Figure 1. Apparatus for the disproportionation of calcium peroxide diperoxyhydrate in a flowing gas stream and RF discharge.

vorable to particle fluidization without agglomeration.

In additional tests (no. 9–11) the reactant batch size was increased and the particles again completely fluidized without agglomeration and showed no evidence of a vigorous reaction during the test. These tests, as well as no. 8, were made with a continuous 5-W RF discharge. It should be possible to operate at higher power, as well as higher reaction chamber pressure, with a pulsed RF discharge (Donohoe et al., 1977).

Conclusions

Visual observations indicated that an RF discharge significantly reduced agglomeration of particles in a fluidizing gas stream, and this observation was consistent with the possibility that the discharge reduced the static charge on the reactant particles. An enhancement of product purity was also seen and was believed to be due to the improved temperature control and more efficient removal of evolved product water when the particles were not agglomerated.

An alternate possibility was that the increased product purity was due to reactive species in the RF discharge. This was not considered a major factor, as the only oxygen present was that released from the reactant, and prior studies had shown no detectable higher oxides when two of the solid product species (CaO_2 and $Ca(OH)_2$) were subject to an RF discharge in oxygen. The possibility that particle deagglomeration or lack of agglomeration was due to increased vigor of the reaction in an RF discharge, with consequent more rapid expulsion of gaseous products from the particles, was also considered. This latter possibility must be accommodated to the fact that observed or recorded evidence of a vigorous reaction was not seen in the RF discharge experiments and product purities were relatively high, whereas in tests where evidence of vigorous reactions was seen the product purities were reduced.

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# On the Number and Stability of Steady States of a Sequence of Continuous-Flow Stirred Tank Reactors

A sequence of CSTR's can have a very large number of possible steady states, even if the number N of such tanks is relatively small. However, only a very few among them can be stable. A conservative upper bound on this feature is developed. Reactions for which a single adiabatic or isothermal CSTR has a maximum of three steady states (two stable, one unstable), a sequence of N CSTR's can have up to $2^{N+1} - 1$ steady states, of which only $N + 1$ are stable, the rest unstable. Some comments about compatibility of the discrete series of mixers model with continuous models (plug flow or plug flow with axial dispersion) for tubular reactors are also made.

Introduction

It is well known that a single reaction occurring in a single continuous-flow stirred tank reactor (CSTR) can give rise to multiple steady states. For an exothermic reaction $A \rightarrow B$ in an adiabatic CSTR (van Heerden, 1953; Bilous and Amundson, 1955; Aris, 1969), a substrate-inhibited enzyme reaction (O'Neill et al., 1971; DeVera and Varma, 1979) or a bimolecular Langmuir–Hinshelwood reaction (Matsuura and Kato, 1967; Luss, 1971) in an isothermal CSTR, the maximum number of possible steady states is

three, of which two (the high and the low conversion steady states) are asymptotically stable and the third (the intermediate conversion steady state) is unstable. The number of steady states of a distributed system, such as a catalyst pellet, depend on its geometry and can be arbitrarily large; however, of these, only a very few are stable, the rest unstable (Aris, 1975).

Many industrial reactions are carried out in a sequence of CSTR's. The steady-state multiplicity and stability characteristics for such a sequence are investigated. This
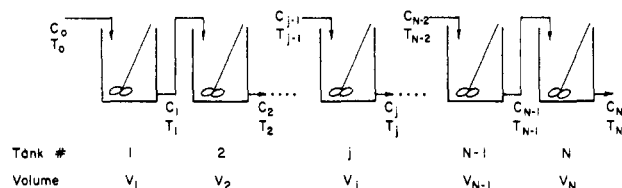
Figure 1. A sequence of N CSTR's.
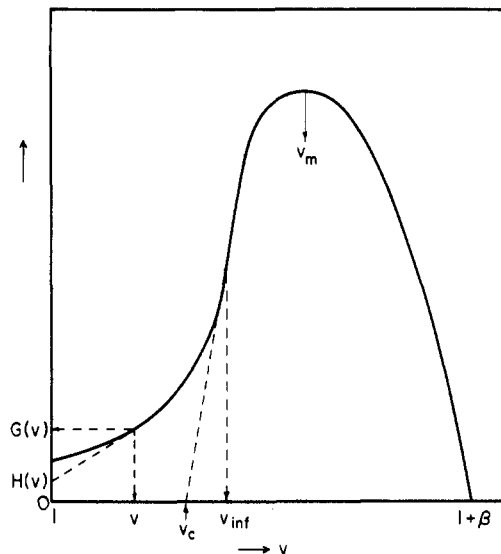
Figure 2. Form of the function $G(v)$.

study has implications beyond the problem of an array of CSTR's, since it is common to model empty tubular (Coste et al., 1961) and fixed bed catalytic (Deans and Lapidus, 1960; Hlavacek and Votruba, 1977) reactors as a sequence of CSTR's.

The System Equations

Consider, as shown in Figure 1, an array of N CSTR's, in which, for example, an exothermic reaction A → B occurs adiabatically. With the symbols as defined at the end, the steady-state mass and energy balances lead to the following system of equations

$$qC_{j-1} = qC_j + V_j f(C_j, T_j) \tag{1a}$$

$$qC_p\rho T_{j-1} = qC_p\rho T_j - V_j(-\Delta H)f(C_j, T_j) \tag{1b}$$

where $j = 1 \rightarrow N$. From eq 1

$$C_j = C_{j-1} + [C_p\rho/(-\Delta H)][T_{j-1} - T_j] \tag{2}$$

so the reactant concentration in tank j, C_j, is related to the temperature, T_j, of the tank.

Introducing the dimensionless quantities

$$u_j = C_j/C_0; \quad v_j = T_j/T_0; \quad \beta = (-\Delta H)C_0/C_p\rho T_0 \tag{3}$$

Equation 2 rearranges to

$$v_j + \beta u_j = v_{j-1} + \beta u_{j-1} \equiv 1 + \beta \qquad j = 1 \rightarrow N \tag{4}$$

since $u_0 = 1 = v_0$. If we further define

$$r(v_j) = f(C_j, T_j)/f(C_0, T_0); \quad \phi_j = V_j f(C_0, T_0)/qC_0 \tag{5}$$

then eq 1 becomes

$$v_j - v_{j-1} = \beta\phi_j r(v_j) \qquad j = 1 \rightarrow N \tag{6}$$

It is now convenient to focus on the case of a first-order reaction, which is representative of all reactions of normal (i.e., positive order) kinetics. For this

$$\beta r(v) \equiv G(v) = (1 + \beta - v) \exp\{\gamma[1 - (1/v)]\} \tag{7}$$

where

$$\gamma = E/RT_0 \tag{8}$$

is the dimensionless activation energy. The physical interpretation of the left- and right-hand sides of eq 6

$$v_j - v_{j-1} = \phi_j G(v_j); \quad j = 1 \rightarrow N \tag{9}$$

is then heat removal due to flow and heat generation due to reaction, respectively, in tank j.

The form of the heat generation function $G(v)$ has been studied by Aris (1969) and others (Varma and Amundson, 1973). In its most severe complexity, it has the form shown in Figure 2, where $G(v)$ has a maximum, v_m and an inflection point, v_{inf} in the range $1 \leq v \leq 1 + \beta$, and H_{min}, the minimum value of

$$H(v) \equiv G(v) - (v - 1)G'(v) \tag{10}$$

is nonpositive. v_m and v_{inf} are readily derived as

$$v_m = \frac{\gamma}{2}\left[-1 + \left\{1 + 4\frac{(1 + \beta)}{\gamma}\right\}^{1/2}\right] \tag{11a}$$

$$v_{inf} = \gamma(1 + \beta)/[\gamma + 2(1 + \beta)] \tag{11b}$$

and $H_{min} \leq 0$ if and only if

$$\beta\gamma \geq 4(1 + \beta) \tag{12}$$

Due to the nature of G, it is straightforward to establish the bounds

$$1 \leq v_1 \leq v_2 \leq \dots \leq v_{j-1} \leq v_j \leq v_{j+1} \leq \dots \leq v_N \leq 1 + \beta \tag{13}$$

for the exothermic ($\beta \geq 0$) case of interest.

Criteria for the Number of Steady States and Their Stability

Rearranging eq 9 as

$$\frac{1}{\phi_j} = \frac{G(v_j)}{v_j - v_{j-1}} \equiv F(v_j); \quad j = 1 \rightarrow N \tag{14}$$

it follows from arguments used before (Luss, 1971; Varma and Amundson, 1973) for a single tank, that unique steady states exist in tank j for all values of ϕ_j if and only if

$$\frac{dF(v_j)}{dv_j} \leq 0 \tag{15}$$

where $v_{j-1} \leq v_j \leq 1 + \beta$.

If condition 15 is violated, $F(v_j)$ will possess a local minimum at v_{j^-} and a local maximum at v_{j^+}, where $v_{j\pm}$ are given as

$$v_{j\pm} = [\gamma(1 + \beta + v_{j-1}) \pm$$
$$[\gamma(1 + \beta - v_{j-1})\{\gamma + 4(1 + \beta)\} \times$$
$$\{v_c - v_{j-1}\}]^{1/2}]/2(1 + \beta + \gamma - v_{j-1}) \tag{16}$$

and

$$v_c = \gamma(1 + \beta)/[\gamma + 4(1 + \beta)] \tag{17}$$

may easily be verified as the value of v where the tangent drawn to the curve $F(v)$ at $v = v_{inf}$ intersects the v axis (see Figure 2).

It is clear from eq 16 that condition 15 holds if and only if

$$v_{j-1} \geq v_c \tag{18}$$

so that if the output v value of the $(j - 1)$st tank exceeds v_c, there is no possibility of multiplicity in the jth tank. If $v_{j-1} < v_c$, then the jth tank will possess multiple steady states if and only if ϕ_j is in the range

$$\phi_{j*} \equiv 1/F(v_{j^+}) \leq \phi_j \leq 1/F(v_{j^-}) \equiv \phi_j^* \tag{19}$$
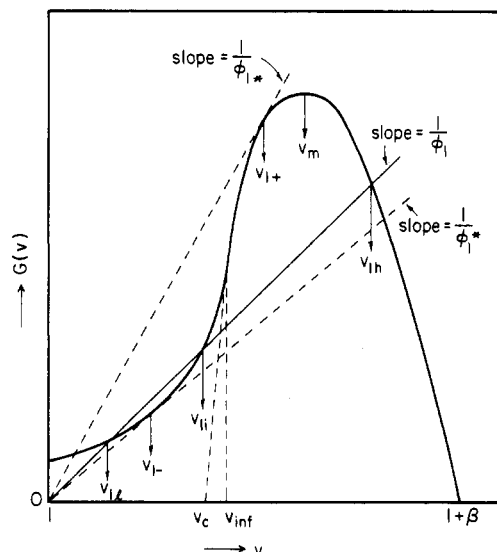
Figure 3. Locations of $v_{1\pm}$, v_{1l}, v_{1i}, and v_{1h}.

Note that for $j = 1$, the first tank in the sequence, (18) reduces to the familar condition

$$\beta\gamma \leq 4(1 + \beta) \tag{20}$$

For $j = 1$, if (20) is violated and $\phi_1 \in (\phi_{1*},\phi_1{}^*)$, then three steady-state solutions exist, and it is convenient to label them as v_{1l}, v_{1i}, and v_{1h} corresponding to the low, intermediate, and high conversion states, respectively. Their locations, as well as those of $v_{1\pm}$, are shown in Figure 3. From previous analyses (Bilous and Amundson, 1955; Aris, 1969) it is apparent that the steady state corresponding to v_{1i} is unstable while those corresponding to v_{1l} and v_{1h} are asymptotically stable. The startup procedure determines which of the steady states among v_{1l} and v_{1h} is actually attained.

As described by eq 9, the input for tank 2 is v_1, for tank 3 it is v_2, and so on. It is convenient to directly consider the jth tank. Given a value of $v_{j-1} < v_c$, and ϕ_j lying in the range prescribed by the strict inequalities of (19), the three possible v_j values may again be labeled v_{jl}, v_{ji}, and v_{jh}. As before, v_{ji} will be unstable and v_{jl}, v_{jh} asymptotically stable if v_{j-1} is either the unique steady state of tank $j - 1$ or one among $v_{j-1,l}$ and $v_{j-1,h}$. Clearly, since $v_{j-1,i}$ is itself unstable, it cannot generate any stable solutions in the jth tank.

Now note that

$$\frac{\partial v_j{}^+}{\partial v_{j-1}} < 0; \quad \frac{\partial v_j{}^-}{\partial v_{j-1}} > 0 \tag{21a}$$

$$v_{j\pm} \rightarrow v_{inf} \text{ as } v_{j-1} \rightarrow v_c \tag{21b}$$

$$v_j{}^- \leq v_{inf} \leq v_j{}^+ \tag{21c}$$

and

$$v_{jh} \geq v_j{}^+ \geq v_{inf} > v_c \tag{21d}$$

so that from eq 18 and 21d, $v_{j-1,h}$ only gives rise to a unique steady state v_j in the jth tank. However, $v_{j-1,l}$ and $v_{j-1,i}$ can generate multiple steady states in the jth tank as long as they violate condition 18, and they necessarily generate multiple states if ϕ_j is also in the range given by (19).

So under conditions described above, for a sequence of two tanks, v_{1l} and v_{1i} can each generate three additional steady states in the second tank. These along with the unique state caused by v_{1h} mean at most seven steady states are possible in the second tank. However, of these, at most three—two generated by v_{1l}, and one by v_{1h}—are asymptotically stable, the remaining four unstable.
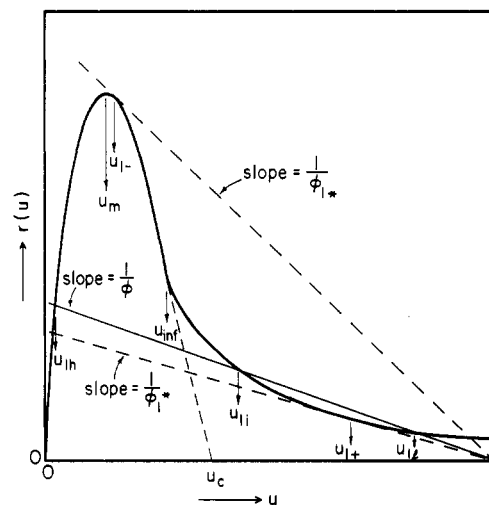

Figure 4. The function $r(u) = u/(1 + \sigma u)^2$ for the isothermal Langmuir-Hinshelwood reaction.

All of the above considerations can be summarized by the statement that *the maximum possible number of steady state values of v_N for an array of N CSTR's connected in series is $(2^{N+1} - 1)$, of which at most $(N + 1)$ are asymptotically stable, the rest unstable.*

Note that although the maximum number of steady states can grow rather explosively as the number N of tanks in series increases, the number of states among them that are stable remains relatively modest. For example, with $N = 8$, the maximum number of steady states possible in the last tank is 511, but of these only 9 are asymptotically stable, the rest unstable.

It should be evident from what has been said above that the number $2^{N+1} - 1$ is in reality a conservative upper bound on the largest number of steady states possible in an array of N CSTR's. However, short of numerical computation for specific reaction systems, it appears to be the best a priori upper bound that can be constructed.

An Example of Isothermal Multiplicity

The above considerations are, of course, not limited to nonisothermal reactions. It is now well established that complex isothermal reactions such as CO and hydrocarbon oxidation on noble metals (Wei, 1975; Hegedus et al., 1977) or olefin hydrogenation on CuO-MnO_2 catalyst (Furusawa and Kunii, 1971) lead to "abnormal" reaction rates of the form

$$r(u) = u/(1 + \sigma u)^2 \tag{22}$$

which give rise to multiple steady states in isothermal CSTR's—and also catalyst pellets—for sufficiently large σ (Luss, 1971; Pereira and Varma, 1978). In its most severe complexity, $r(u)$ has a shape, as shown in Figure 4, which is essentially a mirror image of $G(u)$, and

$$u_m = 1/\sigma; \quad u_{inf} = 2/\sigma \tag{23}$$

$\bar{H}_{min}$, the minimum value of

$$\bar{H}(u) = r(u) + (1 - u)r'(u) \tag{24}$$

is nonpositive if and only if $\sigma \geq 8$. Exactly the same conclusions regarding the maximum possible number of steady states and their stability as for the nonisothermal case are reached again; this time

$$u_{j\pm} = [u_{j-1} \pm \{u_{j-1}(u_{j-1} - u_c)\}^{1/2}]/4; \quad j = 1 \rightarrow N \tag{25}$$

where $u_0 = 1$ and $u_c \equiv 8/\sigma$. Thus u_{j-1} is capable of generating multiple states in the jth tank if and only if

$$u_{j-1} > u_c \tag{26}$$

and then it surely does so if ϕ_j is in the range

$$\phi_{j*} \equiv 1/\bar{F}(u_{j-}) \le \phi_j \le 1/\bar{F}(u_{j+}) \equiv \phi_j^* \qquad (27)$$

where

$$\bar{F}(u_j) \equiv r(u_j)/[u_{j-1} - u_j] \qquad (28)$$

Concluding Remarks

The number of steady states of a sequence of CSTR's *can* be very large; however, only a very few among them are stable. Explicit formulas are given which provide conservative upper bounds on these numbers. For the first-order reaction A → B occurring adiabatically, or the bimolecular Langmuir–Hinshelwood reaction occurring isothermally, an a priori determination can be made, by comparing the output of the $(j - 1)$st tank with a critical value, to indicate whether or not the jth tank can possess multiple steady states.

It is worth remarking that these observations on the number of steady states and their stability characteristics are not necessarily in conflict with the series of mixers model for an empty tubular reactor of finite length. Recall that if the number of such mixers in series approaches infinity (thus, each mixer is of infinitesimally small volume), then a plug-flow model is obtained (Coste et al., 1961) which possesses a unique steady state that is globally stable although it may exhibit parametric sensitivity (Bilous and Amundson, 1956). If V_j is infinitesimally small, then $1/\phi_j$ approaches infinity and the slope of the heat (mass) removal (supply) line passing through $v_{j-1}(u_{j-1})$ is almost infinite. Then even if $v_{j-1} < v_c(u_{j-1} > u_c)$, $\phi_j < \phi_{j*}$; so unique steady states obtain in each tank and hence for the entire reactor.

For a finite axial dispersion characterized by a Peclet number based on the reactor length, Pe, if we take $N = Pe/2$, a relationship which is obtained by comparing the axial dispersion model with the respective equations for the axial dispersion model with the equal-tanks-in-series model (Deans and Lapidus, 1960; Coste et al., 1961), then consistent with the analysis given above, essentially a very large number of steady states are possible at the end of the reactor. For adiabatic tubular reactors with equal Peclet numbers for heat and mass transfer (Amundson and Luss, 1968; Hlavacek and Hofmann, 1970) or for isothermal tubular reactors with axial dispersion in which a complex reaction occurs (DeVera and Varma, 1979), only a maximum of three steady states are obtained when the relevant nonlinear boundary value problems are numerically solved. This anomaly raises some questions about the compatibility of the tanks in series model with the dispersion model which are not readily resolved. In some ways this is a conceptual difficulty which arises when the model of a model is considered (see Aris (1978) for other fine points in this regard). A similar but more perplexing problem arises in population dynamics where the simple deterministic logistic differential equation has a unique globally stable equilibrium point, but its finite difference analogue predicts a variety of unusual dynamic behavior—from stable self-sustained oscillations to apparently random fluctuations implying chaos (May, 1974, 1976).

Although we have deliberately avoided any direct implications for the fixed-bed reactor, it should be evident that the comments made above for empty tubular reactors also hold for the pseudohomogeneous model of a fixed-bed reactor. For the two-phase model, with intrapellet diffusional resistance, however, some caution needs to be exercised. Thus although in the nondiffusion case as shown, the high conversion state in a tank cannot generate multiplicity in any following tank, this appears not to be the case when diffusionally induced multiplicity exists (Hegedus et al., 1977; Oh et al., 1978). It is hoped this note will encourage further investigations in the latter area.

Nomenclature

C = reactant concentration
C_p = specific heat of reaction mixture
E = activation energy
f = intrinsic reaction rate
F = function defined by eq 14
$\bar{F}$ = function defined by eq 28
G = heat generation function
H = function defined by eq 10
$\bar{H}$ = function defined by eq 24
ΔH = heat of reaction
N = number of CSTR's in series
Pe = Peclet number
q = volumetric flow rate
r = dimensionless reaction rate
R = universal gas constant
T = temperature
$u = C/C_0$
$v = T/T_0$
V = CSTR volume

Greek Letters

$\beta = (-\Delta H)C_0/C_p\rho T_0$
$\gamma = E/RT_0$
ρ = density of reaction mixture
$\phi = Vf(C_0,T_0)/qC_0$
σ = adsorption constant

Subscripts

c = critical value
h = high conversion state
i = intermediate conversion state
inf = inflection point
j = jth tank
l = low conversion state
m = maximum value
min = minimum value
0 = inlet to first tank
* = bifurcation values

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