

Comparison of reverse flow and counter-current reactors in case of selective catalytic reduction of NO_x

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Abstract

The paper is focused on the comparison of the reverse flow reactor (RFR) and of the counter-current reactor (CCR) operation, focusing the attention on the interaction between transport phenomena and chemical reactions, as well as on the analysis of the dynamic behavior. A heterogeneous mathematical model was used in order to investigate the performance of both reactor configurations. The role of the thermal balance was stressed. Auto-thermal reactor operation was obtained even when low temperature gas is fed to the reactor. Temperature profiles, reactants conversion inside the apparatus and the response to perturbation in the feeding flow have been used as criteria for comparison. Numerical simulations revealed that RFR has an asymptotic behavior coincident to the CCR, which is technically simpler to be realized. However the domain where the counter-current reactor can be used as a limiting case of the RFR depends on the internal heat transfer coefficient, switching time, flow condition and reactor geometry.

Keywords

Selective Catalytic Reduction, NO_x removal, Reverse-flow reactor, Counter-current reactor, Chromatographic reactor

1. Introduction

The analysis of the complex dynamic interaction between transport phenomena and chemical reactions and the investigation of systems response in case of non-stationary operation offers new possibilities of reactor design and operation. Cottrell [1] suggested the reverse flow reactor operation as an efficient mode of treating dilute gas pollutant mixtures. The operation supposes that the catalyst bed is preheated to a relative high temperature and a cold reactive mixture is feed into reactor. As a consequence of the flow circulation in the reactor it appears a thermal front wave that moves towards the reactor outlet. Keeping the thermal wave inside the reactor is possible if the gas flow direction is periodically reversed. The advantage of this mode of reactors operation is the possibility of achieving auto-thermal reactor behavior even when a low exothermic reaction takes place.

The evaluation of the transient and of the pseudo steady-state (PSS) behavior of the RFR is time consuming, because more than one hundred cycles are generally necessary before the PSS is reached. Finding the limit conditions which can cause extinction, in particular, require a huge number of simulations, using a trial and error approach. The use of a detailed model permits to predict the behavior before the attainment of the PSS and to put in evidence and to understand the characteristics of the system, but it is unpractical for design, sizing and optimization of the bed. Due to these reasons, we considered the possibility of using a simplified model for the RFR in order to achieve practical goals.

Under certain assumptions the behavior of RFR is similar to that of a counter-current reactor, although the last one is much simpler to operate. If similar operating conditions are considered and if an infinitely fast internal heat transfer model is assumed, almost the same solid temperature and gaseous composition profiles can be obtained in the CCR and in the RFR with fast flow reversal.

The aim of the present article is the investigation, by means of numerical simulations, of the performance of RFR and CCR when the Selective Catalytic Reduction (SCR) of NO_x with NH_3 takes place. In particular the influence of the adsorptivity of the catalyst and of the kinetic, will be addressed, because only a precise consideration and quantification of the phenomena taking place inside the catalytic bed provide a reliable means for achieving maximal performance of the reactor for a given size, shape and operating conditions (temperature, gas velocity and pollutant concentrations). Moreover, we will examine the CCR as a limiting model for the RFR with fast flow reversal.

2. Problem Statement, background

Our group recently investigated the behavior of a monolithic reactor operating in flow-reversal and counter-current reactor modes. The counter-current reactor is considered to be built by one tube filled with a monolithic catalyst; the feeding is divided into two halves: one half is introduced from one side and the other half from the opposite side. The reactor can be employed then either as a simple once-through monolith with flow reversal or with a counter-current flow. A heterogeneous mathematical model that assumes no mass and energy dispersive transport, no pressure loss inside the reactor and adiabatic operation was considered. The interface gas concentrations were calculated from the mass balance at the interface assuming that there is no accumulation. The heat and mass transfer coefficients have been calculated using the asymptotic solution for a circular duct with fully developed concentration and temperature profiles Skelland [2]. An Eley-Rideal mechanism is used to model the reaction between NO_x and ammonia. The kinetic model proposed by Tronconi et al. [3] for a V₂O₅/TiO₂ catalyst (with V₂O₅ loading of 1.47%) was used; the reduction reaction is considered to be of first order with respect to each reactant. 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 was assumed. The kinetic model of Tronconi et al. [3] invokes a Temkin-type desorption isotherm, where the activation energy for desorption is a function of the surface coverage. The inlet gases composition is considered constant and equal to the feeding value and the initial concentration of ammonia adsorbed on the catalyst surface is equal to 0. The catalyst is pre-heated to a uniform temperature of 360° C and adiabatic operation is assumed. The other operating conditions are given in Table 1. The system of partial differential equations was solved using the MatLAB solver ode15s [4]; 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) in case of RFR, being the behaviour of the reactor (temperature and concentration profiles) the same within every cycle; in the case of the CCR a steady state solution is obtained after the transient.

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

c_{NO_x}	560 ppmV	Ω	210 molm ⁻³	ν	0.27 m s ⁻¹	ρ_s	2500 kg m ⁻³
c_{NH_3}	560 ppmV	L	0.45 m	t_{sw}	600-1200 s	$c_{p,s}$	0.9 kJ kg ⁻¹ K ⁻¹

3. Results and discussion

When the operation of both reactors is compared, the catalyst bed is supposed to be preheated to a relative high temperature and a cold reactive mixture is feed. If an adiabatic fixed-bed is considered, the cold gas that came from one side of the reactor it is heated up by the hot monolith. As soon as the ignition temperature (T^{ign}) is exceeded, reactants conversion starts and exothermic reaction and heat transfer take place simultaneously. In case of RFR, before the heat front wave formed leaves the reactor, the flow direction is reversed and the hot gas, that comes from the opposite reactor end, delivers its heat to the catalyst support. As a consequence of this flow circulation, in the center of the reactor, temperature rises over T^{ign} .

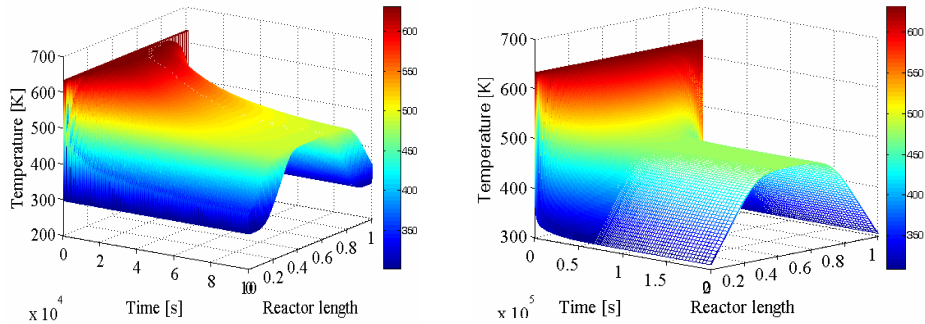


Figure 1. 3D representation transient temperature profile in RFR (left) and CCR (right)

The limit of fast flow reversal leads to a direct correspondence with counter-current operation (Figure 1 and 3). Almost the same temperature profiles are obtained. In case of CCR the gas flow is fed from both reactor ends. In this way the heat of reaction accumulated in the center of the reactor enables the heating up of the cold gas assuring the required T^{ign} . Similar conditions are obtained in the two sections of the monolith channels when the same heat transfer parameters are used and under the assumption that the heat resistance of the catalyst support is negligible. In the CCR the maximum temperature is slightly lower; this because in RFR a better trap of heat released by chemical reaction is obtained as a consequence of reverse flow operation.

When the pseudo-stationary (RFR) or the true stationary (CCR) state is established, similar concentration profiles are obtained (Figures 2 - left and center). Both in RFR and CCR high reactant conversions are obtained. Essential differences appear in case of trapped ammonia profiles on the catalyst surface. Higher quantities of NH_3 are adsorbed inside the RFR (Figure 2 - right).

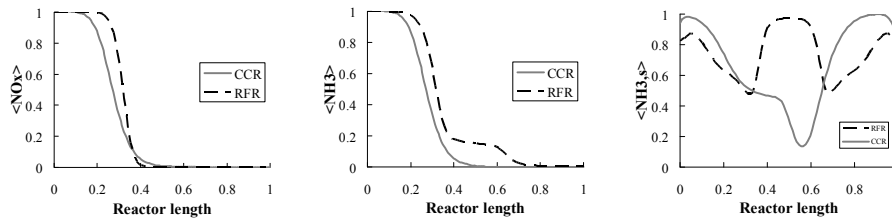


Figure 2 Axial profiles of mean value concentration of NO_x in the RFR and CCR

The asymptotic behavior of the RFR related to the CCR is revealed in Figure 4 in terms of transient temperature obtained. Simulations were made for different switching times ($t_{w/s}$) and all confirmed the same asymptotic behavior. The influence of the inlet gas velocity in both CCR and RFR is shown in Figure 5, higher catalyst temperature (left) and reactants conversions (center) are obtained when the flow rate is low.

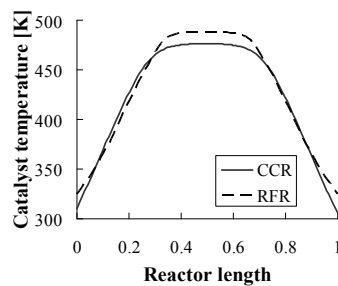


Figure 3 Axial solid temperature profile in the RFR and CCR

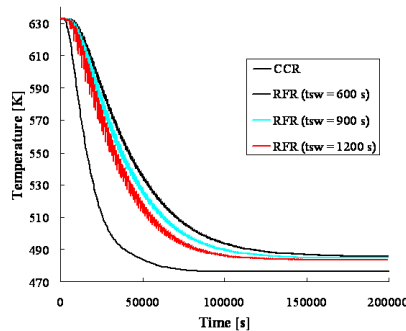


Figure 4 Asymptotic profile of temperatures in case of RFR vs. CCR

In CCR the domain of inlet gas velocity (and thus of feed flow rate) which allows for auto-thermal operation with high conversions is slightly reduced. The gas residence time must be slightly higher in the CCR in comparison to the RFR in order to enable a stable operation.

The CCR, as well as the RFR, is self-adaptive with respect to disturbances that can appear in the inlet flow. This can be seen from the NO_x outlet concentration profiles in Figure 6. The simulations were performed for a time interval of about 10^5 s, which is necessary for achieving the stationary state, and then for other 10^5 s in which ammonia feeding is stopped. The NO_x concentration begins to rise in CCR, after the interruption of the NH_3 feeding, in about $4 \cdot 10^3$ s and in RFR in about $15 \cdot 10^3$ s as a consequence of higher quantities of adsorbed ammonia in the RFR.

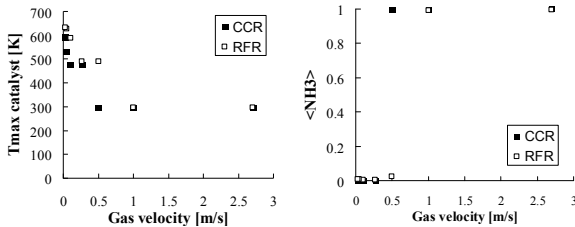


Figure 5 Influence of inlet gas velocity on maximum catalyst temperature (left) and NH_3 conversion (right)

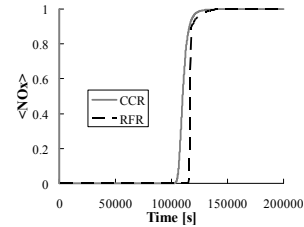


Figure 6 Influence of NH_3 feeding interruption on the NO_x mean value outlet concentration

4. Conclusions

The performances of the counter-current and of the reverse flow reactors, in case of selective catalytic reduction of NO_x with ammonia, have been analyzed. The temperature profiles and the level of conversions achieved, as well as the robustness facing disturbances in the inlet flow revealed a similar behavior of the two types of reactor studied. In addition, in conditions of fast switching of flow direction, in terms of transient temperature, the asymptotic behavior of the RFR related to the CCR was identified. All these enabled us to suggest the CCR as a limiting model for RFR operation, assuming quasi-steady gas balances, which means that the residence time of the gas has to be considerably shorter than the switching period. This analogy provides a simple basis for short-cut calculations, since the steady-state of a counter-current reactor can be computed much easier than the periodic steady-state of a reverse flow reactor.

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