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Network of three catalytic reactors with periodical feed switching for methanol synthesis: bifurcation analysis.

Marco Pota[a], Lucia Russo[b], Erasmo Mancusi[c] and Silvestro Crescitelli[a]

[a] *Dipartimento di Ingegneria Chimica, Università "Federico II", Piazzale Tecchio 80, 80125 Napoli, Italy*
[b]*Dipartimento di Ingegneria Chimica ed Alimentare,Università di Salerno, Via Ponte Don Melillo, 84084, Fisciano(SA), Italy.*
[c]*Facoltà di Ingegneria, Università del Sannio, Piazza Roma, 82100, Benevento, Italy.*

Abstract

In this paper the bifurcation analysis of a network of three catalytic reactors with periodical feed switching for methanol synthesis is carried out and the influence of switch time on the stability and on the performance is addressed. With a methodology based on the construction of discrete maps, the continuation of periodic regimes and the detection of bifurcations are systematically conducted as the switch time is varied. Several complex regimes are found in a wide range of the switch time. Catastrophic transitions from periodic to quasiperiodic and multiperiodic regimes are detected and discussed. These catastrophic bifurcations are found very close to the optimal periodic regime in methanol yield.

Keywords: periodically forced reactor, network of reactors, methanol synthesis.

1. Introduction

Periodically forced catalytic reactors have attracted considerable interest in the last years. Such operation modes possibly overcome thermodynamic and kinetic limitations by changing the feed direction or by periodically changing some operating parameters such as temperature or concentration of the system. Many studies have shown that catalytic reverse flow reactors (RFR), in which the flow direction is periodically reversed, is very efficient to conduct autothermally the purification of industrial off-gas with a low concentration of volatile organic compounds. The RFRs have proven to be cost-effective also for other catalytic processes, in which equilibrium-limited exothermic reactions are carried out (e.g. methanol synthesis (Froment, 1990), ammonia synthesis and oxidation of SO_2 (Matros and Bunimovich (1996)). In these processes, reverting the flow direction produces a bell-shaped temperature profile in the reactor close to the optimal temperature distribution which increases yield and selectivity towards the main product. To overcome some intrinsic disadvantage of the RFRs as the washout effect (the loss of reactants immediately upon the flow reversal), Matros (1985) has suggested a network of catalytic reactors in series equipped with a valve system that allows cyclic permutation of the feed position. Van den Bussche and Froment (1996) studied the feasibility of methanol synthesis in a periodically forced network of three catalytic reactors (the STAR configuration) which gives a higher conversion than the reverse flow reactor. Velardi and Barresi (2002) analyzed the methanol synthesis in a three reactors network with a periodical changing of the feed position, as originally proposed by Matros (1985). Using a brute force analysis they assess that periodic

regimes and autothermal behavior are possible only for two relatively small ranges of the switch time, although the network allows higher conversions than in RFR. In a successive work Velardi et al. (2004) showed that complex dynamics may arise close to the conditions of maximum conversion.
In this framework, nonlinear dynamics tools are proved very successful to predict and completely characterize all regimes as the model parameters are varied.
In this paper, we conduct a systematic study of the dynamic behaviour of a periodically forced network of three catalytic reactors for the methanol synthesis through bifurcation analysis. Using the methodology based on the symmetry properties of a periodically forced network of reactors previously established (Russo et al.2002, 2006), bifurcation diagrams are derived with a continuation technique based on the construction of discrete maps (Russo et al.2002). The switch time is chosen as bifurcation parameter for its relevance on both design and control of the system.

2. The mathematical model.

In the present work, a network of three fixed-bed reactors is considered. Each fixed-bed reactor is modeled as a heterogeneous system with 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 at the reactor wall. A similar model was implemented by Velardi and Barresi (2002) but in the present work we considered a constant value of the total concentration in the gas phase and a pseudo-steady-state hypothesis for mass balance in the solid phase. Within the hypotheses, the mathematical model for the reactors network reads:

$$\frac{\partial T_G^i}{\partial t} = \frac{k_{eff}}{\rho \cdot c_{P,G}} \frac{\partial^2 T_G^i}{\partial x^2} - v \cdot \frac{\partial T_G^i}{\partial x} + \frac{h_f \cdot a_v}{\varepsilon \cdot \rho \cdot c_{P,G}} \cdot (T_S^i - T_G^i), \tag{1}$$

$$\frac{\partial T_S^i}{\partial t} = \frac{\lambda_S}{\rho_S c_{P,S}} \left(\frac{\partial^2 T_S^i}{\partial x^2} \right) - \frac{h_f \cdot a_v}{\rho_S c_{P,S} (1-\varepsilon)} \cdot (T_S^i - T_G^i) + \frac{1}{c_{P,S}} \sum_{i=1}^{n_r} \left[\left(\sum_{k=1}^{n_r} \nu_{i,k} R'_k \right) \left(-\Delta H_{f,i} \right) \right] \tag{2}$$

$$\frac{\partial y_{G,j}^i}{\partial t} = D_{eff,j} \cdot \frac{\partial^2 y_{G,j}^i}{\partial x^2} - v \frac{\partial y_{G,j}^i}{\partial x} + \frac{k_{G,j}}{\varepsilon} \cdot (y_{S,j}^i - y_{G,j}^i) \cdot a_v - y_{G,j}^i \sum_{k=1}^{n_r} \frac{k_{G,k}}{\varepsilon} \cdot (y_{S,k}^i - y_{G,k}^i) \cdot a_v \tag{3}$$

$$k_{G,j} \cdot c_G \cdot \left(y_{S,j}^i - y_{G,j}^i \right) \cdot a_v = \rho_S (1-\varepsilon) \cdot \sum_{k=1}^{N_r} \nu_{j,k} R'_k \tag{4}$$

with the following boundary conditions:

$$\left. \frac{D_{eff,j}}{v} \frac{\partial y_{G,j}^i}{\partial x} \right|_0 = y_{G,j}^i(0,t) - \left[1 - f\left(t-(i-1)\tau\right) \right] y_{G0,j} - \left[f\left(t-(i-1)\tau\right) \right] y_{G,j}^{i-1}(L,t) \tag{5}$$

$$\left. \frac{k_{eff}}{\rho \cdot v \cdot c_{P,G}} \frac{\partial T_G^i}{\partial x} \right|_0 = T_G^i(0,t) - \left[1 - f(t-(i-1)\tau \right] T_{G0} - \left[f\left(t-(i-1)\tau\right) \right] T_G^{i-1}(L,t) \tag{6}$$

$$\lambda_S \left. \frac{\partial T_S^i}{\partial x} \right|_0 = D_{eff,j} \left. \frac{\partial y_{G,j}^i}{\partial x} \right|_L = k_{eff} \left. \frac{\partial T_G^i}{\partial x} \right|_L = \lambda_S \left. \frac{\partial T_S^i}{\partial x} \right|_L = 0 \tag{7}$$

The subscript $j = 1...n_r$ indicates the j-th chemical species while the superscript i=1,2,3 indicates the i-th reactor of the network. For the nomenclature we refer to that adopted by Velardi and Barresi (2002).

The function *f(t)* is a square wave that accounts for the discontinuous feed scheme (Fig.1). The reactors are fed according to the sequence 1-2-3 in the time range $[0,\tau]$; after the first switch, that is in the range $[\tau,2\tau]$, they are fed according to the sequence 2-3-1; then, after the second switch ($t\in[2\tau, 3\tau]$), the reactors are fed as the sequence 3-1-2; the next switch brings the feed sequence to the first one, i.e., 1-2-3, and the permutation cycle restarts.

It is apparent that the vector field changes discontinuously in time, and it recovers the same form after a time $3\tau=T$. Indeed, *f(t)* is a discontinuous periodic function with minimum period T, and the non–autonomous system (1)-(3) is T periodic.

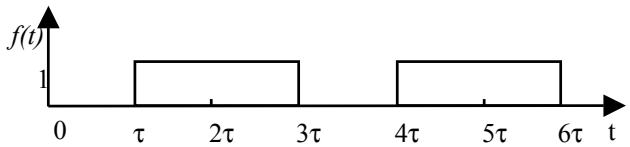

Figure 1 – The forcing function *f(t)* appearing in the boundary conditions of Eqs. (5)-(7).

For methanol synthesis from CO, CO_2 and H_2 over commercial Cu-Zn-Al catalyst, the model is completed by the kinetic equations given by Graaf et al. (1988), based on three independent reactions:

$$\begin{aligned}&(A)\ CO + 2H_2 \rightleftarrows CH_3OH\\ &(B)\ CO_2 + H_2 \rightleftarrows CO + H_2O\\ &(C)\ CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O\end{aligned} \tag{8}$$

The adopted reaction rates, reported in Graaf et al. (1988), are written in terms of partial pressure (Velardi and Barresi, 2002). Here we assumed a catalyst efficiency equal to one.With these hypotheses, the model (1)-(7) is a system of 6 partial differential equations and 6 algebraic equations. The numerical simulations are carried out by discretising the system through a collocation method with 8 collocation nodes for each reactor. The time integration of the discretised system of ODEs is performed with LSODE code. The conditions used for the numerical results are the same adopted by Valardi and Barresi (2002)and they are reported in Table I.

Reactor length	0.5 m
Void fraction	0.4
Catalyst density	1750 Kg m^{-3}
Catalyst void fraction	0.5
Pellets diameter	0.0054 m
Total pressure	50 atm
Y_{H2}^{in}	0.935
Y_{CO}^{in}	0.045
F^{in}	32.65 mol m^{-2} s^{-1}
T_G^{in}	420 K

Table I Conditions adopted in the simulations.

3. Results

The switch time is an important operating parameter as proper forcing may induce reactor ignition and different performances, and it can be used as manipulated variable in a control law. Thus, the knowledge of the bifurcation behaviour of the reactor network as the switch time is varied is of value as it allows a quick and complete characterization of reactor performances in terms of ignition and switch off.
The regime solution diagram shown in Fig. 2 presents the influence of the switch time on network dynamics and it is obtained with the continuation technique described in Russo et al. (2002, 2006). Each point of the diagram is representative of a T-periodic regime.

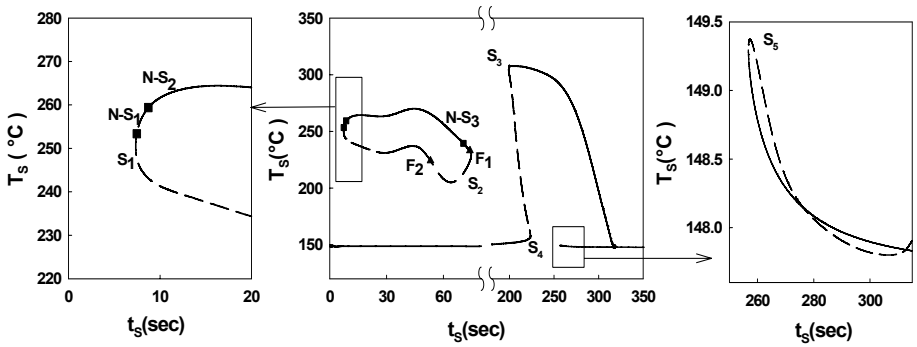

Fig.2. The symmetric T-periodic solution diagram with the switch time, τ, as bifurcation parameter. The solution is reported with the solid temperature at the exit catalyst layer. Solid lines: stable T periodic regimes; dashed lines: unstable T periodic regimes; Fold bifurcations are indicated with the letter S, Flip bifurcations are indicated with the letter F and filled triangles.

The diagram is constituted by two curves: an isola and a mushroom-shaped curve. On the curve with a mushroom shape four fold bifurcations are detected. The two branches, corresponding to $0<\tau<\tau_{S4}$ and $\tau>\tau_{S6}$, are constituted by non-ignited T-periodic regimes where $T^{out}\approx T^{in}$, while the upper branch, delimited by the fold bifurcations S_3 and S_5, corresponds to ignited T-periodic regimes. Then, a multiplicity is detected in the ranges $[\tau_{S3}, \tau_{S4}]$ and $[\tau_{S5}, \tau_{S6}]$. On the T-periodic curve corresponding to the isola delimitated by $[\tau_{S1}, \tau_{S2}]$, different bifurcations leading to complex regimes are detected. These regimes are determined via simulation, and their asymptotic behavior, which varies with the switch time, is reported in Fig.3.
In Fig.3, one thousand iterates of the Poincarè map after transients have died out are plotted for each τ-value. Data have been calculated via numerical simulation starting from one regime solution and the bifurcation parameter has been continuously changed. Once the regime solution was reached, this solution was used as initial condition of the subsequent simulation.
An aperiodic complex regime (quasiperiodic or chaotic) corresponds in Fig.3 to a vertical line for a fixed parameter value, while a kT-periodic regime corresponds to k points placed on a vertical line.
It is apparent from Fig.3 that a quasiperiodic regime exists over a wide range of the bifurcation parameter ([0, 40]). This quasiperiodic regime arises from the subcritical N-S_2 and it coexists with a stable ignited T-periodic regime in almost all range of existence. After a range where only the T-periodic regime exists as ignited regime ($40<\tau<50$), a multiplicity of two 4T-periodic regimes appears. Increasing further the

switch time, windows of multiperiodic and quasiperiodic ignited regimes alternate in a wide range of the bifurcation parameter. The transitions from quasiperiodic regimes to multiperiodic ones are characterized by frequency-locking phenomena (Mancusi et al.2004).

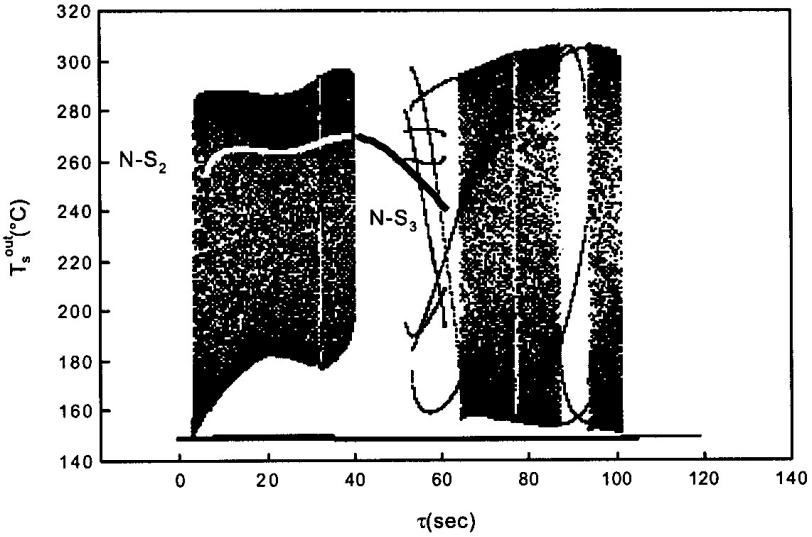

Fig.3. The asymptotic behavior for $\tau \in [0, 110]$. The state is represented by the solid temperature at the exit catalyst layer.

It should be noted that the presence of subcritical, and thus catastrophic, Neimark Sacker bifurcations (N-S_2 and N-S_3 in Fig.2) may lead to plant operating problems. Indeed, when the network operates in a T-periodic regime close to Neimark Sacker bifurcation points N-S_2 or N- S_3, a disturbance in the bifurcation parameter could lead to jump to a quasi-periodic attractor characterized by larger amplitude oscillations of the vector state. Moreover, even far from the Neimark-Sacker bifurcation, the coexistence of operating T-periodic regime with other complex regimes may induce some problems to the process conduction.

Despite of the complexity of the dynamic behaviour of the system, this range of the switch time has a great interest in terms of methanol yield.

Indeed, as it is shown in Fig.4, for low switch time (τ=35.969) and in correspondence of the T-periodic regime, the methanol yield is maximum ($\bar{y}^{out}_{CH_3OH} = 0.0387$). However, the optimal T-periodic regime coexists with a quasiperiodic regime, and then it should be preferred, for safety reasons, a T-periodic regime with a slightly lower yield but in a range of the switch time without multiplicity. For low switch times, this range is very narrow [40,50] and it is embedded in the parameter region where quasiperiodic and multiperiodic regimes can be easily found. It should be noted that, although these complex regimes should be avoided for a safe operation, they are characterized by high average methanol yield. From the other hand, for higher switch time in the range [200,280], although the methanol yield is not maximum, a safe operation can be conducted with a methanol yield comparable with that obtained with a reverse flow reactor (Velardi and Barresi, 2002).

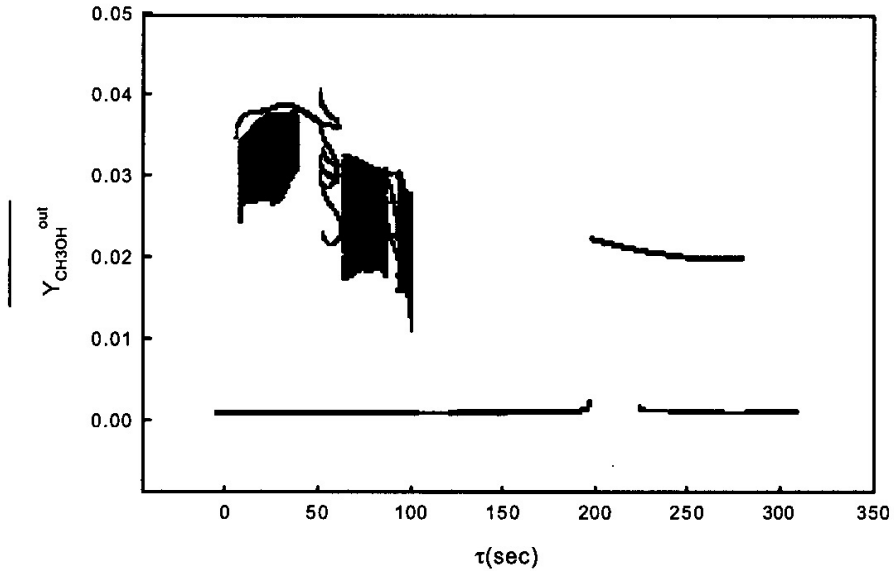

Fig.4. The asymptotic behaviour for $\tau \in [0, 300]$. The state is represented by the average mole fraction of methanol at the exit.

4. Conclusions

In this work a non linear analysis of a network of three catalytic fixed-bed reactors for methanol synthesis has been performed. The bifurcation analysis of the periodic regime is conducted by a continuation technique based on the construction of discrete maps. Using the switch time as bifurcation parameter, two different curves of T-periodic regimes are detected: an isola and a mushroom shaped curve. On the isola catastrophic bifurcations are detected which lead to complex regimes like quasiperiodic and multiperiodic regimes. The complex dynamic behaviour is found only in the range of low switch time values. In this parameter range, despite of the complexity of the dynamics, it was detected the optimal T-periodic regime in yield in methanol. Thus, a suitable control policy should be adopted to operate at low switch times.

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