———, "On the Thermodynamics of Solutions. VII. Critical Properties of Mixtures," *J. Chem. Phys.*, 36, 2002 (1962).

Redlich, O., and J. N. S. Kwong, "On the Thermodynamics of Solutions. V," *Chem. Rev.*, 44, 233 (1949).

Sarashina, E., J. Nohka, Y. Arai, and S. Saito, "Correlation of Critical Locus for Binary Mixtures by the BWR Equation," *J. Chem. Eng. (Japan)*, 7, 219 (1974).

Scott, R. L., "The Thermodynamics of High-Polymer Solutions. IV. Phase Equilibria in the Ternary System: Polymer-Liquid 1—Liquid 2," *J. Chem. Phys.*, 17, 268 (1949).

———, "Thermodynamics of Critical Phenomena in Fluid Mixtures," *Ber. Bunsenges. Phys. Chem.*, 76, 296 (1972).

———, and P. H. Van Konynenburg, "Static Properties of Solutions. 2. van der Waals and Related Models for Hydrocarbon Mixtures," *Discuss. Faraday Soc.*, No. 49, 87 (1970).

Spear, R. R., R. L. Robinson, and K. C. Chao, "Critical States of Mixtures and Equations of State," *Ind. Eng. Chem. Fundamentals*, 8, 2 (1969); "Critical States for Ternary Mixtures and Equations of State," *ibid.*, 10, 588 (1971).

Teja, A. S., and H. W. Kropholler, "Critical States of Mixtures in Which Azeotropic Behavior Persists in the Critical Region," *Chem. Eng. Sci.*, 30, 435 (1975).

Teja, A. S., and J. S. Rowlinson, "The Prediction of the Thermodynamic Properties of Fluids and Fluid Mixtures—IV. Critical and Azeotropic States," *ibid.*, 28, 529 (1973).

Tisza, Laszlo, *Generalized Thermodynamics*, M.I.T. Press, Cambridge, Mass. (1966).

Manuscript received March 11, 1977; revision received June 16, and accepted June 21, 1977.

Multivariable Computer Control of a Butane Hydrogenolysis Reactor:

Part I. State Space Reactor Modeling

A state space model is developed for an existing nonadiabatic packed-bed reactor which experiences axial and radial concentration and temperature gradients resulting from highly exothermic reactions involving several chemical species. The set of partial differential equations is reduced from three to two dimensions using orthogonal collocation. Further use of orthogonal collocation on the quasi steady state version of the differential equations results in a set of coupled algebraic and differential equations from which a linearized low-order state space model is obtained. The model parameters are estimated from reactor data, and the fitted model is used for design and implementation of a multivariable stochastic control schemes on the reactor. These applications are described in parts II and III of this paper.

ARTHUR JUTAN
J. P. TREMBLAY
J. F. MacGREGOR
and
J. D. WRIGHT

Department of Chemical Engineering
McMaster University
Hamilton, Ontario, Canada

SCOPE

The catalytic chemical reactor represents one of the more complicated processes to model in chemical engineering. Because of this, it is essential when deriving a process model to keep in mind the purpose for which the model is to be used. If, for example, the model is to be used as the basis for on-line regulatory control of the reactor, large simplifications to most of the models proposed in the literature must be made. Although most of the models tend to be somewhat complex and, in general, unsuitable for control, by examining the formulation of these models some insight into the important effects occurring within a reactor may be gained, and ideas for simplifying the models for the purposes of control may be found.

Beek (1962) and Froment (1967, 1972) present great insight into the factors surrounding a complex model of a packed-bed reactor including estimation of transport properties and heat transfer effects. More recently, Froment (1974) reviews the current findings in the literature and comments on a number of still unanswered questions in the modeling of chemical reactors. Extensions to Beek's work are provided by Hlavcek (1970), particularly in the area of parameter estimation problems. Parametric sensitivity in fixed-bed reactors is discussed by Carberry and White (1969). Most of these studies address the problems appearing in single reaction systems of specific order under steady state conditions.

There are only a limited number of studies concerned with transient effects in packed tubular reactors. Most of these except Young and Finlayson (1973) appear to neglect radial gradients. Inclusion of both axial and radial gradients gives rise to a set of three-dimensional partial differential equations which presents a very difficult computational problem. Sinai and Foss (1970) consider an adiabatic reactor in which a non-catalyzed reaction occurs in the liquid phase of a solid liquid system. Crider and Foss (1966) attempt to isolate the important factors affecting the dynamics of packed bed reactors although for their system radial gradients are unimportant. Ferguson and Finlayson (1970) make an attempt to analyze the validity of the quasi steady state assumption often used in modeling the dynamics of fixed bed reactors.

The equations describing the dynamics of chemical reactors are often complex, requiring powerful computational techniques for solution. Villadsen and Stewart (1967) and Finlayson (1971, 1974) discuss in detail the application of orthogonal collocation techniques to chemical reaction engineering. Ferguson and Finlayson (1970), Finlayson (1972), and Hanson (1973) also discuss various aspects of orthogonal collocation as applied to reactor dynamics.

Control of present day reactors in the process industry appears to be still somewhat of an art (Lee and Weekman, 1976), except perhaps for control studies on simple CSTR or batch reactors (Marroquin et al., 1973). Multivariable control of plug flow reactors, however, appears to be confined to the literature as a series of simulation studies (Dyring and Kummel, 1973; Seinfeld, et al., 1971; Bertram and Chang, 1971), and the literature is extremely sparse when it comes to application of control techniques to actual processes or pilot plant reactors. Catalytic fixed bed reactors often require a set of partial differential equations (PDE) to fully describe their complex dynamics. A common approach is to reduce this set of PDE's to a set of ordinary differential equations (ODE), often linearized, so that multivariable control and estimation theory can be applied. Michelsen et al. (1973) address this problem on a noncatalytic system which is conveniently solved by orthogonal collocation techniques to produce a small set of ODE's. In a subsequent paper (Vakil et al., 1973) a control scheme is derived for the fixed-bed reactor system. Owing to problems associated with concentration measurements, the system was assumed to have temperature measurements only, and concentration measurements are inferred through a model. Extensions to that work are suggested, including investigation of gas solid systems, where fluid residence time is small compared with thermal transit time; reaction schemes are complex; catalytic reactions occur; reactors are nonadiabatic; and the reactant flow rates are manipulated for control.

The present work addresses the above problems by obtaining a dynamic model of a complex exothermic catalytic reaction system suitable for on-line multivariable process control studies. This paper represents the first of three stages in the control of a pilot scale butane hydrogenolysis reactor. Part I addresses the model formulation and reduction. Part II discusses the experimental analysis and collection of data and model parameter estimation problems. Finally, Part III concludes with the design and implementation of a multivariable control scheme on the pilot reactor using a minicomputer.

CONCLUSIONS AND SIGNIFICANCE

A mechanistic model describing axial and radial concentration and temperature gradients in a nonadiabatic pilot scale fixed-bed catalytic reactor with three independent reactions has been formulated. Through the use of orthogonal collocation in both the radial and axial directions, the three-dimensional partial differential equations were reduced to a low-order state space model in a form suitable for parameter estimation and on-line multivariable control studies. The differential equation models were shown to agree with steady state temperature profile and conversion data taken from the reactor, although detailed fitting of the parameters and a comparison with data collected under dynamic conditions is carried out in Part II of this paper followed by control studies on the reactor in Part III.

In previous applications, radial gradients have not been present partly because of the complexity of the resultant mechanistic models and also because most reaction schemes considered have been less complex or less exothermic than the present study.

Although a specific set of reaction equations was used, the approach is general and could be used for any reaction scheme in a packed-bed reactor. The order of the reduced model is a function of the number of independent reactions and the severity of the axial temperature gradients.

Because reactor effluent concentration measurements are infrequent in the pilot plant system, the model for control purposes was written in terms of axial temperature profiles with an inferential measurement for composition. The performance of these inferential predictions is shown in the applications to follow.

PROCESS DESCRIPTION

The reaction considered here is the hydrogenolysis of butane, a highly exothermic series parallel reaction, carried out over a nickel on silica gel catalyst in a fixed-bed, nonadiabatic tubular reactor. A schematic diagram of the reactor system is presented in Figure 1. The reactor consists of a single 2.045 cm radius tube, 28 cm long, packed with finely divided (average diameter 0.1 cm) catalyst particles. The flow rates of the two feed streams, hydrogen and butane, are controlled using a minicomputer to maintain control of the exit concentrations. In the absence of control, these concentrations would deviate from target owing to internal or external disturbances (for example, catalyst activity fluctuations or wall temperature fluctuations) of a stochastic or deterministic nature. The inlet gases are preheated to wall temperature by passing through a tube filled with silica gel particles, heated by an electrical resistance heater. The wall temperature of the reactor tube is controlled by countercurrent flow of heat transfer oil

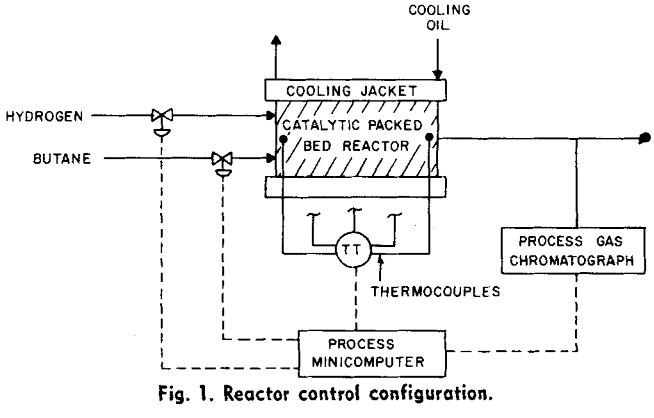

Fig. 1. Reactor control configuration.

through the annulus of a cooling jacket. The oil temperature is controlled externally to the system shown in Figure 1. The reactor wall temperature is equal to the oil temperature and, for all practical purposes, independent of length along the reactor.

Nine thermocouples are positioned inside the reactor at equispaced points along the central axis. Several radially located thermocouples are provided as well as thermocouples to measure inlet and exit gas stream temperatures.

Exit concentration measurements are obtained using an on-line process gas chromatograph (Beckman, Model 6700). Pressure in the reactor is usually set between 100 to 200 kPa, and pressure drop across the reactor is less than 20 kPa.

All data collection and process control is accomplished using a Data General 32 K Nova 2/10 minicomputer to which the reactor process has been interfaced. A Control Software Package (Tremblay, 1975) handles all the data logging and control implementation for the system.

Details of the reactor design, control software package, and process computer interfacing are provided by Tremblay (1977), who designed and built the pilot plant reactor and interfaced it to the minicomputer.

REACTION KINETICS

The butane hydrogenolysis reaction has been studied previously by Orlikas (1970, 1972) and Shaw (1972, 1974). From their analysis, the hydrogenolysis reactions may be represented by the following four (three independent) reactions:

$$\begin{array}{ll} (1) & C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4 \\ (2) & C_4H_{10} + H_2 \rightarrow 2C_2H_6 \\ (3) & C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4 \\ (4) & C_2H_6 + H_2 \rightarrow 2CH_4 \end{array} \qquad (1)$$

The reaction rate models associated with these reactions are given in Appendix 1.

REACTOR MODEL EQUATIONS

An overview of the problems associated with the modeling of fixed-bed reactors has been presented in the scope. Further discussion of the specific assumptions employed for this study follow below.

Catalyst Particle

In this reactor, the gases flow rapidly over solid, porous, catalytic particles. The reaction is highly exothermic and occurs on and within the small, approximately spherical, catalyst particles. Orlikas (1970) and Shaw (1974) determined that there are no interparticle or intraparticle mass transfer limitations.

They also concluded that the effect of pore diffusion on intraparticle concentration profiles is minor and hence that concentration within the catalyst particle is uniform (Levenspiel, 1972).

Under most conditions encountered industrially, catalyst particles remain nearly isothermal (Froment, 1972, 1974; Carberry and White, 1969), even for exothermic reactions. This is especially true for the small catalyst particles considered here. Shaw (1974) provided evidence that this assumption is valid.

The presence of uniform concentration and temperature profiles within the catalyst make the probability of multiple steady states within the particle small. Industrially, this is often the case (Froment, 1972, 1974), and a unique steady state will be assumed here.

In situations where it is not possible to assume uniform catalyst particle profiles, the resulting complications to the model would make it unusable for control; another approach to the problem would have to be sought. We assume that the packed bed may be treated as a continuum insofar as changes occur continuously and smoothly throughout the bed. The ratio of bed diameter to catalyst diameter is about 200, and under these conditions (Hlavacek, 1970) this assumption is valid.

Gas Phase

The reactor operates at low pressure, and we assume the gases obey the ideal gas law.

There is a minor pressure drop across the reactor, and because the reaction is equimolar, we assume (provided temperature rise is not too excessive) that the gas flow may be represented as a movement of a plug down the reactor with constant average velocity, independent of radial position (Paris and Stevens, 1970; Beek, 1962).

Axial diffusion of mass and temperature has been neglected in comparison with bulk flow or convective terms (Beek, 1962; Shaw, 1974; Orlikas, 1970; Froment, 1974). Shaw presents an analysis which shows that mass diffusion can certainly be neglected. There is some evidence (Mears, 1976; Froment, 1974) that small errors may result in steady state models if temperature diffusion terms are neglected, that is, terms resulting from axial heat conduction through the catalyst mass. From an examination of their criteria, these effects are minimal for the fast flowing gases and small catalyst particles in the reactor system considered here. From a control point of view, this assumption is mandatory, since inclusion of these terms, apart from making the equations computationally unfeasible, would force us to deal with multiple steady states in the gas phase, and the solution of a two point boundary value problem, both of which clearly could not be considered for an on-line control model.

Furthermore, for this fast flowing gas-solid system, the difference between gas and solid catalyst temperatures may be considered negligible. Industrial experience appears to support this (Froment, 1974; Gould, 1969). Shaw (1974) presents an analysis to show that there is ample driving force to remove the heat generated by reaction and that essentially no temperature difference existed between catalyst pellet and gas at steady state.

From a control point of view, there is a further problem of measurement. Although, theoretically, it is possible to measure separately the gas and solid temperature, in practice it is difficult. Recent work on a highly exothermic reactor system (Sharma, 1977) in which thermocouples were actually embedded in catalyst particles considerably larger than those in the present study has shown that the dynamic differences between catalyst and gas temperatures are small. For practical measurements of gas temperature only, the thermocouple may be surrounded by a meshed cage. These practices can seriously disrupt flow patterns and are not common industrial practice. There is also the question of measurement error. The difference between gas and solid temperature ($< 5°K$) is of the order of error associated with the thermocouple (Jutan, 1977).

Heat Radiation Between Solid and Gas

Heat transfer by radiation from the solid catalyst to the gas can have a significant effect on the temperature dynamics in the reactor, especially at the high temperatures attainable by highly exothermic catalyzed reactions. According to Hlavacek (1970), heat transfer by radiation need only be considered for operating temperatures in excess of 673°K (400°C), and since our operating temperatures should remain between 520 to 570°K, radiation should not be excessive. However, if radiation became significant, it would have the effect of enlarging the convective heat transfer parameter [see Equations (3) and (4)], and hence this parameter should properly be considered to be an overall heat transfer coefficient. Beek (1962) also includes a radiation term in his correlation for effective radial conductivity λ_{er}; this procedure is used for parameter estimation (Jutan et al., 1977*a*).

Radial Gradients

In this reactor, extensive cooling is provided at the reactor wall to ensure that temperature runaways can be prevented. This cooling can cause steep radial gradients, and temperature drops of up to 55°C have been observed across the radius (2 cm) of the reactor (Tremblay, 1973).

Radial gradients are almost always ignored in any unsteady state analysis of reactor systems, partly because of the resulting complications to the model. In any industrial situation where wall cooling is required for safety or control, radial gradients will exist. Nowhere, to our knowledge, has an attempt been made to include these gradients in any dynamic model, and the majority of dynamic studies avoid systems which exhibit appreciable radial gradients. Our reactor, unavoidably, has significant radial gradients, and these are accounted for in the model.

The Reactor Model

For clarity, a distinction is made between the gas temperature T_g and the solid temperature T_s. This allows two energy balances to be written along with the mass balances for each of the three independent species. The following normalized equations result:

Mass balance

$$\frac{-G_o}{\epsilon L}\frac{\partial C^i}{\partial z} + \frac{D_{er}}{\epsilon R^2 r}\frac{\partial}{\partial r}\left(r\frac{\partial C^i}{\partial r}\right) - \frac{\rho_B R^i}{\epsilon} = \frac{\partial C^i}{\partial t} \tag{2}$$

where $i = 1, 2, 3$ is the component number.

Energy balance: gas

$$\frac{G_oC_{pg}\rho_g}{L}\frac{\partial T_g}{\partial z} + \frac{\lambda_{er}}{R^2 r}\frac{\partial}{\partial r}\left(r\frac{\partial T_g}{\partial r}\right) + ha\rho_B(T_s - T_g) = C_{pg}\rho_g\epsilon\frac{\partial T_g}{\partial t} \tag{3}$$

Energy balance: solid

$$-ha\rho_B(T_s - T_g) + \sum_{i=1}^{3}\Delta h_i R_i(T_s)\rho_B = C_{ps}\rho_B\frac{\partial T_s}{\partial t} \tag{4}$$

The two energy balances may be combined by eliminating the term between them which describes heat transfer between solid and gas, $ha\rho_B(T_s - T_g)$. If the assumption of equal solid and gas temperatures is made and the homogeneous gas/solid temperature is defined as T, Equations (3) and (4) become:

Energy balance: solid/gas

$$\frac{-G_oC_{pg}\rho_g}{L\bar{C}}\frac{\partial T}{\partial z} + \frac{\lambda_{er}}{R^2\bar{C}r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{\sum_{i=1}^{3}\Delta h_i R_i\rho_B}{\bar{C}} = \frac{\partial T}{\partial t} \tag{5}$$

where

$$\bar{C} = [C_{ps}\rho_B + C_{pg}\rho_g\epsilon] \tag{6}$$

is a gas/solid heat capacity term.

Boundary conditions

$$r = 0 \quad \frac{\partial C^i}{\partial r} = \frac{\partial T}{\partial r} = 0 \text{ (symmetry)}$$

$$r = 1 \quad \frac{\partial C^i}{\partial r} = 0; \quad \frac{\partial T}{\partial r} = B_i(T_w - T) \tag{7}$$

$$z = 0 \quad T = T_w \quad \text{for all } r$$

$$C^i = C^i \text{ (inlet) for all } r,\ i = 1, 2, 3 \tag{8}$$

$$t = 0 \quad T = T \text{ (initial) } (r, z)$$

$$C^i = C^i \text{ (initial) } (r, z)\ i = 1, 2, 3 \tag{9}$$

The expressions for the rate equations R^i are given in Appendix 1. We can also identify (Gould, 1969) the thermal (v_T) and concentration (v_C) wave velocities as

$$v_T = \frac{G_oC_{pg}\rho_g}{L\bar{C}} \tag{10}$$

$$v_C = \frac{G_o}{\epsilon L} \tag{11}$$

Equations (2) and (5) represent four coupled, three-dimensional nonlinear partial differential equations. In their present form, a solution (even numerically) is not feasible, and it is necessary to seek some approximation to these equations that will reduce them to a form suitable for use for on-line control. The method of orthogonal collocation is used.

STATE SPACE REACTOR MODEL

In the previous section, a set of partial differential equations which describe the dynamics of the concentration and temperature profiles in our fixed-bed reactor was developed. In this section, these equations are broken down and simplified so as to fit into the framework of modern multivariable control theory which most often requires a model for the process to be expressed as a set of linear(ized) first-order ordinary differential equations in the (state space) form:

$$\dot{\mathbf{x}}(t) = \underline{\mathbf{A}}\mathbf{x}(t) + \underline{\mathbf{B}}\mathbf{u}(t)$$

$$\mathbf{y}(t) = \underline{\mathbf{H}}\mathbf{x}(t) \tag{12}$$

Once the dynamic equations for the system have been expressed in the standard form of Equation (12) and model parameters are estimated, much of the current multivariable control theory may be used to design one or more multivariable control schemes. When we deal with real processes, it will generally not be possible to describe the system exactly in terms of the deterministic state Equations (12), and one can account for noise in the system, modeling errors, and measurement errors by identifying and by adding a stochastic noise term to these equations. This is discussed elsewhere (Jutan et al., 1977*a*).

The first step is to express the set of nonlinear partial differential Equations (2) and (5) in the state space form given by (12). Because we are going from partial differential equations (PDE's) to ordinary differential equations (ODE's), some form of discretization of spatial variables r and z is necessary, so as to produce an ODE in time at each grid point in the z, r domain. In general, these equations will be nonlinear (since the PDE's were nonlinear), and it is necessary to linearize about some operating profile in the z, r domain. This operating profile could be obtained first by solving the steady state versions of the original

PDE's, or by choosing a profile from historical records. Although the discretization problem appears to be relatively straightforward, the following example illustrates that it is not trivial for this system. Assume that five grid points are adequate for discretizing the radial direction r and twenty grid points for axial direction z. This would define a mesh of 100 grid points. At each grid point there are four ODE's in time, one for each of the three concentrations and one for the temperature. Hence, the total number of ordinary differential equations necessary to describe the system would be 400. This is much too large a model for control.

Also, any discretization or lumping procedure in the axial direction would probably have to take into account the position of the hot spot (and discretize more finely here). This would mean that the discretization would have to change for different operating conditions, which is a great disadvantage. The method of orthogonal collocation has been very successfully applied to simplify reactor equations (Finlayson, 1971, 1972, 1974; Ferguson, 1970) and provides a powerful method for transforming PDE's to ODE's.

ADAPTION OF COLLOCATION FORMULAS TO REACTOR SYSTEM

Collocation formulas developed for derivatives (Villadsen and Stewart, 1969) are easily extended to partial derivatives by simply collocating with respect to a single independent variable. For example, the partial derivatives of temperature with respect to r at collocation point r_i are given by

$$r = r_i; \quad \frac{\partial T^{(n)}}{\partial r} = \sum_{j=1}^{n+1} A_{ij}{}^{(n)} T_j{}^{(n)}(z, t) \tag{13}$$

$$r = r_i; \quad \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T^{(n)}}{\partial r}\right) = \sum_{j=1}^{n+1} B_{ij}{}^{(n)} T_j{}^{(n)}(z, t) \tag{14}$$

where $T_j(z, t)$ is written for $T(r_j, z, t)$, a function of z and t. Villadsen and Stewart (1969) and Finlayson (1972) have tabulated values for the collocation weights $A_{ij}{}^{(n)}$ and $B_{ij}{}^{(n)}$.

Radial Collocation

The order of collocation approximation (n) in (13) and (14) necessary to approximate a function is not known beforehand and remains very much a matter of judgment. Experimental measurements (Tremblay, 1973) and an examination of typical temperature and concentration radial profiles in the literature (Finlayson, 1971) indicate that often radial gradients in temperature may be well represented by a quadratic and the corresponding radial concentration profiles by a quartic.

For the symmetric radial profiles in the reactor, a suitable trial function is given by (Villadsen and Stewart, 1967)

$$T^{(n)}(r, z, t) = T(1, z, t) + (1 - r^2) \sum_{k=0}^{n-1} a_k{}^{(n)}(z, t) P_k(r^2) \tag{15}$$

where the $a_k{}^{(n)}$ are unknown coefficients and P_k are Jacobi polynomials.

The technique in applying orthogonal collocation here is to write the three-dimensional differential equations as an enlarged set of two-dimensional equations at the collocation points in r. Extensive use of the boundary conditions is then made to derive relations between the dependent variables at the collocation points and hence eliminate some of them, reducing, in turn, the number of equations.

As illustrated in Figure 1, the axial temperature profile of the reactor is measured by a set of thermocouples located along the reactor bed ($r = o$). These axial temperatures provide some indication of the overall behavior of the reactor.

Temperature Equation

At $r = o$, the energy balance Equation (5) becomes

$$\left. - v_T \frac{\partial T_o}{\partial z} + \frac{\lambda_{er}}{R^2\overline{C}}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)\right]_o \frac{\sum_{i=1}^{3} \Delta h_i R_i \rho_B}{\overline{C}} \right|_o = \frac{\partial T_o}{\partial t} \tag{16}$$

Using L'Hopital's rule

$$\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)\right]_o = \left[2\frac{\partial^2 T}{\partial r^2}\right]_o \tag{17}$$

Orthogonal collocation is now used to obtain an expression for Equation (17) in terms of T_o and the known wall temperature T_w. Using Jacobi polynomials for the approximation (which results in a quadratic temperature profile), two collocation points are obtained at $r = 0.577$, $r = 1.0$. The center point is not a collocation point, and in order to obtain an expression for the temperature at $r = 0$, write (15) in an alternative form (Finlayson 1971) with T symmetric with respect to r

$$T_j{}^{(n)} = \sum_{i=1}^{n+1} d_i r_j{}^{2i-2} \quad j = 1, \ldots, n+1 \tag{18}$$

Evaluating the coefficients d_i in terms of the temperatures at the collocation points, for a first collocation approximation $((n) = 1)$, an extrapolation is obtained to the center point temperature T_o. Dropping the collocation superscript $(n) = 1$ here, write the extrapolation formula as

$$T_o(z, t) = \frac{3}{2} T_1(z, t) - \frac{1}{2} T_2(z, t) \tag{19}$$

where

$$T_j(z, t) = T(r_j, z, t)$$

The boundary condition at the wall has been characterized by Beek (1962) in terms of a Biot number B_i [see Equation (7)]:

$$\left.\frac{\partial T}{\partial r}\right|_{r=r_2} = B_i(T_w - T) \tag{20}$$

The use of the first collocation approximation from Equation (13) [omitting the collocation superscript $(n) = 1$, here] results in an expression for the first derivative in r, at the edge of the bed:

$$\left.\frac{\partial T}{\partial r}\right|_{r=r_2} = A_{21}T_1 + A_{22}T_2 \tag{21}$$

Similarly, an expression for the second derivative may be derived from Equations (14) and (19) and then (17) to give

$$\left.\frac{\partial^2 T}{\partial r^2}\right|_{r=o} = \overline{B}_{01}T_1 + \overline{B}_{02}T_2 \tag{22}$$

where the $\overline{B}_{0j}$'s are functions of the collocation parameters

A_{ij} and B_{ij}. Equating Equations (20) and (21) and using (19), we may eliminate all the temperatures except T_o and T_w. By further substituting the numerical values for the collocation constants A_{ij} and $\overline{B}_{ij}$, we get

$$\left.\frac{\partial^2 T}{\partial r^2}\right|_o = \frac{-2B_i}{(B_i+2)}[T_o - T_w] \qquad (23)$$

and

$$T_2 = T(r=1) = \left(\frac{2}{B_i+2}\right)T_o + \left(\frac{B_i}{B_i+2}\right)T_w \qquad (24)$$

Equation (16) then becomes

$$\left.-v_T\frac{\partial T_o}{\partial z} + \frac{\lambda_{er}4B_i}{R^2\overline{C}(B_i+2)}[T_w - T_o] + \frac{\sum_{i=1}^{3}\Delta h_i R_i \rho_B}{\overline{C}}\right|_o = \frac{\partial T_o}{\partial t} \qquad (25)$$

The temperature equation has now been reduced from a three-dimensional equation in variables (r, z, t) to a two-dimensional equation in variables (z, t). This reduced equation is a function of the axial temperature T_o only, but includes radial information via the wall temperature and Biot number. Radial temperature profiles can be obtained from the collocation Equation (18) or (19).

Concentration Equation

For the radial concentration profiles, standard boundary conditions require a zero first derivative at the reactor center $r = o$ and the reactor wall $r = 1$ (7). A suitable polynomial satisfying these requirements is a quartic, and this requires a second collocation approximation and three collocation points:

$$r_1 = 0.3938 \quad r_2 = 0.8031 \quad r_3 = 1.0$$

Again, the axial point is not a collocation point. Notice also that collocation point $r_3 = 1.0$ for the second collocation approximation coincides with collocation point $r_2 = 1.0$ for the first collocation approximation used in temperature. Writing the concentration equations at points $r_o = 0$ and $r_3 = 1.0$, we get

$r = r_3 = 1.0$

$$\left.-v_C\frac{\partial C_3^i}{\partial z} + \frac{D_{er}}{R^2\epsilon}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)\right]_{r=r_3} - \frac{R^i\rho_B}{\epsilon}\right|_{r=r_3} = \frac{\partial C_3^i}{\partial t} \qquad (26)$$

$r = 0$

$$\left.-v_C\frac{\partial C_o^i}{\partial z} + \frac{D_{er}}{R^2E}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C^i}{\partial r}\right)\right]_{r=0} - \frac{R_i\rho_B}{\epsilon}\right|_{r=0} = \frac{\partial C_o^i}{\partial t} \qquad (27)$$

$$i = 1, 2, 3$$

If we proceed in a similar manner to that followed for the temperature equation, the corresponding concentration equations (for second collocation approximation) are

$$C_o^i = 1.5572\, C_1^i - 0.8922\, C_2^i + 0.3350\, C_3^i \qquad (28)$$

and from (7) and using the form (13) we get

$$\left.\frac{\partial C^i}{\partial r}\right|_{r=r_3} = A_{31}C_1^i + A_{32}C_2^i + A_{33}C_3^i = 0 \qquad (29)$$

where $i = 1, 2, 3$ is the component number. The information that the first derivative is zero at $r = 0$ has already been included by the assumption of the quartic radial profile from which Equation (28) is obtained. For example, from Equation (18) with collocation approximation order $(n) = 2$, we get

$$C_j = d_1 + d_2r_j^2 + d_3r_j^4$$

which provides for symmetry in r and a zero first derivative at $r = 0$, as did the temperature equation. Thus, for the concentration equation, there are only two equations (28) and (29) between the concentration at the four radial points, r_o, r_1, r_2, r_3, and the partial derivative in r may be expressed in terms of C_o at r_o and C_3 at r_3:

$$\begin{aligned}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C^i}{\partial r}\right)\right]_{r=r_3} &= B_{31}C_1^i + B_{32}C_2^i + B_{33}C_3^i = \beta_{13}C_o^i + \beta_{32}C_3^i \\ \left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C^i}{\partial r}\right)\right]_{r=0} &= \overline{B}_{01}C_1^i + \overline{B}_{02}C_2^i + \overline{B}_{03}C_3^i = \beta_{01}C_o^i + \beta_{02}C_3^i\end{aligned} \qquad (30)$$

Substituting Equations (30) into (26) and (27), we get the set of differential equations

$$\left.-v_C\frac{\partial C_3^i}{\partial z} + \frac{D_{er}}{R^2\epsilon}[\beta_{31}C_o^i + \beta_{32}C_3^i] - \frac{R^i\rho_B}{\epsilon}\right|_{r=r_3} = \frac{\partial C_3^i}{\partial t} \qquad (31)$$

$$\left.-v_C\frac{\partial C_o^i}{\partial z} + \frac{D_{er}}{R^2\epsilon}[\beta_{01}C_o^i + \beta_{02}C_3^i] - \frac{R^i\rho_B}{\epsilon}\right|_{r=0} = \frac{\partial C_o^i}{\partial t} \qquad (32)$$

component number $i = 1, 2,$ or $3.$

which, together with the temperature Equations (24) and (25), provides the complete collocation model.

The system has now been reduced to seven, two-dimensional, differential equations, six in concentration and one in temperature, including an algebraic equation for temperatures at $r = 1$. The steady state versions of Equation (31), (32), (24), and (25) were used (Jutan, 1976) using initial reactor parameter values from the literature to obtain comparisons of the reactor model with steady state data (Tremblay, 1973). The highly exothermic nature of the reactions resulted in steep temperature gradients along the z axis. Because of this, a variable step size integration procedure, Hamming's modified predictor-corrector, was used for the simulations. Computation time on a CDC 6400 was about 20 CPU s. By comparison, a fourth-order Runge-Kutta method required about 45 CPU s for comparable accuracy.

Figure 2 compares the axial temperature profile predicted by the model equations with that obtained experimentally. Apart from the difference in entering gas temperatures, these profiles are in good agreement. (The discrepancy in inlet temperatures was caused by the absence of a feed preheater at the time the data were taken. To simplify the PDE model solution, it is convenient to have the gases enter the reactor at the wall temperature. This is

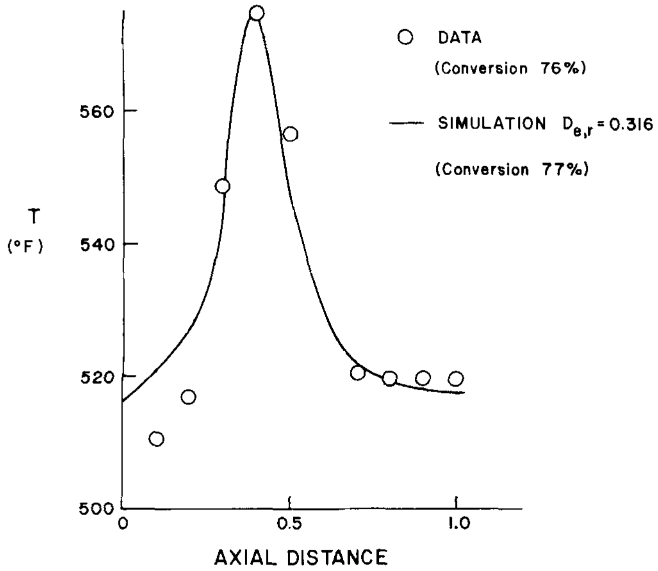

Fig. 2. Comparison of steady state temperature data with simulation profiles.

the case in later studies.) No point concentration measurements are available. Nevertheless, the overall predicted conversion of butane (77%) agrees well with the actual value obtained experimentally (76%). In addition, the model is able to predict variations in hot spot locations and butane conversions observed experimentally (Tremblay, 1973; Tremblay and Wright, 1974). Detailed fitting of actual reactor data is described in Part II of this paper (Jutan et al., 1977*a*).

Although these tests are by no means exhaustive, they provide some confidence in the collocation methods used here. The equations may now be reformulated to obtain a state space model representation [see Equation (12)] for the reactor.

Quasi Steady State Approximation

Up until this point, the development has been perfectly general in the sense that no specific reaction scheme or reactant properties has been assumed in the development of the mathematical model. However, in the present reactor, as with most solid catalyzed gas reactions, the ratio of the concentration wave velocity v_C to the thermal wave velocity v_T [see Equations (10) and (11)] is very large ($\sim$ 1400, here). This, *in effect, implies that the concentration profiles reach a quasi steady state rapidly and that this quasi steady state then follows the slowly changing temperature profile.*

In order to examine the relative dynamics of the concentrations and temperatures in the reactor, a high order (120 $\times$ 120) linearized model was derived from the radially collocated equations. Simulation studies (Jutan, 1976) showed that the concentration responses to a step input in flow rate had reached a quasi steady state within 3 s. Furthermore, since the control studies (Jutan et al., 1977*b*) were to use a 1 min sampling interval, it was clear that the concentration dynamics could be ignored.

The quasi steady state approximation allows the concentration time derivatives to be set approximately to zero in Equations (31) and (32). Note that this does not imply that concentrations are not a function of time, since concentrations are coupled to temperatures in the solution of the above equations, and temperatures obviously change with time according to (25). Incorporating the quasi steady state assumption, the concentration Equations (31) and (32) become

$$\frac{\partial C_3^i}{\partial z} = \frac{D_{er}}{\epsilon R^2 v_C}[\beta_{31}C_o^i + \beta_{32}C_3^i] - \frac{R^i \rho_B}{\epsilon v_C}\Bigg|_{r=r_3} \qquad (33)$$

$$\frac{\partial C_o^i}{\partial z} = \frac{D_{er}}{\epsilon R^2 v_C}[\beta_{01}C_o^i + \beta_{02}C_3^i] - \frac{R^i \rho_B}{\epsilon v_C}\Bigg|_{r=0} \qquad (34)$$

Axial Collocation

Typical concentration profiles along the length of the reactor, obtained from steady state simulations (Jutan, 1976), indicate that these profiles can be approximated by relatively low-order polynomials. However, certain temperature profiles may need a much higher order. The control problem which is discussed in Part III of this paper is to control the selectivity of the reaction as opposed to the conversion of butane. For this case, the axial temperature profiles are not nearly so severe as they are for high conversion. Michelsen et al. (1973) used axial collocation for their reactor and were able to adequately represent the dynamic behavior using six collocation points. Although more collocation points can reduce approximation error, numerical ill conditioning induced by the collocation weights begins to swamp the error.

One of the problems of fitting high-order polynomials to process curves is that the polynomials, if of sufficiently high order, may begin to ripple along the curve, and since these collocation formulas are being used to approximate derivatives, the dangers are apparent. The order of the collocation approximation must be chosen with these facts in mind. It is seen in the next section that the order (n^*) of the state space model becomes equal to the order of the collocation approximation (n), plus 1. A sixth-order collocation approximation was tentatively assumed [$(n) = 6$]. (This implies seven collocation points, excluding $z_o = 0$, where inlet conditions are constant over a sample period.) A nonsymmetric function is required, and Finlayson (1972) suggested one of the form

$$T^{(n)} = T(z=0) + z\sum_{i=1}^{n+1} a_i^{(n)}P_{i-1}(z) \qquad (35)$$

where $a_i^{(n)}$ are coefficients to be determined, P_i are Legendre polynomials, (n) is the order of approximation, and $T^{(n)}$ is a polynomial of order $n+1$. An analogous expression for the first derivative is obtained for collocation point z_i at $z = z_i$:

$$\frac{\partial T^{(n)}}{\partial z} = \sum_{i=1}^{n+1} D_{ij}^{(n)}T_j^{(n)}(z,t) \qquad (36)$$

A corresponding expression for the concentration derivative may be written. The $D_{ij}^{(n)}$ weight may be calculated according to Finlayson (1972), Chapter 5.

A previous analysis (Jutan et al., 1974) approximated the axial derivatives using a finite difference scheme tailored to the expected axial profile for temperature. The study was also more general in that the quasi steady state approximation was not used. This analysis required the time derivatives of concentration to be explicitly accounted for and resulted in large reduced order (eighty equations) state space models for the reactor.

Application to the Reactor Equations

Rewriting Equations (25), (33), and (34) using (36) to approximate the axial z derivative, one obtains a set of $(n+1)$ ODE's from the temperature Equation (25), at $n+1$ (= 7 here) different axial collocation points z_i. Two sets of algebraic equations are obtained from the concentration Equations (33) and (34). The temperature differential equations are obtained as

$$z = z_i; \quad \frac{dT_o^{(i)}}{dt} = -v_T \frac{\partial T_o}{\partial z}\bigg|_{z_i} + \frac{\lambda_{er} 4B_i}{R^2 \overline{C}(B_i + 2)}[T_w - T_o(i)] + \frac{\sum_{i=1}^{3} \Delta h_i R_i \rho_B}{\;}\bigg|_{\substack{r=0\\ z=z_i}} \tag{37}$$

$$i = 1, 2, \ldots n^* \quad \text{where} \quad n^* = n + 1$$

When Equation (36) is substituted for the axial derivatives where they appear, two sets of algebraic equations are obtained from Equations (33) and (34) and a set of $n + 1$ ordinary differential equations from Equation (37). These equations form the basis for a low-order nonlinear model of the reactor and may be used for simulation studies once parameters of the system are obtained.

All equations at this stage are nonlinear, and to obtain the standard state space equation we must linearize the algebraic and differential equations about some operating profile. An operating profile can be calculated from the nonlinear steady state versions of Equations (25), (33), and (34) with (24) by simply setting all time derivatives to zero and integrating the resulting set of nonlinear ordinary differential equations in z. If the radial temperature at the edge of the bed T_2 is expressed in terms of the temperature along the central axis T_o, using Equation (24) the two sets of algebraic equations and the set of ordinary differential equations can be expressed in terms of the deviation variables $\Delta\mathbf{C}_o$, $\Delta\mathbf{C}_3$, $\Delta\mathbf{T}_o$, together with two controls Δu_1, Δu_2 representing the flow rates of the two reactants. The following equations are obtained:

$$\underline{\mathbf{A}}_1\Delta\mathbf{C}_o = \underline{\mathbf{A}}_2\Delta\mathbf{T}_o + \underline{\mathbf{A}}_3\Delta\mathbf{C}_1 + \underline{\mathbf{A}}_4\Delta\mathbf{u} \tag{38}$$

$$\underline{\mathbf{B}}_1\Delta\mathbf{C}_1 = \underline{\mathbf{B}}_2\Delta\mathbf{T}_o + \underline{\mathbf{B}}_3\Delta\mathbf{C}_o + \underline{\mathbf{B}}_4\Delta\mathbf{u} \tag{39}$$

$$\frac{d\Delta\mathbf{T}_o}{dt} = \underline{\mathbf{E}}_1\Delta\mathbf{T}_o + \underline{\mathbf{E}}_2\Delta\mathbf{C}_o + \underline{\mathbf{E}}_3\Delta\mathbf{u} \tag{40}$$

Calling the state space model order $n^* = n + 1$, we get

$$\Delta\mathbf{C}_o = [\Delta C_o^1(z_1), \Delta C_o^1(z_2) \ldots \Delta C_o^1(z_{n^\cdot}), \ldots \Delta C_o^3(z_1) \ldots \Delta C_o^3(z_{n^\cdot})]'$$

$$\Delta\mathbf{T}_o = [\Delta T_o(z_1), \Delta T_o(z_2) \ldots \Delta T_o(z_{n^\cdot})]'$$

$$\Delta\mathbf{u} = [\Delta u_1, \Delta u_2]'$$

and $\underline{\mathbf{A}}_j$, $\underline{\mathbf{B}}_j$, $\underline{\mathbf{E}}_j$, $j = 1, 2, 3, (4)$ are matrices of constants representing the partial derivatives of the various terms in Equations (25), (33), and (34) evaluated at a given operating profile.

It is possible using Equations (38) to (40) to eliminate concentration to obtain a self-consistent set of n^* linear ordinary differential equations in temperature alone.

From (38) and (39)

$$\Delta\mathbf{C}_o = \underline{\mathbf{X}}_1\Delta\mathbf{T}_o + \underline{\mathbf{X}}_2\Delta\mathbf{u} \tag{41}$$

substituting into (40) we get

$$\frac{d\Delta\mathbf{T}_o}{dt} = \overline{\underline{\mathbf{A}}}\,\Delta\mathbf{T}_o + \overline{\underline{\mathbf{B}}}\,\Delta\mathbf{u} \tag{42}$$

where

$$\underline{\mathbf{X}}_1 = (\underline{\mathbf{A}}_1 - \underline{\mathbf{A}}_3\underline{\mathbf{B}}_1^{-1}\underline{\mathbf{B}}_3)^{-1}(\underline{\mathbf{A}}_2 + \underline{\mathbf{A}}_3\underline{\mathbf{B}}_1^{-1}\underline{\mathbf{B}}_2)$$

$$\underline{\mathbf{X}}_2 = (\underline{\mathbf{A}}_1 - \underline{\mathbf{A}}_3\underline{\mathbf{B}}_1^{-1}\underline{\mathbf{B}}_3)^{-1}(\underline{\mathbf{A}}_4 + \underline{\mathbf{A}}_3\underline{\mathbf{B}}_1^{-1}\underline{\mathbf{B}}_4)$$

$$\begin{aligned}\overline{\underline{\mathbf{A}}} &= \underline{\mathbf{E}}_1 + \underline{\mathbf{E}}_2\underline{\mathbf{X}}_1\\ \overline{\underline{\mathbf{B}}} &= \underline{\mathbf{E}}_3 + \underline{\mathbf{E}}_2\underline{\mathbf{X}}_2\end{aligned} \tag{43}$$

In our case, a value of $n^* = 7$ was tentatively assumed to be adequate after simulation with higher orders (up to $n = 11$) resulted in essentially identical profiles. Lower values of n^* (< 5) began showing differences in the profiles.

To investigate the effects of axial collocation and of linearizing the model about a steady state profile, simulation studies with step changes in feed rates were carried out on both the linearized Equations (41) and (42) and on the steady state versions of the reactor Equations (31) and (32) (Jutan, 1976). The combined effects of nonlinearities and axial collocation were shown to have some effect in the simulations, but the importance of these in a model for control purposes can only be assessed in the ultimate performance of the controller on the pilot plant reactor (see Jutan et al., 1977*b*).

Discrete State Space Model

Although the state space model (42), which is now in the standard form of Equation (12), can be used to formulate optimal control schemes, the reactor is to be controlled directly by a digital computer. It will be more convenient to have it in the corresponding discrete form for which the formal discrete solution is well known (Noton, 1965):

$$\begin{aligned}\mathbf{x}(t+1) &= \underline{\mathbf{F}}\mathbf{x}(t) + \underline{\mathbf{G}}\mathbf{u}(t)\\ \mathbf{y}(t) &= \underline{\mathbf{H}}\mathbf{x}(t)\end{aligned} \tag{44}$$

In the state Equation (42), the seven state variables ($n^* = 7$) are the deviation temperatures (about the operating profile) at the n^* collocation points along the central axis of the reactor. In the actual reactor, temperature measurements are available at nine equally spaced points along the central axis. The normalized distances at which these temperature measurements are available are compared with the seven collocation points in Table 1. The nine measured temperatures were converted to seven temperatures at the collocation points by quadratic interpolation using the nearest measurements around these points.

With the seven interpolated collocation temperatures, the measurement Equation (44) becomes

$$\mathbf{y}(t) = \underline{\mathbf{I}}_7\mathbf{x}(t) \tag{45}$$

Concentration as a Function of Temperature

The measurement equation given in (44) is general enough to accommodate the form suggested by Equation (41) for concentration as a function of temperature. Since the concentration variables of interest are the radially averaged concentrations at the reactor exit, Equation (41) has to be modified for averaged concentrations.

TABLE 1. TEMPERATURE MEASUREMENTS AND COLLOCATION POINTS FUNCTION OF NORMALIZED REACTOR LENGTH

Measurements	Collocation points
0.0	0.0
0.034	0.034
0.158	0.169
0.282	0.381
0.407	0.619
0.531	0.831
0.655	0.966
0.779	1.0
0.904	
1.0	

Following Villadsen and Stewart (1967), the radially averaged concentrations throughout the reactor may be obtained using the collocation integration formulas:

$$\overline{C}^i(z,t) = 2\int_0^1 C^i(z,t,r)dr = \sum_{j=1}^{n+1} w_j^{(n)} C^i(z,t,r_j) \tag{46}$$

where $w_j^{(n)}$ are n^{th} order collocation integration weights. Assuming a quartic radial profile for concentration, we get

$$\overline{C}^i = w_1 C_o^i + w_2 C_3^i, \quad i = 1, 2, 3 \tag{47}$$

and in terms of deviation variables

$$\Delta\overline{C}^i = w_1 \Delta C_o^i + w_2 \Delta C_3^i, \quad i = 1, 2, 3 \tag{48}$$

The expression for ΔC_o^i in Equation (41) together with an analogous one for ΔC_3^i may be substituted into (48) to obtain an expression for the vector of radially averaged (deviation) concentrations $\Delta\overline{\mathbf{C}}$ as a function of (deviation) temperatures and (deviation) manipulated variables at the previous time interval in the form

$$\Delta\overline{\mathbf{C}}(t) = \underline{\mathbf{X}}_3 \Delta\mathbf{T}_o(t) + \underline{\mathbf{X}}_4 \Delta\mathbf{u}(t-1) \tag{49}$$

The mixed exit concentration vector $\Delta\overline{\mathbf{C}}_{\text{ex}}$ (at $z = 1.0$) can be obtained by selecting that row of matrices $\underline{\mathbf{X}}_3$ and $\underline{\mathbf{X}}_4$ which correspond to exit conditions for each of the three species. Thus, the three-element vector of radially averaged exit concentrations can be expressed in terms of the temperatures and flows as

$$\Delta\overline{\mathbf{C}}_{\text{ex}}(t) = \underline{\mathbf{M}} \Delta\mathbf{T}_o(t) + \underline{\mathbf{N}} \Delta\mathbf{u}(t-1) \tag{50}$$

Thus, Equation (42) in discrete form together with Equation (50) provides a low-order linearized state space model of the dynamics of a complex reactor system. In Part II of this paper, the parameters of the process models are estimated from plant data, and in Part III a control study using these fitted models is discussed (Jutan et al., 1977*a*, 1977*b*).

APPENDIX 1: BUTANE HYDROGENOLYSIS KINETICS

The kinetics of the *n*-butane hydrogenolysis reaction on a nickel on silica catalyst have been modeled by Orlikas (1970) who did the fundamental work and then by Shaw (1974) who improved the model. They have postulated a mechanism for the reaction based on the following assumptions:

1. Butane and propane are absorbed on the catalyst surface and reaction takes place entirely as a surface catalyzed reaction.
2. The reaction products from these reactions may react further or be desorbed.
3. Because of low probability of breaking two or three carbon bonds simultaneously, reactions converting butane and propane to methane are assumed not to occur.

The net rates of reaction based on these assumptions have been established and are presented below. From a number of treatments with actual experimental data, the parameters have been estimated to yield the best fit.

Reaction Rates of the Reaction Species

Net rate of disappearance of butane:

$$R_{C_4H_{10}} = k/k_o \cdot A \cdot P^{m'}{}_{C_4H_{10}} \cdot P^{n'}{}_{H_2}$$

where $A = k_B \cdot \exp\{-\Delta E_B/RT\}$.

Net rate of appearance of propane:

$$R_{C_3H_8} = \frac{F \cdot R_{C_4H_{10}} - k/k_o \cdot B \cdot P^{m''}{}_{C_3H_8} \cdot P^{n''}{}_{H_2}}{1 + C}$$

where $B = k_{P1} \cdot \exp\{-\Delta E_{P1}/RT\}$

$$C = k_{P2} \cdot \exp\{-\Delta E_{P2}/RT\}$$

Net rate of appearance of ethane:

$$R_{C_2H_6} = \frac{(2 - F) \cdot R_{C_4H_{10}} - R_{C_3H_8} - k/k_o \cdot D \cdot P^{m'''}{}_{C_2H_6} \cdot P^{n'''}{}_{H_2}}{1 + G}$$

where $D = k_{E1} \cdot \exp\{-\Delta E_{E1}/RT\}$

$$G = k_{E2} \cdot \exp\{-\Delta E_{E2}/RT\}$$

Net rate of appearance of methane:

$$R_{CH_4} = 4 \cdot R_{C_4H_{10}} - 3 \cdot R_{C_3H_8} - 2 \cdot R_{C_2H_6}$$

Net rate of disappearance of hydrogen:

$$R_{H_2} = 3 \cdot R_{C_4H_{10}} - 2 \cdot R_{C_3H_8} - R_{C_2H_6}$$

where

F = fraction of butane which reacts to propane
k/k_o = catalyst activity (dimensionless)
k_B = frequency factor for butane (mole/(s·g catalyst·atm$^{(m'+n')}$))
ΔE_B = activation energy for rate of butane cracking (cal/mole)
m' = exponent on butane partial pressure
n' = exponent on hydrogen partial pressure in the butane rate expression
$P_{C_4H_{10}}$ = partial pressure of butane (atm)
P_{H_2} = partial pressure of hydrogen (atm)
k_{P1} = preexponential factor in propane rate expression (mole/(s·g catalyst·atm$^{(m''+n'')}$))
k_{P2} = preexponential factor in propane rate expression (dimensionless)
$\Delta E_{P1}, \Delta E_{P2}$ = activation energies in propane rate expression (cal/mole)
m'' = exponent on propane partial pressure
n'' = exponent on hydrogen partial pressure in the propane rate expression
$P_{C_3H_8}$ = partial pressure of propane (atm)
k_{E1} = preexponential factor in ethane rate expression (mole/(s·g catalyst·atm$^{(m'''+n''')}$))
k_{E2} = preexponential factor in ethane rate expression (dimensionless)
$\Delta E_{E1}, \Delta E_{E2}$ = activation energies in ethane rate expression (cal/mole)
m''' = exponent on ethane partial pressure
n''' = exponent on hydrogen partial pressure in the ethane rate expression
$P_{C_2H_6}$ = partial pressure of ethane (atm)
R_i = rate of disappearance or appearance of component i (mole/(s·g catalyst))
T = reacting temperature (°K)
R = universal gas law constant [atm·cm^3/(mole °K)]

Values of Kinetic Parameters: Shaw (1974)

(a) Butane rate

$k_B = 10^{15.6}$ $m' = 1$
$\Delta E_B = 5.1 \times 10^4$ $n' = -2.34$ (or -2.15)

(b) Propane rate expression

$k_{P1} = 10^{10.6}$ $\Delta E_{P2} = 3.0 \times 10^4$
$k_{P2} = 10^{12.2}$ $m'' = 1.0$
$\Delta E_{P1} = 4.0 \times 10^4$ $n'' = -2.15$ (or -2.08)

(c) Ethane rate expression

$k_{E1} = 10^{4.52}$ $\Delta E_{E2} = 1.6 \times 10^4$
$k_{E2} = 10^{6.81}$ $m''' = 1.0$
$\Delta E_{E1} = 2.6 \times 10^4$ $n''' = -2.21$

ACKNOWLEDGMENT

The work described in this paper was carried out with the financial support of the National Research Council of Canada under grant numbers A6075 and A6854, and also with an industrial grant from Imperial Oil Enterprises, Limited. The support of these organizations is gratefully acknowledged.

NOTATION

a = heat transfer area for catalyst, m^2/kg catalyst

$A_{ij}^{(n)}$ = collocation weights for first derivative

$a_i(z, t)$ = collocation trial function coefficients

$\underline{\mathbf{A}}$ = $n \times n$ dynamic state matrix (12)

B_i = Biot number $(h_w R/\lambda_{er})$

$B_{ij}^{(n)}$ = collocation weights for Laplacian

$\overline{B}_{ij}$ = derived collocation weights

$\underline{\mathbf{B}}$ = control matrix (12)

C^i = concentration of species i, mole/cm^3

$\overline{C}^i$ = radial average concentration of species i, mole/cm^3

C_j^i = concentration of species i at radial collocation point j

C_{ps} = specific heat of solid, J/(kg · °K)

C_{pg} = specific heat of gas, J/(kg · °K)

$\overline{C}$ = specific heat term $[C_{ps}\rho_B + C_{pg}\rho_g\epsilon]$, Equation (6)

D_{er} = effective radial diffusivity (based on empty reactor volume), m^2/s

d_P = catalyst particle diameter, m

$D_{ij}^{(n)}$ = collocation weights, Equation (36)

E = reaction activation energy, J/mole

$\underline{\mathbf{F}}$ = matrix for discrete state space model, Equation (4-56)

G_m = mass flow rate based on area of empty reactor, $kg(m^2 \cdot s)$

G_o = superficial gas velocity, m^3 gas/(m^2 reactor · s)

$\underline{\mathbf{G}}$ = control matrix, Equation (44)

h = heat transfer coefficient particle to fluid, W/(m^2 · °K)

h_w = heat transfer coefficient at reactor wall, W/(m^2 · °K)

$\underline{\mathbf{H}}$ = $m \times n$ measurement matrix (44)

$\underline{\mathbf{I}}_m$ = m^{th} order unity matrix

$N_{Pem,r}$ = Peclet number for radial mass transfer $\left(\dfrac{G_m d_P}{\rho D_{er}}\right)$

$N_{Pem,z}$ = Peclet number for axial mass transfer $\left(\dfrac{G_m d_P}{\rho D_{ez}}\right)$

$N_{Peh,r}$ = Peclet number for radial heat transfer $\left(\dfrac{G_m C_P d_P}{\lambda_{er}}\right)$

N_{Re} = Reynolds number for particles $\left(\dfrac{G_m d_P}{\mu}\right)$

(n), n = order of collocation approximation

n = order of state space model, $(n^* = n + 1)$ (4-51)

$P_i(r^2)$ = orthogonal polynomial symmetric in r

r = radial distance in reactor (normalized)

r_j = radial collocation point j

R = radius of reactor bed, m

R^i = net reaction rate for species i, mole/(kg catalyst · s)

R_i = reaction rate for reaction i, mole/(kg catalyst · s)

T = homogeneous gas/solid temperature, Equation (5), °K

T_j = temperature at radial collocation point j, °K

T_o = temperature along center axis of reactor, °K

T_w = temperature of reactor wall, °K

T_g = gas temperature, Equation (3), °K

T_s = solid (catalyst) temperature, Equation (4), °K

t = time: continuous (s); discrete (min)

$\mathbf{u}$ = vector of manipulated variables

v_T = thermal wave velocity $G_o C_{pg} \rho_g / L\,\overline{C}$, m/(s · m)

v_C = concentration wave velocity $G_o/\epsilon L$, m/(s · m)

$w_i^{(n)}$ = collocation quadrature weights

$\mathbf{x}(t)$ = state vector at sample time t

$\dot{\mathbf{x}}$ = time derivative of state vector (continuous)

$\mathbf{y}$ = vector of output variables

z = axial distance along reactor (normalized)

$'$ = transpose of matrix or vector

$\cdot$ = derivative with respect to time, for example, $\dot{\mathbf{x}}$

Greek Letters

λ_{er} = effective radial thermal conductivity, W/(m · °K)

ρ_B = bulk density of catalyst, kg/m^3

ρ_g = gas density, kg/m^3

Δh_i = heat of reaction for reaction i, J/mole

ϵ = void fraction, m^3 gas in voids/m^3 empty reactor

∇^2 = Laplacian operator

β_{ij} = derived collocation weights

Δ = prefix for deviation variable about steady state or operating point, example $C_o = C_o - C_o$ (steady state)

Subscripts

ex = exit conditions for reactor

i = species number

p = center axial conditions

LITERATURE CITED

Beek, J., "Design of Packed Catalytic Reactors," *Adv. Chem. Eng.*, 3, 203 (1962).

Bertram, D. R. and Chang, K. S., "Optimal Feedforward Control of Concurrent Tubular Reactors," *AIChE J.*, **16**, 897 (1970).

Carberry, J. J. and D. White, "On the Role of Transport Phenomena in Catalytic Reactor Behaviour," *Ind. Eng. Chem.*, **61**, No. 7, 27 (1969).

Crider, J. E. and A. S. Foss, "Computational Studies of Transients in Packed Tubular Chemical Reactors," *AIChE J.*, **12**, 514 (1966).

Dyring, J., M. Kummel, "Analogue Simulation and Control of a Tubular Reactor," *Chem. Eng. J.* Lausanne, **5**, No. 1, 93 (1973).

Froment, G. F., "Chemical Reaction Engineering," *Advances in Chemistry Series 109*, pp.1-34 (1972).

Finlayson, B. A., "Packed Bed Reactor Analysis by Orthogonal Collocation," *Chem. Eng. Sci.*, **26**, 1081 (1971).

———, "Orthogonal Collocation in Chemical Reaction Engineering," *Catal. Rev. Sci. Eng.*, **10**, 1, 69 (1974).

Ferguson, N. B. and B. A. Finlayson, "Transient Chemical Reaction Analysis by Orthogonal Collocation," *Chem. Eng. J.* Lausanne, **1**, 372 (1970).

Finlayson, B. A., *Method of Weighted Residuals and Variational Principles*, Academic Press, N.Y. (1972).

Froment, G. F., "Fixed Bed Catalytic Reactors," *Ind. Eng. Chem.*, **59**, No. 2, 18 (1967).

———, "Fixed Bed Catalytic Reactors: Technological and Fundamental Design Aspects," *Chem. Ing. Tech.*, **46**, 9, 381 (1974).

Gould, L. A., *Chemical Process Control: Theory and Applications*, Addison Wesley, Reading, Mass. (1969).

Hlavacek, V., "Aspects in Design of Packed Catalytic Reactors," *Ind. Eng. Chem.*, **62**, No. 7, 8 (1970).

Hansen, K. W., "Simulation of the Transient Behaviour of a Pilot Plant Fixed Bed Reactor," *Chem. Eng. Sci.*, **28**, 723 (1973).

Jutan, A., J. P. Tremblay, J. F. MacGregor and J. D. Wright, "The Formulation and Reduction of a State Space Model for the Dynamic Behaviour of a Non-Adiabatic Packed Bed Catalytic Reactor," *SOC Report #50*, Faculty of Engineering, McMaster University, Ontario, Canada (1974).

Jutan, A., *State Space Modelling and Multivariable Stochastic Control of a Pilot Plant Packed Bed Reactor*, Ph.D. thesis, McMaster University, Ontario, Canada (1976).

———, J. F. MacGregor, and J. D. Wright, "Multivariable Computer Control of a Butane Hydrogenolysis Reactor, Part II—Data Collection, Parameter Estimation and Stochastic Disturbance Identification," *AIChE J.*, **23**, 742 (1977).

Ibid, "Part III: On-Line Linear Quadratic Control Studies," *AIChE J.*, **23**, 750 (1977).

Lee, W., and V. W. Weekman, "Advanced Control Practice in the Chemical Process Industry: A View from Industry," AIChE J., **22**, 27 (1976).

Levenspiel, O., *Chemical Reaction Engineering,* 2nd edition, John Wiley and Sons, New York (1972).

Marroquin, G. and W. L. Luyben, "Practical Control Studies of Batch Reactors Using Realistic Mathematical Models," *Chem. Eng. Sci.,* **28**, 5, 993 (1973).

Mears, D. E., "On Criteria for Axial Dispersion in Non-isothermal Packed-Bed Catalytic Reactors," *Ind. Eng. Chem. Fundam.,* **15**, 1, 20 (1976).

Michelsen, M. L., H. B. Vakil, and A. S. Foss, "State Space Formulation of Fixed Bed Reactor Dynamics," *Ind. Eng. Chem. Fundam.,* **12**, 3, 323 (1973).

Noton, A. R. M., *Introduction to Variational Methods in Control Engineering,* Pergamon Press, New York (1965).

Orlikas, A., *Kinetic Study of the Hydrogenolysis of n-Butane on Nickel Catalyst,* M.Eng. thesis, McMaster University, Hamilton, Canada (1970).

———, T. W. Hoffman, I. D. Shaw, and P. M., Reilly, "The Hydrogenolysis of n-Butane on a Nickel on Silica Gel Catalyst: I A Kinetic Model," Can. J. Chem. Eng., **50**, 628 (1972).

Paris, J. R., and W. F. Stevens, "Mathematical Models for a Packed Bed Chemical Reactor," *Can. J. Chem. Eng.,* **48**, 100 (1970).

Sinai, J., and A. S. Foss, "Experimental and Computational Studies of the Dynamics of a Fixed Bed Chemical Reactor," *AIChE J.,* **16**, 658 (1970).

Seinfeld, J. H., G. R. Gavalas, and M. Hwang, "Control of Plug Flow Tubular Reactors by Variation of Flow Rate," *Ind. Eng. Chem. Fundam.,* **9**, No. 4, 651 (1971).

Sharma, C. S., *A Study of Catalytic Packed Bed Reactor Behaviour,* Ph.D. thesis Universiety of Salford, England (1977).

Shaw, I. D., *Modelling and Discrimination Studies in a Catalytic Fluidized Bed Reactor,* Ph.D. thesis, McMaster University, Hamilton, Canada (1974).

———, T. W. Hoffman, A. Orlikas, and P. M. Reilly, "The Hydrogenolysis of n-Butane on a Nickel on Silica Gel Catalyst: II Fluidized Bed Studies," *Can. J. Chem. Eng.,* **50**, 637 (1972).

Tremblay, J. P., *Computer Control of a Butane Hydrogenolysis Reactor,* M.Eng. thesis, McMaster University, Hamilton, Canada (1973).

Tremblay, J. P., *Real Time Computer Data Acquisition and Control Systems: An Application to Model Reference Adaptive Control of a Packed Bed Tubular Reactor,* Ph.D. thesis, McMaster University, Hamilton, Canada (1977).

———, "GOSEX—A Generalized Operating Software Executive Program," SOC-NOVA Report #3.01, McMaster University, Hamilton, Ontario (1975).

———, and J. D. Wright, "Computer Control of a Butane Hydrogenolysis Reactor," *Can. J. Chem. Eng.,* **52**, 845 (1974).

Vakil, H. B., M. L. Michelsen, and A. S. Foss, "Fixed Bed Reactor Control with State Estimation," *Ind. Eng. Chem. Fund,* **12**, No. 3, 328 (1973).

Villadsen, J. F. and W. E. Stewart, "Solution of Boundary Value Problems by Orthogonal Collocation," *Chem. Eng. Sci.,* **22**, 1483 (1967).

Young, L. C. and B. A. Finlayson, "Axial Dispersion in Nonisothermal Packed Bed Chemical Reactors," *Ind. Chem. Fundam.,* **12**, No. 4, 412 (1973).

Manuscript received December 14, 1976; revision received June 10, and accepted June 22, 1977.

ARTHUR JUTAN
J. F. MacGREGOR
and
J. D. WRIGHT

Department of Chemical Engineering
McMaster University
Hamilton, Ontario, Canada

Part II. Data Collection, Parameter Estimation, and Stochastic Disturbance Identification

A state space model, developed for multivariable control studies on a pilot plant packed-bed reactor for the hydrogenolysis of butane, is fitted to experimental temperature and concentration data collected under unsteady state conditions. The parameters estimated are the fundamental transport parameters of the packed-bed reactor and a catalyst activity parameter. A discrete stochastic model for the process disturbances is also identified, and a principle component type of procedure is used to reduce its dimensionality and to gain insight into the nature of these disturbances.

SCOPE

Considerable work has been done on the steady state modeling of nonisothermal packed-bed tubular reactors and the estimation of the transport properties in these reactors. Some of the difficulties associated with this estimation problem have been discussed by Beek (1962), Froment (1967, 1974), Hlavacek (1970), and Carberry and White (1969).

For reactor control purposes, an unsteady state or dynamic model of the reactor is required. While a detailed description of the reactor dynamics can be obtained in terms of partial differential equations derived from unsteady state material and energy balances, such a model, used directly, is certainly impractical and unnecessarily complex for process control. Empirical models, such as