CHAOS IN A CONTINUOUS STIRRED TANK REACTOR

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Abstract—A model is derived for a nonisothermal, continuous, stirred tank reactor in which two, exothermic, first order, irreversible reactions are occurring in parallel. A numerical examination of this model reveals that complex periodic and chaotic oscillations are possible. This behavior is studied using linear stability analysis, autocorrelation analysis, and next-amplitude plots. The next-amplitude plots are found to be fractal curves. An examination of the system trajectories shows that in some circumstances the trajectories follow a Möbius-band attractor in state space.

INTRODUCTION

Since the early work by Liljenroth [1] and van Heerden [2], a considerable amount of research has been directed at analyzing the stability of chemically reacting systems. Theoretical and experimental studies, summarized in several review articles [3, 4, 5, 6], have shown that under certain conditions, chemically reacting systems can display oscillatory behavior. In a continuous flow reactor, oscillatory behavior is normally manifested through periodic changes in the reaction temperature and/or the concentrations of reacting species with respect to time.

There are many reasons for the recent interest in oscillatory phenomena in chemical reactors. A few of these are

(1) The fundamental processes occurring in chemical reactors can be more fully understood through a knowledge of the mechanisms by which oscillatory behavior occurs.

(2) Increased conversion of reactants to products, and isolation of low-yield intermediates, can sometimes be obtained by operating a chemical reactor in a cyclical fashion.

(3) Large temperature fluctuations in a chemical reactor can present safety problems, hence, a knowledge of how to predict, and suppress, this behavior is necessary for proper design and operation.

Most of the recent work in analyzing the stability of chemical reactors has been directed at reactor models which have consisted of two ordinary differential equations. The variables considered in these models have usually been either two reactant concentrations [7, 8], or one reactant concentration and the reactor temperature [9, 10, 11]. One of the implications of examining systems of two ordinary differential equations is that the most complex dynamic behavior that can be obtained is a sustained oscillation of the two variables, which can be represented as a limit cycle in the phase plane. However, recent experimental studies [12, 13, 14] have shown that chemical reactors can exhibit

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chaotic behavior (cycles with high periods, or even aperiodic behavior [15]) under certain operating conditions. In order to model such behavior, it is necessary to use a minimum of three ordinary differential equations, as the Poincaré–Bendixson theorem prohibits the existence of chaotic behavior in systems of two ordinary differential equations. This theorem states that a bounded solution of a two-dimensional dynamical system will converge to either a stable steady state, or to a stable limit cycle [16].

The modelling of chaotic behavior in chemical reaction systems is still in its infancy, as only a few studies [14,17] have shown that realistic reaction models can display chaotic solutions. It is the purpose of this work to show that chaotic behavior can be exhibited by a very simple chemical reactor model which consists of three ordinary differential equations.

MODEL DEVELOPMENT

The parallel conversion of two reactants A and B into respective products C and D can be written as

\[
\begin{align*}
A & \rightarrow C \\
B & \rightarrow D.
\end{align*}
\]

If these reactions are carried out in a nonisothermal, continuous flow, stirred tank reactor, then this chemical system can be modelled by a system of three ordinary differential equations, which result from the application of the principles of mass and energy conservation. In deriving the model, the following assumptions will be used:

1. The reactions occur in a continuous flow reactor.
2. The reactor is well mixed so that the temperature and the species concentrations are uniform throughout the reactor.
3. Both reactions are exothermic, and follow first-order Arrhenius rate expressions.
4. There are no volume changes on reaction.
5. The physical properties of the reaction mixture are temperature invariant.
6. The reaction fluid phase contains the only significant thermal capacitance.
7. The temperature of the reactor wall is held constant at the feed stream inlet temperature.
8. The reactor wall heat transfer coefficient is constant.

Using the above assumptions, reactor mass balances for species A and B take the following form:

\[
\begin{align*}
V \frac{d[A]}{dt'} &= Q([A]_0 - [A]) - V[A]k_1 e^{-E_1/RT'} \\
V \frac{d[B]}{dt'} &= Q([B]_0 - [B]) - V[B]k_2 e^{-E_2/RT'}.
\end{align*}
\]

These mass balances, Eqs. (1a–1b), are special cases of the general mass balance for a continuous stirred tank reactor as derived by Aris [18], where, for species A, the general mass balance is given by

\[
\begin{bmatrix}
\text{rate of change of number of moles of } A \text{ in the reactor}
\end{bmatrix} = \begin{bmatrix}
\text{rate of feed of } A \\
\text{rate of withdrawal of } A \\
\text{rate of disappearance of } A \text{ by reaction}
\end{bmatrix}.
\]
Chaos in a continuous stirred tank reactor

A general energy balance can also be written, and it has the following form:

\[
\text{rate of change of energy content} = \text{energy released by reaction} + \text{energy brought in with feed} - \text{energy taken out with products} - \text{energy removed by heat transfer}.
\]

Due to the stated assumptions, the general energy balance for this chemical system has the special form:

\[
VpC_p \frac{dT'}{dt'} = Hr_1 V[A]k_1 e^{-E_1/RT} + Hr_2 V[B]k_2 e^{-E_2/RT} - QpC_p(T' - T_0) - SU(T' - T_0).
\] (1c)

The three balance equations, Eqs. (1a–1c), can be written in the following dimensionless form:

\[
\frac{dY}{dt} = 1 - Y - YDa_1 e^{\gamma_1 T(1+T)}
\] (2a)

\[
\frac{dZ}{dt} = 1 - Z - ZDa_2 e^{\gamma_2 T(1+T)}
\] (2b)

\[
\frac{dT}{dt} = \alpha(\beta_1 YDa_1 e^{\gamma_1 T(1+T)} + \beta_2 ZDa_2 e^{\gamma_2 T(1+T)} - T),
\] (2c)

where

\[
Da_1 = \frac{V}{Q} k_1 e^{-\gamma_1}
\] (2d)

\[
Da_2 = \frac{V}{Q} k_2 e^{-\gamma_2}
\] (2e)

\[
\gamma_1 = \frac{E_1}{RT_0}
\] (2f)

\[
\gamma_2 = \frac{E}{RT_0}
\] (2g)

\[
\beta_1 = \frac{Q(Hr_1)[A]_0}{T_0(SU + QpC_p)}
\] (2h)

\[
\beta_2 = \frac{Q(Hr_2)[B]_0}{T_0(SU + QpC_p)}
\] (2i)

\[
\alpha = 1 + \frac{SU}{QpC_p}
\] (2j)

\[
t = \frac{Qt'}{V}
\] (2k)

\[
T = \frac{T' - T_0}{T_0}
\] (2l)

\[
Y = \frac{[A]}{[A]_0}
\] (2m)

\[
Z = \frac{[B]}{[B]_0}
\] (2n)
STABILITY ANALYSIS

The stability properties of Eqs. (2a-2c) are determined from the Jacobian matrix, which for this system of equations is

\[
J = \begin{bmatrix}
-1 - Da_1 e^{\gamma_1 T(1+T)} & 0 & -\frac{Y\gamma_1 Da_1 e^{\gamma_1 T(1+T)}}{(T + 1)^2} \\
0 & -1 - Da_2 e^{\gamma_2 T(1+T)} & -\frac{Z\gamma_2 Da_2 e^{\gamma_2 T(1+T)}}{(T + 1)^2} \\
\alpha\beta_1 Da_1 e^{\gamma_1 T(1+T)} & \alpha\beta_2 Da_2 e^{\gamma_2 T(1+T)} & -\alpha + \frac{\alpha Y\gamma_1\beta_1 Da_1 e^{\gamma_1 T(1+T)}}{(T + 1)^2}
\end{bmatrix}
\]  

(3)

The eigenvalues of Eqs. (2a - 2c) are solutions of the characteristic equation associated with \( J \), which is given by

\[
-\omega^3 + A_1 \omega^2 - A_2 \omega + A_3 = 0,
\]

(4)

where \( A_1, A_2, \) and \( A_3 \) are the three invariants of \( J \), i.e.,

\[
A_1 = \text{trace}(J) \quad \quad (5)
\]

\[
A_2 = \text{minor of } j_{11} + \text{minor of } j_{22} + \text{minor of } j_{33} \quad \quad (6)
\]

\[
A_3 = \text{determinant}(J) \quad \quad (7)
\]

and, the terms \( j_{11}, j_{22}, \) and \( j_{33} \) are the elements on the main diagonal of \( J \). From Routh’s stability criterion [19], the necessary and sufficient conditions for a steady state to be asymptotically stable are that \( A_1 < 0, A_3 < 0, \) and \( -A_2 + A_3/A_1 < 0 \). If any of these three conditions are violated, then the steady state will be unstable, as at least one eigenvalue will have a positive real part.

A general analytical investigation of when the above stability conditions are violated is not possible due to the complexity of the terms in the Jacobian matrix, and due to the possibility of multiple steady state solutions of Eqs. (2a-2c). A combined analytical and numerical uniqueness analysis [20] has shown that, for certain parameter values, as many as five steady state solutions can exist, each with potentially different stability properties. Certainly a dynamical model which possesses a multitude of coexisting steady states with a diversity of stability properties could be expected to exhibit complex global behavior. However, we shall show that when the parameter values are restricted so that the steady state is necessarily unique, both regular and chaotic cycling may still ensue.

HOPF BIFURCATION FROM A UNIQUE STEADY STATE

Using the techniques outlined by Luss [20], it is possible to show that Eqs. (2a-2c) will have a unique steady state over wide ranges of parameter values. In particular, if \( Da_2 = 2.75, \beta_1 = 0.04, \gamma_1 = \gamma_2 = 25, \) and \( \alpha = 250 \), then a unique steady state exists for all values of \( Da_1 \) and \( \beta_2 \).

For the above parameter values, the stability and character (node, focus, etc.) of the
unique steady state in the $Da_1 - \beta_2$ parameter space were determined by calculating the eigenvalues of the characteristic equation. Shown in Fig. 1 are the regions of equivalent character of the unique steady state, where it is seen that the steady state can be one of four types: (1) an unstable focus (one negative real eigenvalue and two complex conjugate eigenvalues with positive real parts); (2) an unstable node (one negative real eigenvalue and two positive real eigenvalues); (3) a stable focus (one negative real eigenvalue and two complex conjugate eigenvalues with negative real parts); or (4) a stable node (three negative real eigenvalues).

Shown in Fig. 2 are the effects of changing the system parameters such that a stable focus becomes an unstable focus. In this figure, the parameter $\beta_2$ is moved across the lower stability boundary (see insert in Fig. 1), and the effect of this on the time behavior of the dimensionless temperature is illustrated. An examination of the eigenvalues listed in Fig. 2 reveals that as expected a pair of complex conjugate, purely imaginary eigenvalues occurs at the lower stability boundary. At this boundary, we have also numerically determined that the real parts of the complex conjugate eigenvalues have nonzero derivatives with respect to $\beta_2$. Thus, a Hopf bifurcation [21] occurs at the lower stability boundary. An examination (not shown here) of the eigenvalues as $\beta_2$ is moved across the upper stability boundary in Fig. 1 reveals that a Hopf bifurcation also occurs on this boundary.

In all cases, the numerical integration of Eqs. (2a–2c) was performed by using Gear's

![Diagram](image-url)
method for the integration of stiff systems of ordinary differential equations. For most cases, the results were also checked by using a fourth-order Runge-Kutta-Fehlberg [23] method, with fifth-order error estimation, to integrate Eqs. (2a–2c). Hence, two very dissimilar integration methods were used to integrate the system of equations, and similar results were always obtained.

COMPLEX OSCILLATIONS AND CHAOTIC BEHAVIOR

From the work of Lorenz [24], it is now well known that systems of three or more differential equations can exhibit solutions of arbitrarily high period, as well as aperiodic solutions which are not even asymptotically periodic. This type of behavior is frequently referred to as chaotic behavior. For Eqs. (2a–2c), we have found that for certain parameter values the system can display apparently chaotic behavior. The transition from complex periodic behavior to chaotic behavior, and then back to complex periodic behavior is shown in Figs. 3 to 6.

Each of Figs. 3 to 6 are composed of the following three sections: (a) a plot of the time behavior of the dimensionless temperature, (b) an autocorrelation analysis of the
temperature maxima, and (c) a next-amplitude plot for the temperature maxima. In the following we will discuss in turn each of the groups of (a), (b), and (c) sections for Figs. 3 to 6.

In Figs. 3(a) to 6(a), we show the variation of dimensionless temperature with time. The behavior for the first 26 units of dimensionless time has been discarded to eliminate the transient effects of the initial conditions. In each case the initial conditions are $T_0 = 0$, $Y_0 = 0$, and $Z_0 = 0$. We see that, as $\beta_2$ is increased, the simple oscillation displayed...
in Fig. 2 bifurcates into the four maxima per cycle oscillation of Fig. 3(a). As $\beta_2$ is further increased the temperature is shown to behave in a chaotic fashion as in Figs. 4(a) and 5(a). An additional increase in $\beta_2$ results in the temperature once again following a stable periodic trajectory, this time with six maxima per cycle, as shown in Fig. 6(a).

Besides stable periodic oscillations of orders four and six, it is possible to have many other numbers of maxima per cycle (2, 3, 6, 8, 9, 16, etc.) depending on the value of $\beta_2$. In many systems which display chaotic behavior, it has been found [25] that period

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Fig. 5. Chaotic oscillation with two "cap-shaped" curves on the next-amplitude plot ($\beta_2 = 0.0163$, other parameters as in Fig. 2).

Fig. 6. Six maxima per cycle oscillation ($\beta_2 = 0.0165$, other parameters as in Fig. 2).
doubling occurs as the system behavior changes from a stable periodic to a chaotic
solution. In general, for the system of Eqs. (2a–2c), we have found that period doubling
does not occur, although it has been observed for some sets of parameter values.

In Figs. 3(b) to 6(b) we show the results of an autocorrelation analysis on the
temperature maxima. The autocorrelation analysis was performed by first reducing the
complete time series of temperatures obtained from the integration program, into a
vector of temperature maxima, \( T_m(i) \), where \( i \) varies from 1 to \( N \), and \( N \) is the number
of temperature maxima in the time series. The autocorrelation coefficient for \( L \) lag units
[correlation between \( T_m(i) \) and \( T_m(i + L) \)] was then calculated from

\[
AC(L) = \frac{1}{N-L} \sum_{i=1}^{N-L} \frac{[T_m(i) - \bar{T}_m][T_m(i + L) - \bar{T}_m]}{\text{var}(T_m)} \tag{8a}
\]

where

\[
\bar{T}_m = \frac{1}{N} \sum_{i=1}^{N} T_m(i) \tag{8b}
\]

\[
\text{var}(T_m) = \frac{1}{N} \sum_{i=1}^{N} (T_m(i) - \bar{T}_m)^2. \tag{8c}
\]

It is important to realize that the temperature maxima are considered to be equally
separated by one lag unit when they are stored in the vector which only contains the
temperature maxima, even though the maxima were perhaps separated by varying
amounts of dimensionless time in the original unreduced time series.

In Fig. 3(b) the autocorrelation analysis clearly indicates that an oscillation with four
maxima per cycle occurs because the autocorrelation coefficient is equal to 1.0 at a value
of four lag units and at all multiples of four lag units. The large value of the
autocorrelation coefficient at a value of two lag units indicates that the four maxima per
cycle oscillation is very close to being a two maxima per cycle oscillation. This type of
behavior is also shown in Fig. 6(b) where the six maxima per cycle oscillation is clearly
shown by the autocorrelation coefficient having a value of 1.0 at six lag units and at all
multiples of six lag units.

For the chaotic behavior displayed in Figs. 4(a) and 5(a), it is seen that the corre-
sponding autocorrelation coefficients given on Figs. 4(b) and 5(b) are never equal to
one, and in fact they approach zero at large lag values. While only twenty-four lag units
are shown in Figs. 4(b) and 5(b), the autocorrelation coefficients have been calculated for
several hundred lag units, and no long periods of oscillation were detected. This
particular form of autocorrelation analysis, as detailed above, has been found to be a
very useful, and computationally efficient, method of detecting chaotic behavior in the
solution of Eqs. (2a–2c).

In Figs. 3(c) to 6(c) we show the next-amplitude plots, in which successive dimen-
sionless temperature maxima \( T_m(i + 1) \) are plotted against \( T_m(i) \). If a stable periodic
solution exists, this will be shown on a next-amplitude plot by the existence of a finite
number of points which correspond to the number of maxima per cycle in the periodic
oscillation. For example, Fig. 3(c) has only four points on it, and this corresponds to an
oscillation with four maxima per cycle. Similarly, the six maxima per cycle oscillation in
Fig. 6(a) generates a next-amplitude plot containing exactly six points, as shown in Fig.
6(c).

The next-amplitude plots become more complex for the case of chaotic oscillations.
Lorenz, in a series of papers (cf. references in [16]) modelled turbulent fluid flow through
a simplified set of equations. From these, he numerically solved for \( X(n) \), the maximum
kinetic energy of successive waves. He plotted $X(n+1)$ versus $X(n)$, and found that a continuous cusp-shaped curve $y = F(x)$ (with a single maximum value at the cusp) approximated this data. However, as can be seen in Figs. 4(c) and 5(c), the chaotic behavior of Eqs. (2a–2c) does not generate a single curve, rather, at least two curves are visually apparent. This is not to imply that the relationship between $T_m(i)$ and $T_m(i+1)$ is nonunique, but rather, as $T_m(i)$ varies there are an infinite number of switchings between the curves. The curves must be discontinuous because the next-amplitude map is single valued, i.e., a vertical line which crosses through a point on one curve necessarily crosses through no point on the other curve. To our knowledge, this is the first time that next-amplitude plots of the form shown in Fig. 5(c) have been observed. Figs. 3(c) to 6(c) do not represent the full extent of possible forms of the next-amplitude plots, as even more complex forms can exist depending on the choice of parameters.

CHAOS AND FRACTAL CURVES

Shown in Fig. 7(c) is a next-amplitude plot in which three curves are distinctly observable. The chaotic oscillation of the dimensionless temperature which generated this next-amplitude plot is shown in Fig. 7(a), and the autocorrelation analysis is given in Fig. 7(b).

Sections of the curves shown in Fig. 7(c) were expanded to more closely examine their structure. Shown in Fig. 8 are successive magnifications of the regions enclosed in the dashed rectangular boxes. Fig. 8(b) shows quite distinctly that the “single” curve in the dashed box of Fig. 8(a) is actually composed of at least three curves. In Figs. 8(c) and 8(d) it is seen that upon additional magnification, these curves expand into even more curves. It is reasonable to expect that “curves” on the next-amplitude plot shown in Fig. 7 are actually composed of an infinite number of curves, and in fact these are fractal curves in the sense of being self-similar [26]. Specifically, the transverse structure across the roughly parallel curve segments is essentially that of a Cantor set, while on the curves the points appear to distribute themselves densely.

Fig. 7. Chaotic oscillation with emergence of a third curve on the next-amplitude plot ($Da_1 = 10.0$, $Da_2 = 2.75$, $\beta_1 = 0.040$, $\beta_2 = 0.0149$, $\alpha = 250$, $\gamma_1 = \gamma_2 = 25$).
Such a topological structure has been encountered in a number of examples of second-order recurrences which approximate certain three-dimensional dynamical systems that have been used to describe turbulent flow. These recurrences take the form of the Poincaré return map to the flow, i.e., the map which describes the flow on some transverse planar section. A well-known example is the Hénon return map to the Lorenz equations [27].

**TRAJECTORIES IN T–Y–Z SPACE**

While the manner in which the variables $T$, $Y$, and $Z$ change with time is of interest, the forms which they create in three dimensional $T$–$Y$–$Z$ space are of even more interest, as these will delimit the shape of the attractor which the trajectories are following. For the chaotic oscillation shown in Fig. 7, the $T$–$Y$, $T$–$Z$, and $Z$–$Y$ views of the system trajectory are shown on Figs. 9(a)–9(c), respectively. From these two-dimensional views, the complete shape of the three-dimensional trajectory can be constructed.
Fig. 9. Two-dimensional views of the three-dimensional attractor: (a) $T$-$Y$ view (clockwise motion when viewed from above); (b) $T$-$Z$ view (Möbius-band structure is displayed); (c) $Z$-$Y$ view (motion is clockwise); all parameters as in Fig. 7.
Several positions have been labelled in Fig. 9(b) in an attempt to describe the three-dimensional shape of the attractor. If a trajectory starts near position 1 on the front (out of the paper) of the lower band, it will travel from right to left and pass through position 2 such that it is now located on the back (behind the paper) of the upper band at position 3. From there, the trajectory passes under the right-most part of the attractor such that it arrives at position 4 which is on the back of the lower band. The trajectory passes along the inside of the "circular-well" [clearly shown in Fig. 9(a)] in a clockwise fashion until it reaches position 5, which is on the front side of the upper band. From position 5, the trajectory travels over the top of the right-most part of the attractor, ultimately arriving at position 6, which like position 1, is located on the front of the lower band. The trajectory will now repeat itself in a similar way.

This motion is identical to that which would result from following a Möbius-band, hence this attractor should be known as a "Möbius-band attractor." In some respects, this attractor is similar to an idealized attractor described by Rössler [28]. Besides this particular shape, many other forms of the attractor have been observed for other parameter values.

CONCLUSIONS

We have shown that a very simple chemical reactor model consisting of three ordinary differential equations can display complex periodic and chaotic behavior. This behavior has been analyzed by examining autocorrelation coefficients, next-amplitude plots, and state-space trajectories.

Through the use of the autocorrelation analysis we have shown that the chaotic behavior does not contain any high-order oscillations. When only the temperature maxima are used, the autocorrelation analysis is a very useful, and computationally efficient, method of examining complex periodic and chaotic behavior.

We have found that the next-amplitude plots are composed of very complex structures, which upon close examination are found to be fractal curves. We are not aware of any previous observations of structures of this type in next-amplitude plots.

A detailed inspection of the state-space trajectories during a chaotic oscillation has shown that the trajectories follow a Möbius-band attractor. Other more complex forms of the attractor have also been found.

REFERENCES


NOMENCLATURE

\[ A_1, A_2, A_3 = \text{constants in the characteristic equations} \]
\[ [A], [B] = \text{concentrations of } A \text{ and } B \text{ in the reactor} \]
\[ [A]_0, [B]_0 = \text{concentrations of } A \text{ and } B \text{ in the reactor feed} \]
\[ C_p = \text{heat capacity} \]
\[ D_1, D_2 = \text{Damköhler numbers for the two reactions} \]
\[ E_1/R, E_2/R = \text{activation energies for the two reactions} \]
\[ H_{r1}, H_{r2} = \text{heats of reaction for the two reactions} \]
\[ J = \text{Jacobian matrix} \]
\[ J_{11}, J_{22}, J_{33} = \text{elements on the main diagonal of the Jacobian matrix} \]
\[ k_1, k_2 = \text{rate constants for the two reactions} \]
\[ L = \text{number of lags for autocorrelation analysis} \]
\[ Q = \text{reactor volumetric feed rate} \]
\[ S = \text{area for heat transfer} \]
\[ t = \text{dimensionless time} \]
\[ t' = \text{time} \]
\[ T = \text{dimensionless temperature} \]
\[ T' = \text{reactor temperature} \]
\[ T_0' = \text{temperature of the reactor feed} \]
\[ T_m = \text{temperature of the reactor} \]
\[ T_{m1} = \text{dimensionless temperature maximum} \]
\[ T_{m2} = \text{average of the dimensionless temperature maxima} \]
\[ U = \text{reactor heat transfer coefficient} \]
\[ V = \text{reactor volume} \]
\[ Y = \text{dimensionless concentration of species } A \]
\[ Z = \text{dimensionless concentration of species } B \]
\[ \alpha = \text{dimensionless heat transfer coefficient} \]
\[ \beta_1, \beta_2 = \text{dimensionless heat of reaction} \]
\[ \gamma_1, \gamma_2 = \text{dimensionless activation energies} \]
\[ \rho = \text{density} \]
\[ \omega = \text{eigenvalue of the Jacobian matrix} \]