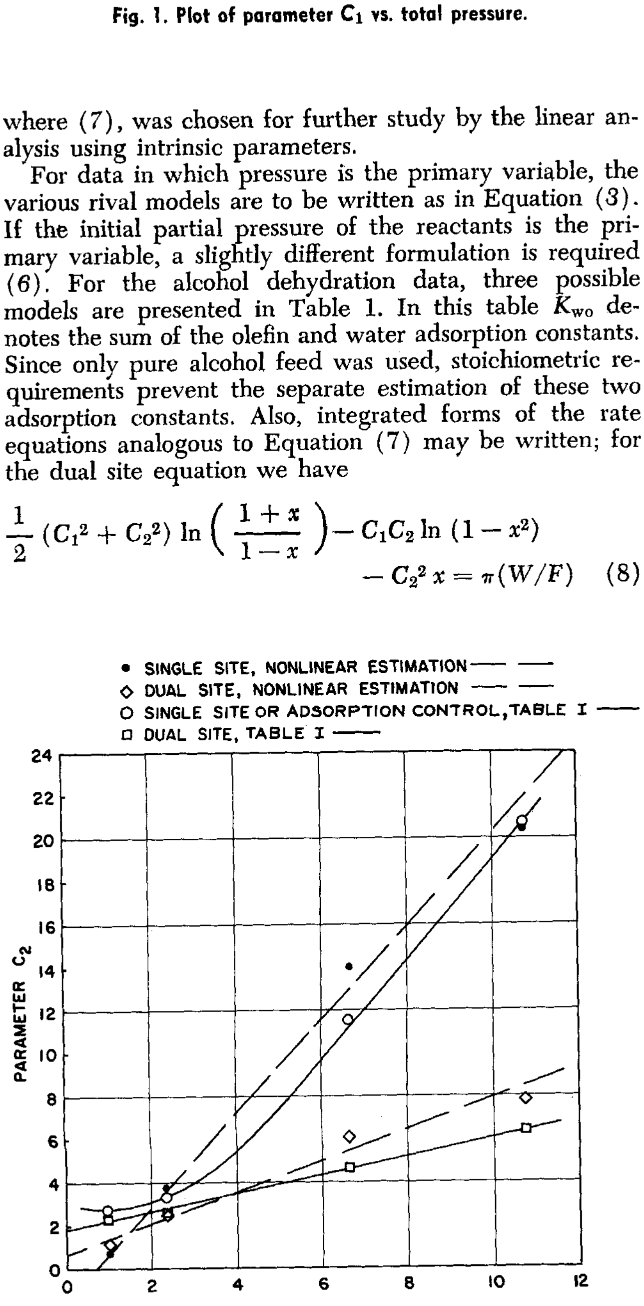

Fig. 2. Plot of parameter C_2 vs. total pressure.

Using the conversion-space time data, initial reaction rates were first obtained by numerical differentiation (Newton's forward approximation). This allows the calculation of C_1 for the models of Table 1. The solid lines of Figure 1 indicate that the adsorption controlled model should be rejected, since the slope of the C_1 plot is nonzero, in contrast to the prediction of Table 1. Neither surface reaction controlled model can be rejected on this basis, however.

For the surface reaction models, then, the dependency of the intrinsic parameter C_2 on pressure should be examined. The use of the equations of Table 1 requires the estimation of the reaction rate at each conversion point. For low conversions this was done by using the differentiated form of Newton's forward interpolation formula, for intermediate conversions Stirling's formula was used, and for high conversion Newton's backward formula was used (*12*). The C_2 values thus obtained are correlated by the solid lines in Figure 2. Note that the dual site values are again correlatable by a straight line, but the single site values of C_2 show definite curvature. Alternatively, the 0.975 atm. value of the single site C_2 could be rejected and the three high pressure points correlated by a straight line. Since the latter procedure results in a significantly negative intercept for C_2 [cf. Equation (5)], either approach eliminates the single site model from further consideration. Note, however, that the intercept from the dual site C_2 plot is somewhat higher than that of the dual site C_1 plot. The 97.5% confidence intervals for these two intercepts do overlap one another. Note that we have seen that the adsorption and the single site surface reaction controlled model have been rejected, *and* the dual site model has been shown to represent both the initial and the high conversion data adequately.

The estimates of the parameters C_1 and C_2 were also obtained by using nonlinear least squares (*10*) with the isobaric data and Equations (7) and (8). The estimates of C_1 and C_2 for each pressure level are correlated by the dashed lines of Figures 1 and 2, respectively. Note that the single site C_1 plot of Figure 1 is now curved, due to the correlation between the C_1 and C_2 values obtained by this simultaneous estimation. The single site C_2 plot of Figure 2 is straight but exhibits a negative intercept [cf. Equation (5)]. The dual site plots, however, are linear in both Figures 1 and 2. Furthermore, the intercepts of the dual site C_1 and C_2 plots are nearly identical, as expected from Table 1. Thus, the analysis with the use of the intrinsic parameters again indicates that the single site model is inadequate, while the dual site model fits both the initial rate data and the high conversion data. The parameter estimates for the dual site model, obtained from the slopes and intercepts of the C_1 and C_2 plots, are reported in Table 2.

TABLE 2. PARAMETER ESTIMATES FOR DUAL SITE, SURFACE REACTION CONTROLLED MODEL

Method	Forward rate constant	Alcohol adsorption constant	Production adsorption constant
Linear estimation of intrinsic parameters, by use of Table 1	12.9	0.064	0.46
Nonlinear estimation of intrinsic parameters, by use of Equation (8)	164	0.017	1.00
Nonlinear estimation of individual parameters	33.9	0.11	1.19

Table 2 also contains estimates of the rate and adsorption constants obtained from minimizing the sum of squares of conversion residuals by using directly the integrated form of the dual site model. These estimates were obtained by combining an equation solving routine with a nonlinear estimation routine so that the sum of squares of residual conversions could be minimized. As is often the case, the estimates thus obtained differ somewhat from the estimates obtained by the other two methods, which are also reported in Table 2. The estimates obtained by the direct nonlinear least squares analysis of the dual site model are generally considered to be better parameter estimates than those reported in the other two entries of Table 2.

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NOTATION

C_1 = intrinsic parameter not multiplied by conversion
C_2 = intrinsic parameter multiplied by the first power of conversion
C_3 = intrinsic parameter multiplied by the second power of conversion
F = molal feed rate, lb.-moles feed/hr.
K = thermodynamic equilibrium constant for overall reaction, atm.
K_A = equilibrium adsorption constant for alcohol, atm.$^{-1}$
K_W = equilibrium adsorption constant for water, atm.$^{-1}$
K_{wo} = sum of equilibrium adsorption constants for water and butylene, atm.$^{-1}$
k = forward rate constant for surface reaction, lb.-moles/(lb.-catalyst)(hr.)
p_A = partial pressure of alcohol, atm.
p_o = partial pressure of butylene, atm.
p_W = partial pressure of water vapor, atm.
r = reaction rate, lb.-moles/(lb.-catalyst)(hr.)
r_o = initial reaction rate for pure feed, lb.-moles/(lb.-catalyst)(hr.)
W = mass of catalyst, lb.
x = conversion, lb.-moles converted/lb.-mole feed
π = total pressure, atm.

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Comments on "Critical Flow of Liquid-Vapor Mixture*"

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Within the restrictions of the model, the authors present a good summary of equations involving two-phase quantities which have been repeatedly used by others, including the maximization of the two-phase flow through manipulation of the slip ratio. Furthermore, it is again noted that the conservation equations are not consistent in the evaluation of the critical flow rates. References noted below (published during the interval of the presentation of the paper and the publication in the *Journal*) will further orient the reader in gaining perspective of the status of the art on critical two-phase flow.

The important contribution claimed by the authors is that their treatment represents a *unified theory*. Although the relationship is now made in a somewhat cautious fashion to irreversible thermodynamics, this reader fails to grasp the justification of the thermodynamic arguments presented. The one-dimensional model almost precludes any basis for examining dissipation through velocity gradients, and consequently provides no insight on *rates* of entropy production.

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