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Multiplicities of temperature wave trains in periodically forced networks of catalytic reactors for reversible exothermic reactions

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ABSTRACT

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 (n_s) of reactor units jumped by inlet and outlet sections on network stability and performance is investigated. Increasing n_s, a greater variety of periodic regimes giving rise to trains of temperature waves characterized by spatial periodicity are detected as the switching velocity varies. These regimes well reproduce the inter-stage cooling effect of multistage fixed bed reactors and, hence, guarantee in general large conversion values. Moreover, an intriguing coexistence between T-periodic and multi-periodic temperature wave trains is revealed, T being the period needed for the system to recover its initial configuration. A T-periodic symmetric wave train characterized by k waves always coexists with a number of $k-1$ stable symmetric kT-periodic regimes, except when symmetry breaking is encountered. The $k-1$ coexisting regimes correspond to wave trains with a number of waves ranging between 1 and $k-1$. 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 n_s.

1. Introduction

Networks (NTWs) of catalytic reactors with periodically switched inlet and outlet sections have been proved to offer an effective technological solution to achieve autothermal operation of exothermic catalytic processes [1]. 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 [1,2]. Moreover, the formation of a declining temperature zone close to the NTW outlet section 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 [3,4]. NTWs of reactors are periodically forced systems which exhibits spatio-temporal symmetries [5]. 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.

When the forced NTW is operated at switching to thermal velocity ratios around unity, these regimes are characterized by a single travelling temperature waves [6]. The switching velocity range over which the NTW can sustain such regimes becomes progressively smaller as the adiabatic temperature rise and/or the feed temperature are decreased. Outside of this range, transitions to multi-periodic, quasi-periodic and chaotic solutions as well symmetry breaking bifurcations can likely occur [7,8].

However, symmetric T-periodic regimes have been also shown to arise at switching to thermal front velocity ratios greater than

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Nomenclature

A_1, A_2	Arrhenius constants
B	dimensionless adiabatic temperature rise
c_p	heat capacity
C	methanol concentration
Da	Damköhler number
D_f	mass axial dispersion coefficient
E_1, E_2	activation energies
$g(t)$	forcing function defined in Eq. (5)
k_e	solid phase axial heat conductivity
L	reactor length
Le	Lewis number
N	number of reactor
n_s	number of reactors jumped by the feed
Pe	Peclet number
R	gas constant
r	reaction rate
S^1	unit circle
t	time
T	temperature (°C)
u	gas rate
v_s	dimensionless gas rate
V_{fr}	reaction front velocity
V_{sw}	switch velocity
V_{th}	purely thermal front velocity
x	methanol conversion
z	axial coordinate
Z_n	cyclic group

Vectors and matrices

$\mathbf{F}$	vector field
$\mathbf{G}_i$	permutation matrix Eqs. (9)–(11)
$\mathbf{p}$	parameters vector
$\mathbf{y}$	state vector

Greek letters

$\tilde{\gamma}$	dimensionless activation energy
γ	generic spatial transformation of a Lie group
Γ	generic Lie group of spatial transformation
Δ	generic Lie group of temporal transformation
ΔH	heat of reaction
δ	generic temporal transformation of a Lie group
ε	reactor void fraction
ϑ	dimensionless temperature
ρ	density
σ	temporal linear transformation
τ	dimensionless switch time
μ	ratio between activation energies
ψ	ratio between Arrhenius constants
ξ	dimensionless axial coordinate

Subscripts and superscripts

0	reference conditions
h	energy balance
in	inlet
m	mass balance

unity significantly extending the domain of operation of the forced NTW. These solutions are characterized by trains of travelling temperature waves and exist within finger-like domains of the parameter space separated by domains of extinguished solutions [9].

It is worth to note in this context that 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 (n_s) between 1 and $N-1$ while keeping unchanged the flow direction through the bed. In this spirit, the stability characteristics and the performance of forced NTWs with inlet and outlet sections jumping $N-1$ reactor units in the flow direction have been recently investigated. When applied to irreversible exothermic reactions, the implemented strategy has been proved to significantly enlarge the domain of stability of symmetric T-periodic regimes [10]. 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. In particular, distinct isolated domains of travelling temperature wave trains have been detected with the proposed strategy while no multiple travelling temperature waves have been found to arise with the traditionally implemented strategy [11]. The analysis of wave trains regimes is of great practical relevance for reversible exothermic reactions. Indeed, these regimes well reproduce the inter-stage cooling effect of multistage fixed bed reactors significantly increasing, compared to single temperature waves, the average outlet conversion as equilibrium limited reactions are considered [4,11].

Despite the practical relevance of these arguments, the potential advantages of different operating strategies remain still largely unexplored. Particularly, no guidelines have been provided on how to select the switching strategy and the operating conditions to produce spatiotemporal temperature and concentration patterns with desired characteristics. Also, no systematic study has been presented on the stability characteristics of periodic regimes corresponding to temperature wave trains arising at switching to thermal velocity ratios greater than unity. 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. A NTW of four catalytic reactors is considered and the effect of varying the number of reactor units jumped by inlet and outlet sections on network stability and performance is investigated. Particularly we study the case when 1, 2 and 3 reactors are jumped by inlet and outlet sections. It should be noted that in the second case the network is equivalent to one with two reactors of double length. Bifurcation analysis is performed enabling to characterize the stability range of periodic regimes and identify domains of coexistence of multiple stable regimes.

The article is structured as follows. In Section 2, the mathematical model of the forced NTW for methanol synthesis and the considered switching strategies are described. In Section 3 the spatio-temporal symmetry properties induced by the considered switching strategies are analyzed. Finally, in Section 4, the results of bifurcation analysis of symmetric T-periodic regimes corresponding to single and multiple temperature waves and the analysis of the coexistence of symmetric T-periodic regimes with nT-periodic symmetric and asymmetric regimes are presented.