COMPARISON OF THE PERFORMANCE OF A REVERSE FLOW REACTOR AND NETWORKS OF NON-STATIONARY CATALYTIC REACTORS FOR CATALYTIC COMBUSTION OF METHANE IN LEAN MIXTURES

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Introduction

Although the operation under unsteady state is generally avoided and continuous operation is preferred in the chemical industry, this mode of operation can often lead to a better performance. Because of this, forced unsteady state reactors are object of increasing interest. In particular, the systems based on the periodic reversal of the feed flow direction, called reverse flow reactors (RFR), and the reactor networks of two (RN2) or three reactors (RN3) in series where the feed position is periodically changed from a reactor to the following one in the sequence seem to be particularly promising (1, 2).

The simple operation procedure of the RFR leads to important advantages in some catalytic processes. So, reverse flow operation is particularly advantageous in the case of the catalytic combustion of lean air-hydrocarbons mixtures, mainly due to its high thermal efficiency. This technology has been implemented industrially for the abatement of VOCs, and the research on this field is still very active. One of the main drawbacks of this technology is the by-pass of relatively large amounts of unconverted hydrocarbons when the flow direction is reversed (2).

Unsteady reactor network consists of a series of fixed bed reactors connected in a closed sequence with periodical variations of the feed position. Contrary to the RFR, the flow direction is maintained in this device. This fact has two important advantages: ensure uniform catalyst utilization and avoid the presence of unconverted gas by-pass.

The scope of the present work was to compare, for similar operation conditions, the performance of a RFR and RN of two and three reactors. Different CH_4/air mixtures of 0.1-1 % were selected as feed for the combustors. It should be taken into account that studies with these kind of reactors working with methane concentrations close to 1 % are very scarce, in spite of their practical interest (these concentrations are very common in real emissions, such as coke ovens or coal mine ventilation systems).

Mathematical model and experimental

A one-dimensional heterogeneous model was used to investigate the influence of the main operating parameters on the stability of the RFR and of the RN; as the radial Biot number is very small, radial temperature gradients were neglected. Pressure loss inside the system was neglected and plug flow, with dispersive transport of mass and energy, was assumed for the gas phase. The transient term was taken into account in the gas phase equations and in the energy equation for the solid phase, while the solid catalytic surface was considered to be in pseudo-steady state condition. The effect of the intraparticle mass

transport was included in the model by means of the effectiveness factor. Details about the model equations, the boundary conditions used, the correlations used to calculate the transport coefficients can be found in further works (3,4).
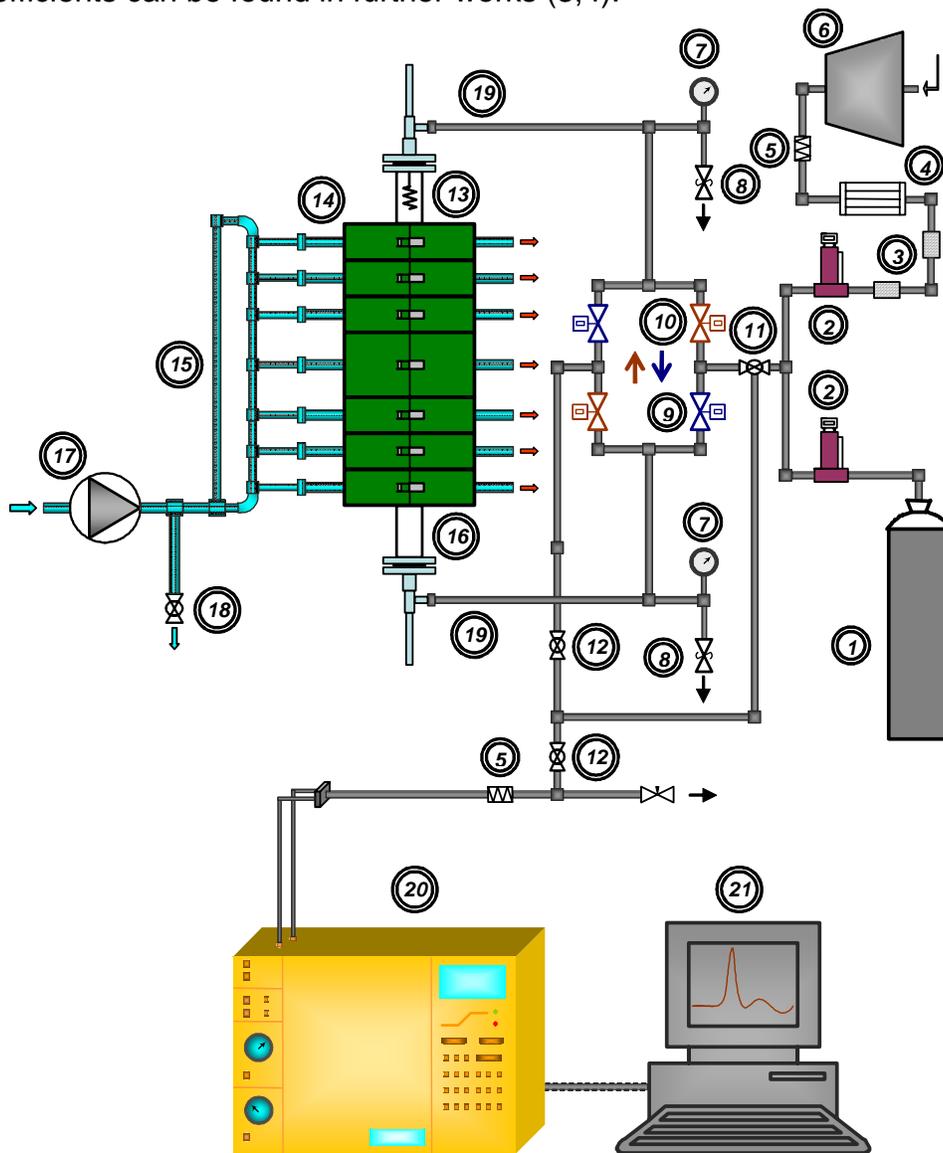
Figure 1. Flow diagram of the experimental apparatus. (1**)** Synthetic mixture air/CH_4. (2) Mass-flow controllers. (3) Oil filters. (4) Cooling dryer. (5) Particles filter. (6) Compressor. (7) Pressure gauges. (8) Relief valves. (9) Solenoid valves (downward flow when closed). (10**)** Solenoid valves (upward flow when closed). (11) Body valve (three-way). (12) Body valve (one way). (13) Preheater. (14) Modular oven. (15) Distribution of cooling air. (16) Reactor. (17) Blower. (18) Body valve (regulation). (19) Flexible tubing. (20) Gas cromatograph. (21) Computer

Simulation results were validated in a novel bench-scale RFR unit (Fig. 1). The reaction chamber consisted of a 0.8 m long and 0.05 m internal diameter cylinder, containing catalyst and inert material. The reactor gaseous feed (1000-10000 ppmV methane in air) was made up by mixing air (from a compressor, filtered) and a mixture of 2.5 % vol. methane in

synthetic air (from a gas cylinder). Mass flow regulators control the flow rate of both gases. A three-way valve, located downstream the mixing point, allows the feed to by-pass the reactor for analytical purposes. The periodical flow reversals are accomplished by means of four solenoid valves. The main innovative feature of this reaction unit is a special temperature control system designed to dynamically compensate the heat losses through the wall, making possible that the reactor works very close to adiabatic conditions. A flow diagram of the apparatus is given in Fig. 1, and a full description of this equipment, as well as the validation of its adiabatic performance can be found in a previous paper (3).

For both simulations and experiments, a commercial Pd/Al_2O_3 catalyst (d_p=0.7 mm, k_0=1.625•10^8 s^{-1}, E_a=9.124•104 J/mol) were considered for these studies. Pseudo-first order kinetics was considered in all the operation range. A surface velocity of 0.1 m/s was considering, neglecting the pressure drop inside the reactor.

Results and Discussion

In order to characterise the performance of these devices it is important to study the influence of the main operating conditions, namely inlet temperature, flow rate and composition, as well as the switching time (i.e. the time interval occurring between two successive changes of the feed position), on the stability of the reactor, in order to find the values (or range of values) of these variables that ensure auto-thermal behaviour. Beside this, the influence of these variables on the temperature profiles that can be reached in the reactor has to be pointed out in order to avoid catalyst overheating and deactivation.
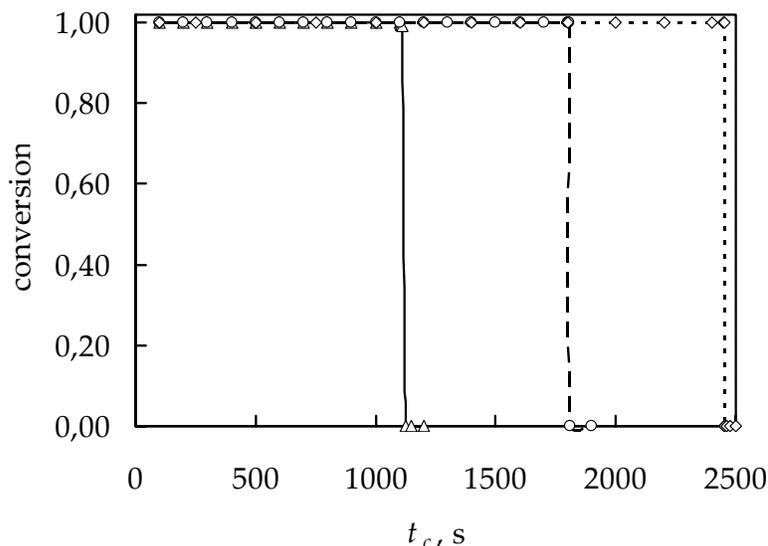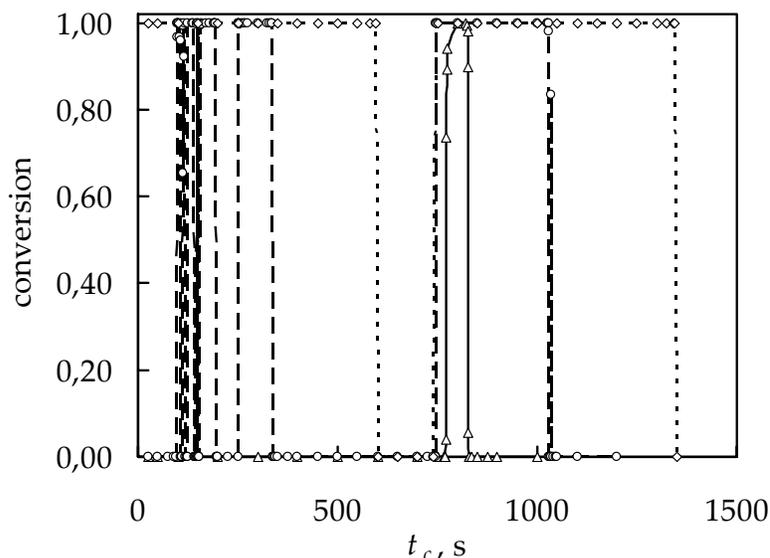

Figure 2. Methane conversion as a function of the switching time in the RFR for various inlet concentrations (—△—: 1000 ppmV, --o--: 5000 ppmV, ⋯◇⋯: 10000 ppmV).

The evolution of the conversion with the switching time is depicted in Fig. 2. It can be observed that the stability of the reactor (the interval of switching time that leads to total methane conversion) increases as the methane concentration in the feed increases. The extinction of the reactor occurs because the zone at which the temperature is high enough to start the reaction moves out of the reactor before the flow direction is reversed. So, as the
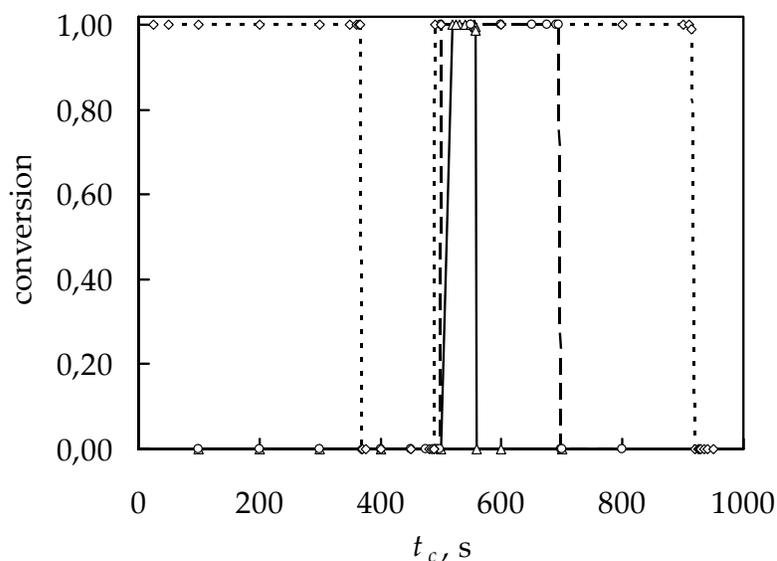
concentration of methane increases, the total amount of heat released is also increased and it is less probable that the zone with enough high temperature to start the reaction moves out the reactor.

Concerning the RN, the stability behaviour is shown in Figure 3 for RN2 and in Figure 4 for RN3 and is much more complex than in the RFR. In particular, while in the RFR stable operation is possible even for very low values of t_c, in the case of the RN a lower limit exists, below which no autothermal operation can be obtained. This different behaviour can be explained considering that in the case of very low switching times only the first reactor of the network is heated by the combustion and, once the feed is moved to the second reactor, more time is required to reach the hot zone as this hot zone has been cooled below the temperature required to start the reaction. Similar behaviour was reported by Fissore and Barresi in a previous work (2), stating that RN leads to narrower stability limits than the RFR.

However, the presence of multiple stable intervals can be observed for the concentration range studied. In the case of RN2 a unique and very narrow stability range is observed at 1000 ppmV (in good agreement with the behaviour reported in the literature), while at 5000 and 10000 ppmV two different stability intervals are observed. The width of the interval observed at higher switching times increases as the methane concentration increases. This result (caused by the highest amount of heat released to the system) suggests that increasing amount of methane leads to more stable operation, being very difficult to work below 5000 ppmV with RN technologies (the stability range is too narrow to ensure a stable operation).

Figure.3. Methane conversion as a function of the switching time in the RN2 for various inlet concentrations (—△—: 1000 ppmV, --○--: 5000 ppmV, ⋯◇⋯: 10000 ppmV).

Figure.4. Methane conversion as a function of the switching time in the RN3 for various inlet concentrations (—△—: 1000 ppmV, --○--: 5000 ppmV, ···◇···: 10000 ppmV)**.**

Concerning to the evolution of the catalytic bed temperature, it increases as the concentration of methane increases for all the configuration studies (as expected), but the behavior is quite different depending on the concentration studied. So, for the most concentrated feed, the maximum temperature found in the RFR is always higher than the corresponding to reactor networks, whereas for lower methane concentrations, maximum temperatures are higher for the reactor networks, especially when working in the high-switching time interval. An important difference between RFR and RN is that the evolution of the maximum temperature with both time (in a given experiment) and switching time (comparing different experiments) is sharper for RN whereas is smoother for RFR. This means that the catalyst used in RN suffer strong more marked temperature variation, which can also affect to the catalytic properties.

Typical temperature profiles for RFR and reactor networks of three reactors are shown in Fig. 5. It is clearly observed the different thermal behaviour of both systems. So, in the case of RFR (Figs. 5a. and 5b.), temperature profiles at both high and low switching times are symmetric, being is observed that the fraction of the reactor with higher zone increases as the switching time decrease. This means that the central part of the reactor (when the catalyst is placed) will be always at the same temperature. In the case of the RN (Figs. 5c. and 5d.) the temperature profiles have two important differences if compared with the RFR. The first one is that the temperature profiles are not periodically repeated with the switching times. So, it is possible to define the so-called temperature profile repetition period (TPRP) as the period of time that needed for the repetition of the temperature axial profile. For the case of the reverse flow reactor, for all the switching times, the TPRP will be always twice the switching time. In the case of reactor networks, the behaviour is different depending on the operation zone. So, in the low switching time zone, the TPRP/t_c ratio shows strong variation with the t_c, with values ranging from 2 to 142 in the case of RN2 and 6 to 87 in the case of RN3. In the high switching time region, the ratio between both parameters is constant and

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equal to 2 and 3, for RN2 and RN3, respectively. This means that the temperature profile moves a the distance corresponding to the reactor length in the switching period when working in the high switching times region, whereas an the low switching time region, it moves a shorter distance.

So, the most outstanding difference of between the temperature profiles of the RFR and the RN is that in the last configuration, all the zones of the reactor bear all the interval of temperatures (from the temperature of the feed to the maximum temperature). This is an important difference with the RFR (the temperature of the central zone is almost constant) and this fact could be negative for the stability of the catalyst, since the thermal shock can affect both mechanical and properties and activity of the catalyst.
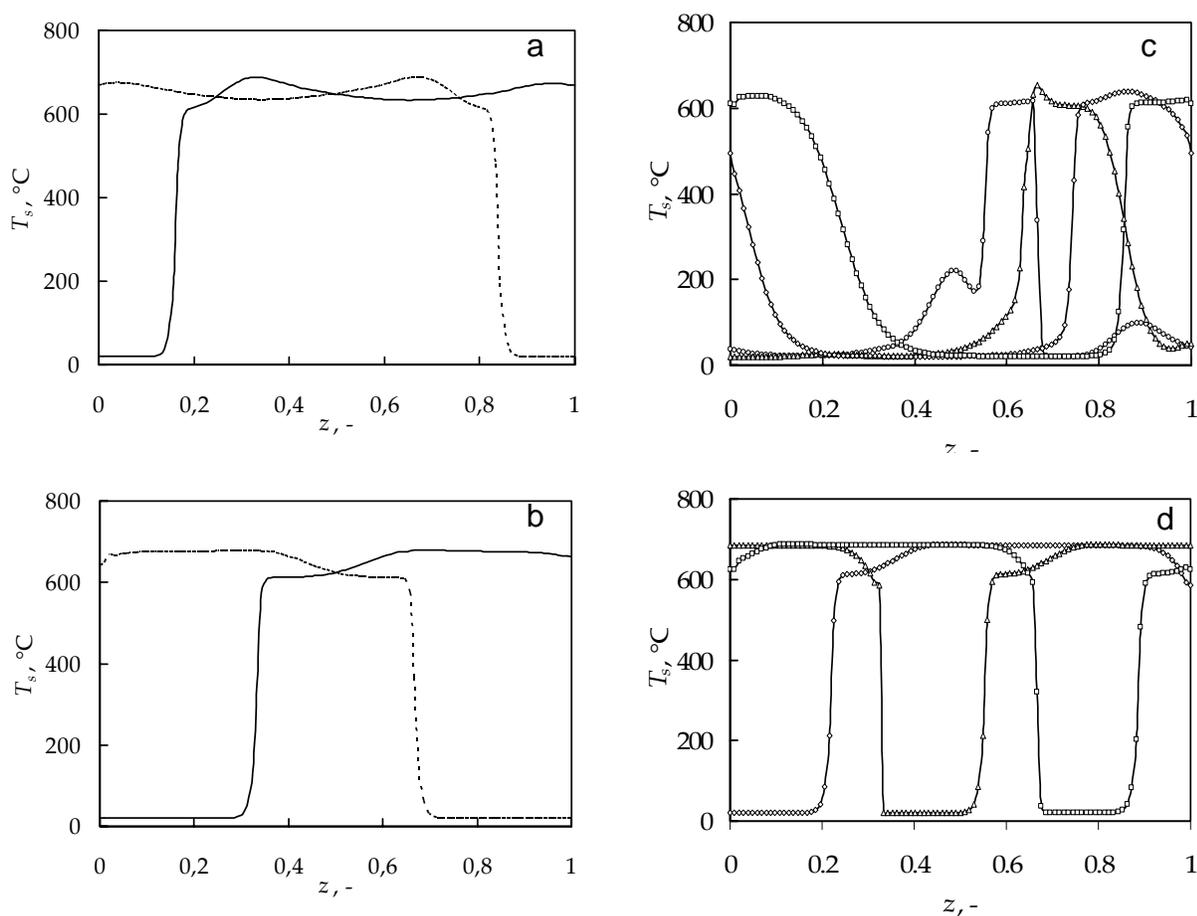
Figure 5. (a-b) Temperature profiles in a RFR at the end of a semi-period when the periodic steady-state has been reached (a) tc = 450 s; _____ t = 29250 s, _ _ _ _ _ _ t = 29700 s; (b) tc = 900 s; _____ t = 27900 s, _ _ _ _ _ _ t = 28800 s. (c-d) Time evolution of the temperature profile in a RN3 ((c) tc = 300 s; ___o___ t = 28800 s, ___D___ t = 29100 s, ___◇___ t = 29400 s, ___□___ t = 29700 s; (d) tc = 600 s; ___◇___ t = 27600 s, ___D___ t = 28200 s, ___□___ t = 28800 s). The inlet methane concentration is 10000 ppmV in the four cases.

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Simulations results concerning to the device that seems to be the best choice, the RFR, were experimentally validated in a bench-scale unit. Figure 6 shows the simulated axial temperature profiles and the actual measurements for three different instants after the PSS was reached, namely the beginning, the middle and the end of a cycle. These results confirm that the behaviour is very close to the adiabatic one, as well as the accuracy attained in the model parameters determination. This conclusion is based not only on the good agreement between experimental measurements and simulated profiles, but also on the absence of local temperature minimums in the central zone of the axial profiles, which are caused by the existence of a non negligible heat flux between the reactor and its surroundings. Similarly, axial temperature profiles do not present local maxima near the inert-catalyst boundary surface. This last effect would reveal an under-utilisation of the treatment capacity of the reactor, since it indicates that the reaction takes place just at the ends of the active section of the bed.
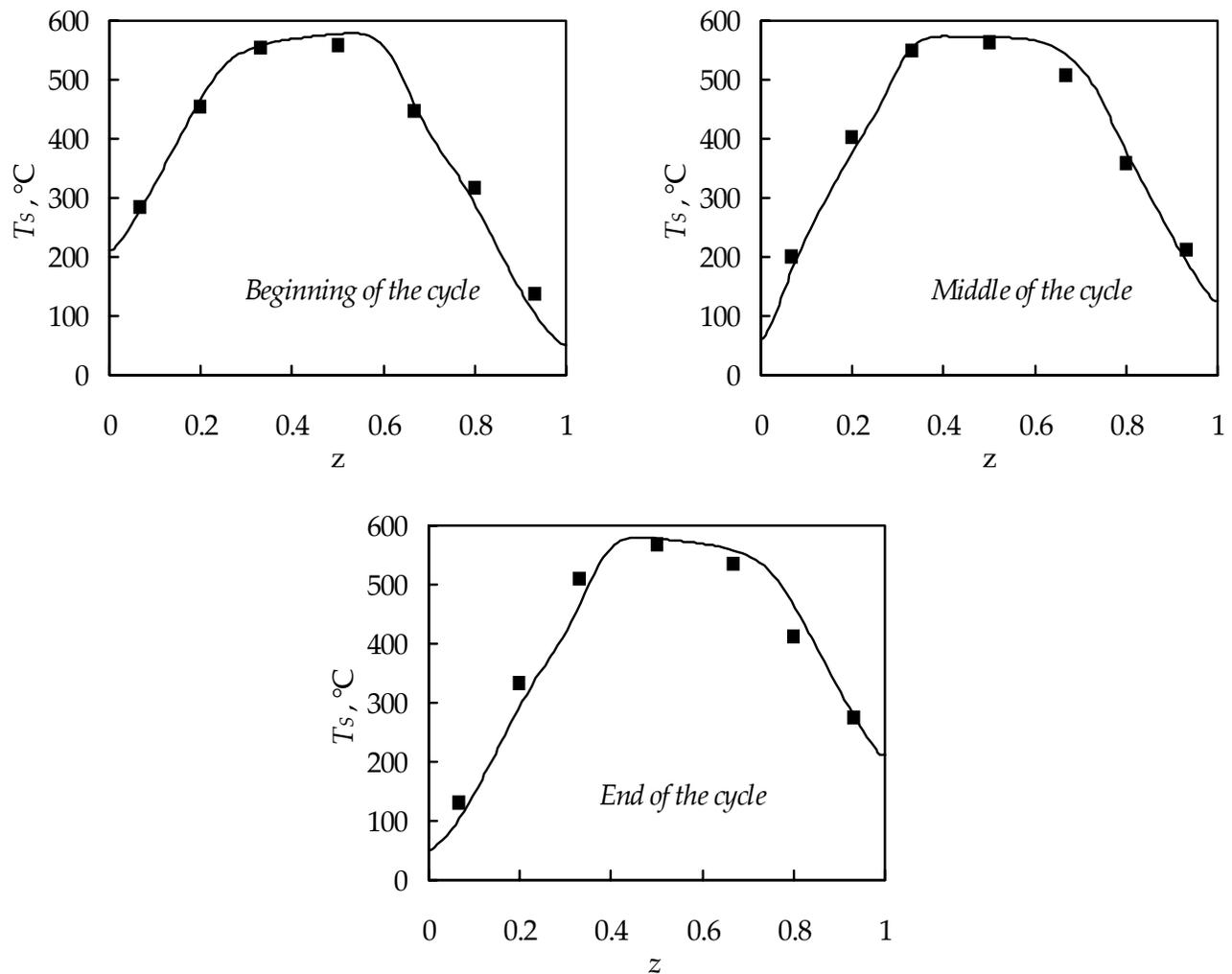
Figure 6. Simulated (solid line) axial temperature profiles and actual measurements (symbols) for different time instants of a RFR cycle, when the PSS was reached ($y_{CH4,0}$ = 3500 ppmV, t_c = 600 s).

Conclusions

The combustion of moderately high methane concentration streams (up to 1% of methane) in different non-stationary reactors has been investigated in this paper. The RFR has been demonstrated to ensure a wider interval of switching time that allows for stable operation and an almost constant temperature profiles is obtained in the central part of the reactor. The reactor networks of two and three reactors exhibits a narrower stability interval and the catalyst suffers important thermal shocks during the operation. At high inlet concentration (10000 ppmV) an other stability interval (at low switching time) appears in the RN3; anyway, even if the stability range of this device is enlarged, the interest in the operation of the reactor with this values of switching times is poor due to the fast temperature changes inside the reactor.

Acknowledgements

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