Improvement of the Performance of a Fixed-Bed Catalytic Reactor by Relaxed Steady State Operation

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The relaxed steady state operation of a tubular fixed-bed catalytic reactor under control of the inlet composition is investigated. It is shown that the performance of such a reactor can be improved under certain conditions by periodically varying inlet concentrations rather than keeping these concentrations time invariant.

In a previously published paper (*1*) the selectivity S of a catalyst has been defined as the set of average rates of product formation attainable under a given set of admissible operations. Depending on the nature of the admissible operations, the correspondingly named (for example, steady state, dynamic, periodic, bang-bang, etc.) selectivity is used. It has been shown that under the assumption of perfect control of fluid concentrations at the catalyst surface, dynamic operation can drastically enlarge the region of attainability and therefore may improve the performance of the process. The following example has been discussed in reference *4*:

$$C_1 \underset{2}{\overset{1}{\rightleftarrows}} A_1 \qquad (1a)$$

$$C_1 + A_1 \overset{3}{\rightarrow} 2P_1 \qquad (1b)$$

$$C_1 \overset{4}{\rightarrow} P_2 \qquad (1c)$$

C_1 is the reactant, A_1 is a chemisorbed component, and P_1 and P_2 are products. Reactions (1*a*) and (1*b*) refer to elementary kinetics, while (1*c*) is an overall reaction. The reactions in (1*a*) are of first order, reaction (1*b*) is of first order with respect to C_1 and A_1, and reaction (1*c*) is of second order. This reaction will also involve species chemisorbed on the catalyst surface. However, in another paper (*1*) it has been shown that for investigations pertaining to relaxed steady state operation, which will be defined shortly, this model may be completely adequate even though the dynamics of the adsorption mechanism in (1*c*) does not appear in the model. For what follows,. the reaction system should be understood only as an example to illustrate the general developments.

Consider now one catalyst particle which is small enough so that mass transfer resistance can be neglected. Also suppose that the product concentration is very small in the environment of the particle and that the reactant concentration u^1 (concentration of C_1) can be controlled dynamically subject to

$$0 \leq u^1 \leq a \qquad (2)$$

This situation is an approximation of conditions near the inlet of a tubular reactor. Under these conditions the set S_{ss} of rates of product formation for the single catalyst particle in steady state is the lower boundary of the double hatched region in Figure 1 (see reference *4*). By mixing products coming from several steady state systems or by slow switching of the control, the convex hull of the steady state selectivity *co* S_{ss} can be obtained (*4*). This is the entire double-hatched region in Figure 1. It has been shown that every point in the hatched region marked S_r can be approximated arbitrarily closely by dynamic operation of the catalyst particle. This means that if P_2 is the desired and P_1 the undesired product, dynamic operation could considerably increase the performance of the system over the performance in the steady state. S_r is the relaxed steady state selectivity corresponding to fast switching of the control. It can be computed easily using only nonanalytical tools of convex set geometry (see reference *4*). The term relaxed steady state refers to a time-invariant condition which is approached in the limit by the state variables of the system as the frequency of the periodic control increases. This is reasonable physically: if the reactant composition in the fluid phase oscillates sufficiently rapidly, the adsorbed concentrations cannot follow and consequently approach a time-invariant state.

The purpose of this paper is to investigate the relaxed steady state of a tubular reactor subject to control of the inlet concentrations. This differs significantly from the problem described above since in the tubular reactor the control of fluid composition is influenced by the accumulation of products along the reactor. The general theory will be applied to the example of Equation (1), and it will be shown that although in a tubular reactor the im-

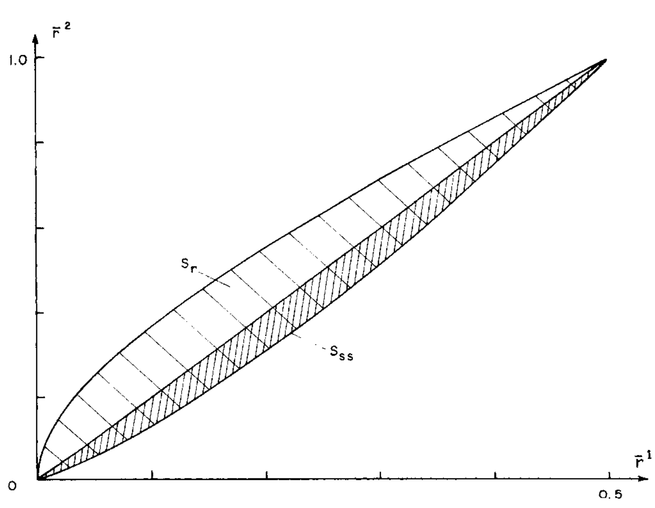

Fig. 1. Attainable sets in rate of formation space for the single catalyst particle.

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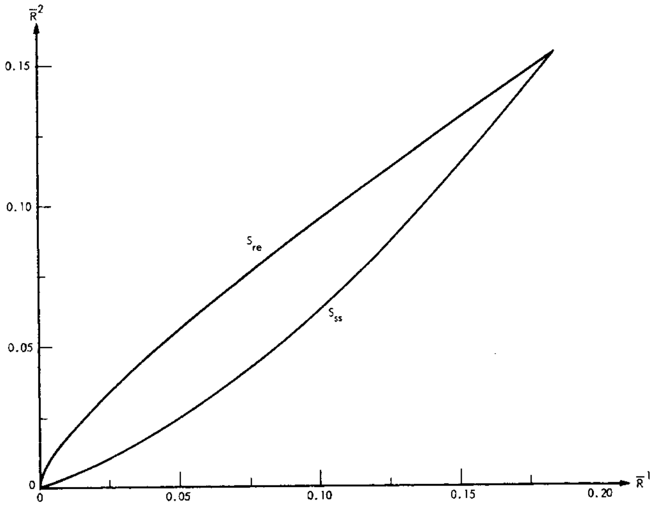

Figure 2.

Fig. 2. Attainable sets in rate of formation space for the tubular reactor.

provement due to dynamic operation is smaller than that for the perfect control case shown in Figure 1, this improvement is still significant. Since in Equation (1) the product desorption is irreversible, there is no induced chromatographic transport associated with the products. Therefore the improvement is due to effects other than those investigated by Gore (3) and others.

DESCRIPTION OF THE MODEL AND GENERAL DYNAMICAL EQUATIONS

It will be assumed that the flow velocity, temperature, and pressure are constant throughout the tube, that there is no longitudinal mixing, and that there is no mass transfer resistance within or around the catalyst pellets which fill the tube. Under these conditions, the operation of the reactor may be described in terms of an l-dimensional vector of fluid concentrations x_g and an n-dimensional vector x_a of adsorbed concentrations as follows:

$$\frac{\partial x_g(z,t)}{\partial t} + v\frac{\partial x_g(z,t)}{\partial z} = f_g\,[x_g(z,t), x_a(z,t)] \quad (3a)$$

$$\frac{\partial x_a(z,t)}{\partial t} = \mathrm{f}_a\,[x_g(z,t), x_a(z,t)] \quad (3b)$$

where the fluid-catalyst ratio is considered in the scaling of f_g such that (3a) becomes the correct mass balance.

We are interested in a periodic operation (5) of the reactor in which all control and state variables are periodic functions of time with period τ. That is

$$\left.\begin{aligned} u(t) &= u(t+\tau) \\ x_g(z,t) &= x_g(z,t+\tau) \\ x_a(z,t) &= x_a(z,t+\tau) \end{aligned}\right\} \text{ for all } t \text{ and } z \quad \begin{aligned}(4a)\\(4b)\\(4c)\end{aligned}$$

In the case of periodic operation we need to pay attention only to one period, say $t \epsilon [0, \tau]$, and the proper boundary conditions are then

$$x_g(0,t) = u(t) \quad (5a)$$

$$x_g(z,0) = x_g(z,\tau) \quad (5b)$$

$$x_a(z,0) = x_a(z,\tau) \quad (5c)$$

The n-dimensional vector $\bar{r}$ of time-average rates of production per unit volume of catalyst is given by

$$\bar{r} = \frac{1}{L}\,\frac{1}{\tau}\int_0^\tau dt\int_0^L g\,[x_g(z,t), x_a(z,t)]\,dz \quad (6)$$

For the example of Equation (1) the rate vectors f_g and f_a are one-dimensional and the rate vector g is two-dimensional. These vectors are given by

$$f_g = [k_2 x_a{}^1 - (k_1 + k_3 x_a{}^1 + k_4 x_g{}^1)x_g{}^1]\left(\frac{1-\epsilon}{\epsilon}\right) \quad (7a)$$

$$f_a = k_1 x_g{}^1 - (k_2 + k_3 x_g{}^1)x_a{}^1 \quad (7b)$$

$$g^1 = 2k_3 x_a{}^1 x_g{}^1, \quad g^2 = k_4 (x_g{}^1)^2 \quad (7c)$$

STEADY STATE OPERATION

In the steady state the reactor is described by

$$\frac{dx_g(z)}{dz} = \frac{1}{v} f_g[x_g(z), x_a(z)] \quad (8a)$$

$$x_g(0) = u \quad (8b)$$

$$0 = f_a[x_g(z), x_a(z)] \quad (9)$$

The integral rates of formation are given by

$$\bar{r} = \frac{1}{L}\int_0^L g[x_g(z), x_a(z)]\,dz \quad (10)$$

For the example in Equation (1), the necessary integrations can be carried out analytically. The result is shown in Figure 2 for the parameters

$$\mu = 1, \quad \beta = 0.3, \quad \rho = 0.5, \quad \theta = 2, \quad (11)$$

where the dimensionless parameters μ, β, θ, and ρ are given by

$$\mu = k_1/k_3 a, \quad \beta = k_2/k_3 a, \quad \rho = k_4/k_3,$$
$$\theta = \frac{Lk_3 a}{v}\left(\frac{1-\epsilon}{\epsilon}\right) \quad (12)$$

and the dimensionless reactor length is unity. In Figure 2 dimensionless average rate of formations $\bar{R}^1$ and $\bar{R}^2$ are used which are defined by

$$\bar{R}^1 = \frac{\bar{r}^1}{2k_1 a}, \quad \bar{R}^2 = \frac{\bar{r}^2}{k_4 a^2} \quad (13)$$

The curve labeled S_{ss} is the set of attainable rates for steady state operation corresponding to inlet concentration u^1 of the reactant C_1 varying between 0 and a.

THE RELAXED STEADY STATE

Returning now to the general system described by Equations (3), assume that the inlet concentrations, which are represented by a point in the control set U, are switched periodically between the values $u_1, u_2, \ldots, u_h$. If τ is the period of the operation, the control is specified as follows:

$$u = u_\nu \quad \text{for} \quad t \,\epsilon\, (t_{\nu-1}, t_\nu) \quad (14a)$$

where

$$t_0 = 0, \quad t_\nu > t_{\nu-1} \quad (14b)$$

and

$$(t_\nu - t_{\nu-1})/\tau = \alpha_\nu, \quad \sum_{\nu=1}^{h} \alpha_\nu = 1 \quad (14c)$$

If τ is sufficiently small the system approximately assumes a relaxed steady state (4). That is, as the fluid concentration within the bed oscillates more and more rapidly, the adsorbed concentration x_a at each position z within the fixed bed approaches a time-invariant condition. Hence for periodic operation with a small period, it can be assumed that x_a is a function of z alone. Then, setting up mass balances for the fluid elements which correspond to the control intervals $[t_{\nu-1}, t_\nu]$ and which move along the reactor with velocity v yields the following set of h vector differential equations:

$$v \frac{dx_{g\nu}(z)}{dz} = f_g\,[x_{g\nu}(z), x_a(z)]; \quad \nu = 1, 2, \ldots, h \tag{15a}$$

The initial conditions are

$$x_{g\nu}(0) = u_\nu \tag{15b}$$

These equations are the relaxed steady state analogs of the steady state Equations (8). Equation (9) is replaced by an integral mass balance over the period

$$0 = \sum_{\nu=1}^{h} \alpha_\nu f_a\,[x_{g\nu}(z), x_a(z)] \tag{16}$$

This equation expresses the essential content of the relaxed steady state concept. By the theorem of relaxed control (6), it can be shown that any solution of (16) can be approximated arbitrarily closely by solutions of (3b) if the fluid concentration x_g switches sufficiently rapidly. In relaxed control rates $\partial x_a/\partial t$ are admitted which are in the convex hull of the rates attainable under ordinary control. Setting the rate (zero in our case) equal to a convex combination of attainable rates f_a corresponds here to a mass balance over the period.

The average rates of formations for the relaxed steady state can be obtained easily by averaging over the period

$$\bar{r} = \frac{1}{L} \sum_{\nu=1}^{h} \alpha_\nu \int_0^L g[x_{g\nu}(z), x_a(z)]\, dz \tag{17}$$

RESULTS FOR AN EXAMPLE

A tubular reactor described by the Equations (7) will be considered in this section. The control will be bang-bang and periodic. Each period τ will consist of two subintervals of length $\gamma\tau$ and $(1-\gamma)\tau$ in which the control u^1 is chosen a and 0, respectively. The relaxed steady state computed is the limiting case for $\tau \rightarrow 0$. For simplicity, dimensionless variables ξ_1, ξ_2, η, φ, and ζ will be introduced as follows:

$$\xi_1 = x^1_{g1}/a, \quad \xi_2 = x^1_{g2}/a \tag{18a}$$

$$\eta = x^1_a/a, \quad \varphi = u^1/a \tag{18b}$$

$$\zeta = z/L \tag{18c}$$

ξ_1 and ξ_2 refer to the gas concentrations of C_1 corresponding to the subintervals of the switching period. φ is the new control variable which will assume values 0 and 1 only.

Equations (15) become [see Equations (7), (12), and (18)]

$$\frac{d\xi_k(\zeta)}{d\zeta} = \theta[\beta - \xi_k(\zeta)]\,\eta(\zeta) - \theta[\mu + \rho\xi_k(\zeta)]\xi_k(\zeta); \qquad k = 1, 2 \tag{19a}$$

The initial conditions are

$$\xi_1(0) = 1, \quad \xi_2(0) = 0 \tag{19b}$$

Equation (16) becomes

$$\gamma\{\mu\xi_1(\zeta) - [\beta + \xi_1(\zeta)]\,\eta(\zeta)\} + (1-\gamma)\,\{\mu\xi_2(\zeta) - [\beta + \xi_2(\zeta)]\,\eta(\zeta)\} = 0 \tag{20}$$

From this it follows that

$$\eta(\zeta) = \mu\bar{\zeta}(\zeta)/[\beta + \bar{\xi}(\zeta)] \tag{21}$$

where

$$\bar{\xi}(\zeta) = \gamma\xi_1(\zeta) + (1-\gamma)\,\xi_2(\zeta) \tag{22}$$

Equations (17) become, after a minor manipulation using (21),

$$\bar{R}^1 = \int_0^1 \frac{[\bar{\xi}(\zeta)]^2}{\bar{\xi}(\zeta) + \beta}\, d\zeta \tag{23a}$$

$$\bar{R}^2 = \int_0^1 \{\gamma[\xi_1(\zeta)]^2 + (1-\gamma)\,[\xi_2(\zeta)]^2\}\, d\zeta \tag{23b}$$

It is easy to integrate the system of Equations (19) numerically. In our calculation Equation (21) was used to compute η in each integration step. [Another possibility is to differentiate (21) with respect to ζ and then to use any standard integration routine to integrate the resulting system of three simultaneous differential equations. This approach can be especially useful when condition (16) does not provide an explicit expression for x_a in terms of x_g and the control parameters α_ν.]

By varying γ from 0 to 1 a curve is traced out in the rate of formation space. This curve for the parameters given by (11) is marked S_{re} in Figure 2. Obviously, the whole region between S_{re} and S_{ss} is attainable by mixing. It is clear that S_{re} is not contained in *co* S_{ss}. Therefore average production rates can be obtained by cycling inlet reactant concentrations which are unattainable with any steady inlet concentration. Also, there are elements $\bar{R}$ of S_{re} which cannot be realized by mixing of steady state productions.

The enlargement of the attainable region by periodic operation is of great importance for reactor optimization.

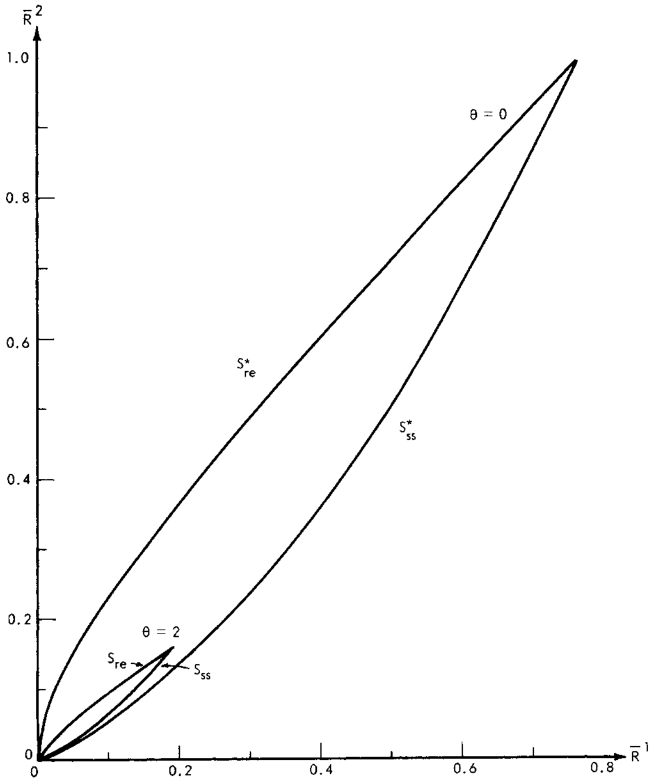

Fig. 3. Attainable sets in rate of formation space for perfect control of the tubular reactor ($\Theta = 0$) and inlet control with $\Theta = 2$.

For the above example in particular, relaxed steady state operation will improve reactor performance for many economic situations where P_2 is the desired and P_1 the undesired product.

It may be of interest to note that the potential increase in performance here is not so large as in the case of perfect control of fluid composition. To illustrate this, the selectivities S^*_{re} and S^*_{ss} for perfect control with $\beta = 0.3$ and $\mu = 1$ are shown in Figure 3 along with the results already shown in Figure 2. The perfect control case arises when there is negligible change in reactant concentration along the reactor. By referring to a dimensionless description of the system, it can be seen that this situation is approached when the dimensionless parameter

$$\theta = \frac{Lk_3a}{v}\left(\frac{1-\epsilon}{\epsilon}\right)$$

approaches zero.

INFLUENCE OF DIFFUSIONAL RESISTANCE AND MIXING

The relaxed steady state is better approximated the faster the switching. If switching becomes faster and faster ($\tau \rightarrow 0$), however, the mathematical model used in this paper becomes inadequate for several reasons. First, the kinetic model will no longer be valid. It breaks down because the steady state approximation for intermediates in the P_2 mechanism, which is implicit in this model, is not valid for very small periods. Effects due to this limitation are discussed elsewhere (*1*), where it is shown that under certain conditions the results obtained with relaxed steady state analysis are still approximately correct. Resolution of the dilemma arising from the use of apparently contradictory assumptions is possible if the characteristic response times for various chemisorbed species are sufficiently different.

Second, diffusional resistance between the bulk fluid and the catalyst surface tends to damp out oscillations of concentrations within the catalyst. Here as in the case of a kinetic restriction, it can be shown that operating with a switching period of optimal length leads to a good approximation of the relaxed steady state under certain conditions (*2*). Results concerning this will be published elsewhere.

Third, longitudinal mixing will damp out oscillation of concentrations in the bulk of the fluid if the switching period is too small. (Usually this will be the case if τ is small compared to the residence time.) However, a switching period which is still so large that the plug-flow assumption is reasonable may be very short as far as approximation to the relaxed steady state is concerned since two entirely separate mechanisms are involved. It can be expected that here, too, an optimum switching period will correspond to a good approximation of the relaxed steady state if the kinetic time constant governing the relaxed steady state approximation is sufficiently larger than the characteristic time governing mixing effects.

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NOTATION

A = adsorbed component
a = maximal concentration of reactant
C = reactant
co = convex hull
f_a = vector of rates of formation of adsorbed components
f_g = vector of rates of formation of fluid components
g = vector of rates of formation of fluid products
h = number of values of control used in periodic operation
k_1, k_2, k_3, k_4 = rate constants
L = length of reactor
P_1, P_2 = products
$\overline{R}$ = vector of dimensionless time-average rates of product formation
$\overline{r}$ = vector of time-average rates of product formation
S = selectivity; point set in average rate of formation space
t = time
u = vector of inlet concentrations
v = fluid velocity
x_a = vector of adsorbed concentrations
x_g = vector of fluid concentrations
z = distance from reactor inlet

Greek Letters

α = fractional length of switching interval [see Equation (14*c*)]
β = dimensionless parameter as defined by Equation (12)
ϵ = void fraction of the fixed-bed reactor
ζ = dimensionless parameter as defined by Equation (12)
η = dimensionless adsorbed component concentration
θ = dimensionless parameter as defined by Equation (12)
μ = dimensionless parameter as defined by Equation (12)
ξ = dimensionless reactant concentration [see Equation (18*a*)]
ρ = dimensionless parameter as defined by Equation (12)
τ = period
φ = dimensionless inlet reactant concentration

Subscripts

e = end of reactor
r = relaxed steady state
re = relaxed steady state obtained by sequence of periodic bang-bang controls with $\tau \rightarrow 0$
ss = steady state
ν = index for switching intervals of periodic bang-bang control

Superscripts

1, 2, . . . = indices denoting components of vector
$*$ = perfect control

LITERATURE CITED

1. Bailey, J. E., and F. J. M. Horn, *Ber. Bunsenges. Phys. Chem.*, **73**, 274 (1969).
2. ——————, and R. C. Lin, accepted for publication in *AIChE J.*
3. Gore, F. E., *Ind. Eng. Chem. Proc. Design Develop.*, **6**, 11 (1967).
4. Horn, F. J. M., and J. E. Bailey, *J. Optimization Theory Appl.*, **2**, 441 (1968).
5. Horn, F. J. M., and R. C. Lin, *Ind. Eng. Chem. Proc. Design Develop.*, **6**, 21 (1967).
6. Warga, J., *J. Math. Anal. Appl.*, **4**, 111 (1962).

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