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Quadratic autocatalysis in an extended continuous-flow stirred tank reactor (ECSTR)

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Abstract

The continuous-flow stirred tank reactor (CSTR) is a standard tool used to investigate the behaviour of chemical processes subject to nonlinear kinetics. A recently proposed variation of the CSTR is the extended continuous-flow stirred tank reactor (ECSTR). This consists of a standard CSTR attached to an environmental tank reactor with mass transfer occurring between them through a membrane. The attraction of studying a reaction scheme in an ECSTR rather than a CSTR is that the former offers the possibility of modifying the behaviour with a larger parameter dimension. We investigate how the behaviour of a prototype non-linear chemical mechanism, quadratic autocatalysis subject to linear decay, changes when it is studied in an ECSTR rather than a CSTR.

It is shown that as process parameters are varied the system exhibits two generic and one non-generic steady-state diagrams. The location of these steady-state diagrams in parameter space is identified. For any set of process parameters periodic behaviour is impossible and there is a unique steady-state solution which is globally asymptotically stable. We show that when the membrane is permeable only to the reactant species (A) that a steady-state diagram can be found which does not exist when it is permeable only to the autocatalyst (B).

Keywords autocatalysis; flow reactor; membrane.

1 Introduction

The continuously stirred tank reactor (CSTR) has been used for decades by chemical engineers to investigate the behaviour of nonlinear processes. In chemical systems nonlinearity may be a consequence of the temperature dependence of rate constants or it may be an intrinsic feature of the underlying chemical mechanism. Starting

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in the 1970s, with the study of the Belousov-Zhabotsinskii reaction, the CSTR has been widely used by physical chemists to study non-linear chemical processes.

In a CSTR there is a continuous flow of reactants into the reactor. Within the reactor all chemical species are instantaneously and homogeneously dispersed. Operating conditions are such that the pH, temperature (for non-isothermal reactions) and other thermodynamic variables are automatically controlled so as to remain constant and spatially uniform. To maintain a constant volume there is a constant outflow from the reactor containing a mixture of products and reactants.

Recently Takinoue et al [10] proposed the extended continuous-flow stirred-tank reactor (ECSTR) as a new tool to investigate and control the behaviour of chemical systems subject to nonlinear dynamics. In an ECSTR a conventional CSTR unit is attached to an environmental tank through a membrane. The membrane permits diffusion of chemical species between the two reactors. It is assumed that no chemical reactions occur within the environmental tank. In [10] the characteristics of an ECSTR were investigated by considering both a model for a general two-variable activator-inhibitor reaction system and a pH oscillator model.

We extend the studies presented in by [10] by investigating the behaviour of a prototype non-linear chemical kinetic system in an ECSTR. The chosen mechanism is quadratic autocatalysis subject to linear decay. This scheme is simpler than those investigated in [10] and accordingly offers less rich behaviour. However, we are able to comprehensively investigate the behaviour of this model. We establish analytic conditions at which the generic steady-state behaviour of the model changes. From these we are able to precisely determine how parameters associated with the operation of the ECSTR influence the steady-state behaviour of the ECSTR. In particular, we identify how the selectivity of the membrane influences the behaviour of the model. This was not investigated in [10].

Quadratic autocatalysis and the closely related cubic autocatalysis have been widely investigated as prototype non-linear chemical kinetic schemes [3, 8, 9]. Although conceptually simple, these schemes qualitatively capture the behaviour of a range of chemical systems [9, page 9]. In particular quadratic autocatalysis has proven to be a simple prototype for more complicated kinetic structures possessed by large families of cooperative biochemical systems, inorganic solution-phase oscillatory reactions, and surface catalysis [2].

The steady-state multiplicity and dynamic behaviour of isothermal autocatalytic reactions in a continuously stirred tank reactor was first investigate by Lin [6, 7]. Lin considered the reaction mechanism

\[ A + B \rightarrow (1 + r)B, \quad \text{rate} = k_1 a^m b^n. \] (1)

The cases \( r = 1 \) and \( r \neq 1 \) were considered in [6] and [7] respectively.

The study of quadratic (and cubic) autocatalytic schemes was popularised by Gray and Scott. In [2] they introduced the two-step reaction scheme

\[ A + B \rightarrow 2B, \quad \text{rate} = k_1 ab, \] (2)

\[ B \rightarrow C, \quad \text{rate} = k_2 b. \] (3)
The first reaction represents a quadratic autocatalytic reaction, with stoichiometry \( A \rightarrow B \), whereas the second reaction represents the decay of the autocatalytic species \( B \). The decay of the catalyst may be the result of further chemical reaction (homogeneous or heterogeneous), be due to poisoning or to physical degradation.

We identify all the different steady-state diagrams that may be observed for the kinetic scheme given by reactions (2) & (3) as parameters associated with the operation of an ECSTR are varied. In particular, we show that when the membrane is permeable only to the reactant species \( A \) that an additional steady-state exists compared to the case when it is permeable only to the autocatalyst \( B \).

2 Equations

2.1 The dimensional model

The model equations are

\[
\begin{align*}
V \frac{da}{dt} &= F (a_0 - a) + F_a (a_m - a) - V k_1 ab, \quad (4) \\
V \frac{db}{dt} &= F (b_0 - b) + F_b (b_m - b) + V k_1 ab - V k_2 b. \quad (5)
\end{align*}
\]

The terms that appear in equations (4) & (5) are defined in appendix A. The main experimental control parameter, i.e. the primary bifurcation parameter, is the residence time inside the CSTR, \( \tau = V/F \).

The parameters associated with the operation of the membrane are the concentrations of reactants inside the environmental tank \( (a_m \& b_m) \) and the flow rates across the membrane \( (F_a \& F_b) \). For a particular choice of membrane the values \( a_m \) and \( b_m \) are fixed. Thus the secondary bifurcation parameters are the concentrations of reactants inside the environmental tank \( (a_m \& b_m) \).

Note that it is assumed that there is tight control of the chemical concentrations inside the environmental tank, i.e. they are maintained at values \( a_m \) and \( b_m \) [10].

From now on we assume that the concentration of the autocatalyst in the feed and in the environmental reactor is zero \( (b_0 = b_m = 0) \). Consequently, in equation (5) the chemical decay term \( -V k_2 b \) may be combined with the term representing removal through the membrane \( -F_b b \) to give a combined removal rate through chemical and physical mechanisms \( -K_r b \). We refer to the term \( K_r \) as the combined removal rate.

2.2 The dimensionless model

By introducing the dimensionless variables defined in appendix A the dimensional model, equations (4)–(5), can be written in the dimensionless form

\[
\begin{align*}
\frac{d\alpha}{dt^*} &= 1 - \frac{\alpha}{\tau^*} + K_a (\alpha_m - \alpha) - \alpha \beta, \quad (6) \\
\frac{d\beta}{dt^*} &= \frac{\beta}{\tau^*} + \alpha \beta - K_r \beta, \quad (7)
\end{align*}
\]
where the parameter groups are defined in appendix A. The initial conditions associated with equations (6) & (7) must be physically meaningful: \( \alpha (t^*=0) \geq 0 \) \& \( \beta (t^*=0) \geq 0 \). From now on we assume that the initial condition is physically meaningful.

In section 3 we need the Jacobian of system (6)–(7). This is given by

\[
J(\alpha, \beta) = \begin{pmatrix}
-\frac{1}{\tau^*} - K_a - \beta & -\alpha \\
\beta & -\frac{1}{\tau^*} + \alpha - K_r
\end{pmatrix}.
\]

3 Results

In section 3.1 we state some results concerning the global behaviour of the system (6) & (7).

In section 3.2 the steady-state solution branches are given. These consists of a washout-branch and a no-washout branch. These are used in section 3.2.1 to derive conditions for which transcritical bifurcations occur and for which the no-washout steady-state branch is physically meaningful. At a transcritical bifurcation points the washout and no-washout solutions intersect and exchange stability. In section 3.3 the local stability of the steady-state solutions is determined.

In section 3.4 asymptotic solutions are presented for the case of large residence times \( (\tau^* \gg 1) \). In section 3.5 we discuss the steady-state diagrams exhibited by the model.

As there is a one-to-one relationship between our dimensionless and dimensional variables we usually refer, for example, to the ‘residence time’ rather than the ‘dimensionless residence time’.

3.1 Global behaviour

In this section we state some global results regarding the system (6) & (7). In section 3.1.1 we show that the region \( \mathcal{R} \) defined by

\[
0 \leq \alpha \leq \alpha_w = \frac{1 + K_a \alpha_m \tau^*}{1 + K_a \tau^*},
\]

\[
0 \leq \beta \leq \frac{1 + K_a \alpha_m \tau^*}{1 + M \tau^*} - \alpha, \quad M = \min (K_a, K_r),
\]

is positively invariant. This means that if the initial concentration is inside the region \( \mathcal{R} \) then the solution of system (6)–(7) remains within the region \( \mathcal{R} \) for all subsequent time. Furthermore, we show that the solution corresponding to any initial condition that it outside the region \( \mathcal{R} \) must eventually enter it; it is ‘exponentially attracting’. The practical consequence of this is that we may only consider initial conditions within the region \( \mathcal{R} \).

In section 3.1.2 we show that the system (6) & (7) can not have oscillatory solutions.

3.1.1 The invariant region
We show that no solution may leave the region \( \mathcal{R} \). We start by showing that no solution component can become negative. Observe that the line \( \beta = 0 \) is invariant as on it we have \( \frac{d\beta}{dt} = 0 \). Along the line \( \alpha = 0 \) we have

\[
\frac{d\alpha}{dt} = \frac{1 - \alpha}{\tau^*} + K_a \alpha_m > 0.
\]

We now show that the concentration of the chemical species \( A \) is bounded. From equation (6) we have

\[
\frac{d\alpha}{dt} = 1 - \alpha \frac{\tau^*}{\tau^*} - \frac{(1 + K_a \tau^*)}{\tau^*} \alpha \quad \text{as} \quad \alpha \geq 0, \beta \geq 0.
\]

It follows that

\[
\alpha(t^*) \leq \alpha_w - [\alpha_w - \alpha(0)] \exp \left[ -\frac{(1 + K_a \tau^*)}{\tau^*} t^* \right]. \tag{8}
\]

Inequality (8) establishes two facts. Firstly, if the initial condition for the species \( A \) is inside the region \( \mathcal{R} \) \( (0 \leq \alpha(0) \leq \alpha_w) \) then the \( \alpha \) component of the solution always remains within it \( (0 \leq \alpha(t^*) \leq \alpha_w) \). Secondly, if the initial condition for the species \( A \) is outside the region \( \mathcal{R} \) \( (\alpha(0) > \alpha_w) \) then the \( \alpha \) component of the solution trajectory must eventually be attracted into it.

Finally, we show that the autocatalytic concentration is bounded. Let \( Z(t^*) = \alpha(t^*) + \beta(t^*) \) (As \( \alpha \) and \( \beta \) are both non-negative so it \( Z \)). Adding equations (6) and (7) we have

\[
\frac{dZ}{dt^*} = 1 + K_a \alpha_m \tau^* - \frac{(\alpha + \beta)}{\tau^*} - K_a \alpha - K_r \beta,
\]

\[
\leq 1 + K_a \alpha_m \tau^* - \frac{(1 + M \tau^*)}{\tau^*} Z \quad \text{where} \quad M = \min(K_a, K_r).
\]

Hence

\[
Z(t^*) \leq \frac{1 + K_a \alpha_m \tau^*}{1 + M \tau^*} \left[ 1 + K_a \alpha_m \tau^* - \frac{(\alpha(0) + \beta(0))}{1 + M \tau^*} \right] \exp \left[ -\frac{(1 + M \tau^*)}{\tau^*} t^* \right].
\]

It follows that if the initial condition is within the region \( \mathcal{R} \) that the solution trajectory must remain in this region. Furthermore, if the initial condition is outside this region then the solution must eventually enter into it.

The use of simple differential inequalities to establish solutions boundedness in these types of systems stems from [4] (though was possibly known much earlier).

### 3.1.2 Periodicity

To show the non-existence of an oscillatory solution we use Dulac’s criteria.

**Theorem 1 (Dulac’s Test [1, 5])** Consider the system

\[
\frac{dx}{dt} = f(x, y),
\]

\[
\frac{dy}{dt} = g(x, y).
\]
Let $D$ be a simply connected region in $\mathbb{R}^2$ and let $\{f(x,y), g(x,y)\} \in C^1(D)$. If there exists a function $\rho \in C^1(D)$ such that
\[
\frac{\partial (\rho f)}{\partial x} + \frac{\partial (\rho g)}{\partial y}
\]
is not identically zero and does not change sign in $D$, then this system does not have any closed paths lying entirely in $D$.

We use the test function $\rho = 1/\beta$. This test function is acceptable. To see this note that if an oscillatory solution exists it can not include any part of the line $\beta = 0$; any solution touching this line can not leave it as $\frac{d\beta}{dt} \bigg|_{\beta=0} = 0$.

Applying Dulac’s Test to the system (6) & (7) with the specified choice for $\rho$ we obtain
\[
\frac{\partial (\rho f)}{\partial S^*} + \frac{\partial (\rho g)}{\partial X^*} = -\frac{1}{\tau^*\beta} - 1 - \frac{K_r}{\beta},
\]
This function is strictly negative inside the positive quadrant. Thus no oscillatory solution can exist that is entirely contained within the positive quadrant. As no solution may leave the positive quadrant there can be no periodic solution only partly contained within it.

### 3.2 Steady-state solution branches

In this section we state the steady-state solutions of the system (6) & (7).

The steady-state solutions are given by

- **Washout branch**
  \[
  (\alpha, \beta) = (\alpha_w, 0), \quad \alpha_w = 1 + K_a\alpha_m\tau^*.
  \]

- **No-washout branch**
  \[
  (\alpha, \beta) = (\alpha_{nw}, \beta_{nw}), \quad \alpha_{nw} = 1 + K_r\tau^* \quad \text{and} \quad \beta_{nw} = \frac{1}{\alpha_{nw}\tau^*} [1 + K_a\alpha_m\tau^* - (1 + K_a\tau^*)\alpha_{nw}].
  \]

The conditions for the no-washout solution branch to be physically meaningful ($\beta_{nw} > 0$) are given in section 3.2.1.

A transcritical bifurcation, at which the washout and no-washout branches intersect, occurs at a positive value of the residence time, $\tau^*_{cr}$, where
\[
Q(\tau^*) = -K_a (\alpha_m - K_r) \tau^* + (K_r + K_a - 1) \tau^* + 1 = 0.
\]
(Transcritical bifurcations occurring at negative residence times are not physically meaningful). When equality (14) holds we have

\[(\alpha_{nw}, \beta_{nw}, \tau_{cr}^*) = (\alpha_w, 0, \tau_{cr}^*).\]

The conditions under which a transcritical bifurcation occur are related to those for which the no-washout branch is physically meaningful. It is useful to note now that the no-washout branch is physically meaningful when

\[Q(\tau^*) < 0.\] (15)

### 3.2.1 When is this no-washout solution physically meaningful?

The no-washout solution is given by equation (11). It is physically meaningful the autocatalytic concentration is positive \((\beta > 0)\). After some algebra we find that this happens when

\[Q(\tau^*) = c_2 \tau^*^2 + c_1 \tau^* + 1 < 0,\] (16)

\[c_1 = K_a + K_r - 1\] (17)

\[c_2 = -K_a (\alpha_m - K_r).\] (18)

Values of the residence time for which \(Q = 0\) correspond to transcritical bifurcations, provided that the corresponding values of the residence time are positive. We consider three cases depending upon if the coefficient of \(\tau^*^2\) is negative, zero and positive respectively.

**Case One:** \(\alpha_m > K_r\) \((c_2 < 0)\).

The steady-state is physically meaningful when

\[\tau^* > \tau_{tr}^* = \frac{-c_1 - \sqrt{c_1^2 - 4c_2}}{2c_2} > 0.\] (19)

The value \(\tau_{cr}^*\) corresponds to a transcritical bifurcation.

**Case Two:** \(\alpha_m = K_r\) or \(K_a = 0\) \((c_2 = 0)\).

Inequality (16) reduces to

\[1 + (\alpha_m + K_a - 1) \tau^* < 0.\]

If \(\alpha_m + K_a \geq 1\) then the steady-state solution is never physically meaningful. If \(\alpha_m + K_a < 1\) then the steady-state solution is physically meaningful when

\[\tau^* > \tau_{tr}^* = \frac{1}{1 - (K_a + \alpha_m)}.\] (20)

The value \(\tau_{cr}^*\) corresponds to a transcritical bifurcation.

**Case Three:** \(\alpha_m < K_r\) \((c_2 > 0)\).
The no-washout solution is physically meaningful between values

\[ 0 < \tau_+ < \tau^* < \tau_-, \]

\[ \tau_{\pm} = \frac{-c_1 \pm \sqrt{c_1^2 - 4c_2}}{2c_2}, \]

when the discriminant \( D \) is positive

\[ D = c_1^2 - 4c_2 = [K_r - (K_a + 1)]^2 + 4K_a (\alpha_m - 1) > 0 \]

and when the coefficient \( c_1 \) is negative

\[ c_1 = K_r + K_a - 1 < 0. \]

In this case there are two transcritical bifurcations at \( \tau^* = \tau_{\pm} \).

The condition \( D > 0 \) gives

\[ \alpha_m > 1 - \frac{[K_r - (K_a + 1)]^2}{4K_a}. \]

Thus the set of conditions for the no-washout solution to be physically meaningful for case three are

\[ K_r < 1 - K_a, \quad (21) \]

\[ K_r > \alpha_m > 1 - \frac{[K_r - (K_a + 1)]^2}{4K_a}. \quad (22) \]

### 3.3 Stability of the steady-state solutions

#### 3.3.1 The washout solution

The Jacobian matrix evaluated at the washout steady-state solution is given by

\[ J(\alpha_w, 0) = \begin{pmatrix} \frac{1}{\tau^*} - K_a & -\alpha_w \\ 0 & \frac{1}{\tau^*} + \alpha_w - K_r \end{pmatrix}. \]

The eigenvalues of this matrix are

\[ \lambda_1 = -\frac{1}{\tau^*} - K_a < 0, \]

\[ \lambda_2 = -\frac{1}{\tau^*} + \alpha_w - K_r, \]

\[ = -\frac{1}{(1 + K_a \tau^*) \tau^*} \cdot Q(\tau^*). \]

It follows that the washout branch is unstable when the no-washout branch is physically meaningful \( (Q(\tau^*) < 0) \). Conversely, the washout branch is stable when the no-washout branch is not physically meaningful \( (Q(\tau^*) > 0) \).
3.3.2 The no-washout solution

The Jacobian matrix for the no-washout branch can be written in the form

\[ J(\alpha_{nw}, \beta_{nw}, \beta_{nw}) = \begin{pmatrix} -\frac{1}{\tau^*} & -K_a & -\alpha_{nw} \\ \beta_{nw} & 0 \end{pmatrix} \].

(23)

This solution branch is stable when \( \text{trace} J < 0 \) and \( \det J > 0 \). We have

\[
\text{trace } J = -\frac{1}{\tau^*} - K_a - \beta_{nw},
\]

\[
\det J = \alpha_{nw} \beta_{nw}.
\]

It follows that when the no-washout branch is physically meaningful (\( \alpha_{nw} > 0 \) and \( \beta_{nw} > 0 \)) it is locally stable.

3.4 Asymptotic solutions

In this section asymptotic solutions are presented along the no-washout solution for large residence times \( (\tau^* \gg 1) \). We have

\[
\alpha_{nw} = K_r + \frac{1}{\tau^*},
\]

(24)

\[
\beta_{nw} \approx \frac{[\alpha_m - K_r] K_a}{K_r} \cdot \left( \frac{K_a^2 + K_a \alpha_m - K_r}{K_r^2} \right) \cdot \frac{1}{\tau^*} + O \left( \frac{1}{\tau^*} \right)^2.
\]

(25)

The no-washout solution branch is physically meaningful at high residence times when \( \alpha_m > \kappa + K_b \). When \( \alpha_m = K_r \) equation (25) simplifies to

\[
\beta_{nw} \approx \frac{1 - K_a - K_r}{K_r} \cdot \frac{1}{\tau^*} + O \left( \frac{1}{\tau^*} \right)^2.
\]

(26)

This solution is physically meaningful when \( 1 - K_a - K_r > 0 \).

3.5 Steady-state diagrams

In this section we use results from section 3.2.1 to show that two generic and one non-generic steady-state diagram are exhibited by the system. We also identify where in parameter space the steady-state diagrams are found.

Before doing we make the following observations. From section 3.1 we know that all solutions are attracted into the closed and bounded region \( \mathcal{R} \). Furthermore, there are no oscillatory solutions within this region. From sections 3.2 & 3.3 for any value of the residence time there is only one stable steady-state solution. It follows from the Poincare-Bendixon Theorem [5, Page 294] that this steady-state solution must be globally asymptotically stable.

(Note that when the washout solution is stable, the no-washout solution is not located within the invariant region as it is not even physically meaningful. When the no-washout solution is stable then the unstable
washout solution has a one-dimensional stable manifold. This manifold is the line $\beta = 0$. Any initial condition not on this manifold is attracted to the no-washout steady-state solution).

The steady-state diagrams depend upon the sign of the difference of the dimensionless concentration of reactant $A$ in the membrane and the dimensionless combined removal rate of the autocatalyst from the flow reactor ($K_r$): $\alpha_m - K_r$. This term determines the sign of the quadratic term in the polynomial $Q$: $c_2 = -K_a (\alpha_m - K_r)$. For a given membrane the removal rate $K_r$ is fixed. However, it is straightforward to change the concentration of the reactant $A$ in the reservoir ($\alpha_m$). Thus it is experimentally possible to change the sign of the coefficient $c_2$.

When the concentration of reactant $A$ inside the environmental tank is greater than the removal rate of autocatalyst from the reactor ($\alpha_m > K_r$, the case $c_2 < 0$) the steady-state diagram is as shown in figure 1 (a). There is one transcritical bifurcation and the autocatalyst concentration is physically meaningful for $\tau^* > \tau^*_{cr}$. From equation (25) the asymptotic limit for large values of the residence time is

$$\lim_{\tau^* \to \infty} \beta_{nw} = \frac{(\alpha_m - K_r) K_a}{K_r} > 0.$$

The steady-state concentration of the autocatalyst may increase or decrease to the limiting value.

When the concentration of reactant $A$ inside the environmental tank is equal to the removal rate of autocatalyst from the reactor ($\alpha_m = K_r$, the case $c_2 = 0$) there is a non-trivial steady-state diagram provided that

$$\alpha_m + K_a < 1.$$

The steady-state diagram for this case is shown in figure 1 (b). There is one transcritical bifurcation at a finite value of the residence time ($\tau^* = \tau^*_{cr}$) and the concentration of the autocatalyst is physically meaningful for values of the residence time greater than this ($\tau^* > \tau^*_{cr}$). From equation (26) at large values of the residence time the concentration of the autocatalyst asymptotes to zero and it can be seen that there is a second transcritical bifurcation ‘at infinity’ ($\tau^*_{tr} = \infty$).

If $\alpha_m + K_a \geq 1$ then the no-washout solution branch is never physically meaningful and the steady-state diagram consists only of the washout solution.

The steady-state diagram 1 (b) also arises when there is no transfer of reactant $A$ across the membrane ($K_a = 0$). This is the steady-state diagram for quadratic autocatalysis in a flow reactor with no environmental tank attached ($K_a = K_b = 0$).

The final case is when the concentration of reactant $A$ inside the environmental tank is smaller than the removal rate of autocatalyst from the reactor ($\alpha_m < K_r$, the case $c_2 > 0$). There is a non-trivial steady-state diagram only when equation (22) holds,

$$K_r < 1 - K_a.$$

Thus there is no non-trivial steady-state solution when $K_a \geq 1$. When inequalities (21) & (22) both hold then the steady-state diagram is as shown in figure 2. There are two transcritical bifurcations at finite values of the residence time ($\tau^*_-$ and $\tau^*_+$). The concentration of the autocatalyst is physically meaningful when the residence time lays between these limiting values ($\tau^*_- < \tau^* < \tau^*_+$). As the value of the autocatalytic concentration
inside the reservoir is increased towards the transition value \((\alpha_m = K_r)\) the value of the residence time at the transcritical bifurcation \(\tau^*_r\) increases towards infinity.

Figure 3 shows the location of the steady-state diagrams in the \(\alpha_m - K_r\) plane for the case \(K_a < 1\). The two functions shown on the figure are

\[
\begin{align*}
\alpha_m &= K_r, \\
\alpha_m &= 1 - \frac{(K_r - (K_a + 1))^2}{4K_a}.
\end{align*}
\]

It is assumed that \(0 < K_a < 1\), as otherwise the trivial steady-state solution occupies the entirety of the region below the line \(\alpha_m = K_r\). (In the trivial steady-state region, the no-washout solution is never physically meaningful and only the washout solution is stable.) The non-generic steady-state diagram shown in figure 1 (b) corresponds to the straight line \(\alpha_m = K_r\) with \(K_r < 1 - K_a\). When \(K_r \geq 1 - K_a\) the non-generic steady-state diagram along the line \(\alpha_m = K_r\) is the trivial steady-state solution.

4 Discussion

In this section we apply our results to consider the operation of two types of ECSTRs which differ only in the selectivity of their membrane. In sections 4.1 & 4.2 we consider the cases in which only the autocatalyst \((B)\) and the reactant species \((A)\) pass through the membrane respectively.

4.1 Only the autocatalyst species \((B)\) passes through the membrane

If only the autocatalyst is able to pass through the membrane then \(K_b > 0\) and \(K_a = 0\). This scenario is equivalent to the reaction occurring within a standard flow-reactor, without a membrane, but with an enhanced decay rate \((\kappa_2)\).

If the combined removal rate is sufficiently low \((K_r = \kappa_2 + K_b < 1)\) then the steady-state diagram is as shown in figure 1 (b). If the combined removal rate is sufficiently high \((K_r = \kappa_2 + K_b \geq 1)\) then the steady-state diagram is the trivial steady-state diagram, i.e. the washout solution is globally stable for any value of the residence time. Thus as the value of the removal rate through the membrane \((K_b)\) is increased there is a transition from the steady-state diagram shown in figure 1 (b) to the trivial steady-state diagram.

4.2 Only the reactant species \((A)\) species passes through the membrane

If only the reactant \(A\) is able to pass through the membrane then \(K_b = 0\) and \(K_a > 0\). The concentration of the species \(A\) in the reservoir, \(\alpha_m\), can be controlled experimentally. We therefore consider the change in behaviour of the system as this value is increased from zero.
Scenario One: $K_a \geq 1$. When $K_a \geq 1$ inequality (21) does not hold. Thus for $\alpha_m < K_r$ (case three) the trivial steady-state diagram is found. When $\alpha_m = K_r$ (case two) the trivial steady-state diagram is again found. When $\alpha_m > K_r$ (case one) then steady-state diagram 1 (b) is found.

Scenario Two: $K_a < 1$ and $K_r > 1 - K_a$. The variation of the steady-state diagrams as $\alpha_m$ is increased from zero is identical to scenario one.

Scenario Three: $K_a < 1$, $0 < K_r < 1 - K_a$ and $1 - \frac{(K_r - (K_a + 1))^2}{4K_a} > 0$ For sufficiently small values for the concentration of species $A$ in the membrane we have $\alpha_m < K_r$ but inequality (22) does not hold: the steady-state diagram is the trivial steady-state diagram. As $\alpha_m$ is increased from zero there is a range of concentrations over which both $\alpha_m < K_r$ and inequality (22) holds (case 3): the steady-state diagram is as shown in figure 2. When $\alpha_m = K_r$ (case 2) the steady-state diagram is as shown in figure 1 (b). When $\alpha_m > K_r$ the steady-state diagram is as shown in figure 1 (a).

Scenario Four: $K_a < 1$, $0 < K_r < 1 - K_a$ and $1 - \frac{(K_r - (K_a + 1))^2}{4K_a} < 0$ The variation of the steady-state diagrams as $\alpha_m$ is varied is identical to scenario three, except that even when $\alpha_m = 0$ the steady-state diagram is the one shown in figure 2.

5 Conclusions

We have analysed the behaviour of a model non-linear chemical scheme, quadratic autocatalysis with linear decay of the autocatalyst, in an extended continuous-flow stirred tank reactor (ECSTR). The ECSTR consists of a flow reactor connected to an environmental tank via a membrane through which one or both of the chemical species may pass. The ECSTR has been proposed by Takinoue [10] as a new tool to investigate the behaviour of chemical systems subject to nonlinear dynamics.

For the prototype system considered here it is possible to completely characterise the global behaviour of the model as parameters are varied. All solution trajectories must enter a closed and bounded region. Oscillatory behaviour is impossible and there is only ever one stable steady-state solution. This solution is therefore globally stable, though there may be a one-dimensional manifold of initial conditions which converge to an unstable steady-state solution.

The concentration of the reactant species $A$ in the reservoir may be readily controlled experimentally. We have used our analytic results to precisely describe how the steady-state diagram of the experimental system may change as this value is increased from zero.

We have shown that when the membrane is permeable only to the autocatalyst ($B$) that there are two generic steady-state diagrams. In order to control the steady-state diagram that is exhibited, the experimentalist must be able to change the flow-rate of the autocatalyst across the membrane. When the membrane is permeable only to the reactant species ($A$) than an additional steady-state is possible. In this case it is possible to control the steady-state behaviour simply by controlling the concentration of the reactant in the environmental tank. Thus
we anticipate that, in general, the change in bifurcation behavior that is exhibited by an ECSTR, compared to that of a CSTR, will be influenced by the selectivity of the membrane.

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A Symbols used

\[ F \] Flowrate through the bioreactor. \( (\text{ls}^{-1}) \)

\[ F_a \] Flowrate of species \( A \) through the membrane. \( (\text{ls}^{-1}) \)

\[ F_b \] Flowrate of species \( B \) through the membrane. \( (\text{ls}^{-1}) \)

\[ K_a \] Dimensionless flow-rate of species \( A \) across the membrane. \( (\text{—}) \)

\[ K_a = F_a/(a_0 k_1 V) \]

\[ K_b \] Dimensionless flow-rate of species \( B \) across the membrane. \( (\text{—}) \)

\[ K_b = F_b/(a_0 k_1 V) \]

\[ K_r \] Combined removal rate of autocatalyst species \( B \) from the reactor. \( (\text{mol s}^{-1}) \)

\[ K_r = V k_2 + F_b \]

\[ K_r^\ast \] Dimensionless combined removal rate of autocatalyst species \( B \). \( (\text{—}) \)

\[ K_r^\ast = \kappa_2 + K_b. \]

\[ Q \] Quadratic function defined by equation 14. \( (\text{—}) \)

\[ a \] Concentration of species \( A \). \( (\text{mol l}^{-1}) \)

\[ a_m \] Concentration of species \( A \) inside the environmental tank. \( (\text{mol l}^{-1}) \)

\[ a_0 \] Concentration of species \( A \) in the feed. \( (\text{mol l}^{-1}) \)

\[ b \] Concentration of autocatalytic species \( B \). \( (\text{mol l}^{-1}) \)

\[ b_m \] Concentration of autocatalytic species \( B \) in the environmental tank. \( (\text{mol l}^{-1}) \)

\[ b_0 \] Concentration of autocatalytic species \( B \) in the feed. \( (\text{mol l}^{-1}) \)

\[ k_1 \] Rate constant for quadratic autocatalysis. \( (\text{mol}^{-1}\text{l s}^{-1}) \)

\[ k_2 \] Rate constant for decay of autocatalyst. \( (\text{s}^{-1}) \)

\[ t \] Time. \( (\text{s}) \)

\[ t^\ast \] Dimensionless time. \( (\text{—}) \)

\[ t^\ast = k_1 a_0 t \]

\[ \alpha \] Dimensionless concentration of species \( A \). \( (\text{—}) \)

\[ \alpha = a/a_0 \]
\( \alpha_m \)  
Dimensionless concentration of reactant \( A \) in the **environmental tank.**  
\( \alpha_m = a_m/a_0 \)

\( \alpha_{nw} \)  
The dimensionless concentration of species \( A \) along the no-washout solution branch.

\( \alpha_w \)  
The dimensionless concentration of species \( A \) along the washout solution branch.  
\( \quad \)  
\( \beta \)  
Dimensionless concentration of autocatalyst species \( B \).  
\( \beta = b/a_0 \)

\( \beta_m \)  
Dimensionless concentration of autocatalyst \( B \) in the **environmental tank.**  
\( \beta_m = b_m/a_0 \)

\( \beta_{nw} \)  
The dimensionless concentration of autocatalytic species \( B \) along the no-washout solution branch.

\( \beta_0 \)  
Dimensionless concentration of autocatalyst species \( B \).  
\( \beta = b/a_0 \)

\( \kappa_2 \)  
Dimensionless decay rate.  
\( \kappa_2 = k_2/(k_1a_0) \)

\( \tau^* \)  
Dimensionless residence time.  
\( \tau^* = a_0k_1V/F \)

\( \tau_{tr}^* \)  
A value of the dimensionless residence time at which a transcritical bifurcation occurs.

**References**


Figure 1: Steady-state diagrams. In (a) there is one transcritical bifurcation whilst in (b) there is a second transcritical bifurcation at infinity. Parameter values. Figure (a): $K_r = 1.0$, $K_a = 0.5$, $\alpha_m = 1.5$. Figure (b): $K_r = 0.7$, $K_a = 0.5$, $\alpha_m = 0.4$.

Figure 2: Steady-state diagram for case 3 ($c_2 < 0$, $c_2^2 - 4c_2 > 0$, $c_1 < 0$. There are two transcritical bifurcations at finite values of the residence time. Parameter values: $K_r = 0.6$, $K_a = 0.25$, $\alpha_m = 0.58$. 
Figure 3: The location of the generic steady-state diagrams shown in figure 1 (a) (Case One) and figure 2 (B) in the $K_r - \alpha_m$ plane when $K_a < 1$. Along the line $\alpha_m = K_r$ the non-generic steady-state diagram is either as shown in figure 1 (b) ($K_r < 1 - K_a = 0.5$) or the trivial steady-state solution ($K_r \geq 1 - K_a = 0.5$). Parameter value: $K_a = 0.5$. 

\[ \text{Dimensionless concentration of species A in the environmental tank} \]
\[ \text{Dimensionless removal rate} \]