

Selective catalytic reduction of NO_x with NH₃ in unsteady-state reactors

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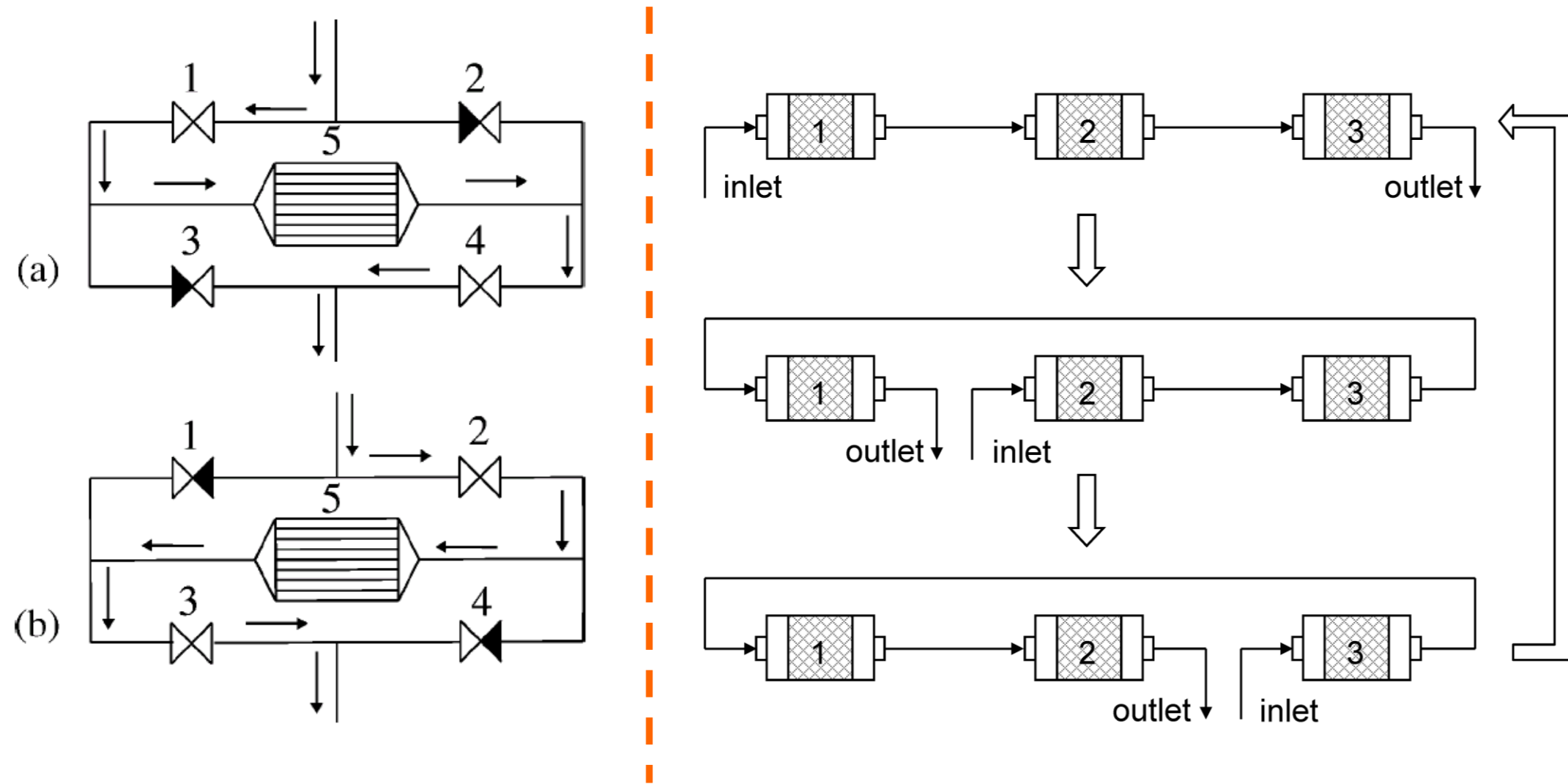
Introduction

Forced unsteady-state catalytic reactors were deeply investigated during the last 40 years by means of numerical simulations and experiments as the unsteady-state operation may significantly enhance the conversion, the selectivity and the productivity and may decrease the operating costs in a wide number of catalytic processes. Unsteady-state operation may arise from variations (periodical or not) in the inlet flow rate, feed composition, temperature or pressure, as well as from the periodical reversal of the feed direction.

The reverse-flow reactor (RFR) with a catalyst that strongly adsorbs ammonia was proposed even recently for the Selective Catalytic Reduction (SCR) of NO_x with ammonia as the RFR operation enables trapping of the ammonia in the bed and minimising its emissions. One of the main problems of such a mode of reactor operation is the emission of ammonia occurring at each switch, due to the reversal of the flow direction.

A reactors network (RN) with periodical change of the feeding position was shown to be an alternative to the RFR as in this system the flow direction is never changed, thus allowing for a further reduction in ammonia emissions, beside fulfilling the requirements on NO_x removal.

Reverse Flow Reactor (RFR) vs Reactors Network (RN)



$$\text{Gas phase mass balance} \quad \begin{cases} \frac{\partial c_A}{\partial t} = -v \frac{\partial c_A}{\partial x} + h_A a_v (c_A^* - c_A) \\ \frac{\partial c_B}{\partial t} = -v \frac{\partial c_B}{\partial x} + h_B a_v (c_B^* - c_B) \end{cases}$$

c_A^* and c_B^* identify the gas concentration at the interface with the solid.

$$\text{Mass balance at the interface} \quad \begin{cases} -h_A a_v (c_A^* - c_A) = r_{red} \cdot \Omega \\ -h_B a_v (c_B^* - c_B) = (r_{ads} - r_{des}) \cdot \Omega \end{cases}$$

$$\text{Solid phase mass balance} \quad \frac{\partial \theta_B}{\partial t} = r_{ads} - r_{des} - r_{red}$$

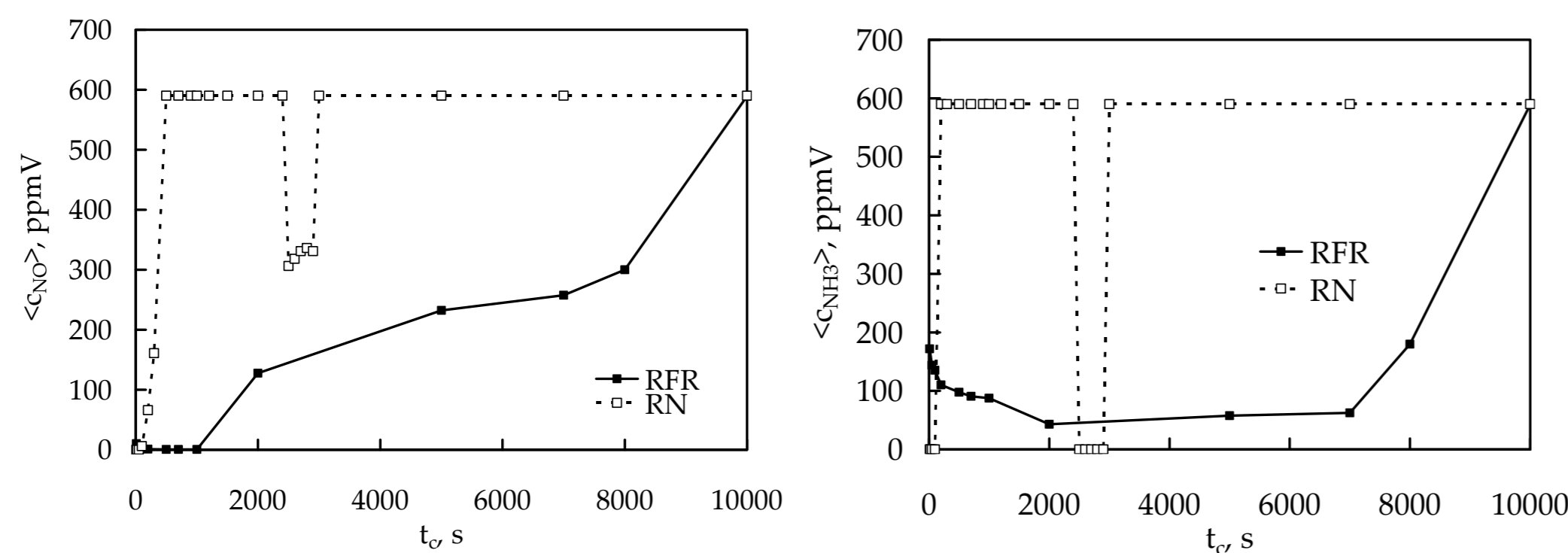
$$\text{Gas phase energy balance} \quad \frac{\partial T_G}{\partial t} = -v \frac{\partial T_G}{\partial x} + \frac{h_T a_v}{\rho_G c_{p,G}} (T_G - T_S)$$

Solid phase energy balance

$$\rho_S c_{p,S} \frac{\partial T_S}{\partial t} = -h_T a_v (T_S - T_G) + r_{red} \cdot \Omega \cdot (-\Delta H_{red}) + r_{ads} \cdot \Omega \cdot (-\Delta H_{ads}) + r_{des} \cdot \Omega \cdot (-\Delta H_{des})$$

The unsteady-state operation mode can allow for trapping the moving heat wave inside the catalytic bed when exothermic reactions take place, thus giving the possibility of exploiting the thermal storage capacity of the catalytic bed, which acts as a regenerative heat exchanger, allowing **auto-thermal operation** when the adiabatic temperature rise of the feed is low.

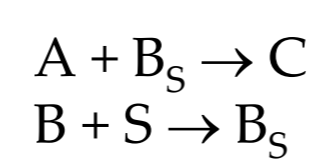
The RN can be competitive with the RFR, allowing for high conversion and achieving lower emissions of NH₃, whose level is subject to even stricter restrictions. The choice of t_c is affected by the dynamic of the heat wave, as too long switching time will lead to reaction extinction, due to the heat removal from the catalyst.



Mean outlet concentration of NO and NH₃ as a function of the switching time in the RFR and in the RN. $v_0 = 0.08 \text{ m s}^{-1} \text{ STP}$.

Mathematical modelling

A heterogeneous mathematical model was used to investigate the performance of the RFR and the RN. An Eley-Rideal mechanism is used to describe the reaction between NO_x (A) in the gas phase and the ammonia (B) adsorbed on the catalyst:



The kinetic model proposed by Tronconi et al. (1996) for a V₂O₅/TiO₂ catalyst (with V₂O₅ loading of 1.47%) is used; the reduction reaction is considered to be of first order with respect to each reactants, the adsorption rate of ammonia on the catalyst surface is assumed to be proportional to the ammonia concentration in the gas phase and to the free fraction of surface sites and the rate of desorption is assumed to be proportional to the concentration of the adsorbed specie. An Arrhenius type dependence of the kinetic constants from the temperature is assumed.

A monolith is considered for the SCR reaction: mass and energy dispersive transport are not taken into account, due to the low conductivity of the monolithic support, and also pressure loss inside the reactor is neglected; adiabatic operation is assumed.

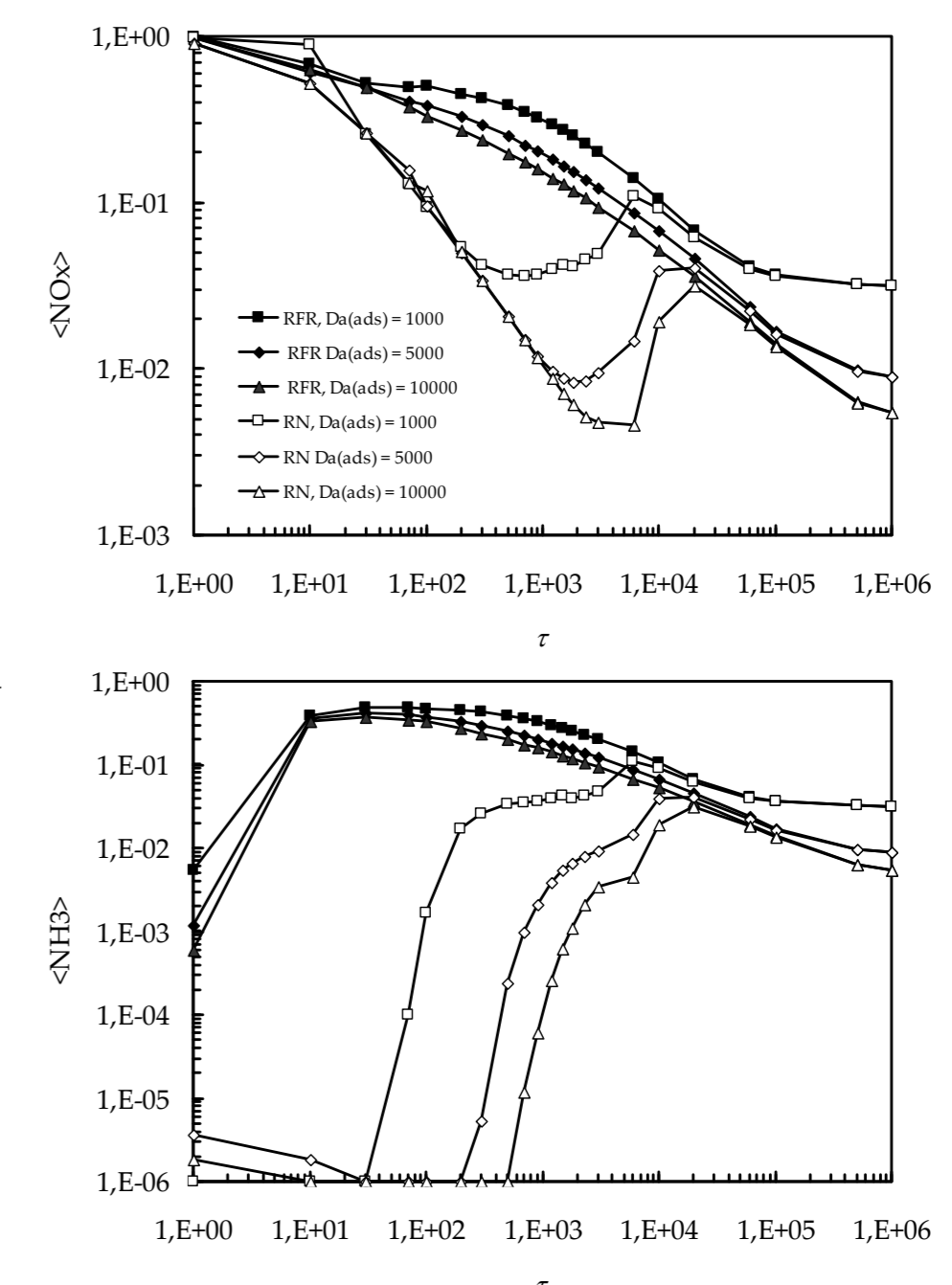
Comparison between the RFR and the RN (T = cost)

When isothermal operation is assumed, as in this case, the switching time is the main operating parameter, particularly for control purposes.

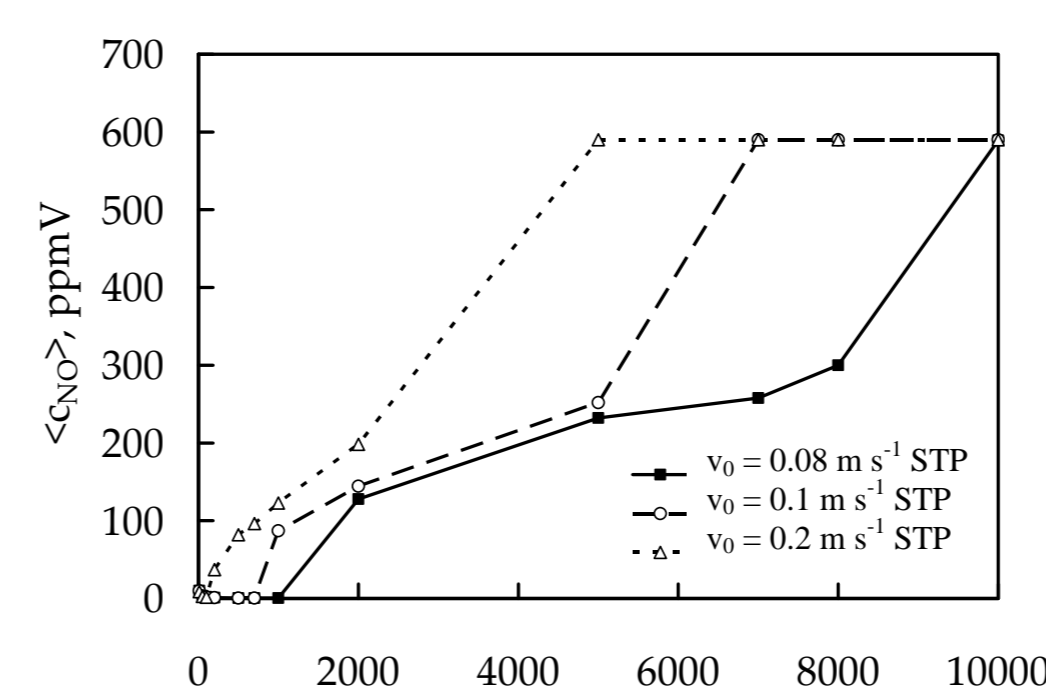
There is a wide range of switching time where the RN exhibits no ammonia emissions and NO_x emissions lower than those obtainable in the RFR; this is a consequence of the absence of wash out; the extent of this "optimal" range is a function of the parameter of the system, namely Da , Da_{ads} , Da_{des} .

$$Da = \frac{k_{red} \Omega L}{v}; Da_{ads} = \frac{k_{ads} \Omega L}{v}; Da_{des} = \frac{k_{des} \Omega L}{v c_A^d}$$

Influence of the switching time on the mean outlet non-dimensional concentration of NO_x (upper graph) and of ammonia (lower graph) for various values of Da_{des} in the RFR and in the RN (isothermal system).

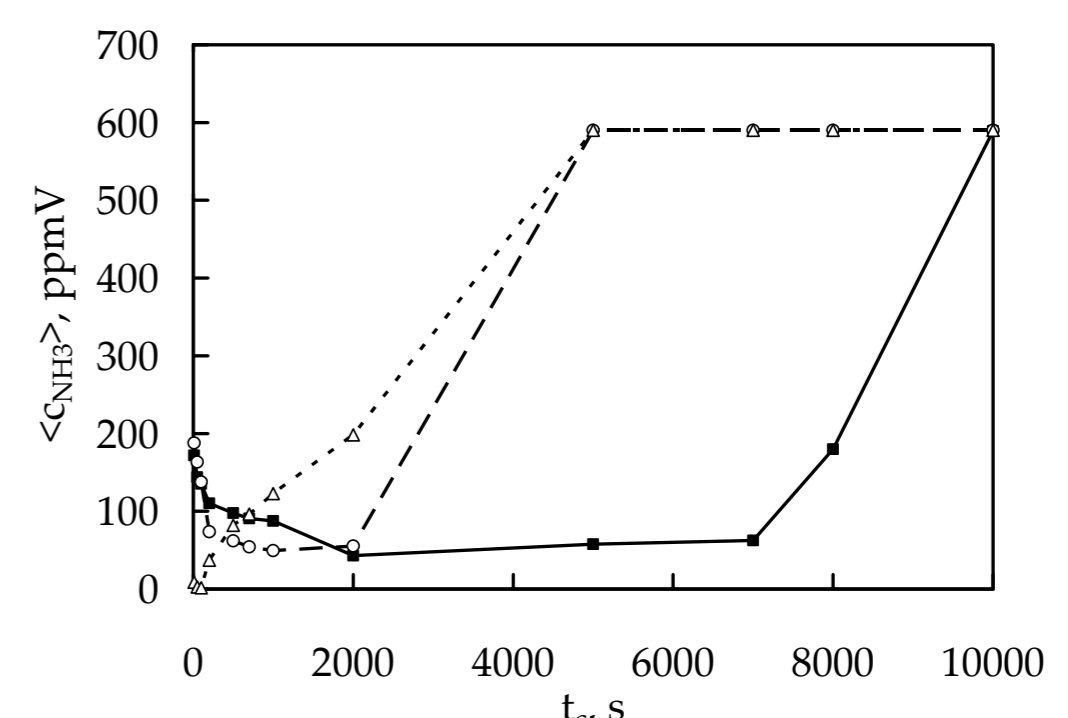


Influence of the surface velocity (RFR)

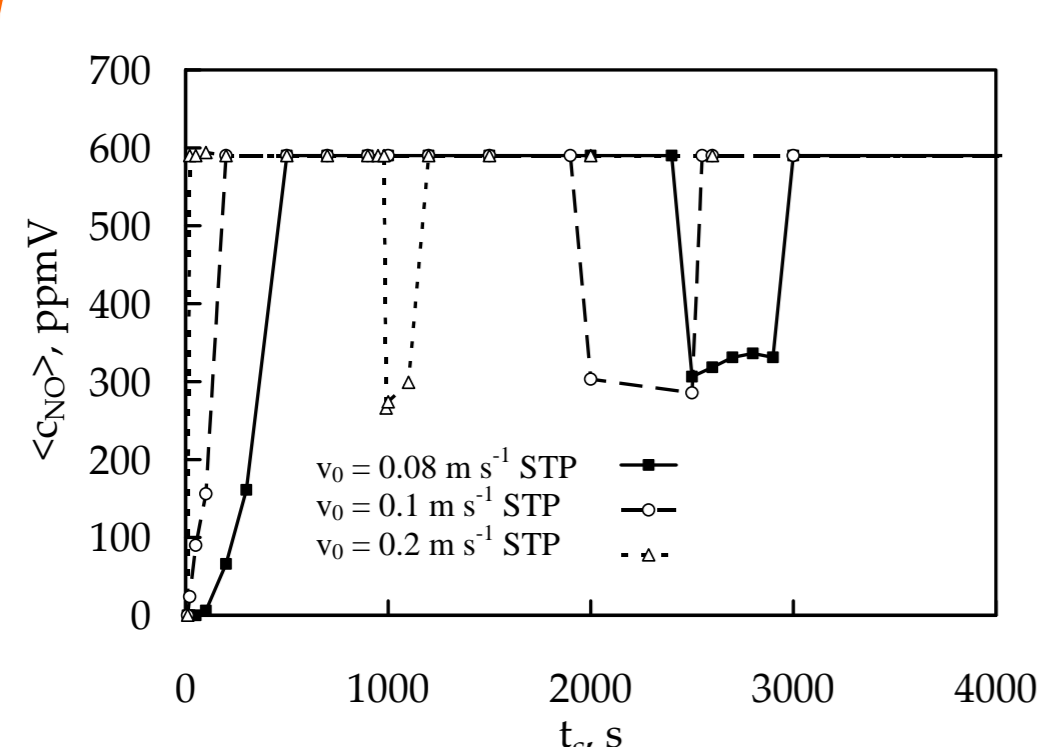


Mean outlet concentration of NO and NH₃ as a function of the switching time in the RFR for various values of the inlet surface velocity.

When the flow rate is increased, the range of switching times that allow for autothermal behaviour is reduced and lower conversion are obtained.

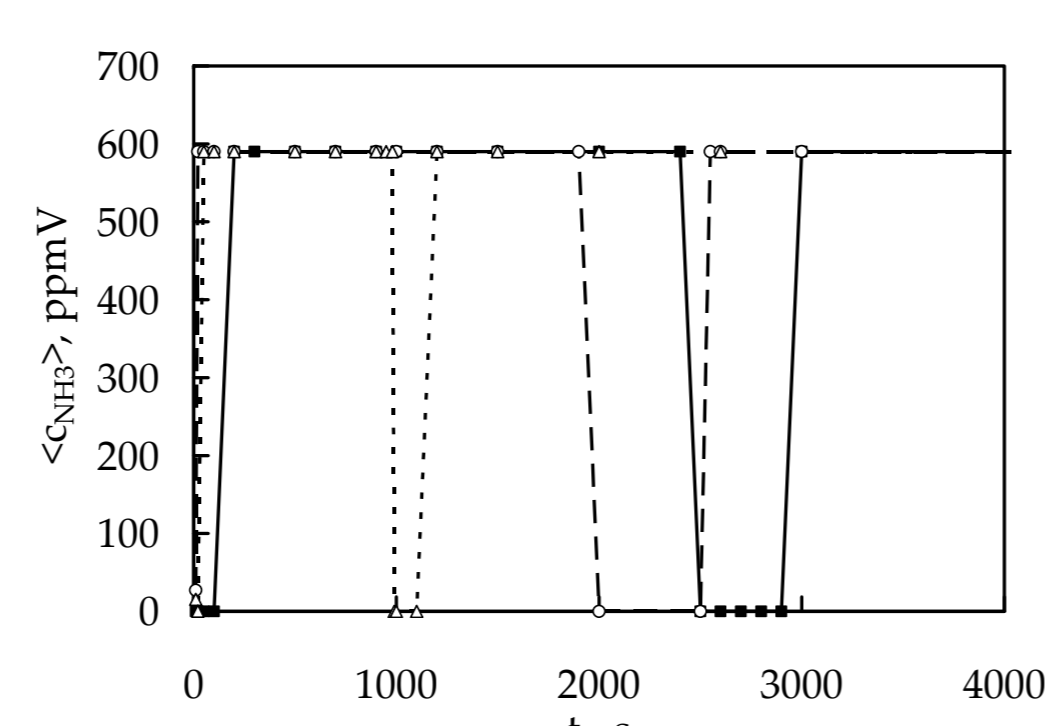


Influence of the surface velocity (RN)

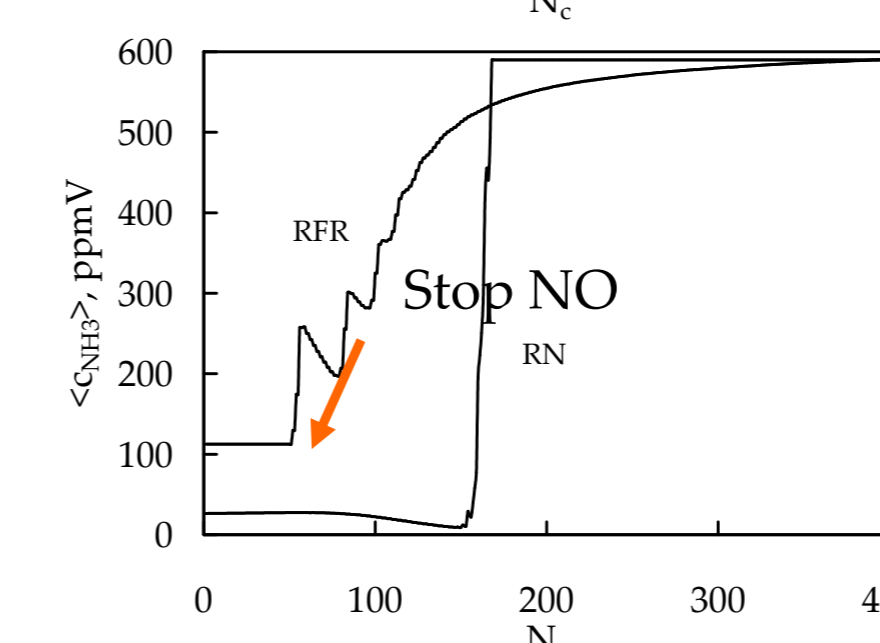
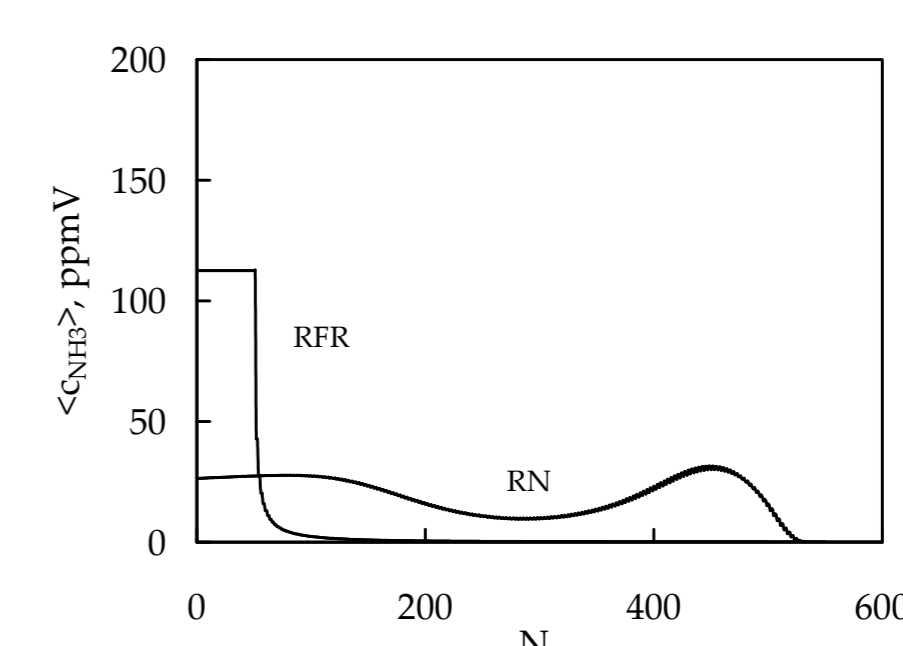
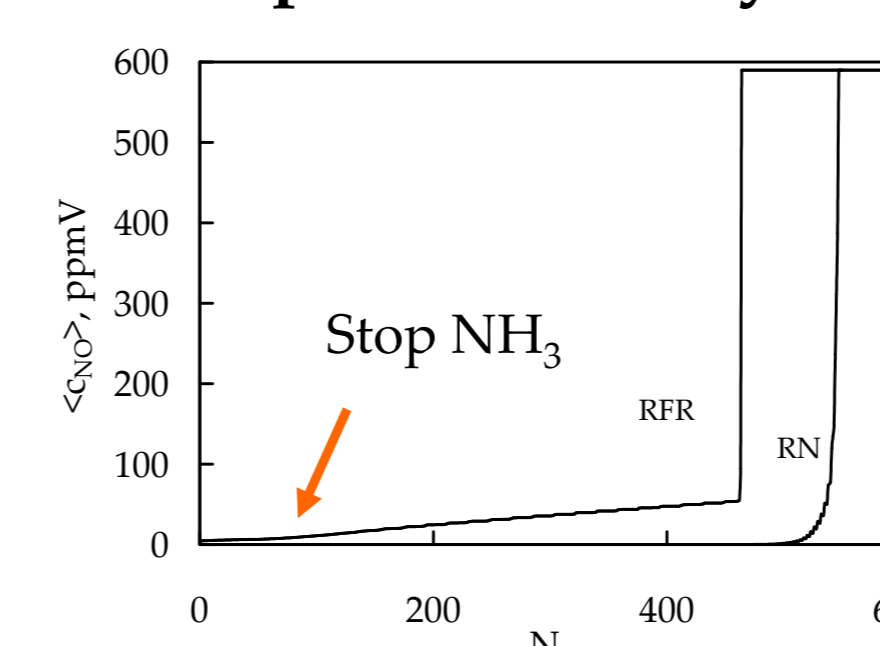


Mean outlet concentration of NO and NH₃ as a function of the switching time in the RN for various values of the inlet surface velocity.

Similarly to the RFR, also in the RN the range of t_c with low NO and NH₃ emissions is reduced at high feed flow rate; moreover, the second interval of t_c where the operation is feasible is not only reduced, but also moved towards lower values of t_c when the flow rate is increased.



Response of the system to disturbances



The RN is much more robust than the RFR, as it allows the fulfillment of the operating constraints also when the feeding concentration is changed and no control action is undertaken.

Moreover, the different dynamics have a strong drawback in the controllability of the system if a feedback control is used and the outlet concentration of both NO and NH₃ is used to monitor the system.