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Multiplicity of Temperature Wave Trains in Periodically Forced Reactors Networks

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Networks of catalytic reactors with periodically switched inlet and outlet sections offer a competitive technological solution to the operation of reversible exothermic reactions. Traditionally, this operation mode is implemented by periodically shifting inlet and outlet sections so as to jump a single reactor unit in the flow direction. Here, a network of four catalytic reactors carrying on the methanol synthesis process is considered and the effect of varying the number of reactor units jumped by inlet and outlet ports on network stability and performance is investigated. Bifurcational analysis is performed to characterize the stability range of periodic regimes and to systematically analyze multiplicities and bifurcations as the switching velocity is varied and at different numbers of reactor units jumped by inlet and outlet sections.

1. Introduction

Networks (NTWs) of catalytic reactors with periodically switched inlet and outlet ports have been proved to offer an effective technological solution to achieve autothermal operation of exothermic catalytic processes (Matros, 1989). The periodic variation of the NTW feeding sequence enables to trap an exothermic reaction front within the bed ensuring the possibility to operate at high conversion regimes even with streams characterized by very low adiabatic temperature rise. Since the NTW keeps unchanged the flow direction, it also prevents the emission of unconverted reactants caused by the inversion of the flow in the RFR. Moreover, the formation of a declining temperature zone close to the NTW outlet sections makes this solution competitive as reversible exothermic reactions are considered, guaranteeing a significant increase in the average conversion due to achievement of more favorable thermodynamic equilibrium conditions (Velardi and Barresi 2002; Sheinman and Sheintuch, 2009). NTWs of reactors are periodically forced systems which exhibits spatio-temporal symmetries (Russo et al. 2002). As a consequence, if T is the system period, that is the time after which the NTW recovers the same feeding sequence, the expected regimes of the forced NTW are symmetric T periodic. Under symmetric regime, each reactor of the NTW exhibits the same spatial profile only shifted of a time corresponding to the switch period.

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When the forced NTW is operated at switching to thermal velocity ratios around unity, these regimes are characterized by a single travelling temperature waves (Sheintuch and Nekhamkina, 2005). Outside of this range, transitions to multi-periodic, quasi-periodic and chaotic solutions as well symmetry breaking bifurcations can likely occur.

Most of the studies on the forced NTW have focused on the implementation of a unique switching strategy. Typically, inlet and outlet NTW sections are shifted in the flow direction so as to jump at switching a single reactor unit. Yet, N-1 alternative operating strategies, N being the total number of reactor units, can be conceived by varying the number of reactor units jumped by inlet and outlet sections between 1 and N-1 while keeping unchanged the flow direction through the bed. When applied to irreversible exothermic reactions, the strategy where N-1 reactors are jumped has been proved to significantly enlarge the domain of stability of symmetric T-periodic regimes (Russo et al., 2007). Moreover, its application in the context of reversible exothermic reactions has been shown to sustain the formation of symmetric T-periodic regimes corresponding to temperature wave trains previously undetected (Mancusi et al., 2010). The analysis of wave trains regimes is of great practical relevance for reversible exothermic reactions as these regimes well reproduce the inter-stage cooling effect of multistage fixed bed reactors. Despite the practical relevance of these arguments, the potential advantages of different operating strategies remain still largely unexplored. These solutions exist within regions of the parameter space separated by domains of extinguished regimes and thus bifurcations delimitating such ranges should be detected. Moreover, the bifurcation analysis of periodic regimes may help in the study of possible coexisting stable and unstable regimes.

In this paper, a systematic study of the effects of different switching strategies on the performance and the stability characteristics of a NTW of catalytic reactors for methanol synthesis is presented. Particularly, a NTW of four catalytic reactors is considered and the effect of varying the number of reactor units jumped by inlet and outlet ports on network stability and performance is investigated. To this aim, bifurcation analysis is performed enabling to characterize the stability range of periodic regimes and identify domains of coexistence of multiple stable regimes.

2. Switching strategies and model equations

We consider a NTW of four identical fixed-bed catalytic reactors, that is N=4. Therefore, three different switching strategies keeping unchanged the flow direction are possible as the number of reactors n_s jumped by inlet and outlet ports in the flow direction is varied: strategy-1, strategy-2 and strategy-3 corresponding to n_s =1, 2 and 3, respectively. The three switching strategies are described in Fig.1. A one-dimensional pseudo-homogeneous model taking into account axial mass and energy dispersive transport is considered for each reactor.

Moreover, it is assumed that the only following reaction occurs:

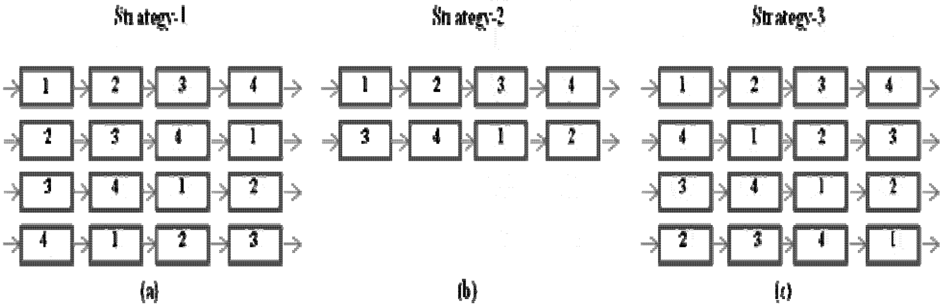

Figure 1: A schematic representation of the three different switching strategies: strategy-1 (a), strategy-2 (b), strategy-3 (c).

$$CO+2H_2 \underset{r_{-1}}{\overset{r_1}{\rightleftharpoons}} CH_3OH \tag{1}$$

The kinetic rate equation employed for this reaction is the one employed in (Sheinman and Sheintuch, 2009). Therefore, the dimensionless mass and energy balances for the i-th reactor of the NTW write as follows:

$$\begin{cases} Le\dfrac{\partial \vartheta_i}{\partial \bar{t}} + v\dfrac{\partial \vartheta_i}{\partial \xi} = \dfrac{1}{Pe_h}\dfrac{\partial^2 \vartheta_i}{\partial \xi^2} + B\ r\left(x_i,\vartheta_i\right) \\ \dfrac{\partial x_i}{\partial \bar{t}} + v\dfrac{\partial x_i}{\partial \xi} = \dfrac{1}{Pe_m}\dfrac{\partial^2 x_i}{\partial \xi^2} - r\left(x_i,\vartheta_i\right) \\ r\left(x_i,\vartheta_i\right) = Da\exp\left(\dfrac{\vartheta_i\tilde{\gamma}}{\vartheta_i+\tilde{\gamma}}\right)\left(1-x_i\left(1+\psi\left(\dfrac{(1-\mu)\tilde{\gamma}^2}{\vartheta_i+\tilde{\gamma}}\right)\right)\right) \quad (\text{ for } i\text{=1,2,3,4}) \end{cases}$$

The definitions for dimensionless variables and parameters and description of all the employed symbols is given in the nomenclature section in Mancusi et al. (2010).
The values of the model parameters are reported in Table-I .

Table 1: Dimensionless parameters with Tin=100°C, T_0=200°C, u_0=1 m/s, z_0=1 m

B=16	ϑ_{in} =-8,2	Pe_h=413	Pe_m=390	Da=0.017
Le=27	γ =39	μ =1.64	$\psi = 3.2\cdot10^8$	L=1/2

Danckwerts boundary conditions are applied at inlet and outlet sections of each reactor and are modified after each cycle to take into account the permutation of the NTW feeding sequence.

3. Bifurcation analysis of periodic regimes

The effect of varying the number n_s of reactors jumped by inlet and outlet sections is here investigated by comparing the spatiotemporal patterns and the bifurcations of periodic regimes detected as the switch time τ varies. Due to the large number of coexisting regimes, we first report in Fig.2 a schematic representation of the periodic solution branches detected with the three considered strategies as τ varies for all the three strategies. In Fig. 2, each isolated branch corresponds to a different periodic regime. The relative widths and the distribution over the switch time domain of the existence ranges of the regimes are only qualitative. Each periodic regime has been characterized by its time period and the number of generated temperature waves. Particularly, periodic regimes giving rise to k multiple temperature waves and with period *n*T are denoted as kW *n*T. Only for periodic regimes giving rise to a single temperature waves, the suffix 1W is replaced by SW. A unique partially symmetric T-periodic regime has been detected and is indicated in Fig.2 with letter A. Symmetric single wave T periodic regimes arise for any switching strategy at switch time values $\tau \cong n_s Le$, that is when the ratio of the switching velocity $V_{sw}=n_s/\tau$ to the thermal front velocity $Vth = 1/Le$ is around unity. At lower τ values, only quasi periodic and periodic regimes characterized by very large period are found with strategy 1(Fig.2a). On the contrary, a rich variety of single and multi waves periodic regimes appear as the switch time is decreased when strategies 2 (Fig.2b) and 3 (Fig.2c) are implemented. All the detected periodic regimes are fully symmetric with the exception of the partially symmetric one computed with strategy-3. The coexistence of multi-waves T-periodic regimes with single and multi waves multi-periodic regimes is also clearly shown in Fig.2. Particularly, independently of the switching strategy, when symmetry is preserved, symmetric kW T-periodic regime always coexist with k-1 kT-periodic symmetric regimes with numbers of waves ranging between 1 and k-1. The only exception to this result is found for the partially symmetric 2W T-periodic regime found with strategy-3. In this case, the two coexisting regimes are T-periodic and partially symmetric regimes. It is worth to remark that the lower switch time values of existence of the periodic regimes can be scaled accordingly to the fundamental characteristic time of the forced NTW, 1/Vth = Le, which represents the inverse of the velocity of a purely thermal front.

Unlike strategy-1, strategies-2 and -3 give rise to symmetric T-periodic regimes corresponding to sequences (or trains) of travelling temperature waves below the range of existence of SW T-periodic regimes, that is at switching to thermal velocity ratios greater than unity. Spatiotemporal temperature patterns of multi-waves symmetric T-periodic regimes detected in this switch time range with strategies-2 and -3 are reported in Fig.3a-b and Fig.3c-e respectively. 3W T-periodic regimes (Fig.3a and Fig. 3d) and 5W T-periodic regimes (Fig.3b and Fig. 3e), characterized by trains of three and five temperature waves respectively, are found for both strategy-2 and -3. Moreover, a 2W T-periodic regime characterized by a train of two temperature waves is observed for strategy 3 only (Fig.3c).

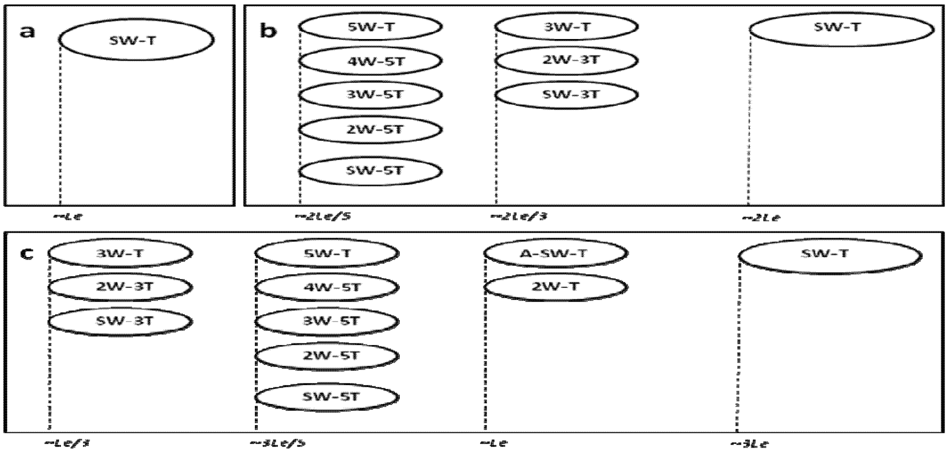

Figure 2 : Schematic representation of the domains of existence of nT-periodic regimes. SW and kW indicate single-wave and multi-wave temperature patterns for strategies 1(a), 2(b) and 3(c) respectively.

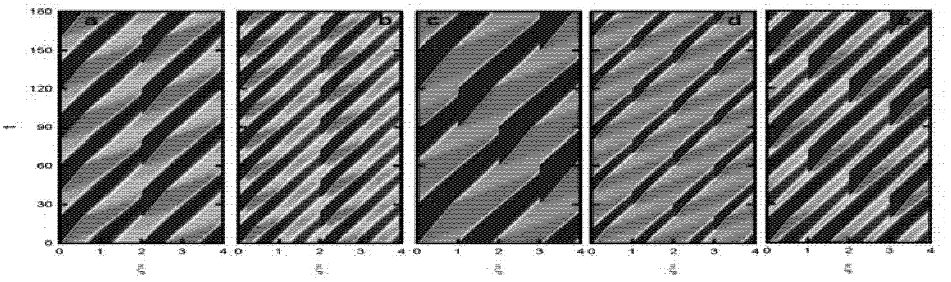

Figure 3 : Spatiotemporal temperature patterns. (a) Symmetric 3W T-periodic regime observed with strategy-2 at =20; (b) Symmetric 5W T periodic regimes observed with strategy-2 at τ=12; (c) Symmetric 2W T periodic regime observed with strategy-3 at τ=30. (d) Symmetric 3W T-periodic regime observed with strategy-3 at τ=10; (e) Symmetric 5W T periodic regimes observed with strategy-3 at τ=18.

From a practical point of view, the kW T-periodic regimes produce average outlet conversions to methanol significantly larger than SW T-periodic ones. Indeed, kW T-periodic regimes well reproduce the inter-stage cooling effect of multistage fixed bed reactors. Accordingly, increasing the number of consecutive temperature fronts results in larger outlet conversions to methanol.Parametric continuation has been therefore performed to detect the bifurcations marking the stability limits and the disappearance of the predicted symmetric multi waves T-periodic regimes (see Fig.4). This analysis reveals that multi-waves symmetric periodic regimes again arise, as found for single temperature waves, over switch time ranges delimitated by saddle node bifurcation points.

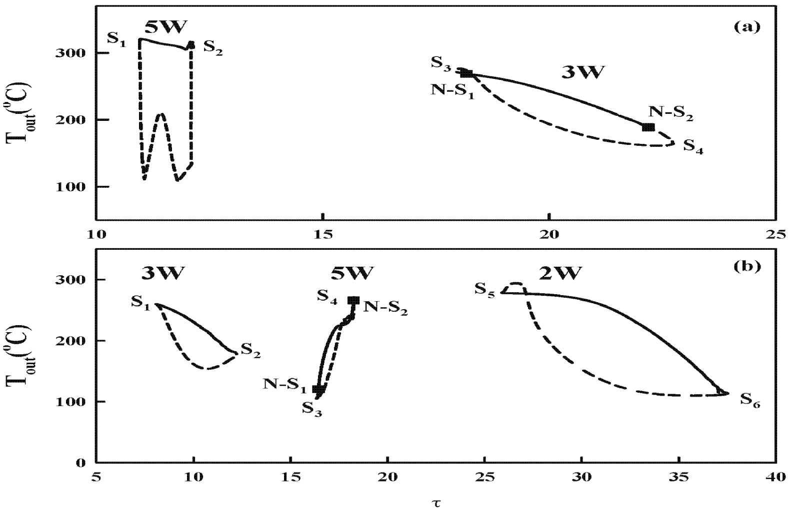

Figure 4 : Solution diagram of kW T-periodic regime for the strategy-2 (a) and for the strategy-3 (b). Filled squares: Neimark Sacker bifurcations (N-S). Saddle-node bifurcations are indicated with the letter S.

However, instability of multi-waves solutions can also occur through Neimark-Sacker bifurcations leading to the emergence of quasi-periodic regimes. Coexistence of symmetric multi-waves T-periodic regimes with other periodic regimes has been also systematically observed. Particularly, when symmetry is preserved, symmetric kW T-periodic regimes coexist with symmetric kT-periodic regimes. The period of the coexisting regimes is equal to the number of waves of the kW T-periodic regime. Moreover, the coexisting regimes are k-1 and their are characterized by numbers of temperature waves varying between 1 and k-1. The only exception to this rule is found in correspondence of the appearance of partially symmetric T-periodic regimes.

As consequence of the reduced number of temperature waves, the regimes coexisting with the symmetric kW T-periodic regimes produce average outlet conversions to methanol lower than those observed for the corresponding kW T-periodic ones. In this respect, symmetric kW T periodic operation is, in general, recommended while transition to the coexisting periodic regimes should be prevented.

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