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Steady-State Multiplicity of a Nonadiabatic Bubble Column with Fast Reactions

A steady-state model is developed for a nonadiabatic bubble column with fast pseudo-*n*th-order reactions. *A priori* bounds are obtained for steady-state temperature and conversion, and analytic necessary and sufficient criteria are derived for the prediction of uniqueness and multiplicity of the steady states as a function of system physico-chemical parameters. For the special case of pseudo-first-order reactions, the occurrence of multiple steady states is shown to be more possible in a bubble column than in a gas-liquid CSTR for equivalent system parameters.

D. T.-J. HUANG
and
ARVIND VARMA
Department of Chemical Engineering
University of Notre Dame
Notre Dame, Indiana 46556

SCOPE

Because of simple construction and excellent temperature control, bubble columns are frequently applied in the process industries. Recently, they are also gaining increasing importance in biotechnology, particularly in fermentations and waste water treatment due to favorable mixing and mass transfer properties combined with low shear stressing of the biological material.

In the operation of gas-liquid CSTRs, the occurrence of multiple steady states has been experimentally observed (Ding et al. 1974) and theoretically explored (Hoffman et al., 1975; Sharma et al., 1976; Raghuram and Shah, 1977; Raghuram et al., 1979; Huang and Varma, 1981). Because a bubble column is quite similar to a CSTR (one with and the other without mechanical stirring), it may be expected that such phenomenon also occurs in bubble columns. However, as far as the authors are aware, no study has been done of the steady-state multiplicity aspects of bubble columns—either experimentally or theoretically.

In this work, a steady-state model is developed for a nonadiabatic bubble column with fast pseudo-*n*th-order reactions and multiplicity analysis (Varma and Aris, 1977) is performed. For the special case of pseudo-first-order reactions, comparisons are also made between bubble columns and CSTRs regarding the relative possibility of the occurrence of multiple steady states.

CONCLUSIONS AND SIGNIFICANCE

Analytic criteria are derived for the prediction of uniqueness and multiplicity of the steady states in a bubble column as a function of system physico-chemical parameters. These criteria along with the model should help provide a rational approach to the design and optimization of bubble columns.

It is found that the region of multiplicity shrinks as the reaction order increases. This feature is the same as that found for single-phase reactors (Tsotsis and Schmitz, 1979; Chang and Calo, 1979).

For the special case of pseudo-first-order reactions, numerical examples applying the data for the chlorination of *n*-decane (Sharma et al., 1976) to the bubble column show that every multiplicity pattern observed in a gas-liquid CSTR is also possible in the bubble column. Moreover, it is found that the possibility of the occurrence of multiple steady states is greater in the bubble column than in the CSTR. It is also shown that information obtained from gas-liquid CSTRs may be helpful in the design and operation of bubble columns.

DEVELOPMENT OF THE MODEL

It was found that for hydrogen-α-methylstyrene system in a bubble column (Sherwood and Farkas, 1966), the liquid phase was well mixed from top to bottom by the bubbling gas flow, although the ratio of height of gas-liquid mixture to column diameter (L/D) was 12 to 35, and the gas phase was in plug-flow. Also for the absorption and sulfuric acid catalyzed hydration of isobutene (Deckwer et al., 1977), it has been reported that conversions calculated from a simple model which treats the

Correspondence concerning this paper should be addressed to A. Varma.
D.T.-J. Huang is presently at Brookhaven National Laboratory, Upton, New York 11973.
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liquid phase as well mixed and the gas phase as in plug flow agree well with the experimental results.

For fast reactions in bubble columns, the height dependence of pressure and gas velocity, and the variations in gas hold-up were found to be negligible (Deckwer, 1976, 1977). These findings along with previous works on gas-liquid CSTRs should support at least partially the assumptions described below.

Assumptions

In this work, the following assumptions are made.

1. The liquid phase is well mixed and the gas phase is in plug flow.
2. The volumetric gas flow rate and the interfacial area are independent of temperature, conversion and position in the column.
3. The resistance to mass transfer in the gas phase, and the heat transfer resistance at the gas-liquid interface are negligible.
4. The liquid phase consists of nonvolatile components so that there are no material and energy losses due to evaporation.
5. The physical properties of the gas and liquid, the liquid-phase mass transfer coefficient, and the heats of solution and reaction are independent of temperature and conversion.
6. Henry's law applies.
7. The liquid feed does not contain any dissolved gas reactant.

Mass Balance

Based on the above assumptions, the gas-phase balance on the gaseous reactant A is, at steady state:

$$F_g L \frac{dA_g}{dZ} = -k_l a A_i E_A^* V \; ; \; Z = 0 \rightarrow L \tag{1}$$

with inlet condition at $Z = 0$, $A_g = A_{gf}$ (1a)

where E_A^* is the reaction factor.

In this work, a fast pseudo-nth-order kinetics on the gas reactant is assumed. The reaction factor is thus (Brian, 1964; Hikita and Asai, 1964):

$$E_A^* = \left[\left(\frac{2}{n+1}\right) k D_A A_i^{n-1}\right]^{\frac{1}{2}} / k_l \; ; \; n \geq 0 \tag{2}$$

Note that $A_l = 0$ is assumed (for fast reactions) and the reaction factor is then the same as the enhancement factor. Also, for fast reactions, the rate of reaction is equal to the rate of absorption:

$$R_A = k_l a A_i E_A^* \tag{3}$$

so that the liquid-phase balance of reactant A can be neglected.

Heat Balance

Since the heat capacity and density of the gas phase are much smaller than those of the liquid phase, the heat content of the gas phase is usually negligible compared with that of the liquid phase. With this fact plus the assumptions 1 and 3, the temperature within the column may be assumed to be uniform for every steady state and the heat content of the gas phase may be lumped into the liquid-phase heat balance.

For the case of the gas and liquid feed temperatures being the same, the overall heat balance then is:

$$(F_g \rho_g C_{Pg} + F_l \rho_l C_{Pl})(T_f - T) + (-\Delta H_s - \Delta H_R) Q V - U S (T - T_c) = 0 \tag{4}$$

where $Q = \frac{1}{L} \int_0^L R_A dZ$ (4a)

Further, from Henry's law,

$$A_i = H_o A_g \exp\left[(-\Delta H_s)/RT\right] \tag{5}$$

and from Arrhenius law,

$$k = k_o \exp\left(-E/RT\right) \tag{6}$$

Note that the F_g-term in Eq. 4 can usually be neglected except when the liquid flow rate is much smaller than the gas flow rate, e.g., as $F_l \rightarrow 0$; also the assumption of same gas and liquid feed temperatures can be readily relaxed. We also note that with Eq. 2 substituted into Eqs. 1 and 3, the k_l-dependence of the heat and mass balances is removed and only the interfacial area from the hydrodynamic problem remains in the model.

Dimensionless Model Equations

With the dimensionless variables and parameters defined in Notation, the mass and heat balance Eqs. 1 and 4 become, after applying Eqs. 2, 3, 5 and 6:

$$\frac{da_g}{dz} = -Da\, a_g^n \exp\left(\frac{y}{1 + y/\gamma}\right); \quad z = 0 \rightarrow 1 \tag{7}$$

at $z = 0$, $a_g = 1$ (7a)

and

$$-\alpha y + DaB\left[\int_0^1 a_g^{(n+1)/2}\, dz\right] \exp\left(\frac{y}{1 + y/\gamma}\right) - \beta(y - y_c) = 0 \tag{8}$$

$n = 1$ CASE

For many gas-liquid reactions, the pseudo-first-order kinetics (on the gas reactant) may be employed and practical situations in which this applies have been discussed before (Bridgwater and Carberry, 1967; Danckwerts, 1970). Especially for the oxidation of thiophenol catalyzed by copper chloride-pyridine solution (Brooks and Smith, 1973), the reaction rate was found to be zero-order with respect to the thiophenol, first-order with respect to the oxygen and to the catalyst. This reaction is very fast, and diphenyl disulphide and water are the only products when it is carried out in a bubble column with high catalyst concentration and/or high reaction temperature.

Analysis

Since y is independent of z, Eq. 7 can be solved with condition Eq. 7a to obtain:

$$a_g = \exp\left[-Daz \exp\left(\frac{y}{1 + y/\gamma}\right)\right] \; ; \; z = 0 \rightarrow 1 \tag{9}$$

Substituting Eq. 9 into Eq. 8 and performing the integration, we get:

$$-\alpha y - B \exp\left[-Da \exp\left(\frac{y}{1 + y/\gamma}\right)\right] + B - \beta(y - y_c) = 0 \tag{10}$$

A Priori Bounds. For exothermic reactions and γ being positive, B is positive and Eq. 10 can be rearranged as:

$$\frac{B + \beta y_c - (\alpha + \beta) y}{B} = \exp\left[-Da \exp\left(\frac{y}{1 + y/\gamma}\right)\right] \tag{11}$$

From Eq. 9, the outlet concentration of gas reactant A is, at $z = 1$:

$$a_{gL} = \exp\left[-Da \exp\left(\frac{y}{1 + y/\gamma}\right)\right] \tag{12}$$

Note that the overall conversion may be defined as $X = 1$

a_{gL}. From Eqs. 9 and 12, since Da cannot be negative, it is readily shown that:

$$0 \le a_g \le 1;\ 0 \le a_{gL} \le 1 \tag{13}$$

Combining Eq. 11 with Eqs. 12 and 13, we get:

$$y_{lb} \equiv \frac{\beta y_c}{\alpha + \beta} \le y \le \frac{B + \beta y_c}{\alpha + \beta} \equiv y_{ub} \tag{14}$$

With the *a priori* bounds as in Eq. 14, the steady-state temperatures can be found from Eq. 10 by trial-and-error, and then the steady-state concentration is obtained through Eq. 9. Because of the similarity of bubble columns to gas-liquid CSTRs, it is not surprising that the *a priori* bounds of this bubble column are exactly the same as those of a CSTR (Huang and Varma, 1981). Note that for the case of γ being negative, B is negative and the *a priori* bounds can be obtained through the same procedure as Eq. 14 is derived.

Note that Eq. 11 may possess multiple solutions for the dimensionless temperature y, and details of this analysis are now reported.

Multiplicity Analysis. Rearrange Eq. 11 as:

$$Da = \left[\exp\left(\frac{-y}{1 + y/\gamma}\right)\right] \ln\left[\frac{B}{B + \beta y_c - (\alpha + \beta)y}\right] \equiv F(y) \tag{15}$$

We note that:

$$F(y_{lb}) = 0;\ F(y_{ub}) = \infty \tag{16}$$

and that $F(y)$ cannot be negative. It is well known that $F'(y) = 0$ (or $d\,Da/dy = 0$) determines the critical points of multiple steady states (Varma and Aris, 1977). From Eq. 15, $F'(y) = 0$ when

$$L(y) \equiv \frac{(\alpha + \beta)(1 + y/\gamma)^2}{B + \beta y_c - (\alpha + \beta)y} = \ln\left[\frac{B}{B + \beta y_c - (\alpha + \beta)y}\right] \equiv R(y) \tag{17}$$

With the *a priori* bounds as in Eq. 14, the characteristics of $L(y)$ and $R(y)$ can be shown to be (Figure 1):

1. $L(y) > 0$ for all $y < y_{ub}$, and $L(y) \to \infty$ as $y \to y_{ub}$.
2. $L(y)$ has a minimum to the left of $y = y_{ub}$.
3. $R(y) < 0$ for all $y < y_{lb}$.
4. $R(y) > 0$ for $y_{lb} < y < y_{ub}$; also $R(y_{lb}) = 0$ and $R(y_{ub}) \to \infty$.
5. $R(y)$ does *not* exist for any $y > y_{ub}$.

Therefore, it is apparent that Eq. 17 has solutions only in the range $y_{lb} \le y \le y_{ub}$.

Before going further, we should mention that throughout the $n = 1$ case, the numerical examples apply the parameters corresponding to the chlorination of *n*-decane (Ding et al., 1974; Sharma et al., 1976). By doing this, comparisons can be made between a bubble column and a CSTR (Huang and Varma, 1981) with the same reaction system, which produces multiple steady states in the CSTR, regarding the possible occurrence of multiple steady states.

It is found that R' ($\equiv dR/dy$) is positive for any finite value of y, noting that all $y > y_{ub}$ should be excluded from consideration as shown above. Furthermore, it is easily verified that $L' = R'$ at $y = y_1$, where

$$y_1 = \frac{1}{2(\alpha + \beta)}\left\{\gamma^2(\alpha + \beta) + 2(B + \beta y_c) - \sqrt{\gamma^4(\alpha + \beta)^2 + 4[B + \beta y_c + \gamma(\alpha + \beta)]^2}\right\} \tag{18}$$

and that $L' < R'$ to the left of $y = y_1$ and $L' > R'$ to the right of $y = y_1$, (Figure 1). Thus, $y_1 \le y_{lb}$ assures that $L' > R'$ for all $y_{lb} \le y \le y_{ub}$. Thus, Eq. 17 has no solution in the range of interest—which guarantees uniqueness.

Uniqueness and Multiplicity Criteria. It can be easily shown that $y_1 \le y_{lb}$, which guarantees uniqueness, is equivalent to the following criteria:

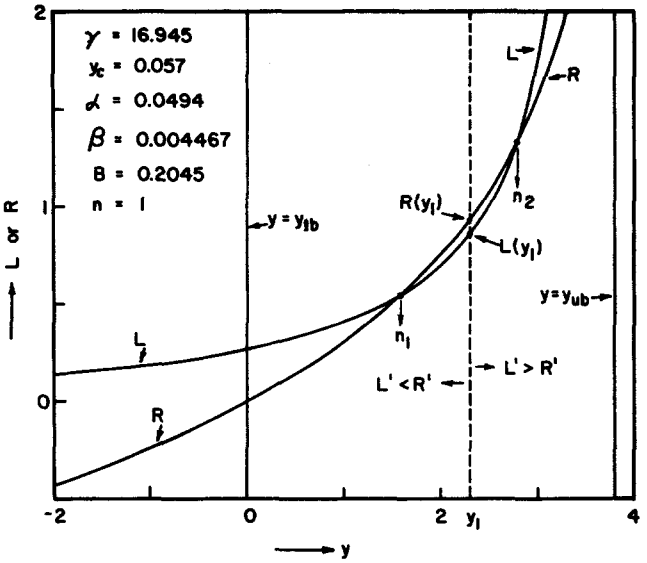

Figure 1. Characteristics of $L(y)$ and $R(y)$.

if

$$\gamma(\gamma - 2) > \frac{2\beta y_c}{\alpha + \beta}, \tag{19}$$

then

$$B \le \frac{[\gamma(\alpha + \beta) + \beta y_c]^2}{\gamma(\gamma - 2)(\alpha + \beta) - 2\beta y_c} \tag{20}$$

guarantees uniqueness. Note that violation of Eq. 19 alone assures unique steady state.

Since Eq. 17 has solutions only when $y_{lb} \le y \le y_{ub}$, and $L'(y_1) = R'(y_1)$, it is readily shown, Figure 1, that $L(y_1) \ge R(y_1)$ is the *necessary and sufficient* condition for uniqueness. The *necessary* condition for the existence of multiple steady states is, therefore, $L(y_1) < R(y_1)$; i.e.,

$$\frac{(\alpha + \beta)(1 + y_1/\gamma)^2}{B + \beta y_c - (\alpha + \beta)y_1} < \ln\left[\frac{B}{B + \beta y_c - (\alpha + \beta)y_1}\right] \tag{21}$$

with y_1 given by Eq. 18. Although the criterion $L(y_1) \ge R(y_1)$ can be used alone to check uniqueness, it is not as explicit as criteria Eqs. 19 and 20; thus, the latter may be used first for the sake of convenience.

It is evident from the relative dispositions of the L and R curves that when Eq. 21 is satisfied, Eq. 17 will lead to exactly *two critical points of multiple steady states*. Denoting the critical points as n_1 and n_2 with $n_1 < n_2$, the sufficient condition for the existence of multiple steady states is:

$$Da_2 < Da < Da_1 \tag{22}$$

where

$$Da_i = \left[\exp\left(\frac{-n_i}{1 + n_i/\gamma}\right)\right] \ln\left[\frac{B}{B + \beta y_c - (\alpha + \beta)n_i}\right];\ i = 1,2 \tag{22a}$$

Note that $dDa/dy \le 0$ for all $n_1 \le y \le n_2$ is the result from Eq. 16 and the slope analysis (Varma and Aris, 1977); thus, $Da_2 < Da_1$ is assured.

Linear Approximation. To avoid the trial-and-error procedure which is necessary to find the exact values of n_1 and n_2, the following approximation is used in Eq. 17 to obtain approximate values of n_1 and n_2:

$$\ln\left[\frac{B + \beta y_c - (\alpha + \beta)y}{B}\right] \approx \frac{\beta y_c - (\alpha + \beta)y}{B} \tag{23}$$

The approximate values of n_1 and n_2 are, thus, found to be:

$$n_1,\ n_2 = \frac{B(\gamma - 2) + 2\beta y_c\gamma \mp D^{\frac{1}{2}}_n}{2[B/\gamma + \gamma(\alpha + \beta)]} \tag{24}$$

with

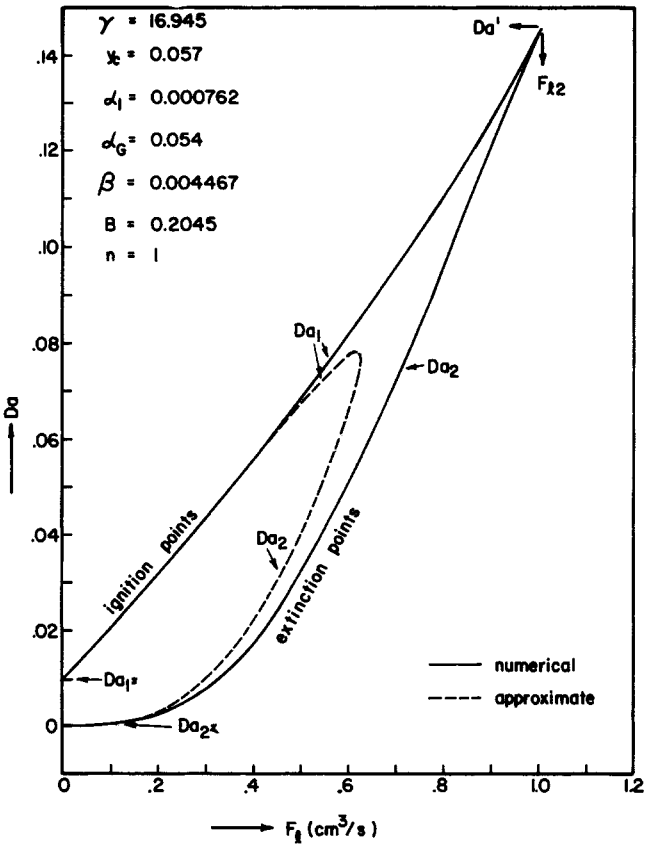

Figure 2. Effect of liquid flow rate on Da_1 and Da_2.

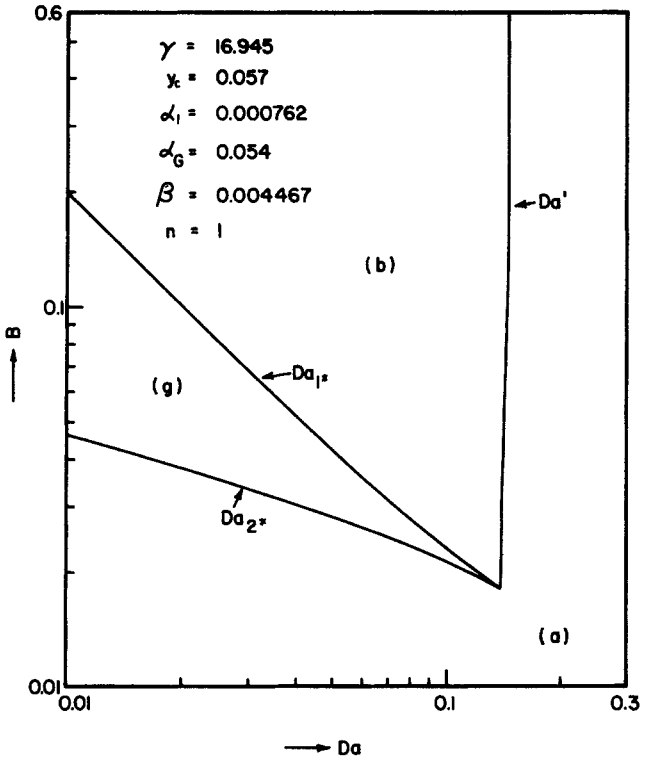

Figure 3. Effect of system parameters on steady-state behavior, Case 1: (a) uniqueness, (b) S-shaped, (g) persistent multiplicity.

$$D_n = \frac{B}{\alpha + \beta}\{B[\gamma(\gamma - 4)[\alpha + \beta) - 4\beta y_c] - 4[\gamma(\alpha + \beta) + \beta y_c]^2\} \quad (24a)$$

These are *exactly* the same as the corresponding values for the nonadiabatic gas-liquid CSTR studied earlier (Huang and Varma, 1981).

The approximation (Eq. 23) is derived from the formula:

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots\ldots ; \; -1 < x \leq 1 \quad (25)$$

with

$$x \equiv \frac{\beta y_c - (\alpha + \beta)y}{B} \quad (25a)$$

From Eq. 14, it is assured that $-1 < x \leq 0$, if we neglect the point of y_{ub}, which is not required in Eq. 17. We note that every term in Eq. 25 is negative, if nonzero; thus, $\ln(1 + x) \leq x$, where $\ln(1 + x)$ approaches x as $x \to 0$ (or $y \to y_{lb}$). Therefore, from Eq. 17, the approximate value of $R(y)$ is smaller than or equal to its exact value, and it is then evident that (ref. Figure 1):

$$n_{1,\,\text{approx.}} \geq n_{1,\,\text{exact}};\; n_{2,\,\text{approx.}} \leq n_{2,\,\text{exact}} \quad (26)$$

Since $dDa/dy \leq 0$ for $n_1 \leq y \leq n_2$, we get

$$Da_{1,\,\text{approx.}} \leq Da_{1,\,\text{exact}};\; Da_{2,\,\text{approx.}} \geq Da_{2,\,\text{exact}} \quad (27)$$

as shown in Figure 2 for an example.

From Eq. 26, we see that the approximate n_1 and n_2 fall inside the *a priori* bounds (Eq. 14) and that the necessary condition for the existence of multiple steady states is obviously $D_n > 0$, i.e.,

$$\gamma(\gamma - 4) > \frac{4\beta y_c}{\alpha + \beta} \text{ first,} \quad (28)$$

and then

$$B > \frac{4[\gamma(\alpha + \beta) - \beta y_c]^2}{\gamma(\gamma - 4)(\alpha + \beta) - 4\beta y_c} \quad (29)$$

We note that the approximate criteria (Eqs. 28 and 29) are exactly the same as the corresponding exact criteria for the gas-liquid CSTR. Thus, it may be said that the linear approximation (Eq. 23) destroys the distributed nature of the mass balance in this bubble column. However, the approximate values of n_1 and n_2 can be used in Eq. 22, which has the distributed system dependence, to obtain a semi-analytic criterion for multiplicity. Figure 2 shows that such procedure results in a rather conservative region for guaranteed multiplicity. It also shows that as Da decreases, e.g., the reaction rate decreases, the approximate multiplicity range approaches the exact range. This is in general expected, because the steady-state temperature then approaches its lower bound y_{lb}.

Results and Discussion

In the operation of gas-liquid reactors, it is quite convenient to vary either the liquid or the gas flow rate or both at the same time. We shall discuss these possible operations and compare their relative possibility for the occurrence of multiple steady states. Also, comparisons with the gas-liquid CSTR will be made.

Fixed Gas Flow Rate (Case 1). It has been found that for a given gas-liquid reactant system, the interfacial area of a bubble column depends on the gas velocity (Deckwer et al., 1974). In this case, with a fixed gas flow rate, the assumption 2 of the model should easily be satisfied.

Since only the liquid flow rate varies, Da and β are fixed and α can be rearranged as:

$$\alpha = \alpha_l + \alpha_G F_l \quad (30)$$

where α_l and α_G are constants.

Figure 2 is found to represent a general case, where Da_1 and Da_2 as in Eq. 22 increase monotonically as F_l increases and $Da_1 = Da_2$ ($\equiv Da'$) at $F_l = F_{l2}$. We note that neither Da_1 nor Da_2 exists for any $F_l > F_{l2}$ and uniqueness is, thus, guaranteed for $F_l \geq F_{l2}$. From Figure 2, three critical points Da_{1*}, Da_{2*} and Da' are obtained, where Da_{1*} and Da_{2*} are the smallest values of Da_1 and Da_2 respectively (i.e., at $F_l = 0$). It has been noted before (Huang and Varma, 1981) that the region between Da_{1*} and Da_{2*}

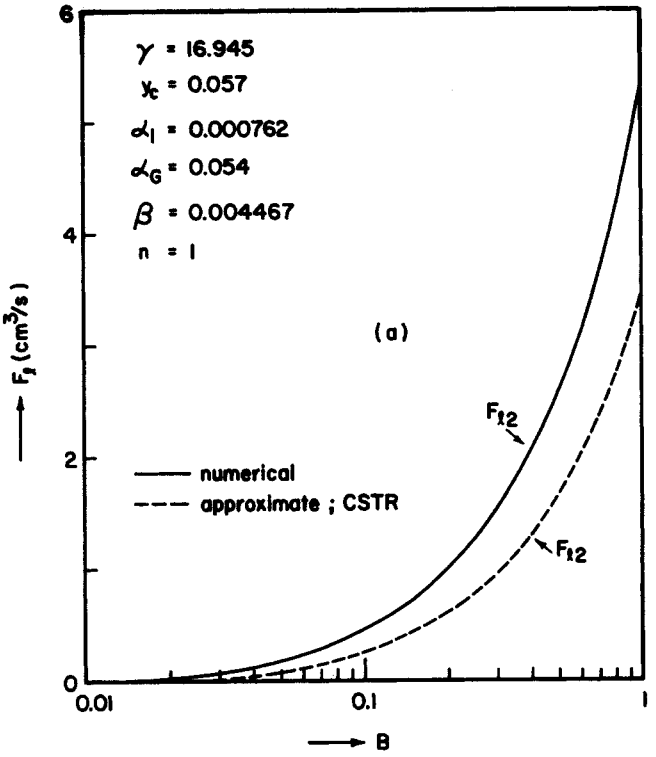

Figure 4. Effect of adiabatic temperature rise on critical liquid flow rate, Case I: (a) uniqueness.

is a region of *persistent multiplicity* with one extinction point but no ignition point; the region between Da_{1^*} and Da' is of S-shaped multiplicity, and uniqueness is guaranteed for $Da \geq Da'$ and $Da \leq Da_{2^*}$.

Figure 3 is a composite of several calculations such as those shown in Figure 2 for a specific value of B, and the steady state behavior is thus classified as a function of the system physicochemical parameters. It can be observed that for very fast reactions, i.e., $Da > Da'$, uniqueness is always assured.

With α as in Eq. 30, condition (Eq. 29) may be converted to the following equivalent:

$$F_{l1} < F_l < F_{l2} \tag{31}$$

where

$$F_{l1},\ F_{l2} = \frac{-b \mp \sqrt{b^2 - 4ac}}{2a} \tag{32}$$

with

$$\begin{aligned} a &= 4\gamma^2\alpha_G{}^2 \\ b &= 8\gamma\alpha_G[\gamma(\alpha_1 + \beta) + \beta y_c] - B\gamma(\gamma - 4)\alpha_G \\ c &= 4[\gamma(\alpha_1 + \beta) + \beta y_c]^2 - B\gamma(\gamma - 4)(\alpha_1 + \beta) + 4\beta y_c B \end{aligned} \tag{32a}$$

It is apparent that condition (Eq. 31) is valid only when $b^2 - 4ac > 0$; otherwise, uniqueness is guaranteed. Then, if $b \geq 0$, F_{l1} is negative and thus $F_{l1} \equiv 0$ must be used in Eq. 31.

From Eq. 31, it is obvious that $F_l \geq F_{l2}$ assures uniqueness. Figure 4 compares the exact values of F_{l2} with the approximate values; the former are obtained from trial-and-error like that shown in Figure 2 and the latter are computed from Eq. 32, which can be shown to be the same as the exact solution of F_{l2} for the CSTR (Huang and Varma, 1981). It is clear that such a comparison compares a bubble column with a CSTR on the critical liquid flow rate. Note that the region (a) in both Figures 3 and 4 is of uniqueness, but that in Figure 3 means uniqueness for all values of F_l and that in Figure 4 means uniqueness for all values of Da (ref. Figure 2).

Figure 4 shows that the region of guaranteed uniqueness for the bubble column (BC) is smaller than that for the CSTR:

$$F_{l2,CSTR} < F_{l2,BC} \tag{33}$$

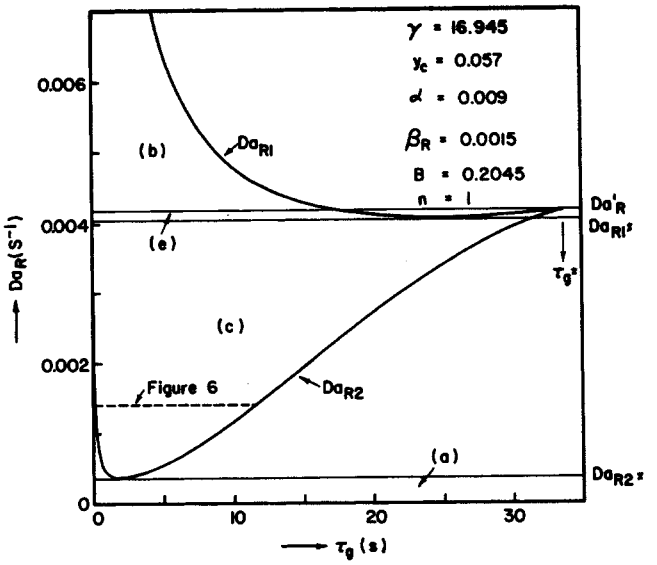

Figure 5. Effect of gas residence time on Da_{R1} and Da_{R2}: (a) uniqueness, (b) S-shaped, (c) isola, (e) mushrooms.

which means higher possibility of multiplicity for the bubble column. Eq. 33 can be shown to be always true from Eq. 29, Figure 2, noting that F_{l2} is the value of F_l where $Da_1 = Da_2$ or the largest F_l for the existence of Da_1 and Da_2. Therefore, we see that information obtained in gas-liquid CSTRs can be quite helpful in the design and operation of bubble columns and vice versa.

From Figure 4, it is also shown that as the adiabatic temperature rise (i.e., the value of B) increases, the liquid flow rate needed to guarantee uniqueness (by bringing away enough heat from the reactor) increases, and so does the possibility of the occurrence of multiple steady states. Note that because of the possible occurrence of persistent multiplicity, these guaranteed unique steady states are of relatively low temperature or low conversion.

Fixed Ratio Flow Rates (Case 2). For this case, α is independent of the individual flow rate but depends on the ratio of the liquid to gas flow rates. Both Da and β are functions of the gas flow rate and can be rearranged as:

$$Da = Da_R\tau_g;\ \beta = \beta_R\tau_g \tag{34}$$

From Eq. 22, the sufficient condition for the existence of multiple steady states for this case is, based on Da_R:

$$Da_{R2} < Da_R < Da_{R1} \tag{35}$$

Note that Da_{R1} is the value of Da_R corresponding to n_1 and Da_{R2} to n_2. Also for this case, care should be taken because the gas holdup (thus, the volume of the gas phase) may change as the gas flow rate varies.

Based on the criterion (Eq. 35), Figure 5 is set up and the critical values Da_{R1^*}, Da_{R2^*} and Da_R' are thus obtained, where Da_{R1^*} is the value of Da_R at the minimum point of the $Da_{R1} - \tau_g$ curve, Da_{R2^*} at the minimum of the $Da_{R2} - \tau_g$ curve and Da_R' denotes the value of $Da_{R1} = Da_{R2}$ (i.e., at $\tau_g = \tau_g^*$). We note that for $\tau_g \geq \tau_g^*$ uniqueness is guaranteed.

Figure 6 represents a plot of the overall conversion vs. the gas residence time, which is identified as an isola in Figure 5. We note that the dashed line in Figure 5 matches the τ_g range of guaranteed multiplicity in Figure 6. It is shown that when the dashed line meets the line Da_{R2}, the intermediate and high conversion branches on the X-τ_g plot coalesce and an extinction point is formed. This is because Da_{R2} corresponds to n_2, the critical point of multiple steady states with higher temperature or conversion. Similarly, when a line similar to the dashed line in Figure 5 intersects the line Da_{R1}, the intermediate branch will meet with the low temperature or conversion branch and an ignition point is formed. This analysis of ignition and extinction points also applies to Case 1 (as shown in Figure 2) and the

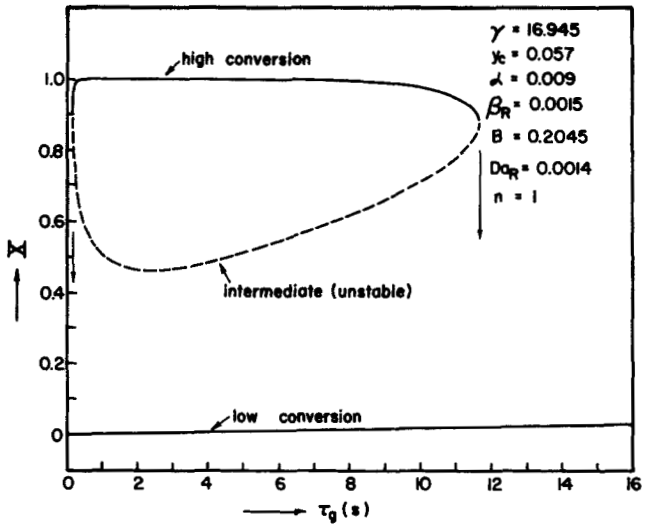

Figure 6. Influence of gas residence time on overall conversion, Case 2.

following Case 3.

Figure 7 collects the critical points Da_R', Da_{R1^*}, Da_{R2^*} and Da_{R2}^*, which is the value of Da_R at the maximum point of the $Da_{R2} - \tau_g$ curve and exists for a relatively small range of B (cf. Uppal et al., 1976). The line $B = B_*$ is the border of regions (a) and (b), and is obtained by trial-and-error. The steady-state behavior is, thus, classified as a function of system parameters.

A comparison of Figures 3 and 7 shows that the value of B below which uniqueness is guaranteed (i.e., B_*) for Case 1 is smaller than that for Case 2. However, for $B > B_*$, uniqueness is always guaranteed to the right of the line Da' for Case 1; but for Case 2, S-shaped multiplicity is always possible to the right of the line Da_R'. Note that all the system physico-chemical parameters are the same for both figures except those characterizing

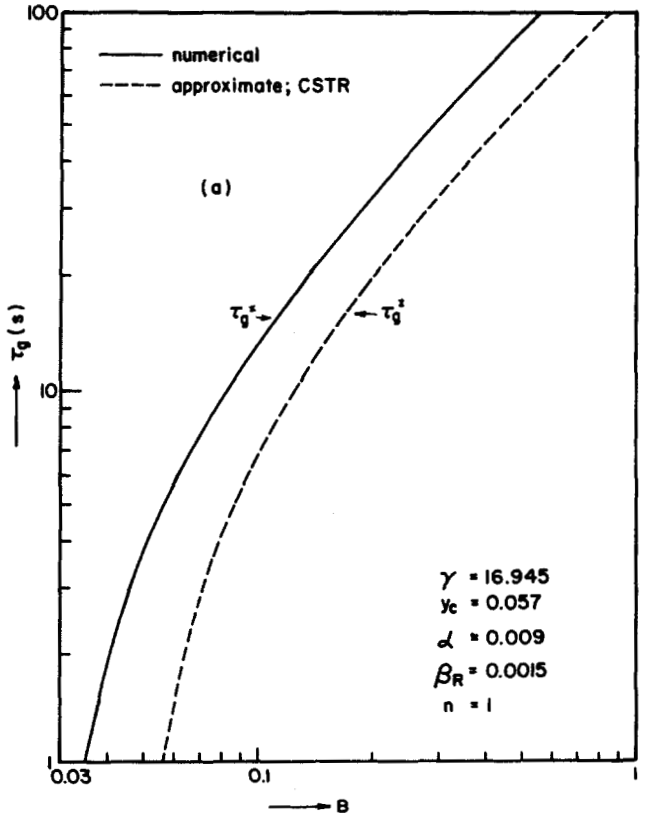

Figure 8. Effect of adiabatic temperature rise on critical gas residence time, Case 2: (a) uniqueness.

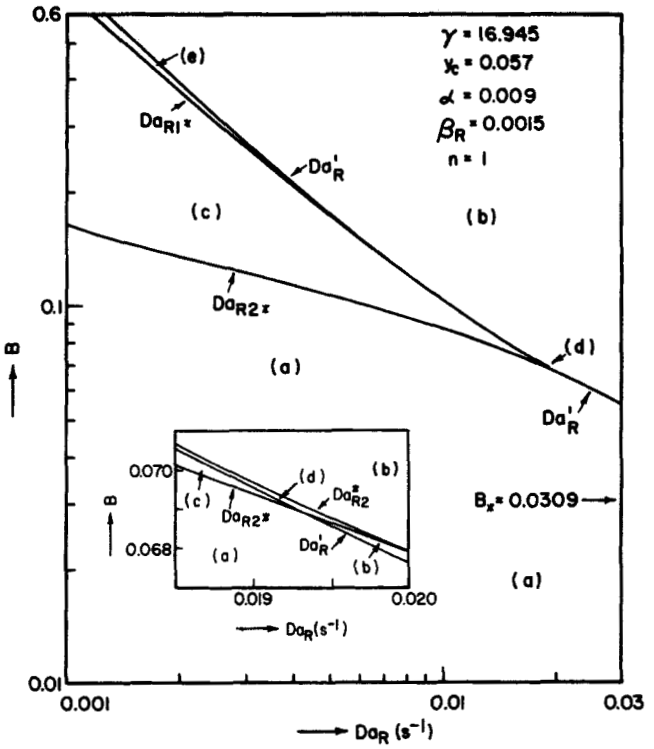

Figure 7. Effect of system parameters on steady-state behavior, Case 2 (a), (b), (c), (e) as in Figure 5, (d) isola + S-shaped.

the individual case. This means that the possibility of multiplicity for Case 2 is greater than that for Case 1, which is anticipated because of more parameters varying with flow rate in Case 2 than in Case 1. Also shown is that Case 1 has only two types of multiplicity patterns (b) and (g) but Case 2 has four, i.e., (b), (c), (d) and (e).

With β in Eq. 34, condition (Eq. 29) may be converted to:

$$\tau_{g^*} < \tau_g < \tau_g^* \tag{36}$$

where

$$\tau_{g^*},\ \tau_g^* = \frac{\gamma(B\gamma - 4B - 8\alpha\gamma) - 4y_c(B + 2\alpha\gamma) \mp 0_2^{\frac{1}{2}}}{8\beta_R(\gamma + y_c)^2} \tag{37}$$

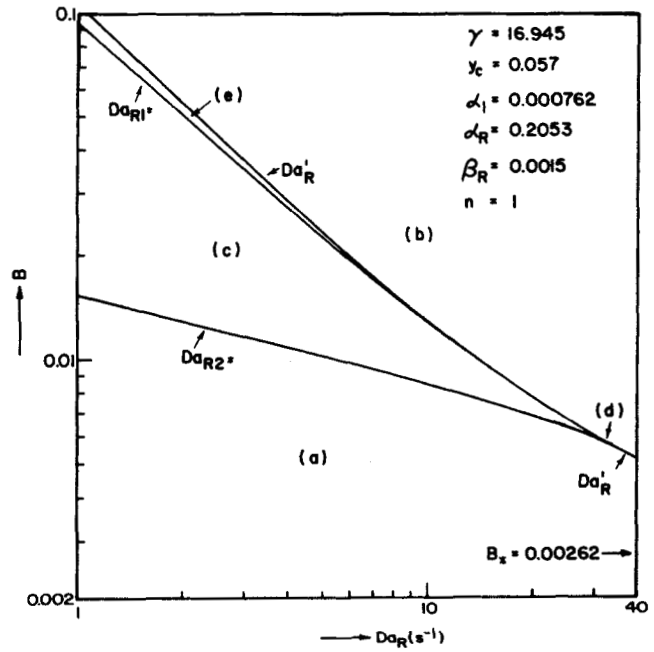

Figure 9. Effect of system parameters on steady-state behavior, Case 3: (a) - (e) as in Figure 7.

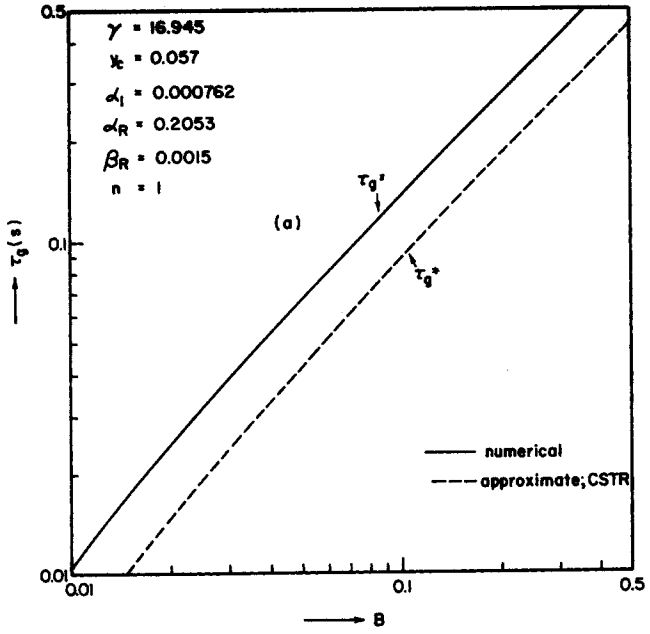

Figure 10. Effect of adiabatic temperature rise on the critical gas residence time, Case 3: (a) uniqueness.

with

$$Q_2 = [\gamma(4B - B\gamma + 8\alpha\gamma) + 4y_c(B + 2\alpha\gamma)]^2 - 16\alpha\gamma(\gamma + y_c)^2(4B - B\gamma + 4\alpha\gamma) \quad (37a)$$

It is found that τ_{g^*} is usually negative and then $\tau_{g^*} \equiv 0$ must be used in Eq. 36. We see that $\tau_g \geq \tau_g^*$ guarantees uniqueness, where τ_g^* has the same characteristic as F_{l2} in Case 1. However, when S-shaped multiplicity occurs in Case 2, these guaranteed unique steady states are on the high temperature or high conversion branch.

Similar to Case 1, it can be easily shown that:

$$\tau_{g,\,CSTR}^* < \tau_{g,\,BC}^* \quad (38)$$

with Figure 8 as an example. It is shown that as B increases, τ_g^* increases sharply. This means that the critical value of the gas flow rate and thus the liquid flow rate should decrease to assure uniqueness. By doing this, either high-temperature steady states are reached because of heat build-up or low-temperature steady states occur owing to the limited supply of the gas reactant. From Figure 5, we note that τ_g^* is in general a rather conservative value of τ_g to guarantee unique steady state. Therefore, plots such as Figures 4 and 8 have only limited utility, and it is plots such as Figures 2 and 5 that give the exact information on multiplicity regions.

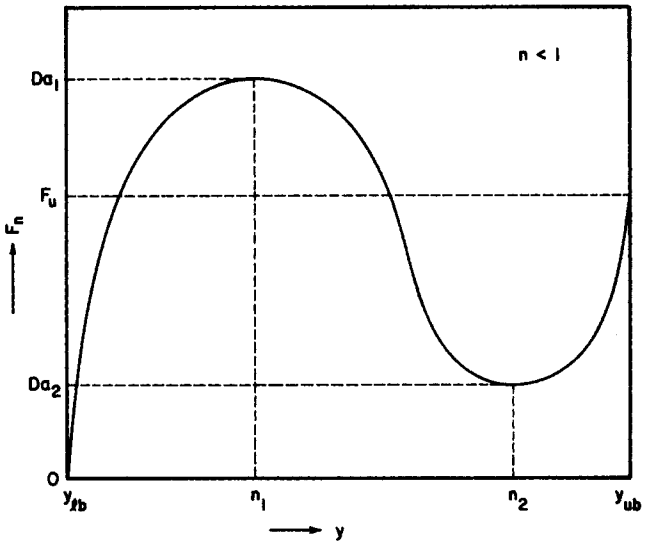

Figure 11. Locus of reactor steady states.

Fixed Liquid Flow Rate (Case 3). Now, the gas flow rate is free to vary. In addition to Da and β varying with τ_g as in Eq. 34, α can be rearranged as:

$$\alpha = \alpha_1 + \alpha_R\tau_g \quad (39)$$

Similar to Case 2, a plot like Figure 9 can be set up to classify the steady-state behavior. A comparison between Figures 7 and 9 seems to indicate that multiplicity is more possible for Case 3 than for Case 2, since B_* for Case 3 is much smaller. However,

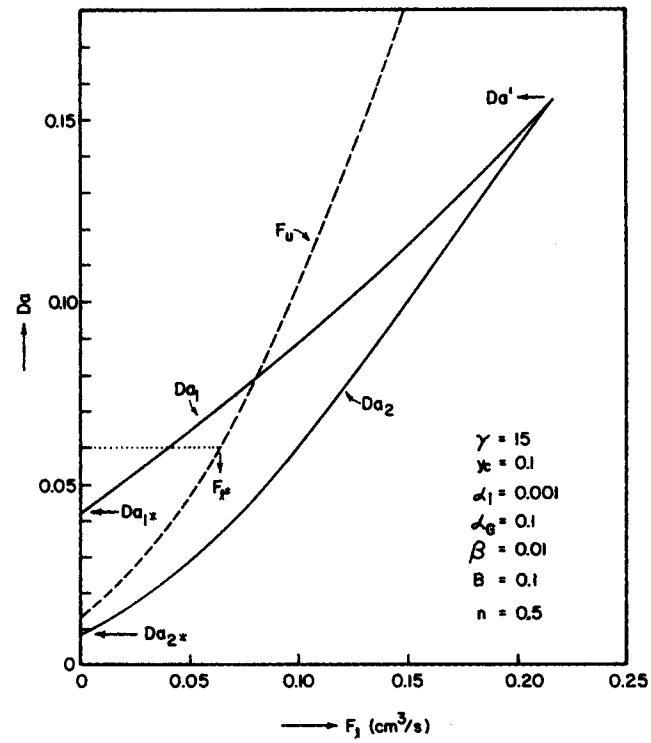

Figure 12. Effect of liquid flow rate on Da_1, Da_2 and F_u.

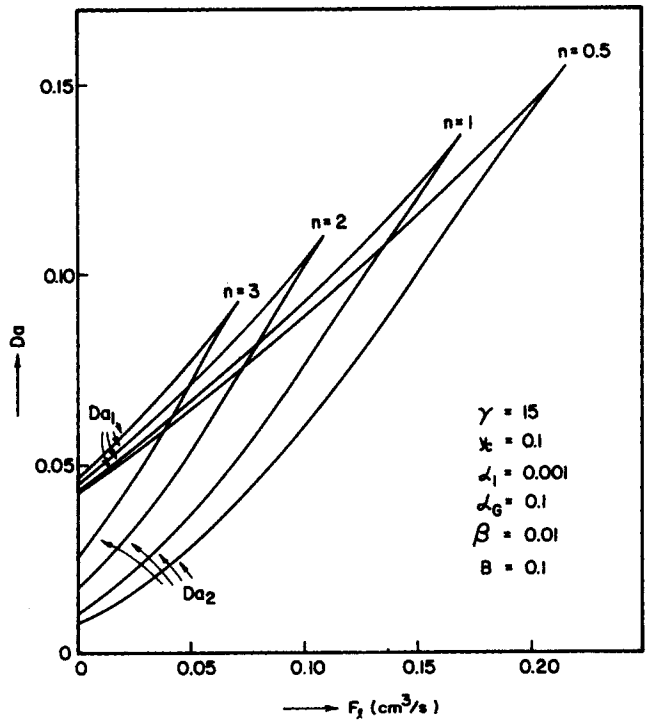

Figure 13. Effect of reaction order on multiplicity region.

from Figure 10, the values of τ_g^* for Case 3 is much smaller than that for Case 2 (cf. Figure 8) for same B values. In Case 3, τ_g^* is so small that uniqueness is virtually always assured. Note that $\tau_g \equiv V_g/F_g$ and the reactor volume for the numerical examples is 400 cm^3. Also note that values of B larger than those shown in the figures can rarely be achieved in gas-liquid reaction systems.

With the rearranged expressions of α and β, condition (Eq. 29) may be converted to condition (Eq. 36) with:

$$\tau_{g^*}, \tau_g^* = \frac{\gamma(\alpha_R + \beta_R)(B\gamma - 4B - 8\alpha_1\gamma) - 4\beta_R y_c(B + 2\alpha_1\gamma) \mp Q_3^{\frac{1}{2}}}{8[\gamma(\alpha_R + \beta_R) + \beta_R y_c]^2} \quad (40)$$

where

$$Q_3 = [\gamma(\alpha_R + \beta_R)(4B - B\gamma + 8\alpha_1\gamma) + 4\beta_R y_c(B + 2\alpha_1\gamma)]^2 - 16\,\alpha_1\gamma[\gamma(\alpha_R + \beta_R) + \beta_R y_c]^2(4B - B\gamma + 4\alpha_1\gamma) \quad (40a)$$

As in Case 2, it is found that Eq. 38 is also true for this case with Figure 10 as an example. Therefore, uniqueness should usually be guaranteed for this case occurring in the CSTR.

From Figure 10, the difference between the exact and approximate values of τ_g^* is rather small for the values of B considered. With uniqueness usually being the case as shown above, τ_g^* in Eq. 40 should be a good approximation for the prediction of the steady-state behavior.

GENERAL CASES ($n \neq 1$)

With $n \neq 1$, Eq. 7 may be solved with condition Eq. 7a to obtain:

$$a_g = \left[1 + \frac{n-1}{2} Da\, z \exp\left(\frac{y}{1 + y/\gamma}\right)\right]^{\frac{2}{1-n}} \quad (41)$$

$n > 1$ Case

Since Eq. 41 satisfies the fact $0 \leq a_g \leq 1$, it is the solution for all $z \geq 0$. Substituting Eq. 41 into Eq. 8 and performing the integration, we get

$$-\alpha y - B\left[1 + \frac{n-1}{2} Da \exp\left(\frac{y}{1 + y/\gamma}\right)\right]^{\frac{2}{1-n}} + B - \beta(y - y_c) = 0 \quad (42)$$

Applying the fact $0 \leq a_g \leq 1$ ($z = 0 \rightarrow 1$) and Eq. 42 with Eq. 41, the *a priori* bounds of the steady-state temperature are found to be the same as in Eq. 14. With $y \leq y_{ub}$, Eq. 42 can be rearranged to:

$$Da = \frac{2}{n-1}\left\{\left[\frac{B + \beta y_c - (\alpha + \beta)y}{B}\right]^{\frac{1-n}{2}} - 1\right\} \exp\left(\frac{-y}{1 + y/\gamma}\right) \equiv F_n(y) \quad (43)$$

We note that $F_n(y_{lb}) = 0$ and $F_n(y_{ub}) = \infty$, and $F_n'(y) = 0$ leads to

$$L_n(y) \equiv \frac{(n-1)(\alpha + \beta)(1 + y/\gamma)^2}{2B}\left[\frac{B}{B + \beta y_c - (\alpha + \beta)y}\right]^{\frac{1+n}{2}} = \left[\frac{B}{B + \beta y_c - (\alpha + \beta)y}\right]^{\frac{n-1}{2}} - 1 \equiv R_n(y) \quad (44)$$

Similar to the $n = 1$ case, it can be easily shown that $L_n(y_n) \geq R_n(y_n)$ assures uniqueness, where y_n is obtained from the following cubic equation:

$$(n+1)(\alpha + \beta)^2 y_n^3 + (n+1)(\alpha + \beta)[2\gamma(\alpha + \beta) - B - \beta y_c]y_n^2 + [\gamma^2(n+1)(\alpha + \beta)^2 - 2\gamma(n+1)(\alpha + \beta)(B + \beta y_c) - 4]y_n + 2\gamma(\gamma - 2) - \gamma^2(n+1)(\alpha + \beta)(B + \beta y_c) = 0 \quad (45)$$

There may be three real solutions from Eq. 45, but we are interested only in the values of $y_n \in (y_{lb}, y_{ub})$ since otherwise uniqueness is always guaranteed. Consequently, the necessary condition for the existence of multiple steady states is:

$$L_n(y_n) < R_n(y_n) \quad (46)$$

where both $L_n(y_n)$ and $R_n(y_n)$ are positive.

It is also readily shown that when Eq. 46 is satisfied, Eq. 44 will lead to exactly two critical points of multiple steady states, denoted as n_1 and n_2 with $n_1 < n_2$. Then, the sufficient condition for the existence of multiple steady states is the same as in Eq. 22 with $Da_i = F_n(n_i)$; $i = 1,2$.

$0 \leq n < 1$ Case

In this case, by the fact $0 \leq a_g \leq 1$, Eq. 41 is a solution only for:

$$z \leq z^* = \frac{2}{Da(1-n)} \exp\left(\frac{-y}{1 + y/\gamma}\right) \quad (47)$$

Note that z^* could be less than, greater than, or equal to 1; these subcases have to be dealt with separately.

Assume first that $z^* \geq 1$. Then, Eq. 41 is the solution for the whole column ($z = 0 \rightarrow 1$); the *a priori* bounds of the steady-state temperature are then the same as in Eq. 14, and Eq. 43 is true also for this case. We note that $F_n(y_{lb}) = 0$ and

$$F_n(y_{ub}) = \frac{2}{1-n} \exp\left(\frac{-y_{ub}}{1 + y_{ub}/\gamma}\right) \equiv F_u \quad (48)$$

where F_u is finite but approaches infinity as $n \rightarrow 1$. The slope of $F_n(y)$ is found to approach infinity as y approaches y_{ub}. As shown in Figure 11, when $Da < F_u$, there are three steady-state levels of dimensionless temperature y satisfying $y < y_{ub}$ and $z^* > 1$. However, for $Da > F_u$, there are only two steady states with $y < y_{ub}$ satisfying $z^* > 1$. This is because at $Da = F_u$, there are two steady states with $y < y_{ub}$ and $z^* > 1$, and a third steady state with $y \equiv y_{ub}$ and $z^* \equiv 1$. Beyond this point, i.e., $Da > F_u$, the third steady state comes with $z^* < 1$ because of the assumption $z^* \geq 1$ being invalid and has to be dealt with separately. Since Eq. 41 can be applied only for $z \leq z^*$, it is clear that when $z^* < 1$, the integral in Eq. 8 should be from $z = 0 \rightarrow z^*$ only. In this case, we get from Eq. 8:

$$y \equiv \frac{B + \beta y_c}{\alpha + \beta} \quad (49)$$

which is equal to y_{ub} and leads to total conversion, i.e., $X \equiv 1$. Under this circumstance, we need a column with only the following length, in cm:

$$Z^* = \frac{2}{\left(\frac{Da}{L}\right)(1-n)} \exp\left[\frac{-(B + \beta y_c)}{\alpha + \beta + (B + \beta y_c)/\gamma}\right] \quad (50)$$

where Da/L is in terms of the reactor cross-section area.

Therefore, we can see that Eq. 44 is good for this $n < 1$ case except at $y = y_{ub}$. Similar to the previous section, it is found that $[-L_n(y_n)] \geq [-R_n(y_n)]$ guarantees uniqueness, where y_n is the same as in Eq. 45. The necessary condition for the existence of multiple steady states is then:

$$-L_n(y_n) < -R_n(y_n) \quad (51)$$

where both $L_n(y_n)$ and $R_n(y_n)$ are negative. Note that we are interested in only $y_n \in (y_{lb}, y_{ub})$. From Eqs. 46 and 51, it is clear that a *general necessary condition* of multiplicity for both $n > 1$ and $n < 1$ cases is:

$$|L_n(y_n)| < |R_n(y_n)| \quad (52)$$

From Eq. 48, with y_{ub} as in Eq. 14, we get:

$$F_u = \frac{2}{1-n} \exp\left[\frac{-(B + \beta y_c)}{\alpha + \beta + (B + \beta y_c)/\gamma}\right] \quad (53)$$

For the case of fixed gas flow rate, and at a given value of Da (thus, $F_u = Fa$), Eq. 53 with Eq. 30 can be rearranged to obtain the critical point of the liquid flow rate:

$$F_{l^*} = \frac{1}{\alpha_G}\left\{\frac{B + \beta y_c}{\ln\left[\frac{2}{(1-n)Da}\right]} - \frac{B + \beta y_c + \gamma(\alpha_1 + \beta)}{\gamma}\right\} \quad (54)$$

beyond which, if there are three steady states, two of them exist with $z^* > 1$ and one with $z^* < 1$. Note that F_{l^*} may be negative and then should be discarded. As shown by the dotted line in Figure 12, when $F_l < F_{l^*}$, the steady state on the upper branch of the $y - \tau_l$ plot (noting $\tau_l \equiv V_l/F_l$) is equal to y_{ub}. In the trial-and-error procedure to obtain $y - \tau_l$ behavior, the value of y_{ub} should be excluded from the numerical search to avoid the certain pitfall. Note that y_{ub} increases as F_l decreases, but when $F_l < F_{l^*}$, $X \equiv 1$ along the high conversion branch; so, no difference exists in the overall conversion along this branch. When there is uniqueness, $F_l < F_{l^*}$ assures a unique $y \equiv y_{ub}$ (thus, $X \equiv 1$).

In summary, it is worth reiterating that the steady-state behavior is always of the type with a unique or three steady states for all values of $n \geq 0$. The additional analysis required for the $0 \leq n < 1$ case originates from the fact that for such kinetics the reactant can be exhausted in a *finite* reactor length.

EFFECT OF REACTION ORDER

For the case of fixed gas flow rate, the exact multiplicity region is shown in Figure 13 for various reaction orders. As can be seen, the region of multiplicity shrinks as the reaction order increases. This feature is the same as that found for single-phase reactors (Tsotsis and Schmitz, 1979; Chang and Calo, 1979). We also note that the critical point of either Da or F_l, i.e., the upper limits of Da and F_l respectively below which multiple steady states exist, also decreases as the reaction order increases. This is found to be generally true and it means that the possibility of the existence of multiple steady states increases as the reaction order decreases.

Although we have not demonstrated them explicitly, it should be evident that all the other types of multiplicity patterns (i.e., isola, mushrooms) that were shown for the $n = 1$ case will all remain feasible for reaction orders $n \neq 1$ as well.

CONCLUDING REMARKS

A mathematical model was developed to predict the steady state behavior of fast pseudo-nth-order reactions in a bubble column. *A priori* bounds were obtained and analytic necessary and sufficient conditions for the prediction of uniqueness and multiplicity were derived for the case of exothermic reactions and γ being positive. For the case of γ being negative, uniqueness is always guaranteed which can be easily shown through the same method applied in the above multiplicity analysis. For the special case of pseudo-first-order reactions, a linear approximation was found leading to uniqueness and multiplicity criteria which are exactly the same as those in the gas-liquid CSTR (Huang and Varma, 1981).

For pseudo-first-order reactions, three cases regarding the operation of bubble columns were discussed. It was found that uniqueness is usually assured for the case of a fixed liquid flow rate; however, this conclusion should be taken with care because some of the assumptions in the model development may not be satisfied for this case. It was also found that the possibility for the occurrence of multiple steady states is higher with a fixed ratio between the gas and liquid flow rates than with a fixed gas flow rate. Finally, it was shown that the possibility for multiplicity in the bubble column is always higher than that in the gas-liquid CSTR for equivalent system parameters.

In conclusion, it is worth noting that in this work, we are interested only in uniqueness and multiplicity of the steady states, and that the important results of the work are expressed in terms of ignition and extinction points, which define the multiplicity region.

The fast pseudo-first-order reaction model is admittedly a simplified one. However, as we have recently shown in the context of second-order reactions in nonadiabatic gas-liquid CSTRs, regions of multiplicity predicted *analytically* for this model compare favorably with those obtained *numerically* for the full second-order reaction model (Huang and Varma 1981a, b). This is not to say that conversions (particularly for the liquid reactant) and temperatures on the various branches within the region of multiplicity are identical for the two models, but only that the multiplicity regions for the two models compare well. Because of the similarity of a bubble column with a gas-liquid CSTR (one with and the other without mechanical stirring), it is expected that the same conclusion holds for the bubble column as well.

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NOTATION

A = concentration of gas reactant, g-mol/cm^3
a = interfacial area per unit column volume, cm^2/cm^3
a_g = dimensionless concentration of gas reactant, A_g/A_{gf}
B = dimensionless adiabatic temperature rise, $(-\Delta H_s - \Delta H_R)A_{gf}\gamma/\rho_l C_{Pl} T_f$
C_p = specific heat, cal/g·K
D_A = diffusivity, cm^2/s
Da = Damköhler number, $aV[2/(n+1)k_o D_A H_o^{n+1}]^{\frac{1}{2}} A_{bf}^{\frac{n-1}{2}}[\exp(-\gamma)]/F_g$
Da_R = parameter, Da/τ_g, s^{-1}
E = activation energy, cal/g-mol
E_A^* = reaction factor
F = volumetric flow rate, cm^3/s
H_o = Henry's law constant
ΔH_R = heat of reaction, negative if heat is liberated with reaction, cal/g-mol
ΔH_s = heat of solution, negative if heat is liberated with dissolution, cal/g-mol
k = nth-order or pseudo-nth-order rate constant, (cm^3/g-mol)$^{n-1}$/s
k_o = Arrhenius frequency factor, (cm^3/g-mol)$^{n-1}$/s
k_l = liquid phase mass transfer coefficient, cm/s
L = height of gas-liquid mixture in the column, cm
R = universal gas constant, cal/g-mol·°K
R_A = reaction rate, g-mol/s·cm^3
S = reactor cooling area, cm^2
T = temperature, °K
U = overall heat transfer coefficient, cal/K·cm^2·s
V = volume of gas-liquid mixture in the column, cm^3
V_g = volume of gas phase, $\epsilon_g V$, cm^3
V_l = volume of liquid phase, $\epsilon_l V$, cm^3
X = overall conversion
y = dimensionless temperature, $(T - T_f)\gamma/T_f$
Z = axial coordinate, cm
z = dimensionless axial coordinate, Z/L

Greek Letters

α = dimensionless parameter, $F_g\rho_g C_{Pg} + F_l\rho_l C_{Pl})/F_g\rho_l C_{Pl}$
α_1 = dimensionless parameter, $\rho_g C_{Pg}/\rho_l C_{Pl}$
α_G = parameter, $1/F_g$, s/cm^3
α_R = parameter, F_l/V_g, s^{-1}
β = dimensionless heat transfer coefficient, $US/F_g\rho_l C_{Pl}$
β_R = parameter, β/τ_g, s^{-1}
γ = dimensionless parameter, $[E - (n+1)(-\Delta H_s)]/2RT_f$
ϵ = fractional holdup in the column
ρ = density, g/cm^3
τ_g = gas residence time, V_g/F_g, s
τ_l = liquid residence time, V_l/F_l, s

Subscripts

c = cooling medium
f = feed
g = gas phase
i = gas-liquid interface
L = top of gas-liquid mixture in the column
l = liquid phase
lb = lower bound
ub = upper bound

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Diffusional Influences on Deactivation Rates

The interrelation between internal diffusion and concentration-independent deactivation is examined using a simple mathematical model. Analytical procedures are developed for evaluating the performance of single catalyst particles in the presence of diffusion and deactivation. By incorporating time-dependent effectiveness factors in design equations, reactor performance under the combined influence of diffusion and deactivation is predicted. By analogy to the effectiveness factor for non-deactivating systems, the concept of a deactivation effectiveness factor is introduced.

S. KRISHNASWAMY

and

J. R. KITTRELL

Department of Chemical Engineering
University of Massachusetts
Amherst, Massachusetts 01003

SCOPE

The design and operation of catalytic reactors are complicated by the phenomenon of catalyst deactivation, whereby the catalyst activity decreases with time on-stream. Furthermore, for reactors utilizing solid catalysts, the presence of mass transfer limitations will have a significant effect on the time scale of decay of catalyst activity. Consequently, an analysis of deactivation data which ignores the masking effects of diffusional limitations will lead to erroneous measurements of deactivation rate constants. Levenspiel (1972) showed that for diffusion-free systems, simple analytical conversion-time relationships exist that predict the behavior of batch and continuous reactors experiencing concentration-independent decay.

However, the bulk of the existing literature on reactor design, under the combined influences of both diffusion and deactivation, deals with computer solutions of theoretical models that are so complex that ease of interpretation is lost. The purpose of the present work is to show that simple analytical conversion-time relationships, similar to those presented by Levenspiel for diffusion-free systems, can be developed for reactors operating under the combined influence of concentration-independent deactivation and diffusional limitations.

S. Krishnaswamy is presently with Gulf Research & Development Co., Harmarville, PA.