

Bifurcation analysis of discontinuous periodically forced reactors

E. Mancusi¹, L. Russo² and G. Continillo¹

¹*Dipartimento di Ingegneria, Università del Sannio, Piazza Roma, 82100, Benevento*

²*Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli "Federico II"*

Piazzale Tecchio 80, 80125 Napoli

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Periodic forcing of chemical processes, as a means to obtain better average performance (in terms of yield, selectivity, conversion) compared to steady-state operation, has been a widely studied subject for a long time (e.g. Bailey, 1973; Matros and Bunimovich, 1996). Particularly, in the last 30 years, the real advantages of forced unsteady-state operation over conventional steady-state regimes of catalytic fixed-bed combustors have been widely supported also experimentally. For such reactors, dynamic regimes are, in many cases, induced by periodically reverting the flow direction while keeping constant feed temperature and composition. For such kind of reactor, named "Reverse Flow Reactor" (RFR), the desired regime is a periodic regime with the same period of the forcing action. However, for certain values of design or operation parameters, a much richer dynamics exists, with multi-periodic, quasi-periodic and chaotic regime solutions. This was found for instance in tubular catalytic fixed-bed combustors (Reháček *et al.*, 1992, 1998; Khinast *et al.*, 1998).

In order to properly design and control periodically forced reactors, it is necessary to accurately describe all the regime conditions when relevant design and operation parameters are changed. The most comprehensive approach to accurately describe changes in stability and nature of regime solutions is the systematic application of bifurcation analysis and of continuation techniques. This approach would be able to characterise all the periodic regimes of these reactors including non-stable regimes such as saddle-type limit cycles (e.g. Doedel 1997; Kuznetsov 1998).

The main difficulties of this approach for RFRs are the non-autonomous nature of the models and the presence of a discontinuous forcing. In fact standard and popular codes for automatic continuation,

¹ Corresponding author Prof. Gaetano Continillo: continillo@unisannio.it

such as for example AUTO (Doedel *et al.*, 1997), CONTENT (Kuznetsov *et al.*, 1996), can be easily applied only to autonomous continuous and discrete systems.

In this work we conduct the bifurcation analysis of periodically-forced systems with time-discontinuous forcing as for reverse flow reactors (RFRs). The technique introduced is based on the application of pseudo-arclength continuation methods to the Poincaré map P obtained numerically (Mancusi *et al.*, 2002; Russo *et al.*; 2002). This method can be applied to a generic periodic system with one or more discontinuities in the mathematical model. The proposed technique permits the continuation of all T -periodic and kT -periodic regimes and also allows to trace out the loci of bifurcation points in a two-parameter space.

A tubular catalytic combustor

The two-phase model of the fixed bed catalytic reactor is essentially the one studied earlier by Reháček *et al.* (1992, 1998). The model considers heat and mass transfer between the gas and the solid-phase, axial dispersion in the gas-phase and axial heat conduction in the solid-phase and cooling through the reactor wall. For simplicity, a constant effectiveness factor and a pseudo steady-state for the mass balance in the solid phase are assumed (Cittadini *et al.*, 1999). The dimensionless mass and heat balances, considering first order reaction on the solid catalyst phase, are in the form:

$$\begin{aligned}
 \frac{\partial \mathbf{a}_g}{\partial t} &= \frac{1}{Pe^m} \frac{\partial^2 y}{\partial z^2} + [1 - 2g(t)] \frac{\partial y}{\partial z} + J_g^m (w - \mathbf{a}_g) \\
 \frac{\partial \mathbf{J}_g}{\partial t} &= \frac{1}{Pe_g^h} \frac{\partial^2 \mathbf{J}_g}{\partial z^2} + [1 - 2g(t)] \frac{\partial \mathbf{J}_g}{\partial z} + J_g^h (\mathbf{J}_s - \mathbf{J}_g) - \mathbf{f}(\mathbf{J}_g - \mathbf{J}_w) \\
 \frac{\partial \mathbf{J}_s}{\partial t} &= \frac{1}{Pe_s^h} \frac{\partial^2 \mathbf{J}_s}{\partial z^2} - J_s^h (\mathbf{J}_s - \mathbf{J}_g) + BhDa(1 - \mathbf{a}_s) \exp \frac{J_s}{1 + J_s/g} \\
 J_s^m (\mathbf{a}_s - \mathbf{a}_g) &= hDa(1 - \mathbf{a}_s) \exp \frac{J_s}{1 + J_s/g}
 \end{aligned}
 \quad g(t) = \begin{cases} 1 & \text{if } 0 \leq \frac{t}{T} \bmod(2) < 1 \\ 0 & \text{if } \frac{t}{T} \bmod(2) > 1 \end{cases} \quad (1)$$

Conventional Danckwerts boundary conditions are assumed for concentration and temperature in the gas-phase. Model details are found in Mancusi *et al.* (2002). Figure 1 reports the solution diagram

obtained by varying the switching time τ . In these diagrams, filled squares represent Neimark-Sacker bifurcation points and filled triangles represent flip bifurcations.

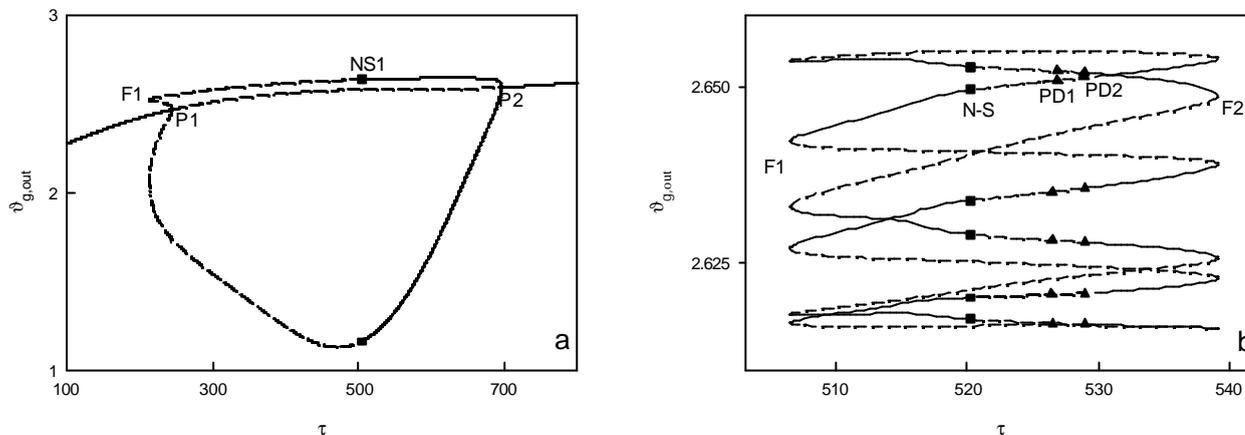


Figure 1 – (a) Solution diagram for τ as the bifurcation parameter. The state is represented by the outlet temperature ($J_{g,out}$) in the gas phase at the inversion time t for symmetric regimes and at time T for asymmetric regimes. (b) Solution diagram of a $6T$ -periodic asymmetric subharmonic regime for τ as the bifurcation parameter.

Starting from low values of τ , the symmetric solution (see Russo *et al.*, 2002) is stable until a pitchfork bifurcation (P1) is met. By further increasing the inversion period, another pitchfork bifurcation (P2) is encountered and the unstable symmetric solution regains stability. Two unstable branches of asymmetric periodic regimes emerge from the subcritical pitchfork bifurcation P1. On these branches a fold bifurcation (F1) is first encountered, then, through a Neimark-Sacker bifurcation (N-S1) these asymmetric regimes become stable. Again, the two G -conjugate asymmetric regimes experience the same bifurcations. Finally these regimes merge and disappear with a supercritical pitchfork bifurcation (P2).

As it is observed in Fig. 1(a), a wide interval of the bifurcation parameter τ exists, in which there are no stable T -periodic regimes. In this range, chaotic, quasi-periodic and kT -periodic subharmonic regimes are found. It is interesting to test the capability of the proposed technique in constructing solution branches for kT -periodic subharmonic regimes for a dynamical system of relatively high dimension. To this aim, the case of a $6T$ -periodic subharmonic regime, earlier described by Reháček *et al.* (1998), is chosen. As a result of the analysis, an even more complex dynamic behaviour, with multistability, is found. By continuation of the 6th iterate of the Poincaré map the solution diagram was obtained and reported in Fig. 1(b). Particularly, Figure 1(b) reports a typical isola of periodic behaviour with resonant

regimes (frequency-locking). This window is bounded by saddle-node bifurcations (F1 and F2). On the stable branches, the system exhibits, as the bifurcation parameter is increased, a Neimark-Sacker (N-S in the figure) and two flip (PD1 and PD2) bifurcations. In this case the two flip bifurcations can exist because the regimes are asymmetric.

Concluding remarks and future developments

The technique presented permits to implement a pseudo-arclength continuation method to analyse models of periodic systems with one or more discontinuities in the governing equations. Thus it is possible to conduct an accurate bifurcation analysis and to characterise resonant solutions by constructing solution diagrams and bifurcation diagrams. The latter permit to identify regions of existence of frequency-locking isolae by determining Arnold angles.

At present, the analysis is demanding in terms of computer time. Constructing Fig1b on an ALPHA STATION 666 Mhz took about 250 hours, 85% of which were used to compute the Poincaré map by means of LSODE routines. Parallelisation of the integration process of the ordinary differential equations is the objective of ongoing work.

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