NOx removal in forced unsteady-state reactors

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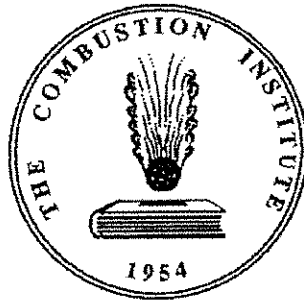
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The aim of this work is to study the feasibility of Selective Catalytic Reaction of NO$_x$ with ammonia in unsteady-state chromatographic reactors, thus coupling chemical reaction and adsorptive mass separation. The network of reactors (RN) was considered as an alternative to the well investigated reverse-flow reactor (RFR): the main advantage is the thermal buffering and the ammonia storage, thus allowing for autothermal operation even when low temperature gas is fed, and avoiding undesired ammonia emission. An Eley-Rideal mechanism was used to model the reaction between NO$_x$ in the gas phase and ammonia adsorbed on the catalyst: this reaction is considered to be of first order with respect to each reactant. Since both RFR and RN can afford autothermal operation with low heat of reaction, isothermal and non-isothermal operation with low temperature feed were investigated by means of numerical simulation. The results obtained with different operating conditions, namely inlet concentration, flow rate and switching time, were compared.

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Introduction

In most chemical processes, the chemical reaction itself is only one of several processes taking place. There are often internal and external separation and heat exchange processes, which are of critical importance for the reaction performance and in the subsequent processing steps. In view of this complex picture, reaction engineering is shifting from conventional reactors operating under steady state to multifunctional reactors. These new type of reactor takes advantage of the coupling of several operations into a single equipment to improve in characteristics, such as yield, productivity, flexibility, safety, and investment and operation costs. Unsteady-state reactors are an example of multifunctional reactors as they can couple chemical reaction and adsorptive separation. Selective Catalytic Reaction (SCR) of NO$_x$ with ammonia is a typical process that can take advantage from this mode of operation. A reactors network (RN) with periodical change of the feeding position, which simulates the operation of a moving bed reactor, was shown to be more effective than the well known reverse-flow reactor (RFR) in order to fulfill the environmental regulamentation. Figure 1 shows the working principle of the RFR and of the RN: while in the latter, the flow direction is periodically reversed, resulting in a non-stationary operation, in the former, the gas flow direction is never changed, thus avoiding the emission of ammonia (whose allowed concentration is lower than that of NO$_x$) that occurs at RFR at every switch, beside fulfilling the NO$_x$ conversion requirements. Since both RFR and RN can afford autothermal operation (Agar & Ruppel,1988; Yeong & Luss, 2003) with low temperature rise, isothermal and non-isothermal operation with low temperature feed were investigated by means of numerical simulation and the performances of both devices were compared in a wide range of operating conditions.
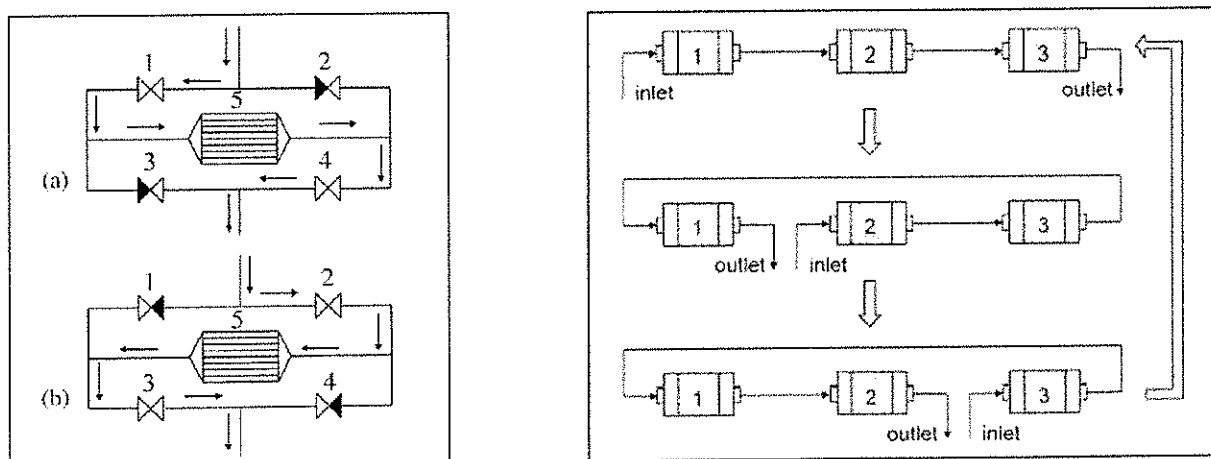

Figure 1. Working principle of the reverse flow reactor (right hand graph) and of a network of three catalytic fixed bed (left hand graph).

The influence of the switching time (t_c) in both reactor configurations was studied. This analysis is important not only as it allows to compare the two devices and to optimise the operation, but also as the switching time is the main operating parameter that can be changed to fulfil the operation constraints. In fact, t_c affects substantially both the thermal buffering and the ammonia storage. The choice of this parameter is affected mainly by the dynamic of the heat wave: too long switching time will lead to reaction extinction, due to the heat removal from the catalyst. Preliminary investigations by means of numerical simulation show the influence of the switching time on the outlet concentration of NH_3 and NO_x in the RFR and in the RN. Since the instantaneous value is variable with time, due to the unsteady-state operation, the mean value of the outlet reactant concentration calculated over a period, once the pseudo-stationary state (PPS) is reached, was observed; the RN configuration resulted to be the better one for a larger range of t_c.

Modelling

A heterogeneous mathematical model was used to investigate the performance of the RFR and of the RN. An Eley-Rideal mechanism was used to describe the reaction between NO_x in the gas phase and the ammonia adsorbed on the catalyst; 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, while 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. The non dimensional mass balances are thus:

$$\frac{\partial C_A^*}{\partial t^*} = -v^* \frac{\partial C_A^*}{\partial x^*} + Pe_A(C_{A,i}^* - C_A^*)$$

$$\frac{\partial C_B^*}{\partial t^*} = -v^* \frac{\partial C_B^*}{\partial x^*} + Pe_B(C_{B,i}^* - C_B^*)$$

$$\frac{\partial \theta_B}{\partial t^*} = Da_{ads}e^{-\gamma_{ads}(\frac{1}{T_S^*}-1)}C_{B,i}^*(1-\theta_B) - Da_{des}e^{-\gamma_{des}(\frac{1}{T_S^*}-1)}e^{\gamma_{des}\frac{\beta\theta_B^\sigma}{T_S^*}}\theta_B - Da_{red}e^{-\gamma_{red}(\frac{1}{T_S^*}-1)}C_{A,i}^*\theta_B$$

for the bulk gas concentration of NO_x, NH_3 and the adsorbed NH_3 respectively. The non-dimensional energy balances are:

$$\frac{\partial T_G^*}{\partial t^*} = -v^* \frac{\partial T_G^*}{\partial x^*} + St \cdot \frac{\rho_0}{\rho_G}(T_G^* - T_S^*)$$

$$\alpha\frac{\partial T_S^*}{\partial t^*} = St(T_G^* - T_S^*) + Da_{red}\Delta T_{ad,red}C_{A,i}^*\theta_B e^{-\gamma_{red}(\frac{1}{T_S^*}-1)}A + Da_{ads}\Delta T_{ad,ads}C_{B,i}^*(1-\theta_B)e^{-\gamma_{ads}(\frac{1}{T_S^*}-1)}A +$$

$$- Da_{des}\Delta T_{ad,des}\theta_B e^{-\gamma_{des}(\frac{1}{T_S^*}-1)}e^{\gamma_{des}\frac{\beta\theta_B^\sigma}{T_S^*}}A$$

The parameters used for the adimensionalization are:

$$x^* = \frac{x}{L}, \quad v^* = \frac{v}{v_0}, \quad t^* = t\frac{v_0}{L}, \quad \alpha = \frac{\rho_S c_{PS}}{\rho_0 c_{P_G}}, \quad A = \frac{\Omega}{C_A^f}, \quad C_A^* = \frac{C_A}{C_{A,0}}, \quad C_{A,i}^* = \frac{C_{A,i}}{C_{A,0}}, \quad C_B^* = \frac{C_B}{C_{A,0}}, \quad C_{B,i}^* = \frac{C_{B,i}}{C_{A,0}},$$

$$T_G^* = \frac{T_G}{T^f}, \quad T_S^* = \frac{T_S}{T^f}, \quad Pe_A = \frac{h_A a_v L}{v_0}, \quad Pe_B = \frac{h_B a_v L}{v_0}, \quad St = \frac{h_T a_v L}{\rho_0 c_{P_G} v_0},$$

$$\gamma_{ads} = \frac{E_{ads}}{RT^f}, \quad \gamma_{des} = \frac{E_{0,des}}{RT^f}, \quad \gamma_{red} = \frac{E_{red}}{RT^f},$$

$$Da_{ads} = \frac{k_{0,ads}e^{-\gamma_{ads}}LC_{A,0}}{v_0}, \quad Da_{des} = \frac{k_{0,des}e^{-\gamma_{des}}L}{v_0}, \quad Da_{red} = \frac{k_{0,red}e^{-\gamma_{red}}L \cdot C_{A,0}}{v_0},$$

$$\Delta T_{ad,ads} = \frac{(-\Delta H_{ads})C_{A,0}}{\rho_0 c_{p_G} T^f}, \quad \Delta T_{ad,des} = \frac{(-\Delta H_{des})C_{A,0}}{\rho_0 c_{p_G} T^f}, \quad \Delta T_{ad,red} = \frac{(-\Delta H_{red})C_{A,0}}{\rho_0 c_{p_G} T^f},$$

Results

Both devices (RFR and RN) were simulated. Isothermal operation was considered at first in order to point out the influence of the unsteady-state operation on the performance of the reactors, without affecting it with the dynamic of the heat wave. Since in the RN performance wash out effect is not present, the mean outlet concentration of both reactants is much lower. As it is shown in Figure 2 the operation in the RN results in lower NO_x emissions with respect to the RFR; moreover, no NH_3 is present in the product stream. The performance of the RN is quite insensitive to the feed flow rate, while in the RFR higher emissions are obtained as a consequence of an increase of the feed flow rate.
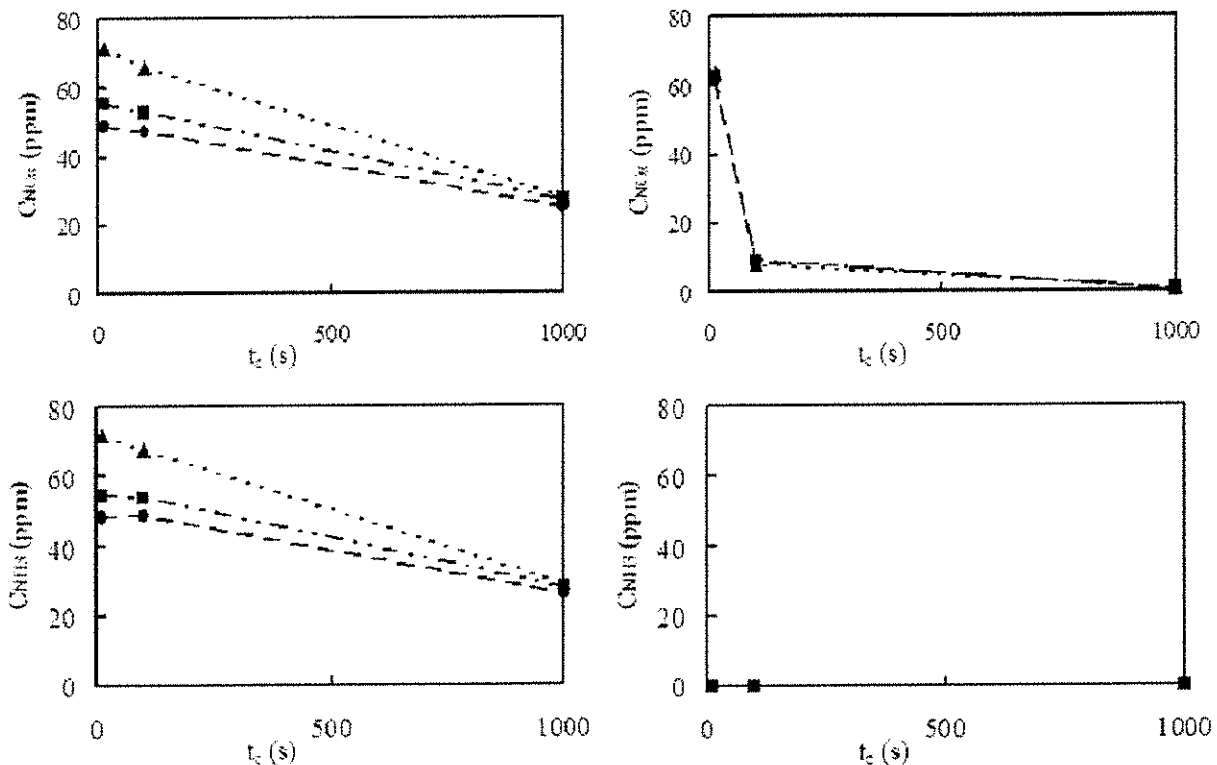

Figure 2.The influence of switching time on the mean outlet concentration of NO_x and of NH_3 in the RFR (on the left) and in the RN (on the right). The temperature of the system is considered to be constant and equal to 250°C. The kinetic model of Tronconi et al.(1996) was used in the simulations. ($- - -\bullet - - - v_0 = 0.053$ m/s; $-\cdots-\blacksquare \cdots-\cdots- v_0 = 0.066$ m/s; $---\blacktriangle--- v_0 = 0.13$ m/s)

As it has been stated in the Introduction, both systems can be considered multifunctional from the energetic point of view as well as they are able to store the heat of reaction in the solid bed, thus allowing for autothermal operation even if the adiabatic temperature rise of reaction is low. This is the case of our reaction in which the pollutants are diluted in a non-reacting atmosphere. This point is very important when considering industrial operation because, if autothermal performance is achieved, the operation costs are lower and, as a consequence, the process is more efficient from the economical point of view. So, after the start up phase, when reaction temperature is reached, the energy supply is stopped.

In order to maintain the autothermal operation the switching time has to be properly chosen. Figure 3 shows an example where the high value of the switching time leads to reaction extinction both in the RFR and in the RN due to the heat removal from the catalytic bed.
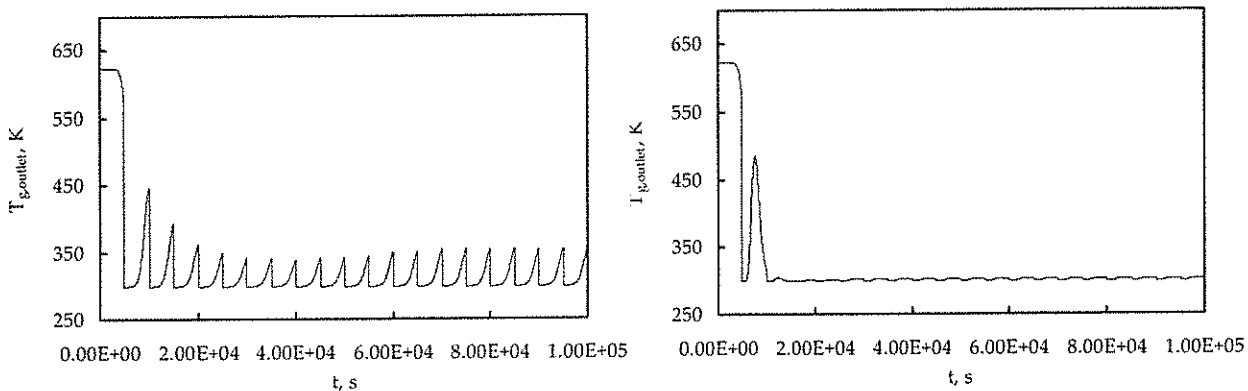
Figure 3.Time evolution of the outlet gas temperature in the RFR (on the left) and in the RN (on the right). t_c=5000 s, v_0 = 0.053 m/s
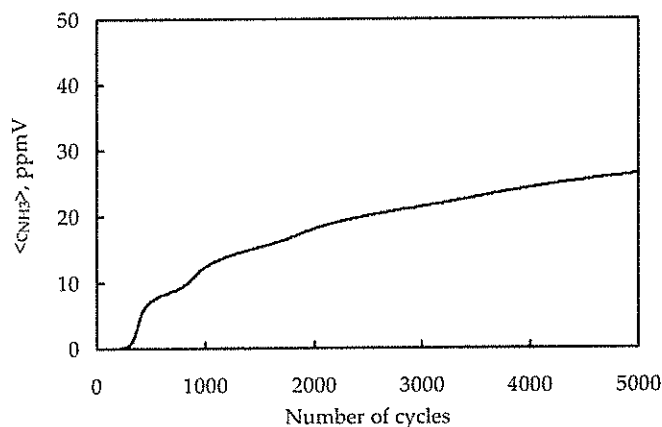

Figure 4. Time evolution of the outlet NH_3 concentration in the RFR. t_c=5 s , v_0 = 0.053 m/s.

In order to reach and to maintain the autothermal operation low values of the switching time are required both in the RFR and in the RN. When stable operation is obtained, the RN gives lower ammonia concentration in the product stream. This can be seen in Figure 4 where the mean ammonia emission (over a cycle) is shown for the RFR in the transient period; the curve for the RN (in the same conditions) is not shown as the NH_3 concentration in the product is negligible.

Acknowledgements

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