Design of a Chemical Pulse Reactor

Steady- State and Pulsewise Operation of a Catalytic Tubular Fixed Bed Reactor with Substrate Inhibition

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The general reaction $X + Y + M \rightarrow P + M$ may — due to substrate inhibition at the catalytic site M — give rise to bistability phenomena in an isothermal tubular fixed bed reactor. The parametric conditions for bistability in the single pellet are studied by a numerical technique. Solution of the steady state equations for a two phase model of the tubular reactor shows that narrow zones with high conversion are possible, similar to ignition zones in nonisothermal catalytic reactors. By a cyclic operation with alternating periods of charging the catalyst phase with substrate and discharging it by chemical reaction, pulses of high product concentration can be generated at the reactor outlet. This is demonstrated by simulation of the system assuming low flow velocity as it is characteristic for reaction columns with liquid mobile phase.

I. Introduction

It is a well known fact in the design of tubular fixed bed reactors (FBRs) that sufficiently exothermic or endothermic chemical reactions may lead to phenomena like multiple stationary profiles of the temperature and chemical concentrations along the reactor, hysteresis behavior, stationary or wandering reaction zones (ignition zones) and even oscillations under constant inlet conditions [1—4]. In order to find out criteria for these effects in the set of technical and chemical parameters of a reactor, there has been a considerable amount of both experimental and theoretical work, the latter being carried out by numerical studies or analytical methods which may lead to a priori predictions for the reactor stability [5, 6].

The basic principle of the mentioned effects is the combination of a nonlinear sigmoid heat production (consumption) rate by the chemical reaction with an approximately linear heat removal (supply) curve leading to multiplicity of steady states.

But while in these cases the nonlinearity in the reaction rate may be characterized as an autocatalysis by the "product" reaction heat, in isothermal systems substrate inhibition is a much more important mechanism giving rise to unusual dynamical behavior. This has been demonstrated e.g. for a continuous stirred tank reactor (CSTR) in which a substrate inhibited enzyme reaction is run [7], as well as for a general isothermal reaction system involving homogeneous catalysis [8]. Furthermore, it has been shown that in the technical hydroformylation process bistability is possible under isothermal conditions, which is due to substrate inhibition by carbon monoxide [9].

It is an interesting question, now, to what extent and under which parametric conditions the same effects that are known from nonisothermal FBRs can also arise in a packed column, in which an isothermal, but substrate inhibited reaction takes place. While there is no way for oscillations to arise in such a reactor, multiple steady states and narrow reaction zones, etc., should be expected under suitable conditions.

Little work has been done in this field until now, although the methodic tools first developed for nonisothermal reactors are at hand. With the growing interest in enzymes as catalysts for technical processes and due to the improvement of enzyme immobilizing techniques in the last years, however, the reactor design for isothermal columns with nonlinear kinetics has become of interest [10—14].

For a substrate inhibited reaction in a column Elnashaie et al. demonstrated the possibility of multiple stationary profiles in a numerical study and DeVera et al. worked out an analytical criterion for predicting uniqueness of steady states [15, 16].

Our aim is to design and describe a mode of operation of a packed column by which due to substrate inhibition and multiplicity of steady states a pulsewise outlet concentration of reaction product can be generated. The idea is to start from

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a state of the system in which the reaction is inhibited all along the reactor bed. This means that for maximal saturation of the catalyst phase with substrate the conversion rate is minimal and the outlet concentration of product is close to zero. If now by an appropriate change of the inlet concentrations the system is switched to the high production state a reaction front will rise at the reactor entrance and will move downstream. For equal velocity of the reaction front and transport velocity of the product this should lead to a strong accumulation of product in a narrow wandering zone. The corresponding pulse of product in the reactor outlet is expected to have a much higher maximum concentration in comparison to the stationary operation in the high conversion state.

It should be mentioned that the situation sketched above is very similar to the formation of hot spots known from exothermal reactions in a tubular catalytic FBR [3]. Besides this, it reminds one of the mode of operation of a laser.

We want to test our hypothesis by simulations of an appropriate reactor model. First, however, we shall analyze the single pellet behavior of the system and the stationary behavior of the tubular reactor model to get criteria for suitable parameters in the simulations.

II. Reaction Mechanism and Single Particle Behavior

Consider the reaction scheme as sketched in Figure 1. We choose a two substrate mechanism because it can still be treated easily but nevertheless represents a large class of catalytic reactions, rather than a one substrate mechanism. The dynamics of the reaction is described by the following set of ordinary differential equations

$$\begin{aligned} \dot{X} &= -k_1 X \cdot M + k_{-1} MX - k_2 X M \cdot X \\ &\quad + k_{-2} MXX , \\ \dot{Y} &= -k_3 MX \cdot Y , \qquad (1) \\ \dot{MX} &= k_1 X \cdot M - k_{-1} MX - k_3 MX \cdot Y , \\ \dot{MXX} &= k_2 MX \cdot X - k_{-2} MXX \end{aligned}$$

together with the conservation condition $M + MX + MXX = M_{\text{tot}}$, where M_{tot} is the total concentration of catalyst (by the dot we indicate the derivative with respect to time). By assuming a pseudo steady state for the species MX and MXX we arrive at an expression for the reaction rate which is dependent on the concentrations of X and Y:

$$-\dot{x} = \mu \frac{y}{1 + \dfrac{x}{K_\text{i}} + \dfrac{K_\text{m} + K_\text{R} y}{x}} := \mu\, \varrho(x, y) . \qquad (2)$$

In Eq. (2) we have introduced the following dimensionless quantities

$$x := \frac{X}{C_\text{r}} , \quad y := \frac{Y}{C_\text{r}} , \quad K_\text{i} := \frac{1}{C_\text{r}} \frac{k_{-2}}{k_2} ,$$

$$K_\text{m} := \frac{1}{C_\text{r}} \frac{k_{-1}}{k_1} , \quad K_\text{R} := \frac{k_3}{k_1} ,$$

where C_r is a reference concentration, e.g., the inlet concentration of y in the reactor. Further,

$$\mu := k_3 M_{\text{tot}} \quad (\text{dim: sec}^{-1})$$

represents the constant of the rate determining reaction step and the total concentration of the catalyst (enzyme). For $y = \text{const}$ Eq. (2) attains the usual form of the rate function for a substrate inhibited enzyme reaction.

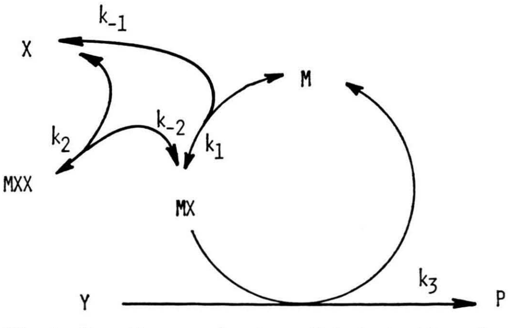

Fig. 1. Reaction mechanism: Substrate X and catalytic site M give rise to complex MX, which reacts with substrate Y to product P. MXX denotes the inhibitory complex and k_i are the rate constants.

For an open reaction system with homogeneous concentrations we now write

$$\begin{aligned} \dot{x} &= q(x_0 - x) - \mu \cdot \varrho \cdot (x, y) , \\ \dot{y} &= q(y_0 - y) - \mu \cdot \varrho \cdot (x, y) \end{aligned}$$

with $y_0 := Y_0/C_\text{r}$ and $x_0 := X_0/C_\text{r}$ being the dimensionless input values of X and Y. Equation (3) may be interpreted as the balance equation of a CSTR (q = volumetric flow rate/reactor volume) or of a single catalyst pellet (microcapsule) with the diffusion resistances lumped at the phase boundary (q = permeability).

For $\dot{x} = \dot{y} = 0$ Eq. (3) yields an algebraic equation in terms of the steady state concentration of x:

$$x_0 - x_{\mathrm{ss}} = \mathrm{Da} \cdot \varrho(x_{\mathrm{ss}}, y_{\mathrm{ss}})$$

with

$$y_{\mathrm{ss}} = y_0 + x_{\mathrm{ss}} - x_0 \tag{4}$$

and

$$\mathrm{Da} = \mu / q \,,$$

where Da, the Damköhler number is a measure for the intensity of the reaction relative to the transport rate in the reaction volume. Equation (4) is equivalent to a cubic polynomial in x_{ss} which may have one or three real positive solutions corresponding to one or two stable steady states of the system. The corresponding curves of x_{ss} vs., say x_0 or y_0 may be monotonic, thus indicating only one possible steady state, or may be S-shaped (hysteresis curves).

A first criterion or necessary condition for the system to allow bistability in the admissible range of x_0 or y_0 is derived from the critical case where the three real roots of Eq. (4) coincide. This condition applied to Eq. (4) yields via elimination of x_0 a complicated implicit function in the fixed parameters of the system. The function may be evaluated numerically for different pairs of two parameters with the others kept constant, thus giving sets of border lines in the parameter space which separate hysteresis regions from those in which only one steady state is possible a priori. This procedure is analogous to the analytic treatment proposed by Luss et al. [6], which in this case, however, does not lead to simple criteria.

From the example presented in Fig. 2 we see that bistability or hysteresis behavior is possible in a reasonable range of parameters. For K_{m}, e.g., values of 10^{-7} to 10^{-1} just fit the experimental data known from most enzymes.

In Fig. 3 a typical series of hysteresis curves x_{ss} vs. x_0 is depicted. On the lower branch of the curves, corresponding to the high conversion state, we have nearly constant x_{ss}, whereas on the upper branch (low conversion state) there is an approximately linear dependence on x_0.

III. Stationary Behavior of the Tubular Reactor

While the steady state behavior of the homogeneous system is readily understood by the analysis of Eq. (4) the fixed bed tubular reactor needs some further treatment.

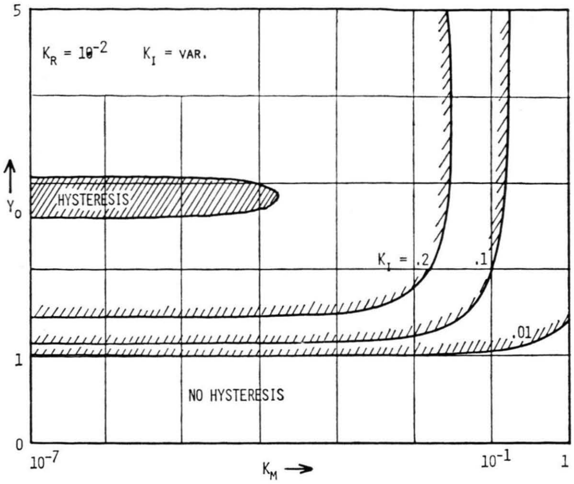

Fig. 2. Section through the hypersurface defining the parametric conditions for the critical case between hysteresis behaviour (two stable steady states) and unique steady state behaviour of the system (Eq. (1)). Scaling for K_{m} is logarithmic.

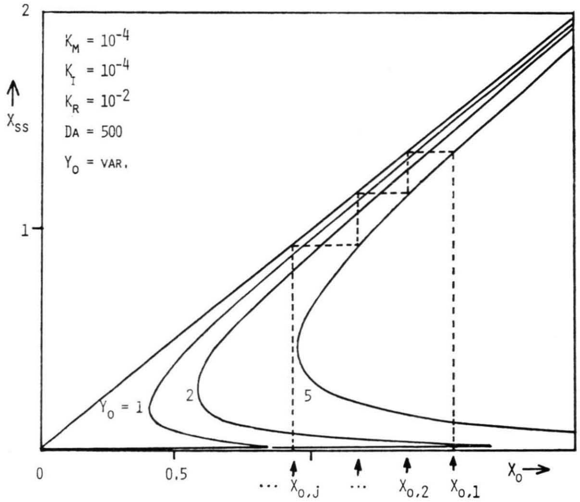

Fig. 3. Hysteresis curves $x_{\mathrm{ss}} = f(x_0)$ for some values of parameter y_0. $x_{0,1} \dots x_{0,n}$ denote a series of feed concentrations in a linear array of ideally mixed cells in which the steady state output concentration of the $(i-1)$-th cell is the feed concentration of the i-th cell (here for $y_0 = \mathrm{const} = 5$).

To get a qualitative idea of the situation let us first consider the reactor as a linear array of ideally mixed cells in which the steady state concentrations of the i-th cell are the feed concentrations of the $(i+1)$-th cell ("mixing cell model"). The stationary concentration profile along the reactor may then be constructed by a graphical procedure using the steady state curves of the homogeneous system [17].

From Fig. 3 we notice for the bistable case:

i) If we start with the low production state in the first cell (at reactor inlet) a jump to the high production state will occur after a finite number j of cells. Whether this "ignition" will be within the reactor length depends on the inlet concentration $x_{0,1}$, the actual shape of the hysteresis curve, and the number of cells by which the reactor has to be represented [17, 18].

ii) Even if the inhibited state is maintained until the reactor outlet, a considerable overall conversion is possible due to the general shape of hysteresis curves for substrate inhibition kinetics (see Chapter II). The closer the upper branch of the hysteresis curve is to the bisector of the $x_{\mathrm{ss}} - x_0$ plane, the lower the overall conversion will be.

(For the sake of simplicity we did not take into account the influence of y_0 and the initial conditions in the above consideration.)

For the numerical calculations we used a two phase rather than a one phase model for the reactor because of the more direct physical interpretation of the parameters. The differential equations for the mobile phase are

$$\frac{\partial x_{\mathrm{m}}}{\partial t} = D_x \frac{\partial^2 x_{\mathrm{m}}}{\partial z^2} - v \frac{\partial x_{\mathrm{m}}}{\partial z} - a_x (x_{\mathrm{m}} - x) \,,$$

$$\frac{\partial y_{\mathrm{m}}}{\partial t} = D_y \frac{\partial^2 y_{\mathrm{m}}}{\partial z^2} - v \frac{\partial y_{\mathrm{m}}}{\partial z} - a_y (y_{\mathrm{m}} - y) \,,$$

$$0 \leqq z \leqq 1 \tag{5}$$

with the boundary conditions

$$\text{at } z = 0{:} \quad D_x \frac{\partial x_{\mathrm{m}}}{\partial z} = v (x_{\mathrm{m}} - x_{\mathrm{m}0}) \,,$$

$$D_y \frac{\partial y_{\mathrm{m}}}{\partial z} = v (y_{\mathrm{m}} - y_{\mathrm{m}0}) \,, \tag{6}$$

$$\text{at } z = 1{:} \frac{\partial x_{\mathrm{m}}}{\partial z} = \frac{\partial y_{\mathrm{m}}}{\partial z} = 0$$

(Danckwerts' boundary conditions) [19].

For the fixed catalyst phase we have

$$\partial x / \partial t = a_x (x_{\mathrm{m}} - x) - \mu \, \varrho (x, y) \,,$$

$$\partial y / \partial t = a_y (y_{\mathrm{m}} - y) - \mu \, \varrho (x, y) \tag{7}$$

with $\varrho(x, y)$ as defined in Equation (2). In Eq. (7) diffusion effects are not accounted for, which would not change, however, the qualitative results via the calculation of effectiveness factors. Neglecting the diffusion term in the mobile phase we derive from Eqs. (5) and (7) for the steady state the ODE

$$\frac{\mathrm{d} x_{\mathrm{m}}}{\mathrm{d} z} = - \frac{1}{v} \mu \, \varrho (x, y) \tag{8}$$

where

$$y = y_{\mathrm{m}} + (a_x / a_y)(x - x_{\mathrm{m}}) \,,$$

$$y_{\mathrm{m}} = y_{\mathrm{m}0} - x_{\mathrm{m}0} + x_{\mathrm{m}} \quad \text{for} \quad D_x = D_y$$

($x_{\mathrm{m}0}$ and $y_{\mathrm{m}0}$: feed values of x_{m} and y_{m})

and x is a solution of

$$a_x (x_{\mathrm{m}} - x) - \mu \, \varrho (x, y) = 0 \,. \tag{9}$$

Equation (8) is integrated numerically with simultaneous solution of Eq. (9), which can be done analytically in our example. In the region of multiple roots of Eq. (9) we select that one which stays on the actual solution branch until a jump to the alternative branch is necessary at $\partial x_{\mathrm{ss}} / \partial x_{\mathrm{m}} = 0$. (This again means neglecting the influence of the initial conditions in the bed on the position of the ignition zone.)

Some examples of the numerical results are depicted in Fig. 4.

The catalyst bed is in the inhibited steady state until the jump to the high conversion state occurs, which is indicated by the dashed lines. The "ignition" zone is shifted out of the bed by either decreasing the inlet concentration of Y or by simultaneously

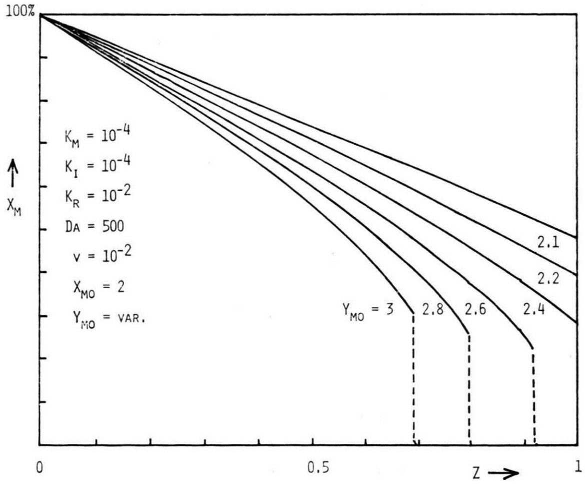

Fig. 4. Steady state profiles of unconverted substrate x in the mobile phase of the two phase tubular reactor model. Decreasing values of $y_{\mathrm{m}0}$ (feed concentration of substrate Y) shift the "ignition" zone towards the end of the reactor.

increasing the inlet concentration of both X and Y with the other parameters being fixed. The value of v has been chosen to be very low, which is suitable for a reaction column with liquid mobile phase.

IV. Pulse Generation in the Tubular Reactor

We want now to present an example of our simulations on a pulsewise operation of the tubular reactor.

Suppose that the set of parameters K_{m}, K_{i}, K_{r}, and k_3 be given for a reaction system. According to the results of Chapters II and III we then choose the other free parameters such that the catalyst phase is in the inhibited steady state along the bed and a sufficiently low overall conversion is given. This may be attained e.g. by low inlet concentration y_0, by relatively high values of both x_0 and y_0 or by a low value of μ corresponding to low catalyst concentration in the fixed bed. μ, on the other hand, should be large enough to guarantee for a rapid transition between the steady states, thus generating a narrow product pulse. The transient solutions of Eqs. (5)—(7) together with an analogous set of equations for the (irreversibly formed) product were computed by a finite element method [20].

In the simulations we neglected the capacity term for y in the catalyst phase, which reduces the number of differential equations by one. This is justified by a relatively high value of a_y e.g. due to a low molecular weight of the substance Y. The simulations show that the same simplification may be applied to x, except for an initial period after the inlet conditions have been changed.

Figure 5 shows the initial steady state profiles for all substances. The reaction is started by both reducing the inlet concentration x_0 to zero and increasing y_0. (A reduction of x_0 alone would also give a product pulse, but to a much lesser extent.) Figure 6 shows how the product peak is forming and wandering downstream for a series of time values after the change in the inlet conditions. We notice that the ascending flank of the peak begins to rise rather flat, which reflects the fact that the system, when driven from the inhibited to the reactive state, runs an appreciable portion of its way near the upper branch of the hysteresis curve until the jump to the reactive state occurs (see Chapter II). The ultimate maximum concentration of the product peak at the outlet is more than sixfold as high as it would be in the high conversion steady state operation for the present set of parameters.

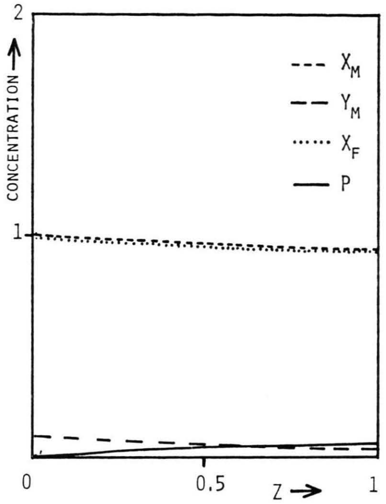

Fig. 5. Initial steady state profiles before the pulse generation, when the reactor is in the low conversion state throughout the length of the bed. The values of the parameters are: $K_{\mathrm{m}} = 10^{-4}$, $K_{\mathrm{i}} = 10^{-4}$, $K_{\mathrm{r}} = 10^{-2}$, $\mu = 10^2$, $a_x = .2$, $a_y = 10$, $D_x = D_y = 10^{-4}$, $v = 10^{-2}$. Subscript $_{\mathrm{m}}$ denotes the mobile phase, $_{\mathrm{f}}$ is for the fixed phase.

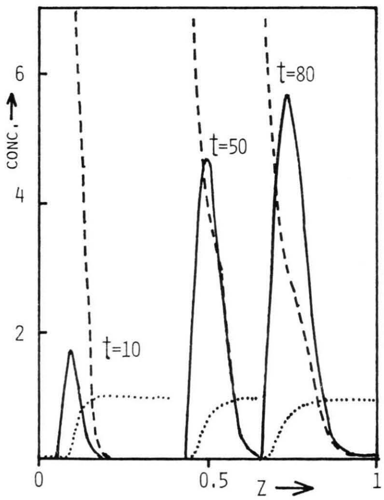

Fig. 6. Development of the concentration profiles for some values of time t after y_{m} has been switched up and x_{m} has been switched down at the reactor inlet. The curves for the different species are indicated as in Figure 5. For the parameters see Figure 5.

Note that the increase of the maximum peak concentration is not linear with t or z because of a broadening of the pulse, which is partly due to the diffusion. The main cause, however, is that the front of the triggering substance Y begins to lag behind the product peak due to the successive consumption by the reaction. As a result, we have a shift of the reaction zone towards the back front of the peak and eventually a "tailing" effect which in another context is known from chromatography (see Figures 7a—c).

Clearly, the optimum design of conditions would be such that the fractions of product and substrate Y will be just separated at $z = 1$, with a slight tailing of the product peak being accepted. Immediately after the reaction front the system may be reset to the inhibited state again, thus initializing a new cycle of "pumping" and "pulsing". In this way a continuous sequence of nearly pure fraction of X (which is recycled), product peak, fraction of Y (recycled) and so on, will appear in the reactor outlet.

V. Concluding Remarks

For a catalytic two substrate mechanism in which one of the reaction partners gives rise to substrate inhibition we analyzed the parametric conditions for bistability in tubular FBR.

It was shown that under the parametric conditions which may fit a column with liquid mobile phase and relatively low flow velocity ignition zones of the reaction are possible. The effect, however, is much less dramatic as compared with examples known from heterogeneous catalytic FBRs with strong exothermal reactions and high interstitial gas velocities (where nearly the total amount of reaction may be lumped in a narrow zone of the bed).

By simulating a cyclic operation of the reaction column we demonstrated the generation of product peaks in the outlet which can be well separated from the fractions of unconverted substrates. In this operation mode the time average of yield would be slightly less than in the stationary case. However, the concentration in the product fraction of the outlet can, due to simultaneous formation and transportation, be strongly increased. This may show a possible way to optimize such a reaction system, e.g., if either concentrating the reaction product is an expensive process or if one of the substrates is available only in diluted concentration.

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Notation

X, Y	concentration of substrates X and Y
M, MX, MXX	concentrations of catalytic sites and the respective substrate complexes,
M_{tot}	total concentration of catalytic sites,
k_{i}	rate constants,
C_{r}	reference concentration,
x, y	dimensionless concentrations in the catalyst phase $= X/C_{\text{r}}$, Y/C_{r},
K_{m}	dimensionless Michaelis constant,
K_{i}	dimensionless inhibition constant,
K_{r}	dimensionless constant $= k_3/k_1$,
μ	$= M_{\text{tot}}\, k_3$,
$\varrho(x, y)$	rate function,
Da	Damköhler number with respect to single pellet,
a_x, a_y	permeabilities for X and Y,
D_x, D_y	diffusion coefficients for X and Y,
z	dimensionless length = axial distance/reactor length,
v	dimensionless interstitial fluid velocity in the FBR.

Subscripts: ss steady state, o inlet, m mobile phase.

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