Stability of Batch Catalytic Fluidized Beds

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This work is a study of the stability of a batch fluidized bed with a simple model. It is shown that multiple steady states can occur with all catalyst particles at the same temperature, some of these states being unstable. If the initial temperature of all the particles is not the same, a special kind of steady state, in which particles of different temperatures can coexist in the bed, might be obtained. The number of these pathological steady states is not finite, and the conversion obtained may be very different from that obtained by a uniform steady state.

The analysis has demonstrated that the initial temperature of the catalyst particles may be a predominate factor in determining the kind of steady state obtained. For the case of uniform catalyst particles, a simple stability analysis has been developed. Several numerical solutions of the transient equations were performed to investigate the possible responses of the system to disturbances of various steady states.

Catalytic fluidized beds have been widely used for about three decades, and, while they were initially applied to petroleum cracking processes, today they are utilized for a wide variety of reactions such as the oxidation of naphthalene and ethylene, production of alkyl chlorides, reduction and fluorination of uranium, etc. A description of many industrial processes using fluidized beds can be found in the book of Zens and Othmer (*1*). Various engineering aspects of fluidized beds have been thoroughly studied, and summaries are available (*1*, *2*).

Westerterp (*3*) treated the stability problem of a fluidized bed as if it were a stirred tank containing only the reactants. He was able to demonstrate the importance of stability considerations for the oxidation of naphthalene; however, his analysis neglected the effect of the presence of the solid particles in the bed.

Nakashio (*4*) investigated the stability of a moving fluidized bed in which combustion occurs, showed that the use of a linearized stability matrix is quite complicated, and derived an approximate method to determine stability.

The purpose of this work is to investigate stability problems associated with the design of a batch catalytic reactor. This reactor is usually built as a cylindrical shell with a support for the catalyst bed. The reactants enter from the bottom through a cone and cause the catalyst particles to be fluidized in the reactor. The reactants leave through a cyclone in which the entrained solids are separated and returned to the bed.

The models derived in this work are for systems with rather simple kinetics, but the methods which will be developed are applicable to systems with complex kinetics. The investigation will include two basic models: all particles have uniform temperature and partial pressure of the reactants, and the system contains at steady state particles of different temperature and partial pressure of the reactants.

PART I: UNIFORM TEMPERATURE MODEL

An important problem in the design of a fluidized bed converter is to determine the flow pattern of the gas through the bed. Experimental data summarized in (*1* and *2*) indicate that the mixing of the gas increases with an increase in diameter of the bed. Hence it may be assumed that in an industrial reactor mixing will be very nearly complete. Askins (*5*) reported that as the diameter of the reactor is increased, the composition of the gas throughout the bed approaches uniformity. Therefore, it is assumed in the models for the batch fluidized reactor that the gaseous reactants are completely mixed throughout the whole bed. The concentration of the reactant is assumed to be low, and the changes in the fractional void volume of the bed due to reaction are neglected.

The catalyst particles are assumed to be small enough so that heat and mass transfer resistances can be lumped at the particle surfaces, and the reaction is assumed to

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take place in the porous volume of the catalyst. All particles have the same size and shape. It is assumed that all the particles have the same temperature and the same partial pressure of the reactants. Though it is not necessary, it will be assumed that only one irreversible reaction $A \rightarrow B$ occurs in the bed. As will be shown later, the same method of treatment can be applied to more complicated kinetics, but no new features are introduced.

Development of Equations

With the above mentioned assumptions the mass and heat balances for the interstitial gas are

$$\frac{q}{VMP}(p_e - p) + a_v k_g (p_p - p) = \frac{\epsilon \rho_g}{MP}\frac{dp}{d\theta} \qquad (1)$$

$$\frac{1}{V} q\ c_g (T_e - T) + \frac{2\pi r h_w}{\pi r^2}(T_w - T) + a_v h_g (T_p - T) = \epsilon \rho_g c_g \frac{dT}{d\theta} \qquad (2)$$

and for each particle

$$s_p k_g (p - p_p) - v_p \alpha k p_p = \alpha v_p \frac{\rho_g}{MP}\frac{dp_p}{d\theta} \qquad (3)$$

$$s_p h_g (T - T_p) + (-\Delta H)\, v_p \alpha k p_p = v_p \rho_s c_s \frac{dT_p}{d\theta} \qquad (4)$$

It is assumed as a first approximation that MP is a constant throughout the whole bed. It is useful to use the following dimensionless groups:

$$\begin{aligned} A &= \frac{\alpha v_p a_v}{\epsilon s_p} & C &= \frac{a_v c_s v_p \rho_s}{\epsilon s_p c_g \rho_g} \\ F &= \frac{(-\Delta H) k_g}{h_g} & H_g &= \frac{a_v k_g MPV}{q} \\ H_T &= \frac{a_v h_g V}{q\ c_g} & H_w &= \frac{2 h_w V}{r c_g q} \\ K &= \frac{\alpha v_p}{s_p k_g} & \tau &= \frac{q\theta}{\epsilon \rho_g V} \end{aligned} \qquad (5)$$

In determining the value of the above parameters use can be made of the relation

$$(1 - \epsilon)\frac{s_p}{v_p} = a_v \qquad (6)$$

By use of the dimensionless groups (5) Equations (1) to (4) can be rewritten as

$$\frac{dp}{d\tau} = p_e - p + H_g (p_p - p) = W(p, p_p) \qquad (7)$$

$$\frac{dT}{d\tau} = T_e - T + H_T (T_p - T) + H_w (T_w - T) = X(T, T_p) \qquad (8)$$

$$A\frac{dp_p}{d\tau} = -H_g K\ k\ p_p + H_g (p - p_p) = Y(p, p_p, T_p) \qquad (9)$$

$$C\frac{dT_p}{d\tau} = H_T F K\ k\ p_p + H_T (T - T_p) = Z(T, p_p, T_p) \qquad (10)$$

Since

$$k = k_o \exp(-\Delta E / R T_p) \qquad (11)$$

these equations are highly nonlinear. Equations (7) to (10) immediately emphasize the need to include the presence of the catalyst particles in any model used to determine instability. To clarify the point let us assume for a moment that the partial pressure and temperature of the gas and the catalyst are the same; that is

$$T = T_p \qquad (12)$$

$$p = p_p \qquad (13)$$

In this special case the four transient equations are reduced to the following two:

$$(1 + A)\frac{dp_p}{d\tau} = p_e - p_p - H_g K k\ p_p \qquad (14)$$

$$(1 + C)\frac{dT}{d\tau} = T_e - T + H_w (T_w - T) + H_T F K k\ p_p \qquad (15)$$

For most gas solid systems $1 + A$ is of order 1, while $1 + C$ is larger by about two orders of magnitude. If one neglects the presence of the particles, $1 + A$ and $1 + C$ should be replaced by 1. This will not change the values of the temperature and partial pressures of the steady state, but it will change the transient behavior of the system. The temperature response of the model with the particles is much slower than that in which the particles are not present. In general, the transient behavior of the system will depend mainly on the initial conditions of the particles and will be almost independent of the initial conditions of the gas. Thus, it is clear that any realistic stability analysis must take into account the presence of the catalyst particles.

Steady State Determination

The steady state equations for the fluidized bed are

$$p_e - p + H_g (p_p - p) = 0 \qquad (16)$$

$$T_e - T + H_T (T_p - T) + H_w (T_w - T) = 0 \qquad (17)$$

$$p - p_p - Kk\ p_p = 0 \qquad (18)$$

$$T - T_p + FKk\ p_p = 0 \qquad (19)$$

Equations (16) and (18) are two linear equations in the variables p and p_p. Their solution yields

$$p_p = \frac{p_e}{(H_g + 1) Kk + 1} \qquad (20)$$

Equation (17) can be rewritten as

$$T = \frac{1}{1 + H_T + H_w}(T_e + H_T T_p + H_w T_w) \qquad (21)$$

Substitution of Equations (20) and (21) into (19) yields

$$Q_I = \frac{(1 + H_w)(T_p - T^*)}{1 + H_w + H_T} = \frac{F\ p_e\ Kk}{(H_g + 1) Kk + 1} = Q_{II} \qquad (22)$$

where

$$T^* = T_e + H_w T_w / (1 + H_w) \qquad (23)$$

Both Q_I and Q_{II} are functions of T_p only. Q_I is a straight line, while Q_{II} is a sigmoidal curve. A schematic description of Q_I and Q_{II} is given in Figure 1. Each intersection of Q_I and Q_{II} describes a possible steady state. In this case there might be one or three possible steady states.

The above method may be used for more general situations with simultaneous and consecutive reactions with complex kinetics. In these cases, however, a numerical procedure must be substituted for the analytical one described above. The heat generation function Q_{II} will be more complicated and will, in general, have several bumps in it; multiple steady states are possible.

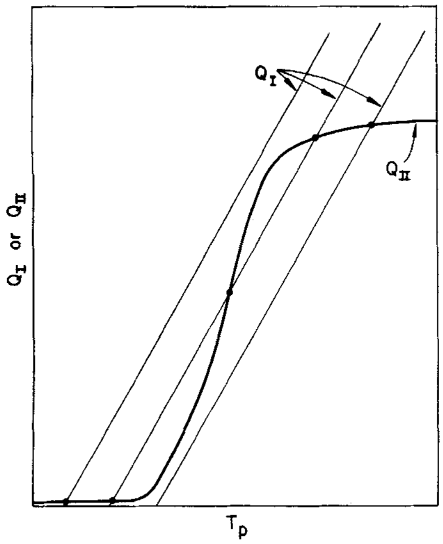

Fig. 1. Schematic illustration of steady state determination.

Stability Analysis

It is of interest to analyze the steady states for local asymptotic stability, that is, to determine which are stable or unstable to small perturbations. This will be done, as was done in previous work (*6*), by linearization about the steady state values of the transient Equations (7) to (10) and by checking the character of the eigenvalues of the appropriate linear system. The linearized equations may be conveniently written in terms of the vector of disturbances from the steady state and a Jacobian matrix, whose elements are evaluated at the steady state, as

$$\frac{d}{d\tau}\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = \frac{\partial(W, X, Y, Z)}{\partial(p, T, p_p, T_p)} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} \tag{24}$$

where

$$\begin{aligned} a_1 &= p - p_{ss} \\ a_2 &= T - T_{ss} \\ a_3 &= p_p - p_{pss} \\ a_4 &= T_p - T_{pss} \end{aligned} \tag{25}$$

The characteristic equation corresponding to the Jacobian matrix of Equations (7) to (10) has the form

$$\begin{bmatrix} b_{11} - \lambda & 0 & b_{13} & 0 \\ 0 & b_{22} - \lambda & 0 & b_{24} \\ b_{31} & 0 & b_{33} - \lambda & b_{34} \\ 0 & b_{42} & b_{43} & b_{44} - \lambda \end{bmatrix} = 0 \tag{26}$$

$$b_{11} = -(H_g + 1),\ b_{13} = H_g$$

$$b_{22} = -(1 + H_T + H_w),\ b_{24} = H_T$$

$$b_{31} = H_g/A,\ \ b_{33} = -H_g(1 + Kk)/A = -H_g p/A p_p$$

$$b_{34} = -H_g\, \Delta E\, Kk\, p_p/RT_p^2 = H_g\, \Delta E\,(T - T_p)/ART_p^2\, F$$

$$b_{42} = H_T/C,\ \ b_{43} = FH_TKk/C = FH_T(p - p_p)/C\ p_p \tag{27}$$

$$\begin{aligned} b_{44} &= \frac{H_T}{C}\left(\frac{\Delta E}{RT_p^2} FKk\, p_p - 1 \right) \\ &= \frac{H_T}{C}\left(\frac{\Delta E}{RT_p^2}\,(T_p - T) - 1 \right) \end{aligned}$$

Equation (26) may be written as

$$\lambda^4 + A_1\,\lambda^3 + A_2\,\lambda^2 + A_3\,\lambda + A_4 = 0 \tag{28}$$

and the coefficients A_i may be written in terms of the principal minors of the Jacobian matrix. For the above case

$$-A_1 = \left(\frac{\partial W}{\partial p}\right)_{ss} + \left(\frac{\partial X}{\partial T}\right)_{ss} + \left(\frac{\partial Y}{\partial p_p}\right)_{ss} + \left(\frac{\partial Z}{\partial T_p}\right)_{ss}$$

$$\begin{aligned} A_2 &= \frac{\partial(W, X)}{\partial(p, T)_{ss}} + \frac{\partial(W, Y)}{\partial(p, p_p)_{ss}} + \frac{\partial(W, Z)}{\partial(p, T_p)_{ss}} \\ &\quad + \frac{\partial(X, Y)}{\partial(T, p_p)_{ss}} + \frac{\partial(X, Z)}{\partial(T, T_p)_{ss}} + \frac{\partial(Y, Z)}{\partial(p_p, T_p)_{ss}} \end{aligned} \tag{29}$$

$$\begin{aligned} -A_3 &= \frac{\partial(W, X, Y)}{\partial(p, T, p_p)_{ss}} + \frac{\partial(W, X, Z)}{\partial(p, T, T_p)_{ss}} + \frac{\partial(X, Y, Z)}{\partial(p, p_p, T)_{ss}} \\ &\quad + \frac{\partial(W, Y, Z)}{\partial(p, p_p, T_p)_{ss}} \end{aligned}$$

In this way the following values are obtained for the A_i's:

$$\begin{aligned} A_1 &= -(b_{11} + b_{22} + b_{33} + b_{44}) \\ A_2 &= b_{11}(b_{22} + b_{33} + b_{44}) + b_{22}(b_{33} + b_{44}) \\ &\qquad + b_{33}b_{44} - b_{13}b_{31} - b_{34}b_{43} \\ A_3 &= -b_{11}(b_{22}b_{33} + b_{22}b_{44} + b_{33}b_{44} - b_{24}b_{42} - b_{34}b_{43}) \\ &\quad + b_{22}(b_{13}b_{31} - b_{33}b_{44} + b_{34}b_{43}) + b_{24}b_{33}b_{42} \\ &\quad + b_{13}b_{31}b_{44} \\ A_4 &= b_{11}b_{22}(b_{33}b_{44} - b_{34}b_{43}) + b_{13}b_{31}(b_{24}b_{42} \\ &\quad - b_{22}b_{44}) - b_{11}b_{24}b_{33}b_{42} \end{aligned} \tag{30}$$

A steady state is defined to be locally asymptotically stable if a small disturbance will damp out with time. This occurs only if all the eigenvalues of the characteristic Equation (28) will have negative real parts. The Routh Hurwitz (*8*) criterion is usually used; however, not all of Routh Hurwitz conditions are independent, and simpler conditions have been devised by Lienard and Chipart (*8*). The use of their criteria yields the following conditions for a fourth-order polynomial:

$$\begin{aligned} &\text{(i)} && A_1 > 0 \\ &\text{(ii)} && A_2 > 0 \\ &\text{(iii)} && A_1A_2A_3 > A_1^2A_4 + A_3^2 \\ &\text{(iv)} && A_4 > 0 \end{aligned} \tag{31}$$

Obviously the four conditions for stability (31) become rather involved owing to the complicated expressions for the A_i's (30). If one carries out all the necessary algebra, it can be shown that condition (iv) of (31) reduces to

$$\frac{1+H_w}{1+H_w+H_T}\left[\frac{p}{p_p}(H_g+1)-H_g\right] > \frac{\Delta E}{RT_p^2}(T_p-T) \qquad (32)$$

By differentiating Equation (22) it can be shown that Equation (32) is equivalent to the condition

$$\frac{dQ_I}{dT_p} > \frac{dQ_{II}}{dT_p} \qquad (33)$$

Thus, one of the necessary conditions for stability is that the rate of change of the heat removal from the system be larger than the rate of change of heat generation with respect to particle temperature. This slope condition immediately proves that the intermediate steady state is unstable. The simple physical meaning for the other three conditions is not apparent.

The first condition $A_1 > 0$ gives

$$2+H_g+H_T+H_w+\frac{H_g}{A}\,\frac{p}{p_p} - \frac{H_T}{C}\left[\frac{\Delta E}{RT_p^2}(T_p-T)-1\right] > 0 \qquad (34)$$

while the second condition $A_2 > 0$ gives

$$\frac{H_g}{A}\,\frac{p}{p_p}\left[H_g\left(1-\frac{p_p}{p}\right)+2+H_w+H_T\left(1+\frac{1}{A}\right) - \frac{H_T}{C}\,\frac{\Delta E}{RT_p^2}(T_p-T)\frac{p_p}{p}\right] + (H_g+1)\cdot$$
$$\cdot(1+H_T+H_w) - \frac{H_T}{A}\left[\frac{\Delta E}{RT_p^2}(T_p-T)-1\right](2+H_g+H_T+H_w) > 0 \qquad (35)$$

For most fluidized bed systems H_T/C is of order 1, and $\frac{\Delta E}{RT_p^2}(T_p-T)$ is much smaller than 1. Hence, one can immediately conclude that both conditions (34) and (35) are always satisfied.

The third condition $A_1A_2A_3 > A_1^2A_4 + A_3^2$ is extremely complicated, and no way was found by which it could be argued that this condition should be satisfied in practice. Such a conclusion would be desirable, since it would mean that the slope condition is both necessary and sufficient for asymptotic stability. All the numerical examples used in this work seem to imply this result; however, no proof of this could be found.

Example 1. Consider the following numerical example:

$a_v = 500$ sq.ft./cu.ft.
$c_s = 0.2$ B.t.u./lb./°F.
$c_g = 0.25$ B.t.u./lb./°F.
$h_g = 10$ B.t.u./hr./sq.ft./°F.
$h_w = 30$ B.t.u./hr./sq.ft./°F.
$k_g = 1$ lb. mole/hr./atm./sq.ft.
$k = 2.5 \exp\left(20.7 - \frac{15{,}000}{T}\right)$ lb. mole/hr./atm./cu.ft.
$M = 48$ lb./lb. mole
$P = 1$ atm.
$p_e = 0.1$ atm.
$q/V = 75$ lb./hr./cu.ft.
$r = 2$ ft.
$T_e = 600$°R.
$T_w = 720$°R.
$\alpha = 0.4$
$\epsilon = 0.7$
$-\Delta H = 8\ 10^4$ B.t.u./lb. mole
$\rho_s = 60$ lb./cu.ft.
$\rho_g = 0.1$ lb./cu.ft.

or in dimensionless form:

$A = 0.17142$
$C = 205.74$
$F = 8{,}000$
$H_g = 320$
$H_T = 266.667$
$H_w = 1.6$
$Kk = 0.0006 \exp\left(20.7 - \frac{15{,}000}{T}\right)$

By plotting the curves Q_{II} and Q_I vs. T_p it was found that three steady states are possible. The values of the four variables at the three steady states are given in Table 1. For each steady state the stability matrix was computed and the coefficients of the characteristic Equation (28) were determined. The eigenvalues were determined by solution of the fourth-order polynomial by use of the Newton-Raphson method. The values of the eigenvalues are reported in Table 1. It can be seen that in this case all the eigenvalues are real. The middle steady state is unstable since it has an eigenvalue with a positive real part. For all three steady states the absolute value of the first eigenvalue is much smaller than that of the other three, and the behavior near the steady state will be determined mainly by this eigenvalue.

TABLE 1. PRESSURES, TEMPERATURES, AND STABILITY EIGENVALUES FOR THE STEADY STATES OF EXAMPLE 1

	First steady state	Second steady state	Third steady state
p	0.09352	0.06704	0.006822
p_p	0.09350	0.06694	0.006531
T	690.445	758.344	912.764
T_p	690.607	759.167	915.094
λ_1	−0.00632	0.00610	−0.00898
λ_2	−0.91177	−1.26387	−12.6008
λ_3	−270.3147	−270.731	−270.7236
λ_4	−2186.977	−2183.084	−2258.0596

It is interesting to note that the difference in partial pressure and temperature of the gas and the catalyst is rather small, especially for the first steady state. This is mainly due to the fact that the particles in the fluidized bed are usually very small and have a large value of a_v. Thus the transfer resistances are quite small.

Numerical Solution of Transient Equations

The solution of the transient equations enables one to verify the stability analysis and to determine the response to large disturbances. The transient Equations (7) to (10) were integrated in this work by use of a modified Runge-Kutta-Gill routine with an adjustable increment size. While there is no theoretical difficulty in the solution of this initial value problem, some numerical difficulties arose during this work. It was found that unless the dimensionless time increment was kept quite small, of the order of 0.0002, numerical errors caused the solution to blow up. For such increment size the time of integration for one unit of τ was 30 sec. on the CDC-1604 computer. In certain cases, as shown in Figure 4, the duration of the transient was about 1,000 units of τ; hence the computer time required for such a numerical analysis was extremely large. It is necessary to find some way to avoid the need to use such small increments.

It is of interest to determine the reason for the numerical sensitivity of the transient equations. Define

$$\Delta P = p - p_p \tag{36}$$

and divide Equation (9) by A and subtract it from (7) to obtain

$$\begin{aligned}\frac{d\Delta P}{d\tau} &= p_e - p + H_g K k\, p_p/A - H_g\left(1 + \frac{1}{A}\right)\Delta P \\ &= f(p, p_p, T_p) - H_g\left(1 + \frac{1}{A}\right)\Delta P \end{aligned} \tag{37}$$

Now

$$f(p, p_p, T_p) > 0$$

Hence if ΔP is positive for some τ, it must remain positive for any larger τ. During the transient computations ΔP becomes very small as can be seen from Figures 2, 3, and 4. If the increment size is too large while Equations (7) to (10) are integrated, p_p may become larger than p owing to a numerical error. It was found that these errors do not tend to damp out with time but rather to grow until the solution blows up.

To overcome this difficulty and yet use large integration steps, the following device was tried successfully. Equations (7) to (10) were first integrated by using a very small integration step size, until p and p_p were almost equal. (The difference was less than 1% of their absolute value.) At this point it was assumed that both p and p_p remained the same throughout the transient behavior. The change with time of p and p_p was determined from this point on by use of Equation (14). A few numerical examples have shown that the error which was introduced by this technique is very small. In certain cases T and T_p become almost equal. In such cases Equations (8) and (10) may be replaced by (15). Once Equation (14) was used instead of (7) and (9), the increment could be increased by a factor of 100, and no numerical problems were encountered. If, in addition, Equations (8) and (10) were replaced by (15), the integration increment could be further increased.

As previously mentioned, the approach to the steady state in the fluidized bed is slow compared with the behavior of continuous stirred-tank reactors. The use of the above simplifying technique might be the only feasible way to carry out transient computations. For example, to compute the transient behavior shown in Figure 4 from the four differential equations one needs 25 hr. of computation on the CDC-1604. Use of the four equations up to $\tau = 2$ and then Equations (14) and (15) would require less than 4 min. for the whole transient computation.

Figure 2 shows the transient behavior of the system when the particles are initially heated to the temperature of the first steady state. The particle and gas temperature and pressure become almost identical after a short time ($\tau = 0.02$), and the system approaches the steady state very quickly. Figure 3 shows the transient behavior when the particles are initially at the temperature of the third steady state. Also, in this case the approach to the steady state is rapid. Figure 4 shows the transient behavior when the particles are heated to a temperature lower by 0.1°F. than the temperature of the second steady state. As can be seen also in this case, the particles and gas temperature and pressure become almost equal after a rather short time. The second steady state is unstable, and the system drifts away from it very slowly and reaches the first steady state at $\tau = 1{,}500$. It was found that if the initial particle temperature was higher by 2°F., the system would go to the third steady state. This, however, is not shown here, since the behavior would not show any new characteristics.

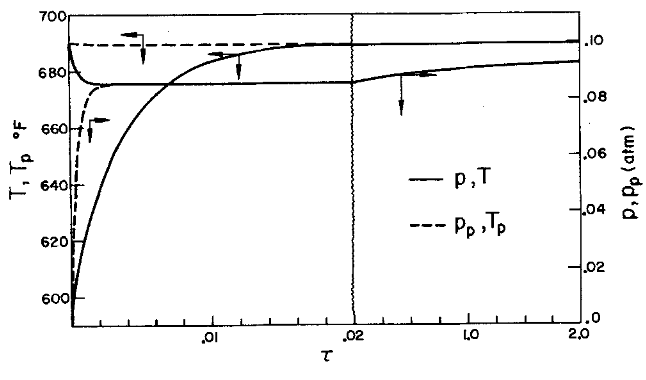

Fig. 2. Approach to first steady state.

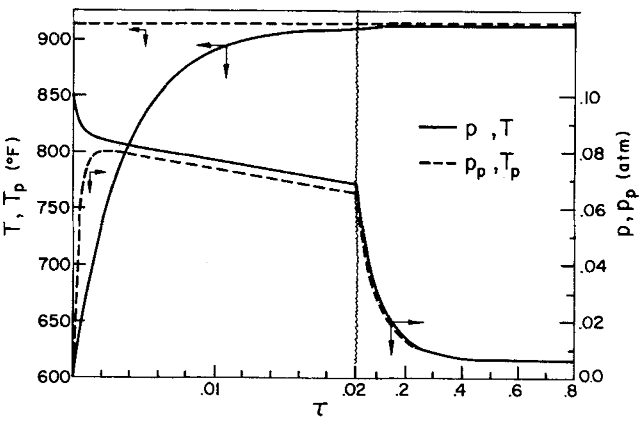

Fig. 3. Approach to third steady state.

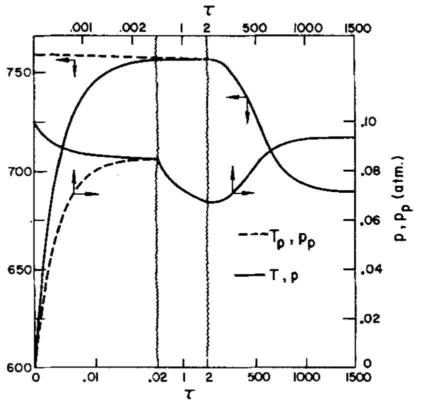

Fig. 4. Shift from second to first steady state.

As can be seen from the above three examples, the initial catalyst temperature will determine which steady state will be approached. In all the examples the initial partial pressure in the particles and the initial partial pressure and temperature of the gas had little effect. This is because the heat capacity of the particles is much higher than that of the gas, and no matter what the initial temperature of the gas is, it very quickly approaches the initial temperature of the solid. It can also be seen that the temperature response of the system is slow. This is also due to the high ratio between the heat capacity of the catalyst to that of the gas. If the system did not contain the catalyst particles, the term $1 + C$ in Equation (15) could be replaced by 1, and the temperature derivative would be larger by about two hundred times.

PART II: NONUNIFORM PARTICLE TEMPERATURE DISTRIBUTION

In the first model it was assumed that all catalyst particles in the batch fluidized bed had the same temperature and partial pressure during the transient and steady behavior. In practice it may often happen that the initial temperature of the various particles is not uniform, and it is important to determine whether this affects the number of possible steady states and their stability.

It was shown (3) that for given gas conditions a catalyst particle might have more than one steady state. Thus, it can be guessed intuitively that under certain conditions a batch fluidized bed might possess a steady state under which different particles are at different temperatures, while the temperature and the reactant partial pressure of the mixed gas are uniform throughout the entire bed. Clearly, such a steady state could be reached only if the initial particle temperature was not uniform.

Development of Equations

In this model it is assumed that the gas is ideally mixed in the batch fluidized bed. The catalyst particles consist of n groups, each one containing a fraction x_i of the total number of particles. The temperature and partial pressure of the reactant are the same for all particles which belong to the same group.

The gas heat and mass balances are

$$p_e - p + H_g\left(\sum_{i=1}^{n} x_i p_p{}^i - p\right) = \frac{dp}{d\tau} \tag{38}$$

$$T_e - T + H_w(T_w - T) + H_T\left(\sum_{i=1}^{n} x_i T_p{}^i - T\right) = \frac{dT}{d\tau} \tag{39}$$

and the heat and mass balances for group i of the particles are

$$\left.\begin{array}{ll} H_g(p - p_p{}^i) - H_g K k^i p_p{}^i = A\dfrac{dp_p{}^i}{d\tau} & (40) \\ H_T(T - T_p{}^i) + F H_T K k^i p_p{}^i = C\dfrac{dT_p{}^i}{d\tau} & (41) \end{array}\right\} i = 1 \text{ to } n$$

Steady State Determination

To determine the number of possible steady states from a given initial temperature distribution, one must investigate the possible solutions of the following system of equations:

$$p_e - p + H_g\left(\sum_{i=1}^{n} x_i p_p{}^i - p\right) = 0 \tag{42}$$

$$T_e - T + H_w(T_w - T) + H_T\left(\sum_{i=1}^{n} x_i T_p{}^i - T\right) = 0 \tag{43}$$

$$\left.\begin{array}{ll} p - p_p{}^i - K k^i p_p{}^i = 0 & (44) \\ T - T_p{}^i + F K k^i p_p{}^i = 0 & (45) \end{array}\right\} i = 1, 2, n$$

If one substitutes Equations (44) and (45) into Equations (42) and (43), the following gas enthalpy balance is obtained:

$$T(1 + H_w) - (T_e + H_w T_w) = \frac{H_T}{H_g} F(p_e - p) \tag{46}$$

or

$$p_e - p = B(T - T^*) \tag{47}$$

where

$$B = \frac{H_g(1 + H_w)}{H_T F} = \frac{M P\, C_p(1 + H_w)}{(-\Delta H)} \tag{48}$$

$$T^* = (T_e + H_w T_w)/(1 + H_w) \tag{49}$$

For any group of particles at steady state, the following relation, obtained by dividing (45) by (44), should hold:

$$Y_I = p_e\frac{(T_p{}^i - T)}{p} = \frac{(T_p{}^i - T)p_e}{p_e - B(T - T^*)} = \frac{F\, p_e K k^i}{1 + K k^1} = Y_{II} \tag{50}$$

A schematic figure of Y_I and Y_{II} is given in Figure 5.

Now Y_I is a linear function of $T_p{}^i$ for T fixed. If one considers two different values of T, say T_1 and T_2, and solves the corresponding linear equations simultaneously for Y_I and $T_p{}^i$, one obtains

$$T_p{}^i = \frac{p_e + BT^*}{B}$$

$$Y_I = \frac{p_e}{B}$$

at the intersection and this is independent of T. Hence all straight lines Y_I with T as a parameter intersect at a common point S as shown on Figure 5. Note that at the point of intersection $T_p{}^i$ corresponds to the maximum temperature, since from Equation (47) when $p = 0$

$$p_e = B(T_{\max} - T^*) \tag{51}$$

so that

$$p = B(T_{\max} - T) \tag{52}$$

and

$$\frac{p_e}{p}(T_{\max} - T) = T_{\max} - T^* \tag{53}$$

Consider first the case in which for each T there is only one intersection between the Y_I — Y_{II} curves. This means that the only possible steady states are those for which the temperature of all particles is uniform. The steady state values are determined by checking which of the values of T (and the corresponding values of T_p) satisfy the enthalpy equation (43). Another simpler approach for this special case is to determine the uniform temperature steady state by the methods developed in Part I. Thus, in this case there may be a single steady state (as, for example, case b of Table 2) or three steady states (as for case g of Table 2).

Consider now the case in which for a given value of $T = T'$ there exist three intersections between the Y_I and Y_{II} curves for $T_p = T_a, T_b, T_c$. This means that for $T = T'$ the particle steady state equations (44) and (45) can be satisfied only for the above three temperatures. Thus, if the system is at steady state, no more than three groups of particles of different temperature can coexist in the fluidized bed. This conclusion is for the special shape of the Y_{II} curve obtained for one reaction. If consecutive or parallel reactions occur, the shape of the Y_{II} curve may be such that more than three groups of particles of different temperatures can coexist.

In the construction of the Y_I lines, use was made of the gas enthalpy balance, which was obtained from a combination of Equations (42) and (43). Hence, if one can determine the x_i which will satisfy the gas energy balance [Equation (43)] for $T = T'$ and $T_p = T_a, T_b, T_c$, one will automatically satisfy the gas mass balance [Equation (43)]. In such a case the system of Equations (42) to (45) is satisfied, and the fluidized bed will possibly contain three different groups of particles of different temperatures. The problem is to find three x_i which will satisfy Equation (43) subject to the restrictions

$$\sum_{i=1}^{3} x_i = 1 \tag{54}$$

and

$$x_i \geqq 0 \tag{55}$$

Thus, there are two linear equations, (43) and (54), for determining the values of the three variables x_1, x_2, x_3, and it appears that for some values of T there may not be a unique solution but rather a spectrum of possible values of x_i. However, in the stability analysis it will be proved that at any steady state there can coexist at most two groups of particles of different temperatures (the high and low temperature particles). Thus, for any value of T, T_p^1, T_p^2, the values of x_1 and x_2 will be uniquely determined from the two linear equations (43) and (54).

Stability Considerations

It is of interest to determine the effect of a small perturbation on the temperature and pressure of one group of particles, on the assumption perturbation does not affect the other groups of particles and the gas. Thus we will determine which group of particles is stable by linearizing the particle equations (40) and (41) for any i.

Define

$$p_p^i - p^i_{p,ss} = w^i \tag{56}$$

$$T_p^i - T^i_{p,ss} = y^i \tag{57}$$

The linearization yields

$$\frac{dw^i}{d\tau} = a_{11}w^i + a_{12}y^i \tag{58}$$

$$\frac{dy^i}{d\tau} = a_{21}w^i + a_{22}y^i \tag{59}$$

where

$$a_{11} = -H_g(1 + Kk^i)/A$$

$$a_{12} = -H_g \,\Delta E\, Kk^i p_p{}^i/ART_p{}^{i^2}$$

$$a_{21} = H_T F K k^i/C$$

$$a_{22} = H_T(-1 + \Delta E F K k^i p_p{}^i/RT_p{}^{i^2})/C \tag{60}$$

The necessary and sufficient conditions that Equations (58) and (59) will have asymptotic solutions tending toward zero are

$$(1 + Kk^i) > \Delta E F K k^i p_p{}^i/RT_p{}^{i^2} \tag{61}$$

$$\frac{H_T}{C} + \frac{H_g}{A}(1 + Kk^i) > \frac{H_T\,\Delta E}{CRT_{p^{i2}}} FKk^i p_p{}^i \tag{62}$$

Condition (62) can be rewritten as

$$1 + \frac{H_g C}{H_T A}(1 + Kk^i) > \frac{\Delta E}{RT_p{}^i} FKk^i p_p{}^i \tag{63}$$

If $H_gC/H_TA \geqq 1$, condition (61) implies condition (62). By definition

$$\frac{H_g C}{H_T A} = \frac{MPk_g c_s}{\alpha\ h_g}\ \frac{\rho_s}{\rho_f} \tag{64}$$

For gas solid systems the predominate factor is ρ_s/ρ_f, since it is very large and the other term is usually of order 1 or more. Thus condition (61) usually implies condition (62).

From Equation (50) one can obtain

$$\frac{dY_I}{dT_p{}^i} = \frac{p_e}{p} \tag{65}$$

$$\frac{dY_{II}}{dT_p{}^i} = \frac{Fp_eKk^i\ \Delta E}{(1 + Kk^i)RT_{p^{i2}}} \tag{66}$$

From the steady state equation (44)

$$\frac{p_p{}^i}{p} = 1 + Kk^i \tag{67}$$

so that

$$\frac{dY_{II}}{dT_p{}^i} = \frac{p_eFKk^ip_p{}^i\ \Delta E}{(1 + Kk^i)RT_{p^{i2}}} \tag{68}$$

From the above it is clear that condition (61) is equivalent to

$$\frac{dY_I}{dT_p{}^i} > \frac{dY_{II}}{dT_p{}^i} \tag{69}$$

or that the slope of Y_I must be greater than that of the sigmoidal curve Y_{II} at the point of intersection. Thus, from the three possible steady states for the particles, only the first and third are stable, while the second one is unstable. This means that a stable steady state for Equations (42) to (45) can consist of a mixture of at most two groups of particles of different temperatures.

Discussion of Possible Steady States

To determine a possible steady state one must satisfy Equation (43) and the restrictions

$$\begin{gathered} x_1 + x_2 = 1 \\ x_1 > 0,\ x_2 > 0 \end{gathered} \tag{70}$$

Substitution of Equation (70) into (43) yields

$$x_2 = \frac{(1 + H_w)(T - T^*)/H_T - (T_p{}^1 - T)}{T_p{}^2 - T_p{}^1} \tag{71}$$

where $T_p{}^1$ and $T_p{}^2$ are the two stable particle temperatures for the given value of T obtained from the Y curves.

For each T, values of $T_p{}^1$ and $T_p{}^2$ are determined from the Y curves. The corresponding values of x_1 and x_2 are uniquely determined from Equations (43) and (71). There usually is a continuous range of values of T for which there is more than one intersection between the Y curves. If restriction (55) is satisfied for x_1 and x_2, there will be a steady state for this value of T. Thus there are in certain cases an infinite number of possible steady states, each state corresponding to one value of T but over a continuous range of T. The initial conditions of the system will determine which steady state will be reached. Hence it is essential to perform a stability and transient analysis of the system.

In most cases, x_2 is small, since H_T is large and the value of $T_p{}^2 - T_p{}^1$ is also large. It can be seen that an increase in H_w tends to increase the value of x_2. H_w is inversely proportional to the diameter of the bed, and hence it will be large for reactors with small diameter. Therefore, x_2 would be larger in a pilot plant than in a full scale reactor. Thus, the occurrence of steady states for which different particles have different temperatures may lead to difficulties in design scale up. Since the value of x_2 is small, its presence might not be detected by measuring devices, even though the presence of these hot spots could have an important effect on the yield of the reactor.

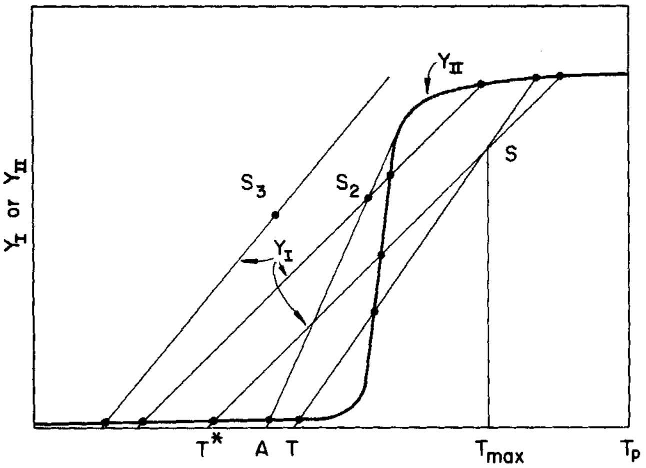

Fig. 5. Schematic illustration of Y_I and Y_{II} curves as a function of T_p.

When the value of x_2, as computed by Equation (71), is nonpositive, there cannot be a steady state under which particles of different temperatures coexist in the bed. Thus it can be seen that an increase of H_T, the dimensionless heat transfer coefficient between the two phases, can prevent the occurrence of this undesirable phenomenon.

It is of interest to determine the effect of the temperature of the gas on the value of x_2. Several typical cases will be discussed, and the numerical values of the parameters of these examples are given in Table 2. It will be shown that the shape of the $x_2 - T$ curve can be determined from the knowledge of the shapes of the $Y_I - Y_{II}$ [Equation (50)] and $Q_I - Q_{II}$ [Equation (22)] curves.

Consider first the case for which the $Q_I - Q_{II}$ curves have one intersection, that is, a unique uniform temperature steady state. If the S point is in such a position that for each T there is a unique intersection between the Y_I and Y_{II} curves, only uniform temperature steady states can exist. Hence, in this special case a unique steady state exists as in case b.

If the location of the S point is like that of S_2 in Figure 5, then for a certain range of gas temperatures two groups of particles of different temperatures can coexist in a steady state. This occurs for case a of Table 2, and Figure 6*a* describes the change of x_2 with T. In certain cases x_2 may attain a maximum for some T, but it can be zero only for one value of T. The reason being that if the $Q_I - Q_{II}$ curves intersect only once, a unique uniform temperature steady state exists.

If the $Q_I - Q_{II}$ curves have three intersections, three uniform temperature steady states can exist, and the situation is more involved. The simplest case occurs when the S point is located such that there is a unique intersection between the $Y_I - Y_{II}$ curves for $T^* \leqq T \leqq T_{\max}$. This means that only uniform temperature steady states can exist. In this case three steady states are possible as in case g.

The situation becomes more complex if for a given range of values of T there are three intersections between the $Y_I - Y_{II}$ curves. To discuss this case define by U_1, U_2, and U_3 the temperatures of the steady states predicted by the uniform temperature model ($U_1 < U_2 < U_3$). $T = U_2$ is the unstable uniform temperature steady state. It is known a priori that $x_2 = 0$ for $T = U_1$, U_2, and U_3. In this case x_2 obtains a positive value for $T > U_1$, and its value changes continuously with T. Near $T = U_1$ the increase in the value of $(1 + H_w)(T - T^*)/H_T$ is larger than the increase of $T_p{}^1 - T$ with T. Thus, as can be seen from Equation (71), in this range x_2 increases with increased values of T. (The change in the value of $T_p{}^1 - T_p{}^2$ is rather small in this range.) As T is further increased towards U_2, the value of $T_p{}^1 - T$ increases faster than $(1 + H_w)(T - T^*)/H_T$, and as a result x_2 decreases with increasing values of T until $x_2 = 0$ for $T = U_2$. For $T > U_2$, x_2 becomes negative. This means that for $T > U_2$ there can be no steady state with particles with two different temperatures. Thus, in this case there are three (one unstable) uniform temperature steady states and an infinite number of steady states for which $U_1 < T < U_2$ with two groups of particles having different temperatures in the bed. Note that for each value of T the temperatures of the two groups of particles have to be determined from the Y_I Y_{II} curves.

Figure 6*b* describes the variation of x_2 with T for two examples (cases e and f). The close similarity of the values of x_2 for the two examples is not accidental. For both cases the same rate equation and values of T^* and $F/(1 + H_w)$ were chosen. Thus, both cases have the same $T_{\max}$ and S point. This means that for a given T both have the same Y_I curve. For each $T_p{}^i$ the value of Y_{II} for the two cases is proportional to F. The S point is located to the right of the Y_{II} curve and is similar to point S in Figure 5. Hence for a given T the values of $T_p{}^1 - T$ and $T_p{}^2 - T$ for both cases are approximately proportional to F, or in this specific case to $1 + H_w$. From Equation (71) it is clear that if both $T_p{}^1 - T$ and $T_p{}^2 - T$ are exactly proportional to $1 + H_w$, the values of x_2 for both cases would have been identical.

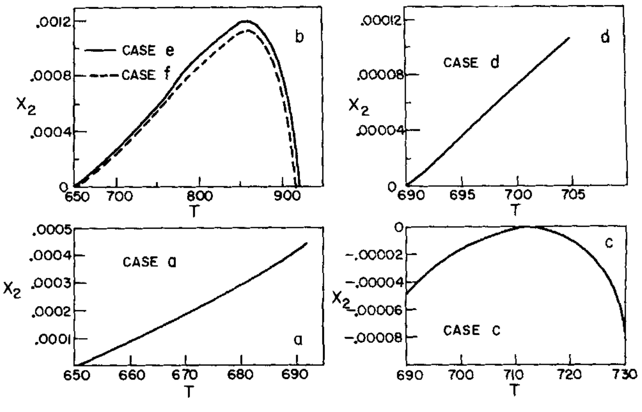

Fig. 6. Change of x_2 with T.

A special case might occur if the common point is like S_2 in Figure 5. In such a case two groups of particles can coexist in the bed for gas temperatures in the range $U_1 < T \leqq A$, where $A < U_2$. For each T the values of $T_p{}^1$ and $T_p{}^2$ are determined from the $Y_I - Y_{II}$ curves. In this case the value of x_2 will change as a function of T in a manner similar to that of the case in which there is a unique uniform temperature steady state. The change of x_2 with T for such a case is described in Figure 6*d*. (This is the same case as used in the example of Part I.)

A special degenerate case is case c in which the first two uniform temperature steady states, U_1 and U_2, have degenerated into one. (The Q_I curve is tangent to the Q_{II} curve.) Hence U_1 and U_2 are one point for which there is a uniform temperature steady state ($x_2 = 0$). As was explained above for $T > U_2$, the values of x_2 are always nonpositive, and in this range there cannot be a steady state with two groups of particles with different temperatures coexisting in the bed. An example of such a case is shown in Figure 6*c*.

From the above it can be concluded that if a mixture of particles of different temperatures can coexist at steady state, the number of possible steady states is not finite. The steady state temperature of the gas can change continuously over a spectrum of temperatures. The above steady states can be obtained only if the initial temperature distribution of the particles is not uniform. To avoid the phenomena of obtaining such steady states the reaction should be started when the temperature of the particles is as uniform as possible.

Transient Computations

The numerical solution of the transient equations, (38) to (41), is of importance since it is the only way to determine which steady state the system would approach from prescribed initial conditions. The number of equations to be integrated is $2n + 2$, where n is the number of groups of particles with different temperatures which are to be considered for the transient case. The computations were carried out with a Runge-Kutta-Gill routine with a self-adjusting step size, so that the numerical error could be kept smaller than a prescribed value. It was found that in order to avoid numerical instabilities the step size for τ must be of the order of 10^{-4}. With two groups of particles of different temperatures used, the integration time on a CDC-1604 computer was between 5 and 10 min. for each unit of τ depending on the case. In order to avoid excessive computer time, it was decided to perform the transient computation only for cases where n was either 2 or 3. Use of a faster computer would enable one to investigate more complex cases.

All transient examples were carried out for cases for which there is an infinite number of possible steady states. Under these conditions the steady state temperature of the gas is a continuous function of x_2.

The first transient computations were done for case a. The analysis predicts that in this case (Figure 6*a*) there will be an infinite number of possible steady states. The initial conditions determine which possible steady state will be obtained. Figure 7 describes the behavior of a system in which most of the particles are initially at a temperature of 654°R., while a very small fraction of the particles ($x_2 = 0.000035$) is at the very high temperature, 1,422°R. It can be observed that the values of $T_p{}^1$ and $p_p{}^1$ become indistinguishable from T and p after a very short time. The heat capacity of the very hot particles is small compared with that of the other group of particles or the gas. As a result the temperature of the hot particles changed comparatively fast (about 60°F. in the first unit of τ), while the temperature of the other group of particles remained practically unchanged during that period of time. The hot particles are first cooled, but at $\tau = 1.5$ they start to heat up to the steady state value. At $\tau = 12$ the system has reached a steady state $T_p{}^1 = 654$, $T_p{}^2 = 1{,}408$, and $x_2 = 0.000035$. It should be mentioned that in accordance with the uniform temperature model, under these conditions a unique steady state exists for which the temperature of all particles is 650°R.

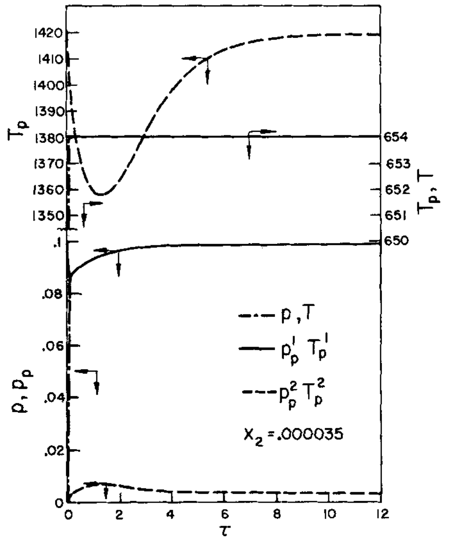

Fig. 7. Transient behavior case a, initially two groups of particles.

The stability analysis predicted that at most two groups of particles of different temperatures could coexist in the bed at steady state. This result was checked in the following example. Figure 8 describes a system almost identical to that just considered. The only difference is in the presence of an additional small fraction of particles ($x_3 = 0.000065$) of high temperature. Since the difference between the values of p and T and of $p_p{}^1$ and $T_p{}^1$ becomes very small afer a very short time, only the value of p and T are shown in this and the other figures. It can be seen that the third group of particles cooled quickly to the temperature of the particles of group 1, and its partial pressure rose to that of group 1. At $\tau = 6$ the system is identical to the system of Figure 7 at $\tau = 6$. By comparison of Figures 7 and 8 it can be seen that the presence of the additional hot particles had almost no effect on the transient response of the particles in groups 1 and 2. The system approached the same steady state in both cases. At steady state conditions the temperature difference between the two groups of particles is 760°F.

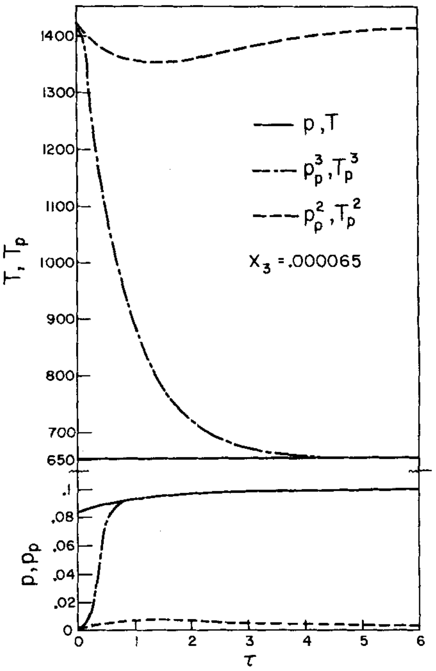

Fig. 8. Transient behavior case a, initially three groups of particles.

In order to obtain a steady state with two groups of particles having different temperatures, the initial temperature of the particles must be nonuniform. The initial distribution of the temperatures of the particles determines which steady state will be obtained. Under certain conditions the system may finally reach a steady state for which

TABLE 2. DATA FOR NUMERICAL EXAMPLES

Case	a	b	c	d	e	f	g
F	8,000	1,200	10,450	8,000	8,000	20,000	7,000
H_w	0.8	1.6	1.6	1.6	0.0	1.5	0.0
Kk	A	B	B	B	A	A	A
T_e	650	600	600	600	650	650	650
T_w	650	720	720	720	650	650	650
Possible uniform temperature steady states	1	1	2	3	3	3	3
T_p of first ss	650.003	1,058.07	711.779	690.607	650.005	650.005	650.004
T_p of second ss	—	—	988.768	759.167	921.503	921.111	932.16
T_p of third ss	—	—	—	915.094	1,316.782	1,320.500	1,232.79

$H_g = 320$
$H_T = 266.667$
$p_e = 0.1$
$A = 0.0006 \exp (28.4 - 25{,}000/T)$
$B = 0.0006 \exp (20.7 - 15{,}000/T)$

the temperature of all the particles is uniform. Figure 9 describes such a case. The initial conditions are almost identical to those shown in Figure 7; the difference is that the initial temperature of the hot particles is lower (1,200°R.). In this case the particles are cooled rather quickly, and at $\tau = 6$ the system can be considered to be of uniform temperature. From this time on, the system drifts towards the uniform temperature steady state. At $\tau = 700$ the system is finally cooled to the steady state value ($T_p = 650.003$).

In the above examples the system reached either one of the infinite steady states for which two groups of particles of different temperatures coexist in the bed, or the unique uniform temperature steady state, depending on the initial temperature distribution. It is of interest to investigate the behavior of a system for which there are an infinite number of nonuniform temperature steady states and two stable uniform temperature steady states. Such computations were done for case e of Table 2.

Figure 10 shows the response of a system in which two kinds of particles existed initially. Most of the particles were initially at 740°R., while a small fraction of hot particles ($x_2 = 0.0005$) was at 1,450°R. The steady state value of T for this value of x_2 was determined from Figure 6b. From the $Y_I - Y_{II}$ curves it was found that in order to bring the system to steady state, the hot particles must be cooled to 1,405°R. This happened rather quickly, and the steady state was reached at $\tau = 4$. No overshoot occurred during the cooling of the hot particles. The temperature of the colder particles was practically unchanged during this short time. Note that the steady state temperatures of the two groups of particles T_p^1 and T_p^2 are obtained from the $Y_I - Y_{II}$ curves. The values of T_p^1 and T_p^2 differ from the temperatures of the particles at either one of the two stable uniform temperature steady states (see Table 2).

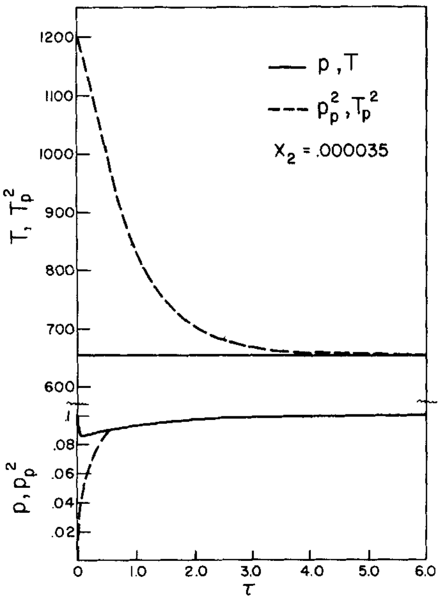

Fig. 9. Transient behavior case a, initially two groups of particles.

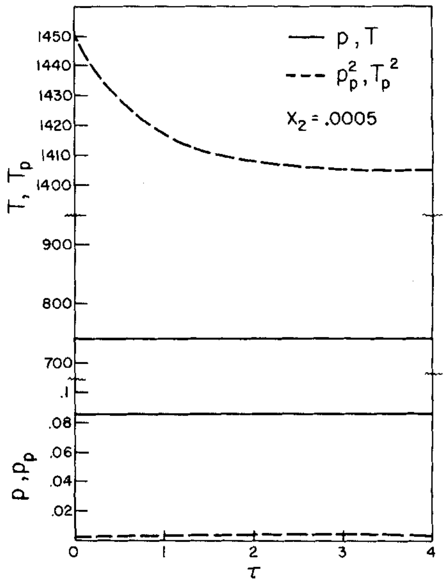

Fig. 10. Transient behavior case e, initially two groups of particles.

The initial temperature of the colder particles has an important effect on the steady state which is finally approached. Figure 11 describes a system in which the initial temperature of the colder particles is 660°R. as compared with 740°R. for the system described in Figure 10. The temperature of the hot particles is the same for both systems. But while the system described in Figure 10 approached a steady state for which two groups of particles of different temperatures coexist at steady state, this is not the case in the system described in Figure 11. In this case the hot particles were cooled from the initial value of 1,450° to 661°R. during the first eight units of τ. During that period the second group of particles was heated by 1°F. After $\tau = 8$ the system acted as a system with a uniform temperature and approached very slowly the steady state temperature of 650.003. (This is not shown in the figure.)

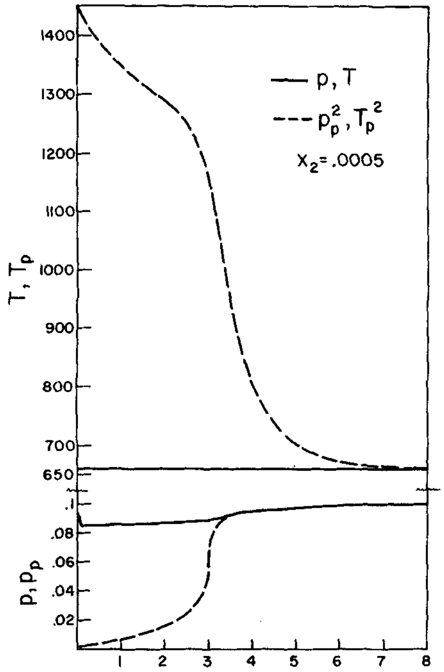

Fig. 11. Transient behavior case e, initially two groups of particles.

SUMMARY

It was shown that a batch fluidized bed may have more than one steady state, some of which are highly unstable. If the initial temperature of all the catalyst particles in the bed is not uniform, a special kind of steady state, in which particles of two different temperatures can coexist in the bed, might be obtained. The number of these pathological steady states and the conversion obtained may be very different from those obtained by a uniform particle steady state.

The analysis has shown that the initial temperature of the catalyst particles is the predominate factor in determining the kind of steady state the system will obtain. For the case of uniform catalyst particles a simple stability criteria has been developed. Several numerical solutions of the transient equations were performed to investigate the possible responses of the system to disturbances of various steady states.

ACKNOWLEDGMENT

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NOTATION

a_v = interfacial area per unit volume
A = dimensionless constant
b = terms of determinant
c = specific heat
C = dimensionless group
ΔE = activation energy
F = dimensionless group
H_g, H_T, H_w = dimensionless heat transfer coefficients
h_w = heat transfer coefficient between wall and gas
h_g = heat transfer coefficient between gas and catalyst
k = reaction constant
k_g = mass transfer coefficient
K = dimensionless group
M = molecular weight
P = total pressure
p = partial pressure of reactant
p_p = partial pressure of reactant absorbed by catalyst particle
q = gas mass flow rate
r = radius of fluidized bed
R = gas constant
s_p = area of particle
T = temperature
T^* = reference temperature
v_p = volume of a particle
V = volume of bed
x = weight fraction of a group of particles
Y_I, Y_{II} = curves
y = temperature perturbation
w = pressure perturbation

Greek Letters

α = void fraction of particle
λ = eigenvalue
ϵ = void fraction of bed
θ = time
ρ = density
τ = dimensionless time

Subscripts and Superscripts

e = entrance conditions
g = of the gas
p = of the particles
s = of the solid
ss = at steady state value
w = of the wall
i = of particles of group i

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