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Original
NOx removal in forced unsteady-state chromatographic reactors / Fissore, D., Barresi, A., Botar Jid, C.C.. - In: CHEMICAL ENGINEERING SCIENCE. - ISSN 0009-2509. - STAMPA. - 61:10(2006), pp. 3409-3414. [10.1016/j.ces.2005.11.060]

Availability:
This version is available at: 11583/1397681 since: 2016-11-17T16:04:41Z

Publisher:
PERGAMON-ELSEVIER SCIENCE LTD

Published
DOI:10.1016/j.ces.2005.11.060

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13 October 2026

This is an electronic version (author's version) of the paper:

Fissore D., Barresi A. A., Botar-Jid C. C. (2006). NOx removal in forced unsteady-state chromatographic reactors. Chemical Engineering Science (Elsevier), 61(10), 3409-3414. DOI: 10.1016/j.ces.2005.11.060.

NO_x removal in forced unsteady-state chromatographic reactors

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Abstract

The feasibility of the Selective Catalytic Reduction (SCR) of NO_x with ammonia in unsteady-state reactors is investigated by means of numerical simulations. A reactors network (RN) with periodical change of the feeding position is shown to be an alternative to the well investigated reverse-flow reactor (RFR) in order to fulfil the requirements on NO_x conversion and ammonia emissions. Non-isothermal operation was studied, with low temperature feed, and the influence of the switching time on the mean outlet concentration of NH_3 and NO_x was investigated, as well as the response of these devices to perturbations in the pollutant feed concentration.

Keywords

Selective Catalytic Reduction, NO_x removal, Reverse-flow reactor, Reactors Network, Chromatographic reactor.

Introduction

Forced unsteady-state catalytic reactors were deeply investigated during the last 40 years as the unsteady-state operation may significantly enhance the conversion, the selectivity and the productivity and may decrease the operating costs in some catalytic processes. Reverse-flow operation, for example, allows trapping the moving heat wave inside the catalytic bed when exothermic reactions take place: the catalytic bed acts as a regenerative heat exchanger, allowing auto-thermal behaviour when the adiabatic temperature rise of the feed is low (see, for example, the reviews of Matros & Bunimovich (1996) and Kolios, Frauhammer & Eigenberger (2000)).

The idea of using a RFR to remove a pollutant A with a reactant B, for which the maximum allowable emission is much lower than that for the first one, was firstly proposed by Agar & Ruppel (1988), who suggested to carry out the Selective Catalytic Reduction (SCR) of NO_x with ammonia in a RFR using a catalyst that strongly adsorbs the ammonia, thus minimizing its emissions and providing an effective response to reactant fluctuations in the feed rate; the result is a cromatographic operation. The paper of Agar & Ruppel motivated the works of Kallrath et al. (1994), Falle et al. (1995), Noskov et al. (1996), Synder & Subramaniam (1998). In all the works concerning the SCR of NO_x with NH_3 in RFR appeared in the literature the temperature rise in the reactor was assumed to be negligible and isothermal operation was studied. This assumption allowed to simplify the analysis, enabling to focus on the impact of the operation conditions and mode on the dynamic features caused by the trapping of one reactant in the reactor. The adiabatic rise in NO_x removal is usually of the order of 10-20 K, but the temperature rise in a RFR will be a multiple of this value, thus allowing, for example, autothermal operation when low temperature gas is fed to the reactor. In these conditions, as it was stressed in the conclusion of the work of Yeong & Luss (2003), the choice of the switching time will be affected also by the dynamics of the heat wave, as too long switching time will lead to reaction extinction, due to the heat removal from the

catalyst. In our work the SCR of NO_x will be investigated in non-isothermal conditions: in our opinion in fact, if a commercial catalyst is used (and thus it is not possible to modify the chemical activity and adsorptive capacity to improve the operation) the main advantage which can be achieved through the forced unsteady-state operation is the possibility to store the heat of reaction (beside storing adsorbed ammonia). The influence of the switching time will be stressed also because the switching time is the main operating parameter that can be changed to fulfil the operation goals.

Nevertheless the RFR exhibits the problem of wash out, i.e. the emission of unconverted reactants occurring when the flow direction is reversed. Noskov et al. (1996) proposed to feed the ammonia in the middle of the reactor in order to avoid wash out of unconverted ammonia; anyway, a long semi-cycle period causes the reactant concentration to be very low in half of the reactor at the end of the semi-cycle and this may lead to a rather large temporal emission of the pollutant upon the flow reversal. Yeong & Luss (2003) investigated also the possibility of feeding ammonia only during a fraction of the semi-cycle, but concluded that continuous ammonia feeding is more efficient than a discontinuous one on every cycle.

The problem of wash out in the RFR was previously addressed by Barresi's group at the Politecnico of Torino (Brinkmann et al. (1999); Velardi & Barresi (2002); Fissore, Barresi & Baldi (2003)) who proposed a Reactors Network (RN) made of two or three reactors connected in a closed sequence as an alternative configuration. Figure 1 shows the working principle of a RN of three reactors: a set of three-way valves enables to change the feed position, thus simulating a moving bed and achieving a sustained dynamic behaviour. In this way the flow direction is maintained, ensuring a uniform catalyst exploitation and avoiding wash out. As a consequence in this paper the possibility of carrying out the SCR of NO_x with ammonia using the RN will be investigated, in order to overcome the problems aroused with the RFR and to avoid the complex feeding configurations proposed in the literature.

The model

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:

$$A + B_S \rightarrow C \tag{1}$$

$$B + S \rightarrow B_S \tag{2}$$

The kinetic model proposed by Tronconi at al. (1996) for a V_2O_5/TiO_2 catalyst (with V_2O_5 loading of 1.47%) is used; the reduction reaction is considered to be of first order with respect to each reactants:

$$r_{red} = -k_{red} c_A^* \theta_B \Omega \tag{3}$$

where θ_B is the ammonia surface coverage and c_A^* is the concentration of reactant A at the gas-solid interface. 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:

$$r_{ads} = k_{ads} c_B^* \left(1 - \theta_B\right) \Omega \tag{4}$$

while the rate of desorption is assumed to be proportional to the concentration of the adsorbed specie:

$$r_{des} = k_{des} \theta_B \Omega \tag{5}$$

An Arrhenius type dependence of the kinetic constants k, k_{ads} and k_{des} from the temperature is assumed

$$k_{red} = k_{0,red} e^{-\frac{E_{a,red}}{RT_S}} ; \quad k_{ads} = k_{0,ads} e^{-\frac{E_{a,ads}}{RT_S}} ; \quad k_{des} = k_{0,des} e^{-\frac{E_{a,des}}{RT_S}} \tag{6}$$

The kinetic model of Tronconi et al. (1996) invokes a Temkin-type adsorption isotherm, where the activation energy for desorption is a function of the surface coverage:

$$E_{a,des} = E_{a,des}^0 \left(1 - \beta \theta_B{}^{\sigma}\right) \tag{7}$$

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. Thus, the system of partial differential equations that describes the process dynamics is the following:

- gas phase mass balances:

$$\frac{\partial c_A}{\partial t} = -v\frac{\partial c_A}{\partial x} + h_A a_v \left(c_A^* - c_A\right) \tag{8}$$

$$\frac{\partial c_B}{\partial t} = -v\frac{\partial c_B}{\partial x} + h_B a_v \left(c_B^* - c_B\right) \tag{9}$$

The value of c_A^* and c_B^*, the gas concentration at the interface, can be calculated from the mass balance at the interface, assuming that there is no accumulation:

$$-h_A a_v \left(c_A^* - c_A\right) = r_{red} \tag{10}$$

$$-h_B a_v \left(c_B^* - c_B\right) = \left(r_{ads} - r_{des}\right) \tag{11}$$

- solid phase mass balance:

$$\Omega\frac{\partial \theta_B}{\partial t} = r_{ads} - r_{des} - r_{red} \tag{12}$$

- gas phase energy balance:

$$\frac{\partial T_G}{\partial t} = -v\frac{\partial T_G}{\partial x} + \frac{h_T a_v}{\rho_G c_{p,G}}\left(T_G - T_S\right) \tag{13}$$

- solid phase energy balance:

$$\rho_S c_{p,S}\varepsilon\frac{\partial T_S}{\partial t} = -h_T a_v \left(T_S - T_G\right) + r_{red}\left(-\Delta H_{red}\right) + r_{ads}\left(-\Delta H_{ads}\right) + r_{des}\left(-\Delta H_{des}\right) \tag{14}$$

The mass transfer between the gas phase and the catalyst surface was estimated by means of the correlation of Votruba et al. (1975a, 1975b), while the heat transfer coefficient was estimated assuming the analogy between heat and mass transfer.

The operating conditions are given in Table 1 and refer to a lab-scale installation. Inlet composition of the gases is considered constant and equal to the feeding value and the initial concentration of ammonia adsorbed on the catalyst surface is equal to 0 in all the reactor configurations considered; the continuity of the gas concentration and temperature is imposed between the reactors of the network.

The system of partial differential equations (8) - (14) was solved by discretising the domain of the spatial variable into a grid of 100 points, equally spaced, thus obtaining a grid-independent solution. The MatLAB solver ode15s, which is a quasi-constant implementation of the Numerical Differentiation Formulas in terms of Backward Differences (Shampine & Reichelt, 1997) was used to solve the system; the relative and absolute tolerances were set equal to the square root of the working machine precision. After a transient period, the solution of the system evolves towards a periodic-steady state (PSS): the behaviour of the reactor (temperature and concentration profiles) is the same within every cycle.

The results

Figure 2 shows the temporal evolution after the transient (i.e. when the periodic steady-state has been reached) of the outlet concentration of NO and NH_3 in a RFR. Even if autothermal operation is possible (the feed is at ambient temperature), in correspondence of the flow reversal there are spikes in the emissions of both NH_3 and NO. The results obtained in the RN made up of three reactors, with the same amount of catalyst and similar operating conditions are not shown as there are no emissions of NH_3 and of NO due to the constant flow direction which prevents wash out of unconverted reactants and ensures a uniform exploitation of the catalyst.

As it has been stated in the introduction the switching time is the main operating parameter. The mean value of the outlet reactant concentration calculated over a period, once the PSS is reached, is shown in Figure 3 both for the RN and for the RFR as a function of the switching time. As far as the emissions of NO are concerned, the RFR exhibits stable behaviour in a wide range of t_c, from few seconds, to about 10,000 s, but only for t_c lower than 1000 s the mean outlet concentration of NO is lower than 10 ppmV. At higher values of the switching time, the outlet concentration increases, due to the lower temperature in the system which is a consequence of the heat removal form the catalyst. As expected, the RN has a

different behaviour: autothermal operation with low NO emissions at low value of t_c can be obtained, but in a narrower range. Moreover, there is a second range of t_c where autothermal operation is allowed, but the conversion of NO in the RN is lower than that obtained in the RFR. Anyway, in both intervals of t_c the emissions of NH_3 are lower than those obtained in the RFR. It must be pointed out that the analysis of the influence of the switching time is of straightforward importance as it is the most important parameter that can be used for control purposes, ensuring proper operation (in terms of low emissions) when the inlet parameters (in particular the inlet flow rate) change.

The influence of the superficial velocity on the results obtained both in the RFR and in the RN is shown in Figure 4 where the mean outlet concentration of NO and NH_3 is given as a function of the switching time for three values of the surface velocity. The higher is the inlet flow rate, the narrower is the range of switching time where autothermal operation with high conversion is obtained both in the RFR and in the RN. Moreover the second interval of t_c where the operation is feasible in the RN is not only reduced, but also moved towards lower values of t_c when the flow rate is increased.

The RFR (and the RN) are known to respond much more efficiently than a fixed bed working in steady-state to any perturbation in the pollutant feed rate and/or concentration. In particular, if the operation is carried out using a fixed concentration of NH_3, the adsorbed NH_3 may be used to remove NO_x when its concentration is higher than the stoichiometric; similarly, if the concentration of NO_x is lower than the stoichiometric, the catalyst may adsorb the NH_3 in excess. We have considered two extreme situations: in the first no NH_3 is fed, in the second the flow rate of NO is set equal to zero; in both cases the system is initially in the PSS condition and the switching time is not changed, in order to highlight the robustness of these devices to face disturbances without any control actions. Figure 5 evidences the mean outlet NO (upper graph) and NH_3 (lower graph) concentration as a function of the number of cycles; the stop in ammonia feeding takes place after 50

switches both in the RFR and in the RN (grapf A and B). It is important to stress that the RN shows higher stability with respect to the RFR: the more uniform exploitation of the catalyst allows for unitary NO conversion for about 400 cycles, while the NH_3 adsorbed and not consumed by the reduction reaction is removed from the system quite constantly in the time. In the RFR the response is quite different: the NO concentration in the effluent gas starts immediately increasing, while the NH_3 concentration in the effluent gas, whose value was higher than that of the RN because of wash out, quickly decreases. When no more ammonia is adsorbed on the catalyst, the outlet NO concentration becomes equal to the inlet value. Moreover, the different dynamics shown in Figure 5 have a strong drawback in the controllability of the system. If a feedback control is used and the outlet concentration of both NO and NH_3 is used to monitor the system, it is quite difficult to understand in the RN that something dangerous is happening as the outlet NO and NH_3 concentration remain constants for a long time interval and the transition to the extinction is quite rapid. The opposite is the behaviour of the RFR where the response of the outlet concentrations of NO and NH_3 to the disturbance is much more rapid. The same conclusions are valid when the response of the RFR and of the RN are compared in the case of stop in the NO feeding (Figure 5, graph C).

Conclusions

The feasibility of the Selective Catalytic Reduction (SCR) of NOx with ammonia in the RFR and in the RN has been investigated by means of numerical simulations.

Non-isothermal operation was considered evidencing that autothermal operation is feasible also with low temperature feed. The choice of the switching time is affected not only by the dynamic of the trapping of one reactant, but also 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. The higher is the inlet flow rate, the narrower is the range of switching time where autothermal operation with high

conversion is obtained.

The resulting optimal value of the switching time both for the reverse-flow reactor and for the network of reactors with periodically varying feeding position is quite low (the order of magnitude is few seconds), due to the dimension of the catalytic reactor that has been chosen which refer to a lab-scale installation. The scale-up of these reactors to the industrial size is still an open problem as the increased dimensions of the catalytic bed will alter the dynamic of both the heat and mass storage. Increasing the length of the bed could be an effective way to achieve autothermal behaviour with higher values of the switching time, but this issue, i.e. the scale up of the results to the industrial size, is beyond the scope of this work and will be the subject of a future paper.

Finally the response of the RFR and of the RN to disturbances in the feed composition has been investigated, evidencing that the robustness of the RN is higher, even if the controllability is poorer than in the RFR.

The scale-up of these reactors to the industrial size is still an open problem as the increased dimensions of the catalytic bed will alter the dynamic of both the heat and mass storage and this issue is beyond the scope of this work and will be the subject of a future paper.

Acknowledgements

Claudiu Cristian Botar-Jid is grateful to the European Commission for a Marie Curie Training Site Fellowship that supported him during his stage at Politecnico di Torino (SICOFOR Contract Nr. HPMT-CT-2001-00343). Thanks are due to the Italian Ministry of University and Research (PRIN - 2002 2094284) for the financial support to this work.

Notation

a_v	specific surface of the catalyst, $m^2\ m^{-3}$
c	gas phase concentration, mol m^{-3}
c^*	concentration at the gas-solid, mol m^{-3}
c_p	specific heat, J $kg^{-1}\ K^{-1}$
E_a	activation energy, J mol^{-1}
h_i	mass transfer coefficient for the i-th species, m s^{-1}
h_T	heat transfer coefficient, J $m^{-2}\ s^{-1}\ K^{-1}$
$-\Delta H$	heat of reaction, J mol^{-1}
L	reactor length, m
k	kinetic constant
k_0	frequency factor
N_c	number of cycles
r	rate of reaction, mol $s^{-1}\ m^{-3}$
R	gas constant, J $K^{-1}\ mol^{-1}$
t	time, s
t_c	switching time, s
T	temperature, K
v	gas velocity, m s^{-1}
x	spatial coordinate, m

Greeks

β	parameter for the surface coverage dependence
ε	monolith void fraction
θ	surface coverage
ρ	density, kg m^{-3}
σ	parameter for the surface coverage dependence

Ω	catalyst capacity, mol m^{-3}

Subscripts and Superscripts

0	inlet condition
ads	adsorption
des	desorption
red	reduction
A, B	reactants
G	gas phase
S	solid phase

Abbreviations

PSS	Periodic Steady-State
RN	Reactors Network
RFR	Reverse Flow Reactor
SCR	Selective Catalytic Reduction
STP	Standard Temperature and Pressure

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Table 1 Values of the main operating parameters used in the simulations.

c_{NO_x}	590 ppmV
c_{NH_3}	590 ppmV
Ω	210 mol m^{-3}
ε	0.65
L	0.45 m
ρ_S	2500 kg m^{-3}
$c_{p,S}$	0.9 kJ kg^{-1} K^{-1}

List of figures

Figure 1 Practical implementation of a network of three catalytic fixed bed reactors with periodically varying feeding position.

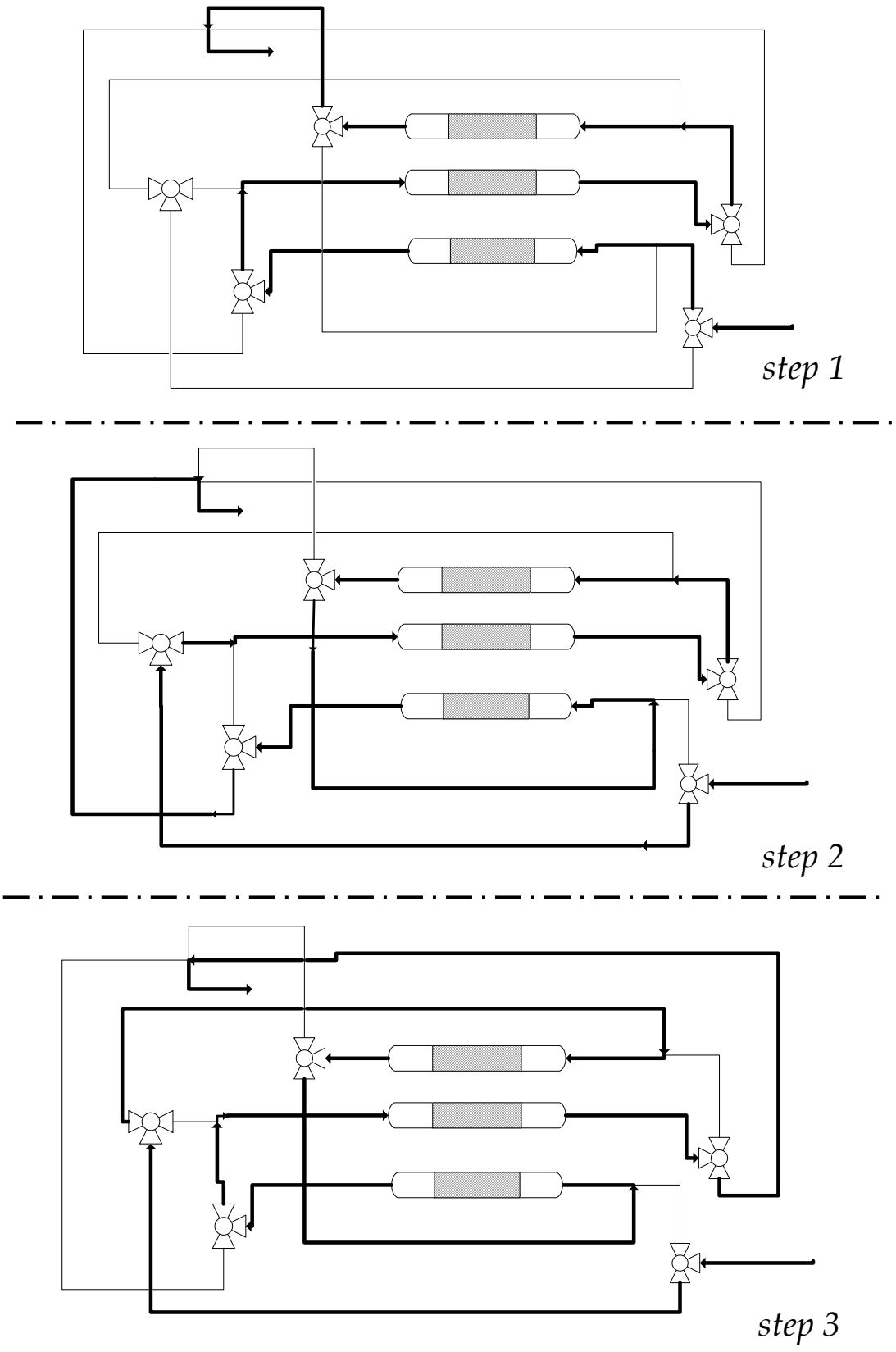
Figure 2 Temporal evolution of the outlet NO (upper graph) and NH_3 (lower graph) emissions in a RFR. t_c = 10 s, v_0 = 0.08 m s^{-1} STP.

Figure 3 Mean outlet concentration of NO (upper graph) and NH_3 (lower graph) as a function of the switching time in the RFR and in the RN. v_0 = 0.08 m s^{-1} STP.

Figure 4 Mean outlet concentration of NO (upper graph) and NH_3 (lower graph) as a function of the switching time in the RFR (on the left) and in the RN (on the right) for various values of the inlet flow rate (–■– v_0 = 0.08 m s^{-1}, –○– v_0 = 0.1 m s^{-1}, –Δ– v_0 = 0.2 m s^{-1} STP).

Figure 5 Mean outlet concentration of NH_3 (graph A) and of NO (graph B) in the RFR and in the RN as a function of the number of cycles when feeding of NH_3 is stopped after 50 cycles. Mean outlet concentration of NH_3 (graph C) in the RFR and in the RN as a function of the number of cycles when feeding of NO is stopped after 50 cycles. t_c = 20 s, v_0 = 0.08 m s^{-1} STP.

Figure 1



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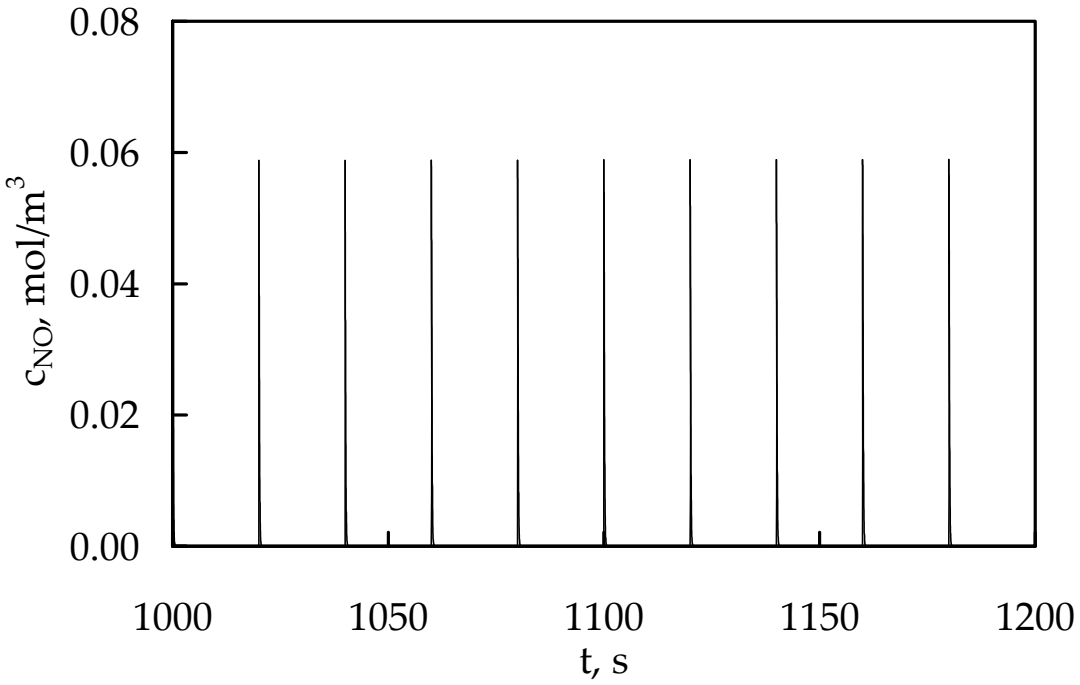
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t, s

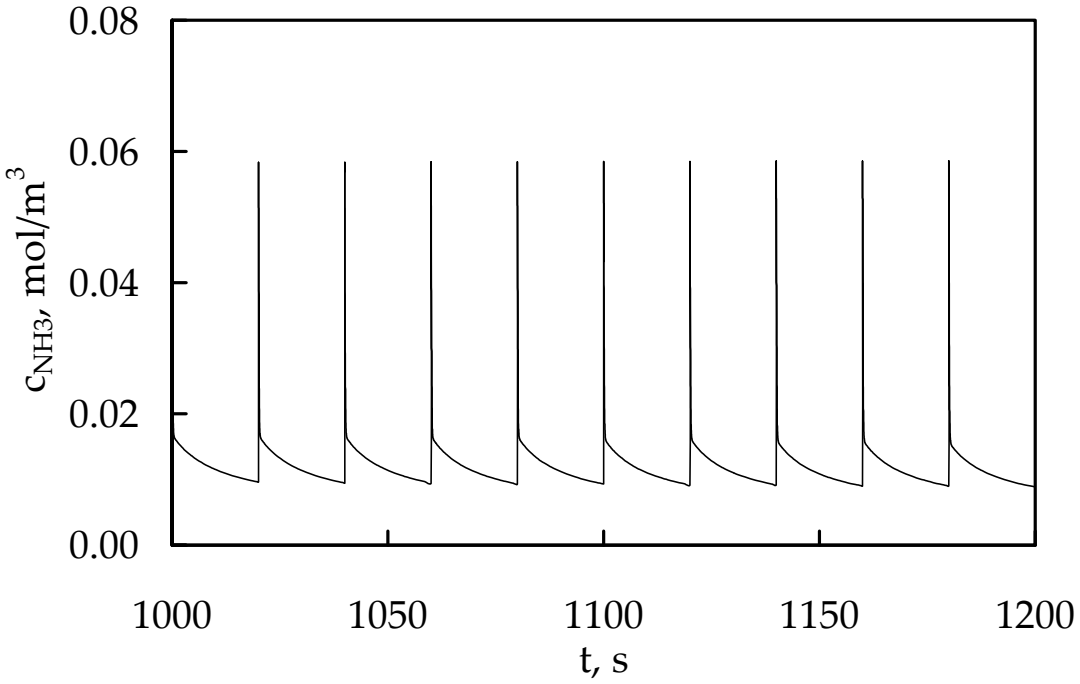
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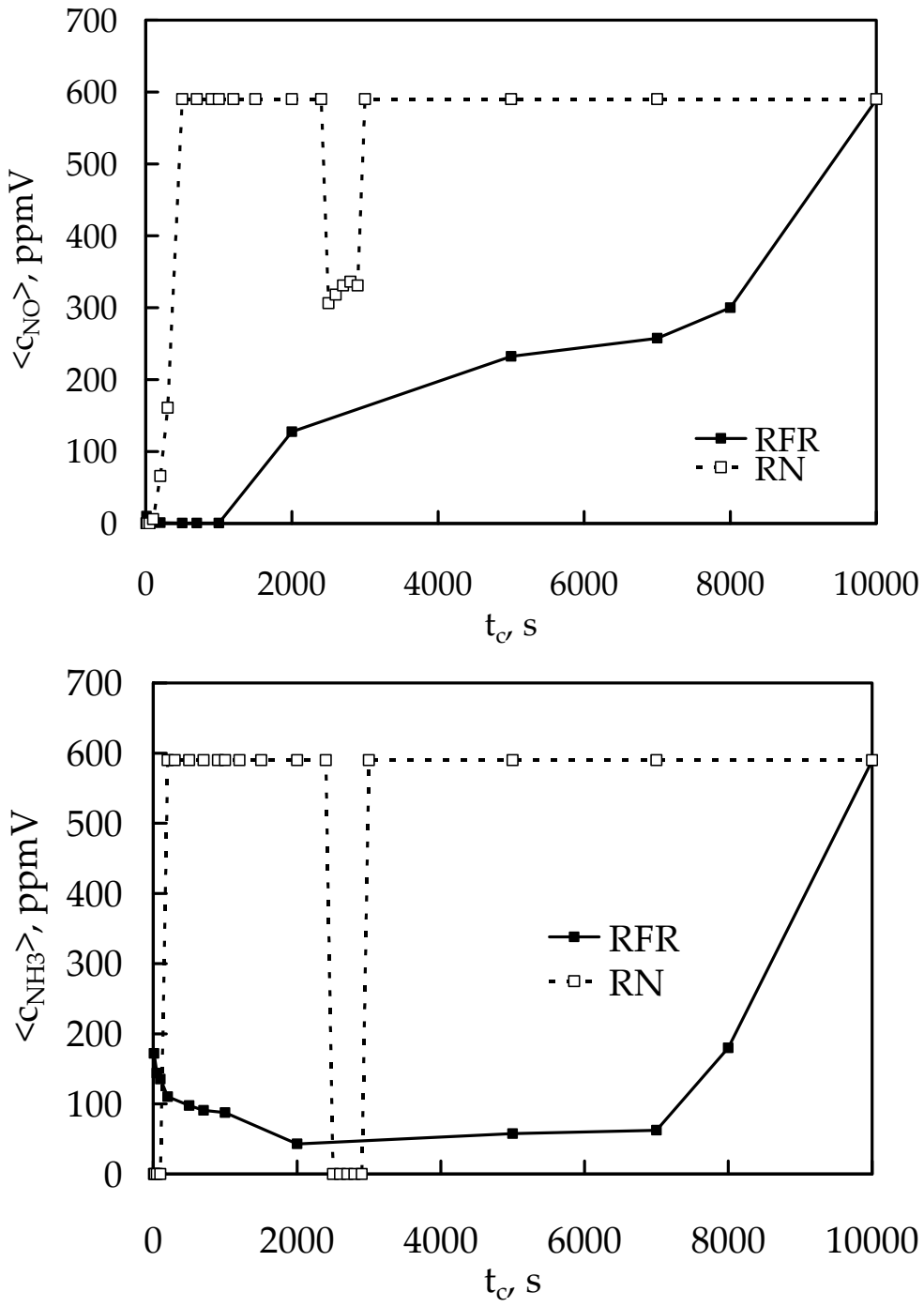
Figure 3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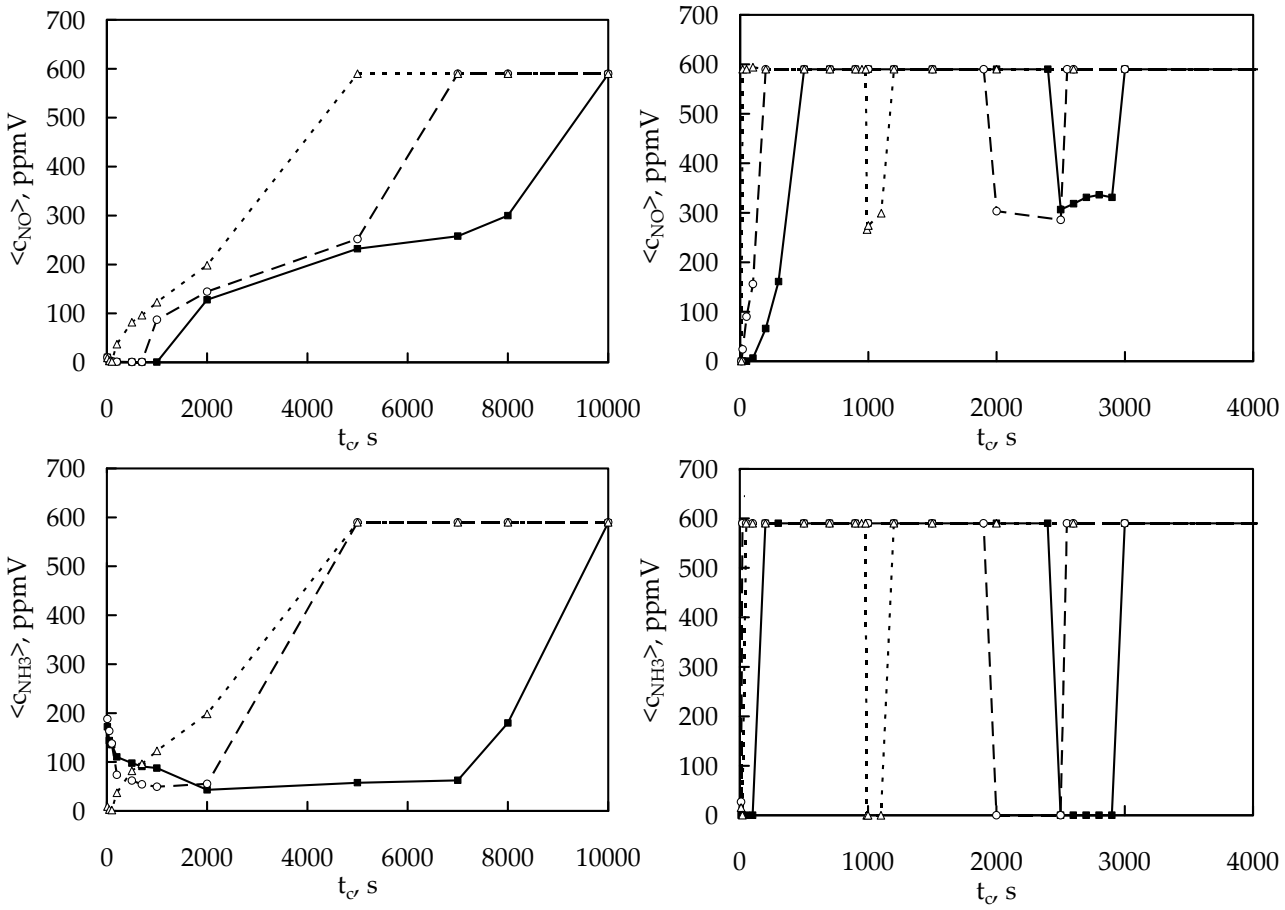
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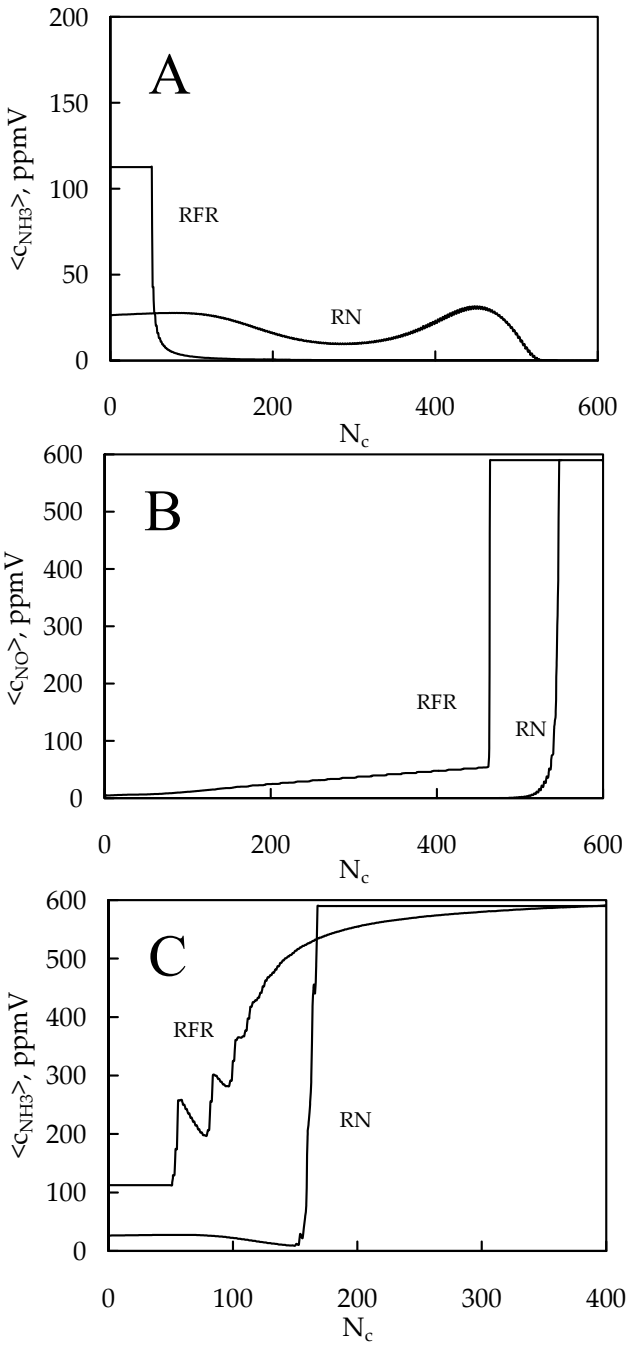
Figure 5