Routes to Chaos in a Reverse-Flow Fixed-Bed Catalytic Combustor

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ABSTRACT

Dynamic simulations and continuation of periodic solutions are conducted to accurately describe the complex dynamic behaviour of a tubular Reverse-Flow Reactor (RFR). Spatio-temporal symmetry proprieties of the reactor model are used to understand complex phenomena and several routes to chaos. The spatio-temporal symmetry influences not only the bifurcation of periodic solution, but also the bifurcation of chaotic regimes and route to chaos. Indeed, special kinds of intermittency are observed and studied. Dynamic regimes are enhanced by the typically high exothermicity and stiff kinetics of combustion reactions.

INTRODUCTION

In the past 30 years, the real advantages of forced unsteady-state operations over conventional steady-state regimes of catalytic fixed-bed reactors have been widely supported (Matros & Buninovich, 1996). Special attention has been devoted to Reverse Flow Reactors (RFR) for catalytic combustion characterized by the periodic alternation of feed introduction between the ends of the packed-bed, in such a way as to trap the high-temperature reaction front. The heat produced by the reaction is thus trapped in the central portion of the reactor; hence it is possible to conduct autothermal operation with gases containing low amounts of combustibles. Recent applications and experimental investigations in RFR have demonstrated that catalytic processes can be enhanced not only for irreversible reactions but also for reversible reactions. Among typical catalytic processes studied with this approach are, for instance: sulphur dioxide oxidation (Boreskov and Matros 1983; Snyder and Subramanian 1993); catalytic combustion (Eigenberger and Nieken 1994).

The rational design and operation of an RFR requires efficient prediction of its performance, in terms of accurate dynamic simulation of spatio-temporal temperature/concentration profiles. Generally, the basic solution of periodically forced systems, such as RFR reactors, is a periodic solution with period equal to the forcing period, namely the double of the switch period. The most common approach to detect periodic regimes is direct simulation. However, dynamic simulations of an RFR are usually very time-consuming because the periodic regimes are attained only after several hundreds of flow reversals.

Furthermore, as model parameters are varied, a cooled RFR can exhibit very complex dynamic behaviour such as multiple stable solutions, subharmonic, quasi-periodic and chaotic solutions (Řeháček et al. 1998; Khinast et al., 1999). Except for some critical parameter values, the behaviour predicted by single- and two-phase models is qualitatively very similar. In fact, complexities in the dynamics are mainly due to heat losses or cooling (Khinast et al., 1999) and to heat axial dispersion (Řeháček et al. 1998).

To properly design a RFR reactor, it is fundamental to foresee any stability change of regime solutions due to changes in the model parameters. In this work, the application of continuation techniques and bifurcation theory proves to be a very powerful tool. Mathematical models of RFR reactors are non-autonomous dynamical systems (namely the vector field explicitly depends on time) with discontinuous periodic forcing. Thus, standard software built for the bifurcational analysis of autonomous systems (like AUTO, Content etc.) cannot be used. However, recently Russo et al. 2002 studies have proposed several techniques to study the stability and to continue periodic solutions of RFR reactors (Russo et al. 2002). In RFR reactors, two routes to chaos have been discovered in previous works: torus doubling bifurcations (Khinast et al. 1999), and torus breakdown (Řeháček et al. 1998). Among these results, particularly interesting is the presence of symmetric and asymmetric solutions (Řeháček et al. 1998; Khinast et al., 1999).

Nevertheless, the role of the symmetry in the bifurcation scenario of a RFR reactor is not well understood. Russo et al., 2002, presented a methodology to study bifurcations of periodic regimes in a class of periodically forced reactors with a spatio-temporal symmetry. The methodology is based on the property that spatio-temporal symmetric systems have a Poincaré map that is an iterate of another map. In this paper, we first assess that a tubular RFR model has a spatio-temporal symmetry.
solution to more complex solutions such as subharmonic, quasiperiodic and chaotic solution, we have conducted a bifurcational analysis of a cooled RFR reactor, previously studied via direct simulations by Řeháček J. et al. 1998.

We will show that the spatio-temporal symmetry of a RFR reactor provides new insights in the complex dynamic behaviour of a RFR reactor. The spatio-temporal symmetry imposes several constraints on the dynamics: for example, some types of bifurcation of symmetric periodic solutions cannot occur (Russo et al. 2002). Here we have used symmetry concepts to conduct an accurate bifurcation analysis and to understand the transition to chaotic regimes and its relevant bifurcations. We will show how, in the routes to chaos, intermittency can be influenced by the symmetry of the system.

MATHEMATICAL MODEL

The reverse-flow catalytic combustor (sketched in Figure 1) is described by a one-dimensional heterogeneous distributed model.

Fig. 1 Schematic of a Reverse-Flow Reactor

The model considers heat and mass transfer resistance between the gas and the solid phase, axial dispersion in the gas phase, axial heat conduction in the solid phase and cooling through the reactor wall. A constant effectiveness factor is assumed. Similar assumptions were made by Řeháček et al. (1998): in the present work, a pseudo steady-state hypothesis for mass balance in the solid phase is assumed. The dimensionless mass and heat balances considering first order reaction on the solid catalyst phase are in the form:

\[
\begin{align*}
\frac{\partial y}{\partial t} &= \frac{1}{Pe_x^r} \frac{\partial^2 y}{\partial z^2} + \left[ \frac{\partial y}{\partial z} - 2g(t) \frac{\partial y}{\partial z} \right] + J_y^* (y_i - y) \\
\frac{\partial \theta}{\partial t} &= \frac{1}{Pe_x^c} \frac{\partial^2 \theta}{\partial z^2} + \left[ \frac{\partial \theta}{\partial z} - 2g(t) \frac{\partial \theta}{\partial z} \right] + J_e^* (\theta_i - \theta) - \varphi (\theta_i - \theta) \\
\frac{\partial \theta}{\partial t} &= \frac{1}{Pe_x^i} \frac{\partial^2 \theta}{\partial z^2} - J_y^* (\theta_i - \theta_i) + B \eta Da (1 - y) \exp \frac{\theta}{1 + \theta / \gamma} \\
J_y^* (y_i - y) &= \eta Da (1 - y) \exp \frac{\theta}{1 + \theta / \gamma}
\end{align*}
\]

Conventional Danckwerts boundary conditions are assumed for concentration and temperature in the gas phase; no flux at both ends in the solid phase is imposed.
The periodic forcing \( g(t) \) takes into account the periodic inversion of the flow. It is a discontinuous function, like a periodic square wave, and defined as:

\[
g(t) = \begin{cases} 
1 & \text{if } 0 \leq t \mod(2) < 1 \\
0 & \text{if } t \mod(2) > 1 
\end{cases}
\]

where \( \tau \) is the period of switching, while the minimum period of \( g \) is \( T=2\tau \). The function \( g(t) \) is one for the flow from the left, and it is zero for the flow from the right. Substituting Eq. 4 into Eq. 1, we obtain a periodic system of tree partial differential equations whose unknowns are \( y_s(z,t) \), \( \theta_s(z,t) \) and \( \theta_\omega(z,t) \).

Time integration has been performed reducing the infinite-dimensional PDE system to a finite-dimensional system by block-orthogonal collocation technique on subdomains. For the investigated parameter ranges, a good numerical accuracy is obtained with twelve collocations points and the finite elements. To study the dynamical behaviour of this system, simulations and bifurcational analysis have been performed making use of the concept of the Poincaré map \( P \). In general, a periodic orbit of a continuous-time system may intersect a Poincaré section \( k \) times before closing onto itself: fixed points of the \( P \) map correspond univocally to \( T \)-periodic orbits of the continuous-time system; fixed points of \( P_k \) correspond to \( k \)-th-order subharmonic solutions of the continuous-time system.

**SPATIO-TEMPORAL SYMMETRIES**

As demonstrated in Russo et al. (2002), periodic forcing may induce symmetry properties into mathematical models of chemical reactors. Symmetry properties are defined as invariance properties with respect to a set of transformations that forms a group, namely a symmetry group. Symmetric systems with only spatial symmetry have a vector field that is invariant respect to transformations, involving only spatial variables. On the contrary, a spatio-temporal symmetric system has a vector field invariant under the application of transformations that also involve the temporal variable. It can be shown (Russo et al., in preparation, 2004) that a tubular RFR mathematical model has a spatio-temporal symmetry. This symmetry is only due to the presence of the forcing function and imposes several constraints on the underlying dynamical system. First of all, this property is reflected by the presence of both symmetric and asymmetric regimes. Denoting with \( A \) the \( \omega \)-limit set of a generic regime, we define a spatio-temporal symmetric regime as follows:

\[
A = G(A)
\]

This definition includes discrete travelling wave regime solutions as well as more complex regimes as quasi-periodic and chaotic regimes. A peculiar property of systems with spatio-temporal symmetry is that the Poincaré map is the iterate of another map. In our case, it is possible to define a smooth map \( H \) whose second iterate coincides with \( P \). This map, which is not a stroboscopic map because it is not an orbit sampling, is related to the Poincaré map by the relation:
Equation (6) represents the essence of the spatio-temporal symmetry in Eqs. (1)-(3) and poses strong constraints to its dynamics and possible bifurcations. In fact, symmetric regimes cannot possess all bifurcations that an asymmetric periodic solution may have. Particularly, symmetric regimes cannot exhibit generic flip bifurcations (Swift & Wiesenfeld, 1984). Moreover, non-generic bifurcations, such as pitchfork bifurcations, become generic (Kuznetsov, 1998).

RESULTS

One of the typical routes to chaotic attractors is intermittency. There are many examples, especially in hydrodynamics, of experimental and numerical observation of this phenomenon. Intermittency in fluid mechanics refers to the state in which the laminar flow is interrupted by turbulent outbreaks or bursts at irregular intervals. In spatially extended physical systems, spatio-temporal intermittency is one of the different forms of spatio-temporal chaos. Although in many systems this phenomenon originates in the spatial structure of the physical problem, it has been shown, theoretically and experimentally, that temporal intermittency can exist in dynamical systems with a finite number of modes. In this context, intermittent chaos is the phenomenon shown by systems exhibiting long sequences of periodic-like behaviour (“laminar” phases) separated by comparatively short chaotic eruptions. The first classification of this transition has been presented by the pioneering work of Pomeau and Manneville, 1980. They proposed three types of intermittencies, also called Type I, Type II and Type III.

![Patterns of Type-III intermittency in the Reverse-Flow Reactor: (a) τ=245.1, (b) τ=245.0](image)

For values of the generic control parameter $r$ less then a critical values $r_i$, the dynamical system has an attracting limit cycle. Thus the system oscillates in a regular fashion and is stable to small perturbations. An example is given in Figure 2(b), which shows a time series in the RFR, where the control parameter in this case is the switching time $\tau$. As $r$ slightly exceeds the threshold value $r_i$ (the intermittency threshold), the system response consists of long stretches of oscillations (laminar phases) that appear to be regular and closely resemble the oscillatory behaviour for $r<r_i$, but this regular behaviour is intermittently interrupted by chaotic outbreaks (turbulent bursts) at irregular intervals. An example is shown in Fig. 2(a). With increasing $r$, the laminar phases between two consecutive bursts become shorter and shorter and difficult to recognize. As $r$ is increased further, eventually the laminar phases disappear and the response becomes fully irregular. It is possible to define a mean time $F(r)$ between the bursts. As $r$ approaches $r_i$ from above, the average time between bursts approaches infinity:

$$\lim_{r \to r_i} F(r) = +\infty$$

The attractor orbit thus becomes always laminar so that the motion is periodic. As afore described, in the intermittency mechanism, as a control parameter $r$ exceeds the intermittency threshold $r_i$, the system response explodes into a larger attractor with the old periodic attractor being a subset of the new chaotic attractor. Thus, as a result of the bifurcation, a periodic orbit is replaced with chaos rather than with a nearby stable periodic
orbit. This is implied by the fact that, during the burst, the trajectory goes far away from the vicinity of the periodic orbit that exists for \( r \leq r_i \). This necessarily implies that the stable attracting periodic orbit either becomes unstable or is destroyed as \( r \) is increased through \( r_i \). Three kind of generic bifurcations which meet these requirements are the saddle-node bifurcation, the subcritical Hopf bifurcation, and the subcritical period doubling bifurcation of a periodic orbit. Pomeau and Manneville, 1980, labelled the intermittency mechanism associated with these bifurcations as type I, type II, and type III, respectively. Since our system, due to symmetry, cannot exhibit subcritical period doubling bifurcation of symmetric solutions, the type-III intermittency must be related to a subcritical pitchfork bifurcation.

![Fig. 3 Solution diagram for \( \tau \) as the bifurcation parameter. The state is represented by the outlet temperature (\( \vartheta_{\text{g,out}} \)) in the gas phase.](image)

Figure 3 reports a solution diagram for our system. Type-III intermittency, in fact, is encountered in correspondence of the P1 subcritical pitchfork bifurcation, when \( \tau \) assumes the critical value, equal to 245.075 (cfr 245.0 and 245.1 corresponding to Fig. 2b and 2a respectively). This gives rise to symmetric chaos that exists in the whole range of \( \tau \) between P1 and the NS1 Neimark-Sacker bifurcation. Astride of NS1 a Type-II intermittency is observed (Fig. 4). Here the time series for two different initial conditions, picked in correspondence of the two just–become–unstable G-conjugate asymmetric periodic solutions, represented in the upper and lower unstable branch, slightly left of the NS1 bifurcation value of \( \tau \). It is observed how both time series, after a short seemingly periodic behaviour, begin to dance between the two “ghost” periodic solutions, marking each transition with a burst. It is also observed how the system moves from an asymmetric solution pair to a symmetric chaos.

Finally, it must be noted that, in general, the loss of stability of a periodic orbit via one of the aforementioned three generic bifurcations is not sufficient for intermittency to occur. The other necessary condition is the existence of a global “relaminarization” mechanism that repeatedly rejects the trajectory towards the neighbourhood of the original periodic orbit (ghost or phantom orbit). Otherwise, the trajectory will always revisit the ghost orbit.

**CONCLUSIONS**

The spatio-temporal symmetry of a catalytic reverse-flow combustor influences the routes to chaos like intermittency phenomena. The understanding of this peculiar mechanism is important to correctly predict the reactor behaviour when periodic solutions lose stability. Particularly, bursts are catastrophic events that can damage the catalyst bed for the extremely high values of the temperature that can be reached by the system. Moreover, intermittency is hard to identify by simulation only, and bifurcation analysis proves to be a reliable tool.

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1 As a remainder, in the Hopf bifurcation of a periodic orbit the orbit goes unstable by having a complex conjugate pair of Floquet multipliers pass thought the unit circle; in the saddle-node bifurcation, a stable Floquet multipliers (inside the unit circle) and a unstable Floquet multipliers (outside the unit circle) come together and coalesce at the point +1; in the subcritical period doubling bifurcation a Floquet multiplier goer from inside to outside the unit circle by passing through -1.
Fig. 4 Patterns of Type-II intermittency in the Reverse-Flow Reactor; $\tau = 498.0$

REFERENCES


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