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REVIEW

INTRICATE CSTR DYNAMICS

Kil Sang CHANG, Jae Youn KIM*, and Hyun-Ku RHEE**

Korea Advanced Energy Research Institute, P.O. Box 7, Daeduk Science Town, Chung-Nam, Korea
*Korea Explosives Group, Research and Engineering Center, P.O. Box 340, Daeduk Science Town, Chung-Nam, Korea
**Department of Chemical Engineering, Seoul National University, Seoul 151-742, Korea

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Abstract—Various dynamical characters of continuous stirred tank reactors (CSTR) are introduced with respect to the effects of reaction types, extra thermal capacitance, periodic forcing, and coupling of CSTRs. The subject includes the classical dynamics of two-dimensional model and the variety of complex dynamics in three or higher dimensional systems such as periodic bifurcations to torus or chaos, aperiodic oscillations on invariant torus, and universal dynamics of alternating periodic-chaotic sequences with $k \cdot 2^{\nu}$-cycles for every natural number k. Particularly this review intends to bring about the problems that the engineers must be prepared to encounter in solving various physical systems including chemically reacting systems.

INTRODUCTION

One of the most mysterious and particular things in nature may be the catastrophic feature of states, which usually brings about an abrupt change in equilibria and dynamics as well with a very slight change of ambient conditions. A chemically reacting system is in this respect an intricate model to exhibit a variety of multiple equilibria and complex dynamical behavior depending on the extent of reaction, temperature and other control variables.

The multiplicity and stability of steady states in a chemically reacting system was first mentioned by Liljenroth[1] in 1918. However, this work was unnoticed and lay dormant until lately. Similar work by Semenov[2] in 1928 was also neglected until rediscovered recently. The regions of attraction of different steady states and some dynamic aspects were mentioned by Burton[3] in 1939 and Denbigh[4,5] in 1947 and 1948. Although some Russian works[6-8] were also published in 1940s, they obviously did not seem to have had any real influence to the Western world. Van Heerden's paper[9] of 1953 on the autothermic chemical reactors discussed the stability of steady states with the fundamental concept of slope conditions of heat generation and removal curves.

The rigorous analysis on stability was put forward by Bilous and Amundson[10] in 1955, and thereafter a flood of papers have rushed on the stability and dynamics of chemically reacting systems. They used the Liapunov first method in analyzing the local stability of the steady states and did show some phase plots of concentration and temperature trajectories using an analog computer. It is notable that they expected up to five steady states for consecutive reaction A→B→C. More extensive survey of multiplicity and dynamics were reported by Aris and Amundson in 1958[11]. They illustrated how the trajectories change in the phase plane as the proportional feedback controller gain is increased. They also showed the existence of undamped oscillations in the form of limit cycles and possible bifurcation of limit cycles and possible bifurcation of limit cycles at the critical value of parameter where the steady state loses its stability.

These papers inspired many other workers to have interests in this field and a large number of studies have since been performed concerning the modeling of reaction systems, dynamic aspects of multiple steady states and mathematical tools for the existence and stability analysis of limit cycles[12-21]. They have involved the second Liapunov method to determine the region of asymptotic stability of a steady state [12-24], averaging technique to predict the presence and stability of limit cycles[15,16], perturbation technique to predict the form of a limit cycle[17,18], and Fourier type analysis of limit cycles[19]. In the meantime, Uppal et al.[20,21], using a two-dimensional method of a nonisothermal CSTR with a first order irreversible exothermic reaction, have displayed the various dynamical features that occur around some bifurcation points such as saddle-node or

**To whom all correspondence should be addressed.

Hopf bifurcations which give rise to a new branch of steady state solutions or the creation of periodic solutions. They have also shown that there are homoclinic bifurcations in which the unstable manifold of a saddle returns to itself to give a solution with infinite period. This paper might well deserve high-evaluation for the establishment of all the dynamic characters which can be found in two dimensional chemical reaction systems.

When the system is three dimensional or higher, much more complex dynamics and steady state behavior can be expected. Golubitsky and Keyfitz[22] introduced the singularity theory[23,24] to the steady state analysis of chemically reacting systems, and other workers[25-28,39] successfully applied this method in predicting all the possible types of bifurcation diagrams and the critical parameter values of changes. Meanwhile, there has been found a complex feature of dynamics which exhibits nonperiodic oscillative motions called chaotic behavior. Kahlert et al.[29] found chaos in a CSTR with two consecutive reactions, the first exothermic and the second endothermic. Similar behavior has been found by Jorgensen and Aris[30] for the same reacting system with both exothermic reactions. In this case some complex dynamic behavior and bifurcation pattern have been identified. This simple three dimensional model was chemically more realistic than previously formulated system of Belousov-Zhabotinskii reaction[31-35] which can exhibit chaotic motions. Since then, many scientists and engineers have indulged in excavating this new field of science, and many chaotic motions have been observed in various chemical reaction systems.

In this review, we intend to show some significant dynamic characters in CSTR systems with respect to the contexts of processes rather than to give complete method of analysis which is still far from the solution. Furthermore, we expect this subject, even with scope of experimental studies, may bring the notion that one must be prepared to encounter chaos as well as varieties of phenomena in physical and engineering systems.

STEADY STATES AND STABILITY

Chemical reaction model of CSTR is usually expressed as an autonomous set of ordinary differential equations,

$$\frac{dx}{dt}=f(x), \quad x(0)=x_0. \tag{1}$$

Such systems usually appear highly nonlinear and can exhibit a variety of multiple steady states and dynamics. The diversity of multiplicity in steady state behavior makes the global analysis very difficult. For physical reasons, the steady state behavior is often analyzed by examining the dependence of these steady states on a distinguished parameter.

Let the steady state of Eq.(1), depending on a parameter λ, be the solution of algebraic equation

$$f(x, \lambda)=0. \tag{2}$$

In a large sense of steady state to include the cyclic motions, Eq.(2) may be replaced by with the concepts of fixed points in the map[36],

$$x=F(x, \lambda)=\phi_T(x, \lambda) \tag{3}$$

where F is a map for flow ϕ, and T is the lowest value of time called period. It may be noticed that the solution of Eq. (2) can explain the static behavior of steady states.

For the moment the standard approach of solution of Eq. (2) would be the application of implicit function theorem. If we let x_0 be the nonsingular solution of Eq. (2) for a specific parameter λ_0, the implicit function theorem insures the existence of unique smooth curve of solution $x=x(\lambda)$ satisfying $x_0=x(\lambda_0)$ in the small neighborhood of λ_0. Furthermore, with the smoothness of solution curve, it follows that $dx/d\lambda$ exists and satisfies

$$f_x[x(\lambda), \lambda]\frac{dx}{d\lambda}=-f_\lambda[x(\lambda), \lambda]. \tag{4}$$

The solution branch of Eq. (2) can provide us with the steady state behavior depending on a parameter change, saying bifurcation diagram. The continuation process, however, fails at the singular point, $f_x(x, \lambda)=0$. To solve this problem, Keller[37] introduced the method of branch switching at singular points, and Doedel and Heinemann[38] used the continuation technique for the computation of periodic solution branch to investigate the oscillatory behavior of a CSTR with consecutive reactions. Meanwhile, the qualitative aspects of bifurcation diagrams can be well established with the elementary catastrophe theory[39]. The singularity theory was first introduced by Golubitsky and Schaeffer[23]. By the application of the theory to the chemically reacting systems, various features of bifurcation diagrams have since been discovered[22,24-28]. The theory required first one to determine the highest order singularity of the equilibrium equation, say organizing center, from which we can predict the maximal number of feasible solutions and the bifurcational feature around that point. The organizing center is characterized by the largest number k satisfying,

$$f=\frac{\partial f}{\partial x}=\frac{\partial^2 f}{\partial x^2}=\cdots\cdots=\frac{\partial^k f}{\partial x^k}=0, \quad \frac{\partial^{k+1} f}{\partial x^{k+1}}\neq 0 \tag{5}$$

The solution of Eq. (5) is called the singularity of codimension k, around which one may expect up to k + 1 multiple steady states. This theory, however, can provide us with the local feature of possible bifurcation diagrams, and does not seem to be useful for the analysis of more complex systems. For the global analysis of the system, one must need to incorporate with physical and mathematical rigor. More precise explanation on this topic is beyond the scope of this review, for which one may consult the references above mentioned.

The dynamic character of a system is determined by the multiplicity feature and properties of steady states, and it has been straightforward matter to determine the stability property of steady state, the stability is in a physical sense the property that a disturbed state will return to the steady state if a small perturbation is given to that system. The stability of a steady state point can be determined more easily for the linearized systems, and it has been a general concept that the linearized system can accurately describe the dynamic character of a nonlinear system in a sufficiently small neighborhood of a steady state point[40].

Let the linearized system of Eq. (1) be

$$\frac{dx}{dt}=\mathbf{A}x,\quad \mathbf{A}=[\partial f_i/\partial x_j]. \qquad (6)$$

Then the stability can be determined directly by the eigenvalues of **A**, and the question of the stability reduces to one of investigating the nature of the roots of the characteristic equation of matrix **A**. To make one more comprehensive, we introduce the Liapunov method.

Let us consider the quadratic function

$$v=(x, \mathbf{B}x) \qquad (7)$$

where **B** is symmetric matrix and $(x, \mathbf{B}x)$ denotes the scalar product of vectors x and $\mathbf{B}x$. Since x is a function of time, v is also a function of time and the time derivative of function (7) is

$$\frac{dv}{dt}=(dx/dt, \mathbf{B}x)+(x, \mathbf{B}dx/dt) \qquad (8)$$

From the system Eq. (6)

$$\frac{dv}{dt}=(\mathbf{A}x, \mathbf{B}x)+(x, \mathbf{BA}x) \qquad (9)$$

Since **B** is symmetric, the following rule holds,

$$(x, \mathbf{B}y)=(\mathbf{B}^T x, y) \qquad (10)$$

and then the Eq. (9) becomes

$$\frac{dv}{dt}=[x, (\mathbf{A}^T\mathbf{B}+\mathbf{BA})x]. \qquad (11)$$

Now, let $\mathbf{C}=\mathbf{A}^T\mathbf{B}+\mathbf{B}\,\mathbf{A}$. Then **C** is a symmetric matrix and the Liapunov's asymmetric stability can be expressed as follows: If there exists a positive definitive matrix **B** for any given symmetric negative definite matrix **C**, then the origin is asymmetrically stable. The direct Liapunov method can calculate the region of stability by defining a region of phase plane inside which all state variables tend to the steady state for a stable system. However, the basic difficulty with the direct method is that there are no straightforward schemes for producing Liapunov functions. Even though we can find the Liapunov function for a linearized system, the region of stability may be too small. This method has been applied to the stability problems by some authors[12-14] with very limited success.

The dynamic character of a system can be more complicated when we come across the bifurcation phenomena of undamped oscillatory motions. The critical point that a spiral sink (damped oscillation) loses its stability with continuously changing parameters is called the *Hopf bifurcation point*, and a limit cycle surrounding an equilibrium point emerges from that point[41]. The stability of a limit cycle can be determined from the map by the concept of the contraction mapping in metric spaces; i.e., if the Jacobian matrix of the map F denoted in Eq. (2) at the fixed point has a modulus less than 1, the point is stable.

$$|F'(x)|<1 \qquad (12)$$

Thus if $|F'(x)|>1$, the point is unstable and points near the fixed point move far away from it. The stability region can also be determined in the parameter space satisfying the condition(12).

Consider a T-periodic solution $x(t)$ with $x(t)=x(t+T)$ in flow systems (1). Let $\mathbf{A}(t)=\partial f/\partial x$ be the T periodic variational matrix on the closed orbit $x(t)$. Then we have the following system as

$$\frac{dx}{dt}=\mathbf{A}(t)x \qquad (13)$$

Now let $X(t)$ be the matrix solution of Eq.(13) satisfying

$$\frac{dX}{dt}=\mathbf{A}X,\quad X(0)=\mathbf{I} \qquad (14)$$

The eigenvalues of the monodromy matrix $X(T)$, derived from the condition of Eq.(12) as the Jacobian matrix of the Poincare map[36] in the periodic orbit, are called the *Floquet multipliers* and can determine the stability of a limit cycle.

Since the periodic solution $x(t)$ can only be found numerically, the Floquet multipliers are obtained numerically by integrating Eq. (14) following the closed orbit of period T. Note that one of the Floquet multipliers is always +1 if the solution is exactly located. If the remaining other multipliers lie inside the unit circle, the periodic solution is stable. If any one of the multipliers leaves the unit circle, the periodic orbit loses its stability and a bifurcation takes place. In particular, if one of the multipliers leaves the unit circle through +1, this corresponds to a turning point in the periodic branch (tangent or saddle-node bifurcation), and if one of the multipliers leaves the unit circle through −1, the periodic branch splits into a stable periodic solution of twice the period. This bifurcation is called *flip* or *period doubling* and often occurs repeatedly culminating in a chaotic motion. Another case is when a complex conjugate pair leaves the unit circle. In this case the periodic orbit bifurcates into a doubly periodic oscillation on an invariant torus. Another bifurcation type is associated with a homoclinic orbit for which the unstable manifold of a hyperbolic saddle point returns to itself coalescing with stable manifold with infinite period. When a parameter crosses a boundary through such a point, there exists a family of periodic orbits[36]. The unstable manifolds can cause various bifurcations when they collide with an attractor. Sudden changes from a periodic or chaotic motion are mostly from this kind of collision.

A periodic orbit, for instance, even though it is an attractor, is intrinsically a part of unstable manifold of a steady state, and thus the dimension of the unstable manifold of limit cycle is one plus the number of multipliers that leaves the unit circle. In the following sections, one may be encouraged to bear in mind those notions as the instability, bifurcations, manifolds, limit cycles, period doubling, chaos, etc., and must put them together in connection with the analytical schemes.

SYSTEMS AND DYNAMICS

1. Single reaction

The dynamic character of a CSTR (See Fig. 1) is usually represented as the mass and energy balances of all reacting species

$$V\frac{dC}{dt} = \lambda q C_f + q(1-\lambda)C - qC - VR(C,T) \quad (15)$$

$$V\frac{dT}{dt} = \lambda q (T_f - T) - \frac{hS}{\rho C_p}(T - T_c) + \frac{(-\Delta H)V}{\rho C_p} R(C,T) \quad (16)$$

Uppal et al.[20,21] have shown the complete analysis of bifurcation and dynamical behavior for their two dimensional model of CSTR with two first-order irreversible exothermic reaction $A_1 \rightarrow A_2$, and

$$R(C,T) = k_0 \exp\left(-\frac{E}{RT}\right)C \quad (17)$$

Taking Damköhler number [$Da = K_0\, \tau\, \exp(-E/RT_f)$] and reactor residence time ($\tau = V/q\lambda$) as parameters, they investigated all possible types of bifurcation diagrams and typical dynamic characters in the phase space. The bifurcation diagram of zero solution varies from simple sigmoid (See Fig. 2) to mushroom and isola (See Fig. 3) associated with the creation or extinction of periodic branches. They classified the typical dynamic feature of their CSTR model into nine types (See Fig. 4) depending on the specific regions divided by various bifurcation points.

Several interesting bifurcational features of two dimensional model have been observed from the figures. The transitions A-B and E-F, for which a stable periodic branch emerges from the critical point around the unstable focus, are the supercritical cases of Hopf bifurcation. Meanwhile, the transitions B-D, C-H, and G-J are called the subcritical Hopf bifurcations, for which an unstable periodic branch emerges from the

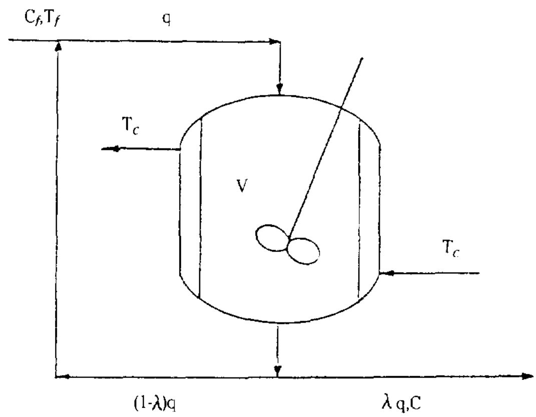

Fig. 1. Schematic view of CSTR with recycle.

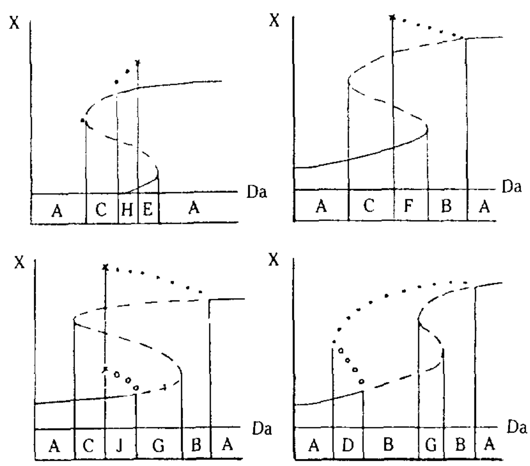

Fig. 2. Various types of bifurcation diagrams with Damkohler number [20].

—: Stable Steady State, ---: Unstable Steady State, ···: Stable Limit Cycle, ∘∘∘: Unstable Limit Cycle

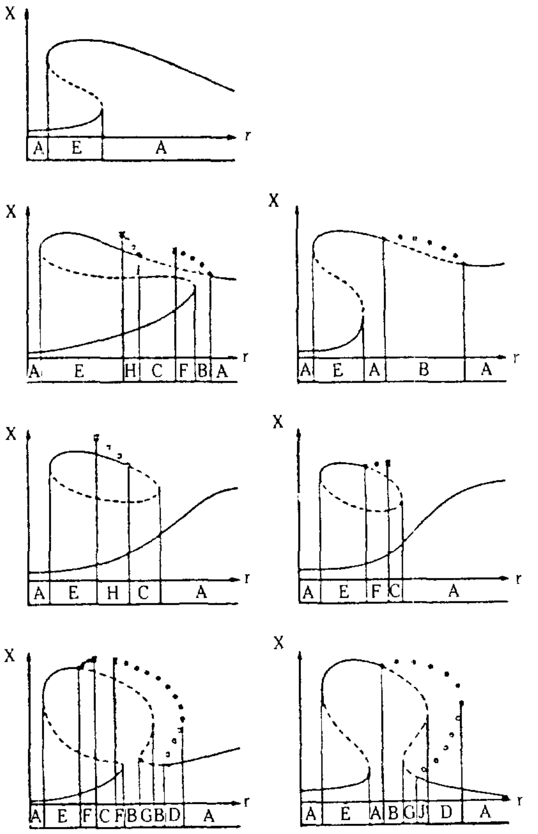

Fig. 3. Various types of bifurcation diagrams with residence time [21].

—: Stable Steady State, ---: Unstable Steady State

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critical point around the stable focus. This kind of Hopf bifurcation point can be obtained by seeing when the Jacobian matrix of the linearized system has a pair of complex eigenvalues crossing the imaginary axis. The tangent or saddle-node bifurcation like the transition A-D is associated with two limit cycles, one stable and one unstable coalescing each other. This bifurcation point can be obtained when one of the Floquet multipliers leaves the unit circle through $+1$, and corresponds to a turning point in the periodic branch. Another interesting bifurcation type is associated with the homoclinic orbit(transition E-H, C-F), in which a limit cycle, stable or unstable, generates or disappears merging with the separatrix of a saddle point. Also one may observe the type of bifurcation that a stable limit cycle disappears suddenly by colliding with an unstable limit cycle (transition J-C). This kind of bifurcations cannot be easily ascertained in many cases since all the unstable periodic orbits are hardly perceived. Some authors[42] use the word crises for this type of collisions even though their cases are related with the chaotic attractors

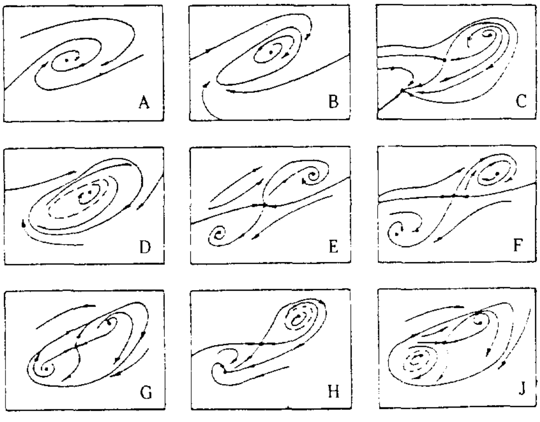

Fig. 4. Possible phase diagrams in two-dimensional system [21].

2. Consecutive reactions

The two dimensional autonomous model, however, can not exhibit more complicated behavior than a simple periodic motion associated with those bifurcations above mentioned. More complex dynamics may be expected in three or higher dimensional systems. Using three dimensional model of a CSTR with two consecutive reactions Kahlert et al.[29] found chaos for the first reaction exothermic and the second endothermic. The presence of a well defined attractor, shaped as folding and stretching intricacy of strips, is an indication of the chaotic behavior of the system (See Fig. 5). This change proceeds by succession of period doubling bifurcations to some limit through a typical *Feigenbaum cascade* of nonlinear transformation[36,43], beyond which the attractor changes its character and becomes chaotic. The period doubling or flip bifurcation occurs when any of the Floquet mul-

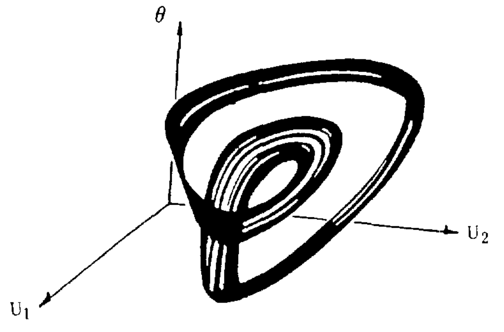

Fig. 5. Chaotic attractor of the consecutive reaction system [29].

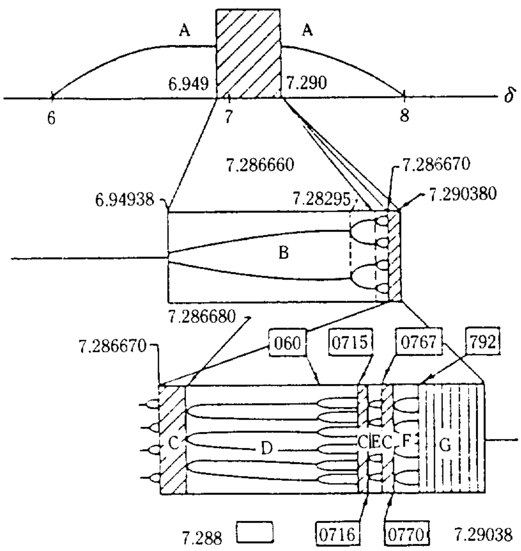

Fig. 6. Bifurcation pattern with parameter $\delta(=hS/q\rho Cp)$ [30].

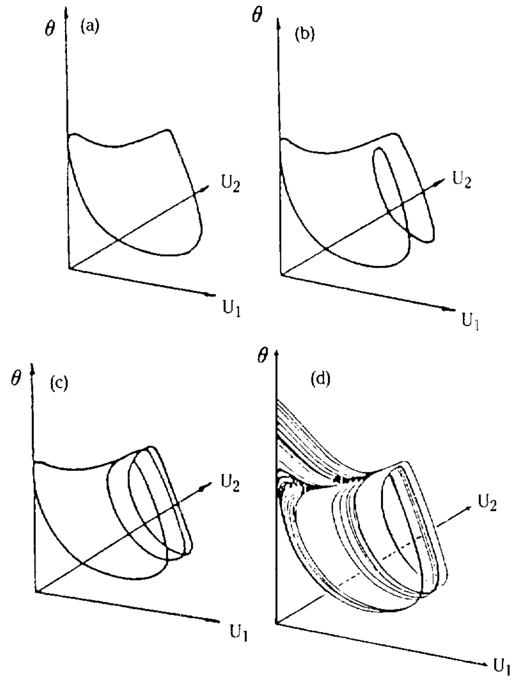

Fig. 7. Sequence of period doubling (a,b,c) and chaotic trajectory (d) [30].

tipliers leaves the unit circle through -1. Then the periodic solution becomes unstable and the unstable manifold forms a Möbius band such as can be obtained from an open strip by twisting half turn and connecting both ends. The trajectories on the surface of the band tend to the boundaries and form a stable cycle with the period almost twice the original periodic orbit.

Similar behavior has been found by Jorgensen and Aris[30], who studies the same reacting systems with both exothermic reactions. For this systems, some more complex dynamic behavior has been identified in the bifurcation pattern of the system. The various types of dynamic regimes is shown in Fig. 6 with the bifurcation parameter $\delta(=h\ S/q\ \rho\ C_p)$. Regime A corresponds to the case where a stable limit cycle is present with unstable focus. Regime B corresponds to the case where period doubling occurs up to the emergence of a chaotic regime C. Regimes D, E, and F correspond to interlude situations separating the occurrence of a chaotic behavior, where periodic solutions and chaos seem to coexist. As can be seen in the figure, the regimes are getting smaller as the bifurcation propagates, and thus at this point the numerical accuracy of the integration technique becomes critical. For better understanding of the system behavior one may need some significant physical and theoretical insight. Some of the periodic solutions characteristic of regime B and C are shown in Fig. 7.

3. Thermal capacitance effect

Now we may consider the effect of the thermal capacitance of the reactor with exothermic irreversible reaction $A_1 \rightarrow A_2$. Then the reactor model (15,16) may need energy balance equation for the solid mass of the reactor,

$$V_M \frac{dT_M}{dt} = \frac{h_M S_M}{\rho_M C_{pM}} (T - T_M) \tag{18}$$

and the term on the right-hand side must be added to the equation (16) with negative sign. This obviously does not affect the zero solution of the system. However, in dynamic character and stability of steady states, this was known to affect greatly. Planeaux and Jensen[44] made a thorough analysis for this effect using normal form theory[45]. They found some new dynamical behaviors not previously observed in the single reaction CSTR problem, including periodic bifurcations to invariant torus and an isolated branch of periodic solutions which contains no Hopf bifurcation points (See Fig. 8).

The periodic bifurcation to invariant torus can be noticed by the Floquet multipliers that the complex conjugated pair leaves the unit circle. In this case the system can show doubly periodic oscillations just like the motion on an invariant torus. Figure 9 shows three dimensional quasiperiodic oscillations seemingly doubly periodic. Though it was not shown whether the torus propagates further bifurcations displaying ergodicity, the tori branch is thought to extinct by colliding with the separatrix of the saddle type equilibrium

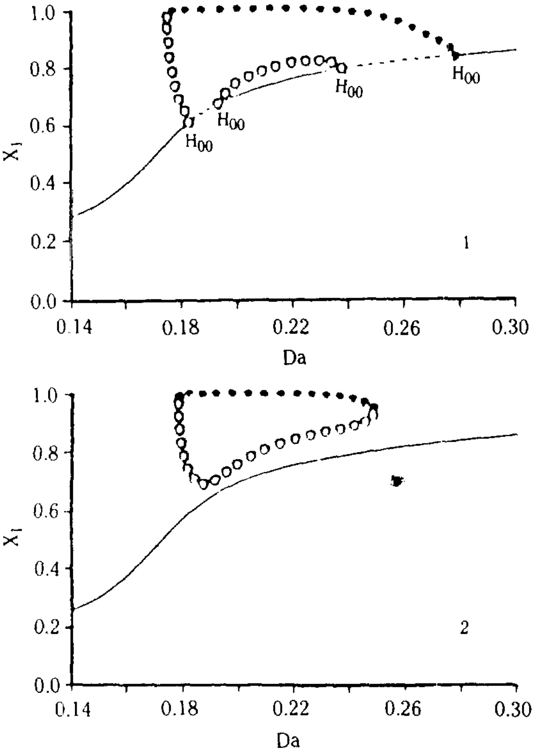

Fig. 8. Isola of periodic solutions [44].

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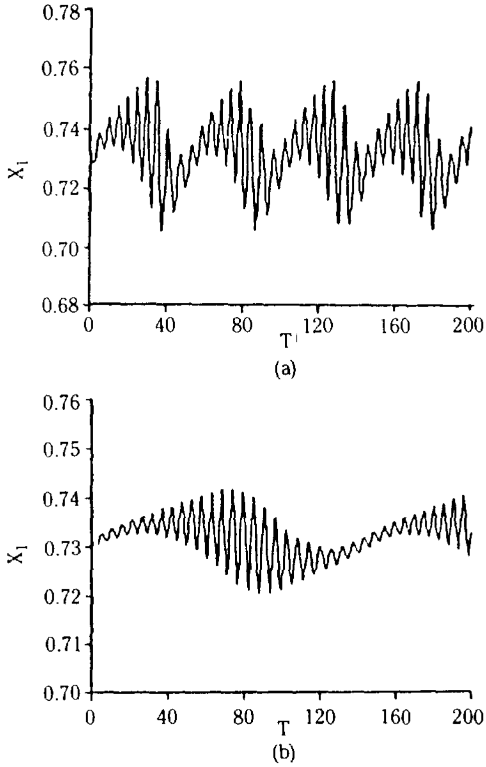

Fig. 9. Various quasi-periodic oscillations [44].

point bringing about a complex homoclinic explosion. It is very interesting to observe the dynamic motion on the invariant torus near homoclinic orbit, a tortuously tangled feature of manifolds as Silikov[46] has suggested. At this moment, however, we may be satisfied with the fact that three dimensional system, obtained by adding the extraneous thermal capacitance effect without changing the equilibrium states of the system, can show different variety of dynamical behavior.

4. Forcing effect

The effect of an external periodic forcing with the natural frequencies of chemically reacting systems gives rise to some interesting dynamic features. The interest in the periodic operation of chemical reactors was first surged in the late 1960s and early 1970s with the idea that the periodically operated processes might produce advantages over steady state processes in terms of mean conversion rate[47-49], and the subject is reviving in recent years.

Now we put into the system equations, [eqs. (15) and (16)], the forcing that the coolant temperature is varied according to

$$T = a \sin \omega t + \overline{T}_c \tag{19}$$

The forcing of nonlinear oscillators then makes the system nonautonomous and can be considered to increase the dimension of the autonomous system by one with the parametric variation of the amplitude and the frequency in coolant temperature. Mankin and Hudson[50] have shown by putting the forcing amplitude change on the basic state of periodic oscillation that the reactor state can change from quasi-periodic to chaos through a sequence of period doubling bifurcations. In their observation for much smaller forcing amplitude than the autonomous(natural) oscillations of the reactor, there appeared also multiple oscillatory states where both states are either periodic or one periodic and the other chaotic. This would be a very interesting feature that can be deduced from the idea that there cannot exist only static point in a periodically forced system and the steady states in autonomous system begin oscillations when periodic forcing is given to the system.

Kevrekidis et al.[51] have studied the same system in some detail with the variation of the forcing amplitude and frequency ratios with respect to the natural oscillations of the autonomous system. For the convenience of visualization they used the stroboscopic mapping that can produce the trajectory at every period of time in the forcing term, so that the closed or-

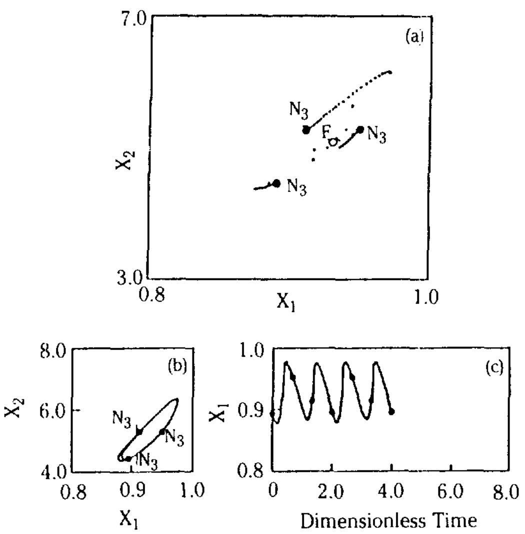

Fig. 10. (a) Stroboscopic view of transient starting (b) Phase plane projection of the oscillations (c) Transient response with time [51].

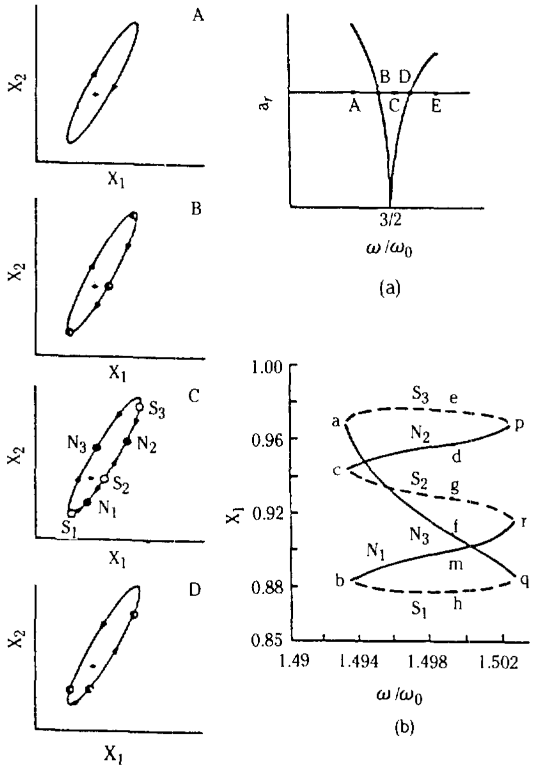

Fig. 11. One-parameter cut through 3/2 resonance horn with $a_r = 0.5$ and bifurcation diagram on invariant torus [51].

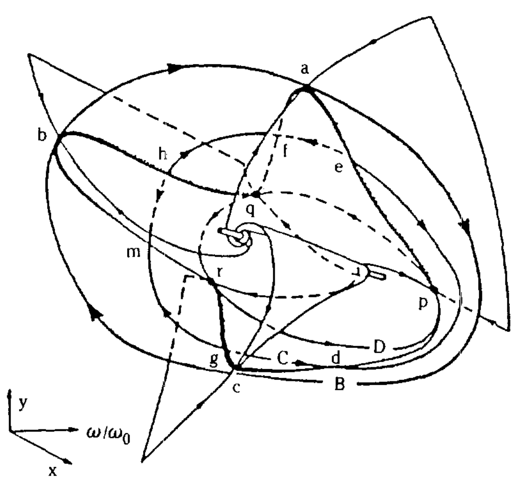

Fig. 12. Perspective view of the three reactions B, C and D of Figure 11 with letters showing corresponding points in Figure 11 [52].

bits are reduced to a finite number of discrete points and the space filling trajectories appear closed curves. They also used the Floquet multipliers to predict the loss of stability by observing whether any multiplier crosses the unit circle in the complex plane. One interesting phenomenon they typically observed is entrainment that when the frequency ratio of forcing to natural is close to any rational number (p/q) the period of response oscillation becomes an integer multiple of the forcing period. Therefore, in the resonance region (horn-like) with its tip at $\omega/\omega_0 = p/q$ one can find an attractor of period p(actually p times the period of forcing) and this oscillatory motion appears in the mapping as p discrete points with q loops in their phase space of the forced system.

Figure 10 shows the stroboscopic view of transient oscillations at amplitude ratio $a_r = 0.5$ and $\omega/\omega_0 = 1.498$ close to the unstable focus of period 1(F1) gradually approaching to the stable node of period 3 (N3) and two loops as in the 3/2 resonance. Figure 11 illustrates the sequential events of otions as the forcing frequency moves across 3/2 resonance at constant amplitude ratio ($a_r = 0.5$). At A there exists a quasi-periodic attractor appearing as an invariant circle with stroboscopic mapping. At B the onset of entrainment as shown in Figure 11, three saddle-node points appear as periodic points on the invariant circle. Crossing through the horn as ω/ω_0 moves, the saddles and nodes move apart from each other in C and recombine at the other entrainment boundary D with different pairing. Meanwhile, the arrows indicating the rotation orientation of a phase point change from B on the invariant circle, and at E quasi-periodicity appear again. The perspective view of the three regions B, C and D of Figure 11 is shown in Figure 12. Further increase in forcing amplitude is known to lead the motion in the resonance horn to bifurcate to a chaotic motion without sequential period doublings.

Similar behaviors were found in other chemical reaction systems such as homogeneous autocatalytic reaction or bimolecular surface reaction[52,53]. The response patterns of periodically forced systems include the interplay between entrainment and quasi-periodicity for small and intermediate forcing amplitude or chaotic motions for some specific regions. One may note here that the forced system can be thought only a special case of a cascade system and thus the understanding of this system helps to elucidate the coupling mechanisms and interaction between reactors.

5. Coupled CSTRs

The coupled reactor system is an extension of single reactor system such that the output of the first reactor acts as a forcing to the second. Varma[54] has shown in the general case of N CSTRs in series that there can be up to 2^{N+1}-1 steady states and no more than N + 1 can be stable. The stability of a cascade system may be determined by the product of the Jacobians of each reactor. However, this does not hold if any counter-current flow is present. For a two CSTRs system with recirculation, the region of existence of multiple steady states and stability were investigated through the analysis of the eigenvalues of the Jacobians[55]. Some case studies also have been done including the test for the direction of bifurcation of limit cycles[56]. Mankin and Hudson[57], by coupling two CSTRs with heat and mass transfer, have found chaotic motions through period doubling bifurcations with the increase of coupling strength.

Typically to investigate the coupled effect of two CSTRs, Chang and Aris[58] devised counter currently cooled CSTRs in which a first-order reversible exothermic reaction takes place. This system may be worthy of attention in relation to the optimal design of coupled CSTRs to obtain a better productivity. Taking into account the coolant dynamics, the system can be represented as a set of six ordinary differential equations. In

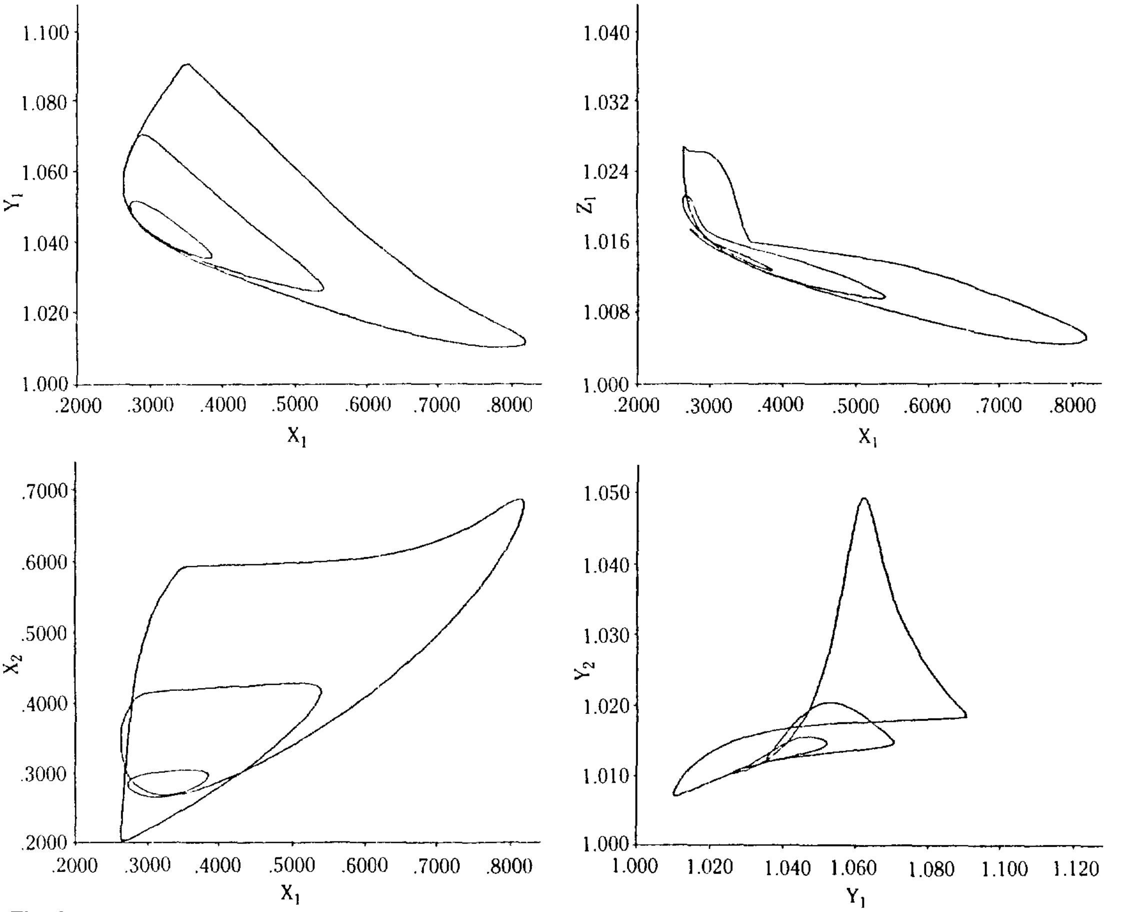

Fig. 13. Stable period of 3T solution [58].

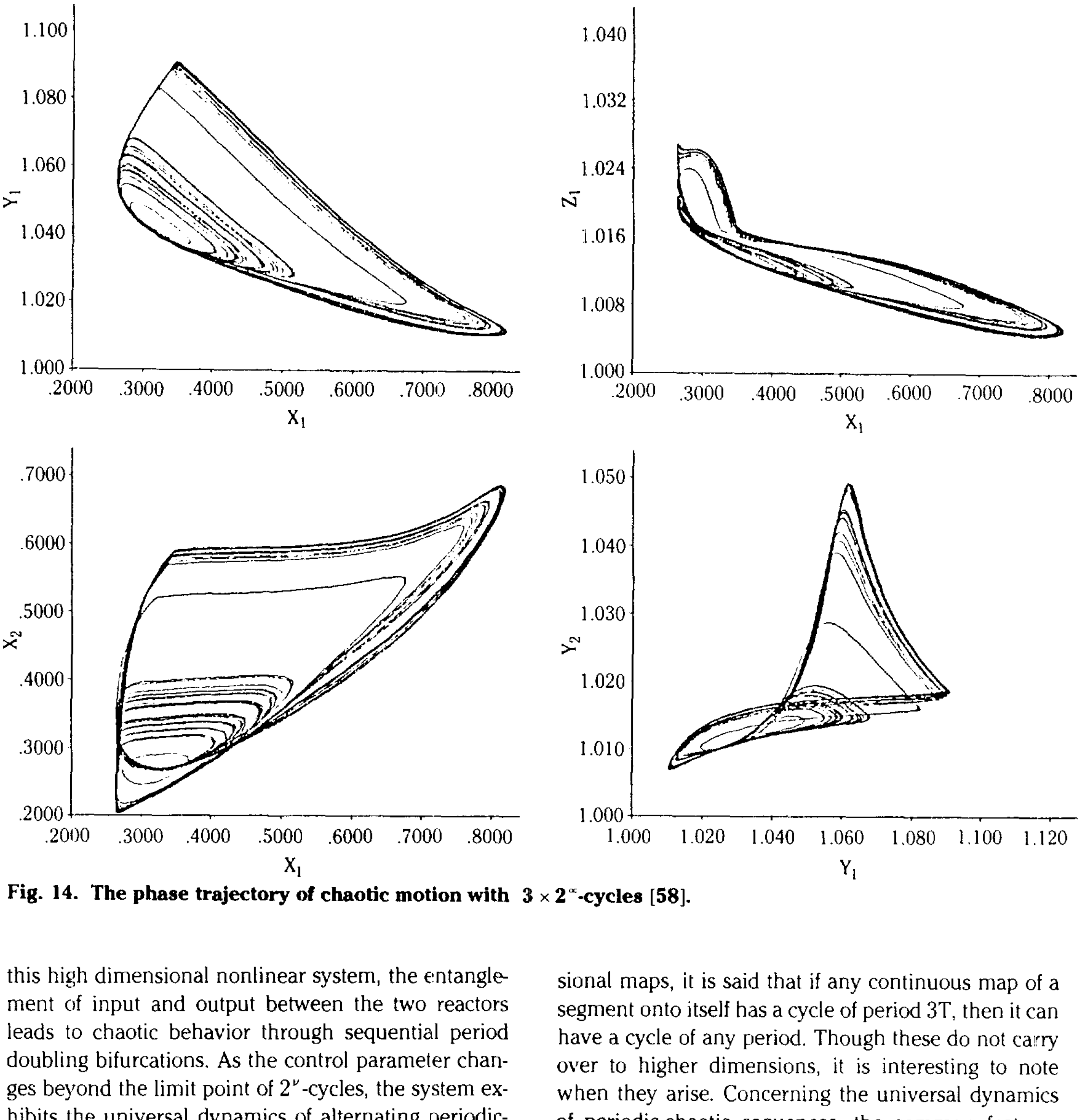

Fig. 14. The phase trajectory of chaotic motion with $3 \times 2^{\infty}$-cycles [58].

this high dimensional nonlinear system, the entanglement of input and output between the two reactors leads to chaotic behavior through sequential period doubling bifurcations. As the control parameter changes beyond the limit point of 2^{ν}-cycles, the system exhibits the universal dynamics of alternating periodic-chaotic sequences with $k \cdot 2^{\nu}$-cycles for every natural number k. Such changes from chaotic motion may result from the collision of the chaotic attractor and a coexisting unstable fixed point or periodic orbit: they have been called *crises* [42]. Such crises may result in the sudden destruction of the chaotic attractor and its basin of attraction, or cause a nonchaotic attractor and ultimately to replace it. During the sequences of $k \cdot 2^{\nu}$-cycles found in this system, k takes from 1 through 7 in the regime. Typically period 3T solution and chaotic $3 \times 2^{\nu}$-cycles are shown in Figure 13 and 14, respectively. Period 3T solutions, in a certain sense, can be regarded as an indicator of chaotic dynamics in mapping or flow. By the theorems[59,60] for one dimensional maps, it is said that if any continuous map of a segment onto itself has a cycle of period 3T, then it can have a cycle of any period. Though these do not carry over to higher dimensions, it is interesting to note when they arise. Concerning the universal dynamics of periodic-chaotic sequences, the common features can be noted as that the sequences are finite; i.e., successive states exist for comparable ranges in parameter space, and the route by which a period state becomes chaotic is in most cases through period-doubling bifurcations.

CONCLUDING REMARKS

We have discussed the various chemical reaction systems involved with a CSTR or CSTRs for some qualitative aspects. Chemical reactions, depending on the physical and chemical properties of the reacting species and mechanisms, can be varied from quite simple to complex structure of reaction steps. Excluded from this review are some complex reaction systems such as Belousov-Zhabotinskii well known for its periodic and aperiodic behavior of dynamics[32,35,36,61,70] and chain reactions of polymerization[62-66]. Regarding biochemical systems, the dynamic character of the predator-prey species growing in a chemostat is also worthy of attention[67,68]. Beside those reaction systems, there are various incorporation of chemical reaction steps revealing oscillatory motions (periodic or aperiodic), which we have not described in detail due to the limitation of space. Considering the whole contexts of substance, we find that this subject has not been completely put in order to resolve the whole dynamic aspects of reaction systems, and there is plenty of room for experimental studies. Engineers must be prepared to encounter chaos as well as varieties of phenomena that the theoreticians have been incorporated into the structure of the subject. Considering the aperiodic or chaotic motions of systems, it is quite a delicate matter that just a nearby point can be the future state (or could be a past state) far away from the present time. We finally hope that this review may help the reader surveying the whole works of this research field. In addition, the works of Razon and Schmitz[69] and Hudson and his colleagues[32,70-73] may deserve special mention as introducing the most thorough treatment, using both experiment and theory, of chaos in the context of chemical reactors.

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