Modelling and Simulation of a Catalytic Fixed Beds Network Operated in Forced Unsteady State Conditions

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The work presents an analysis of a network of catalytic fixed beds operated in forced unsteady state regime by changing periodically the feed point. As a case study it is considered the process of waste gases decontamination by VOC combustion. The process is mathematically described by a heterogeneous one-dimensional model. The study reveals the existence of a tight interval of time durations between two successive feed point shifts, ensuring the stabilization of operation (quasi steady state regime). Among the working parameters, the strongest influences on process state and operation stability have the gas flow rate and feed composition. The study of temperature and conversion sensitivity in respect with model parameters evidenced the highest dependence in respect with solid-gas heat transfer coefficient and axial thermal conductivity of solid.

Keywords: catalytic fixed bed, unsteady state, combustion, mathematical model, simulation

Continuous process operation in forced unsteady state conditions (FUSC) has been studied since the early 1960s. These studies highlighted the potential of increased process efficiency by this type of operation: increased conversion and selectivity, reduced catalyst deactivation, autothermal behaviour [1]. In the class of catalytic fixed bed reactors, two types of FUSC are presently the most investigated: reverse-flow operation (RFR) of single bed reactors and the network of fixed beds (NFB) operated with periodical change of feed point. The RFR operating technique was firstly described by Frank-Kamenetsky (cited in [2]) and developed by Boreskov and Matros [3]. Two major advantages of this technique are usually exploited practically: (i) the possibility of using the thermal storage capacity of the catalytic bed, which operates as a regenerative heat exchanger, thereby allowing an autothermal behaviour even at low concentrations of the reactants, and (ii) a specific temperature profile along the bed, favorable for reversible exothermic reactions.

Vanden Bussche and Froment [4] and Velardi and Barresi [5] analyzed the concept of fixed beds network, unsteady-state operated by changing periodically the feeding point, which can achieve a higher conversion, as compared to a single reverse flow reactor. Botar-Jid et al. [6] investigated the NOx reduction with ammonia in a reverse flow reactor, highlighting the similarities of this system with a steady-state counter-current reactor.

Other types of fixed bed catalytic reactors operated in forced transitory state were described by Boreskov and Matros [3], Brinkmann and Barresi [7] and Kolios and Eigenberger [8].

The aim of this paper is to evaluate, by modeling and simulation, the unsteady state operation of the fixed beds network with periodical change of the feed point, the stabilization mechanism of temperature space and time evolutions (pseudo-steady state), as well as aspects regarding the process sensitivity in respect with working variables.

As case study, it is considered the gas effluents treatment by catalytic combustion. Given the relatively low feed concentration of volatile organic compounds in these applications, the adiabatic temperature increase in the combustion reactor is limited, which makes advantageous the realization of autothermal operation by unsteady-state operation [1,9-12]. The importance of the catalytic combustion as a gas cleaning method is underlined in a series of published works [13-15].

The network of fixed beds operated in forced unsteady state regime

To illustrate the principle of this system, we consider a network of two or more fixed beds operated adiabatically, interconnected in such a way that each bed can be fed either from the preceding one or from the fresh reactant line. Similarly, the effluent of a bed can be fed to the next bed or, alternatively, evacuated to the exit line. In figure 1 is presented a network of three beds A,B and C, that can be connected to the reactant inlet feed and products outlet line respectively, in any sequence (ABC, BCA or CAB), by a set of six valves V1, V2...V6. Each bed consists of an inert solid zone (with no catalytic activity) at bed entrance and a second catalytic zone preceding the outlet.

The operation principle of a NFB consists in contacting a low temperature (usually the ambient one) gas flow, containing the reagents, with the solid of the network beds, initially heated at a relatively high temperature. The incoming gas will be heated by the solid of the first contacted bed (say A) and will arrive on the catalytic zone, at a temperature permitting the light-on of the chemical

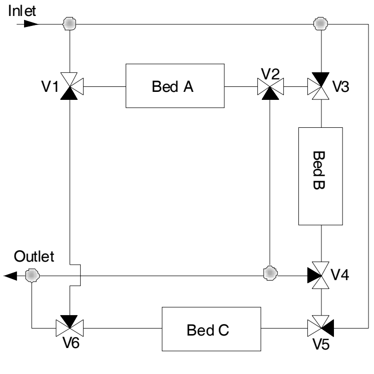

Fig. 1. A three beds network with periodical change of feed point

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reaction. On the catalyst zone, due to the exothermic reaction, the temperature of the gas will increase to some extent and the reaction will continue on the catalyst zones of next beds, B and C. In time, continuing the gas feed and its preheating, it is developing a cold zone of solid in the first bed, which is extending continuously towards the bed exit. After a time interval (t_s), that we'll further call 'switching time', the feed position is changed (by acting the set of valves), so that the bed A (the first one in the previous stage) becomes the last one in the new stage, and the sequence order becomes BCA. During the sequence (stage) BCA, a cooled solid zone appears at the entry of B and the former cooled zone of A will be continuously heated by the gas coming from the beds B and C. After an identical feed duration (t_s) over the sequence (stage) BCA, a subsequent switch of feed position leads to reactor sequence CAB, the same phenomena occurring also in this stage. Continuing the switching of feed point in the same manner, after a sufficiently high number of shifts, the process is either extinguished (by cooling the solid under the reaction light-off temperature) if the switching time is not properly selected, or stabilized in such a way that the axial evolutions of temperature and concentration are repeating periodically. A number of switching times equaling the number of beds of the network is called period (t_p) (for the network presented in figure 1, $t_p=3t_s$).

A particular matter in the modeling of unsteady processes is the validity of kinetic relations obtained from steady-state data for the physical and chemical process steps, during unsteady operation. However, this issue is usually neglected, lacking relations and parameter values well verified in unsteady state conditions.

Mathematical model and numerical method

In the published studies, the behavior of adiabatic unsteady operated fixed bed reactors is described by mathematical models of different complexities: one-dimensional pseudo homogeneous models with plug flow of gas phase and heat transport in the solid phase by conduction [1,16] or heterogeneous one dimensional models considering concentration and temperature inter-phase gradients [12,17-19]. The most comprehensive mathematical model for unsteady operated catalytic fixed beds, with periodical switching of feed point, appears to be the one-dimensional heterogeneous one with axial mass and heat dispersion, which will be adopted in this study.

In the case of single reactions, as VOCs combustion, the mathematical model of an unsteady process occurring inside a fixed catalytic bed operated adiabatically includes VOCs (A) mass balance equations in the gas phase (1) and solid phase (2), as well as the heat balance equations for the gas phase (3) and solid (4) respectively:

$$\varepsilon\frac{\partial Y_{AG}}{\partial t}=\varepsilon D_L\frac{\partial^2 Y_{AG}}{\partial z^2}-u\frac{\partial Y_{AG}}{\partial z}-k_G a_v\left(Y_{AG}-Y_{AS}\right) \tag{1}$$

$$k_G a_v C_t\left(Y_{AG}-Y_{AS}\right)=\rho_{cat}\eta_i r_A\left(Y_{AS},T_S\right) \tag{2}$$

$$\varepsilon\rho_G c_{pG}\frac{\partial T_G}{\partial t}=\varepsilon\lambda_{LG}\frac{\partial^2 T_G}{\partial z^2}-u\rho_G c_{pG}\frac{\partial T_G}{\partial z}+\alpha a_v\left(T_S-T_G\right) \tag{3}$$

$$\rho_S\left(1-\varepsilon\right)c_{pS}\frac{\partial T_S}{\partial t}=\left(1-\varepsilon\right)\lambda_{LS}\frac{\partial^2 T_S}{\partial z^2}+\left(-\Delta H_{RA}\right)\rho_{cat}\eta_i r_A\left(Y_{AS},T_S\right)-\alpha a_v\left(T_S-T_G\right) \tag{4}$$

The surface reaction kinetics is considered of first-order with respect to VOCs concentration (a kinetic appropriate for hydrocarbons combustion on noble metal catalysts):

$$r_A=k_1(T_s)C_{AS}; \quad k_1(T_s)=k_0\ \exp\left(-\frac{E_A}{RT_s}\right) \tag{5}$$

Initial conditions for all the beds:

$$t=0,\ 0\le z\le L,\ Y_{AG}=0; \quad T_G=T_S=T_i;$$

The boundary conditions are of Dankwerts type, the axial coordinate origin (z=0) representing the feed point and z = L the exit of each catalytic bed: (6)

$$z=0,\ t>0, \qquad u\cdot\left(Y_{A0}-Y_{AG}\right)=-\varepsilon D_L\frac{\partial Y_{AG}}{\partial z} \tag{7}$$

$$\rho_G u\, c_{pG}\left(T_{G0}-T_G\right)=-\varepsilon\lambda_{LS}\frac{\partial T_G}{\partial z} \tag{8}$$

$$\frac{\partial T_S}{\partial z}=0$$

$$z=L,\quad t>0; \qquad \frac{\partial Y_{AG}}{\partial z}=\frac{\partial T_G}{\partial z}=\frac{\partial T_S}{\partial z}=0 \tag{9}$$

The nonlinear partial differential equations (PDE) systems, as equations (1) to (4), are traditionally solved by orthogonal collocation or finite difference methods. Our trials to use the finite elements orthogonal collocation led to some inconveniencies (essentially oscillations of numerical solutions), so, despite its higher calculation time, we preferred the finite difference method in the variant known as the method of lines. This involves approximating by finite differences the derivatives with respect to axial coordinate (z) and the integration of the resulted ordinary differential equations system with respect to time [20,21]. An effective discretization of the space variable is supposing intervals of adequate sizes, corresponding to the migration speed of temperature and concentration fronts [22]. The transport parameters involved in the balance equations (1)-(4) were calculated by using published relations [9]. The gas-solid mass and heat transfer coefficients were considered as averages of several published correlations [23]. The physical properties of the reaction system are presented in table 1. A non-uniform distribution (egg-shell) has been taken into account for the platinum on alumina commercial pellets, which have relatively large dimensions. In spite of small thickness of Pt layer inside the pellet, the internal diffusion can limit significantly the overall process kinetics. To include this limiting effect, it is calculated an internal effectiveness factor by relation:

$$\eta_i=\frac{\overline{r}_A}{r_A(C_{AS},T_S)}=\frac{3}{\left(1-\xi_1^3\right)\varphi^2}\frac{\left(\xi_1\varphi^2-1\right)\sinh\varphi\left(1-\xi_1\right)+\varphi\left(1-\xi_1\right)\cosh\varphi\left(1-\xi_1\right)}{\xi_1\varphi\cosh\varphi\left(1-\xi_1\right)+\sinh\varphi\left(1-\xi_1\right)} \tag{10}$$

$$\text{With } \varphi=R\sqrt{\frac{k_1\left(T_S\right)}{D_{ef}}}; \quad \xi_1=\frac{R-\delta_c}{R}; \tag{11}$$

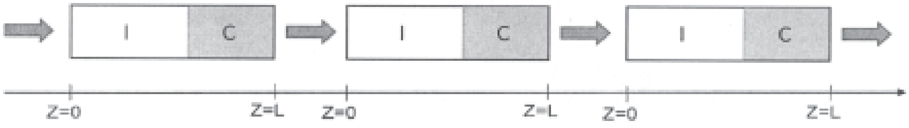

Fig. 2. Axial coordinate values in a succession of the inert and catalyst zones for a three bed network (I – inert; C- Catalyst)

Results and discussions

A network of three fixed beds having the characteristics given in table 1 was simulated by the numerical integration of the PDE system (1) to (4) as described above, dividing the axial coordinate of each bed into 200 intervals. Preliminary trials showed that the use of fewer intervals lead to significant integration errors. In figure 3 are shown the calculated evolutions of the gas and solid temperatures along the networks (reactor) beds, at various moments of operating time, starting with a uniform temperature of the solid. A first observation is that the differences between the temperatures of solid and gas are generally very small, the only significant differences appearing at the entrance of first (feeding) bed, during the incipient time interval, just after the start of gas feeding (fig. 3A).

Due to the difference between the solid and gas temperatures (the gas is fed at ambient temperature), the gas is heated by the contacted solid in the first bed. Consequently, an expanding cooled zone of solid develops in the vicinity of the feed point of the first bed, as result of gas preheating. Thus, the remaining high-temperature front of the solid is continuously moving in time, towards the outlet of the first bed. The velocity of temperature front migration depends on the gas feed rate and the ratio between specific heat capacities of the solid and gas phases.

Since the volume heat capacity of the solid is approximately three orders of magnitude higher than that of the gas, the temperature front velocity is much lower than the gas flow velocity along the bed. After the change of the gas feed point, the former feeding (first) bed becomes the last one, and an extending cold solid section appears similarly in the vicinity of the entry in the new feeding bed. On the other hand, the zone cooled in the previous stage (former first bed) is heated by the high temperature gas mixture coming from preceding beds (fig. 3A). From the thermal point of view, keeping a stable operation of the reactor requires to choose the time interval between two successive feed point shifts (the switching time) so that the high temperature front to overlap in a largest extent the catalytic zones, where the chemical process takes place. As the solid in the vicinity of bed entrance serves merely as heat reservoir than reaction catalyst, it is advantageous to be made of inert material. Due to the accumulation of heat in the solid phase, the maximum temperature rise in the solid bed at pseudo steady-state is greater than the adiabatic temperature increase and the conversion is almost complete. This explains the possibility of auto-thermal operation for gas mixtures with low VOCs concentration. From the figure 3B it can be seen that the chemical transformation occurs with significant rates only on the catalyst zones having the temperature higher than the level necessary to light-on the chemical transformation.

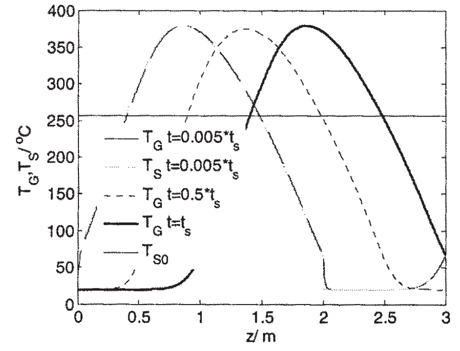

Fig. 3A. Gas and solid temperature

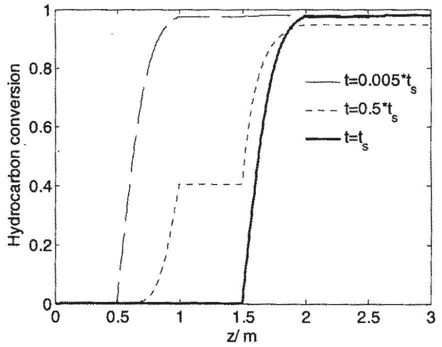

Fig. 3B. Time and space conversion evolutions during a stage (three beds network; pseudosteady state, t_s= 6100 s)

Pseudo steady state attainment

Simulation studies of the NFB operated in forced unsteady state by periodic change of feed point evidenced a narrow range of switching time guaranteeing the stabilization of a pseudo-steady state (stabilizing switching time). In the same time it was observed a strong dependence of the stabilization switching time interval on the number of the beds in the network. In figure 4 is presented the stabilization intervals for networks of two, three and four beds. In all three cases the total length of the bed is 3 m and the cumulated length of the catalyst zones is 1.5 m. The simulation results confirm the literature

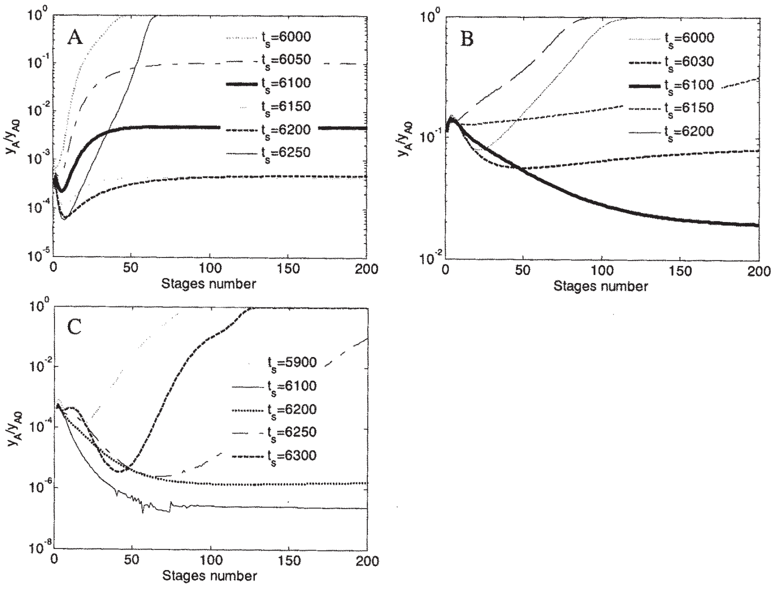

Fig. 4. Stabilization interval for a fixed beds network operated with periodical feed point change. A. Two beds network; B. Three beds network; C. Four beds network

Table 1
CATALYST AND INERT MATERIAL CHARACTERISTICS

Parameter	**Symbol**	**Value**
Catalyst and inert bulk density (kg m^{-3})	ρ_s	2220
Average diameter of the catalyst particle (m)	d_p	0.006
Thickness of the particle layer impregnated with Pt catalyst (m)	δ_c	0.0008
Solid pellet void fraction	ε	0.4
Specific solid-gas interface area of packing (m^2_{GS}/m^3_{bed})	a_v	$\frac{6(1-\varepsilon)}{d_p}$
Catalyst and inert thermal conductivity (J m^{-1} s^{-1} K^{-1})	λ_s	0.18
Catalyst and inert specific heat (J kg^{-1} K^{-1})	$c_{p,s}$	1000
Gaseous mixture feed temperature (°C)	T_0	20
Initial solid beds temperature (°C)	T_i	257
Feed molar fraction of reactant	Y_{A0}	0.0003
Pressure (bar)	p	1
Gaseous mixture superficial velocity (m s^{-1})	u_0	0.4
Reaction rate constant (mol $bar^{-1}s^{-1}$ kg^{-1})	k_0	$0.18 \cdot 10^5$
Activation energy (J mol^{-1})	E_A	57800
Reaction heat (kJ mol^{-1})	ΔH_{RA}	-1323
Gas specific heat (J kg^{-1} K^{-1})	$c_{p,G}$	1373

data stating that in a series of reactors operated with periodic change of the feed point, the stabilization interval decreases when the number of beds increases [24,25].

The identified stabilizing intervals were roughly 6050-6200 s for two beds, 6030-6150 s for three beds and 6100-6200 s for four beds networks. In the case of the irreversible combustion reaction investigated in this study, we found only one stabilization interval, corresponding to high values of switching time. Nevertheless, in an analysis of the methanol synthesis in a network of three fixed beds operated autothermally in forced unsteady state, Velardi and Baressi [5] identified two intervals of stabilizing switching times, one for low values (smaller than 20 s, and the other for higher values (between 160 and 205 s).

As in the case of RFR, the achievement of the pseudo steady state is conditioned by the equality between the total amount of heat discharged with the gas leaving the network and the total amount of heat released in the reaction, during a stage. If the total heat released in the reaction during a stage is less than the total heat discharged by the gas, the heat stored in the bed and consequently the average bed temperature decrease continuously from stage to stage, leading to a gradual time decrease of hydrocarbon conversion and finally the process extinction. In the analysis of pseudo-steady state stabilization and numerical integration accuracy, we used the heat balance per stage of network operation. The error in its accomplishment is expressed by the equation [26]:

$$e=\frac{Q_{CS}+Q_R-Q_P}{Q_{CS}+Q_R}100 \qquad (12)$$

where: Q_{cs} - the total heat transferred from the solid to the gas phase; Q_R - the amount of heat generated in combustion reaction; Q_p - the heat withdrawn from the network by gas phase (all reported to the switching time). In the working conditions, with the calculation method presented above, the stabilization of pseudosteady state was characterized by a heat balance error under 3% in all the runs.

Untransformed reactant emissions following feed point shifting

An inconveniency of the unsteady fixed bed operation with periodic feed point switches consists in small emission of untransformed reactant during short time intervals following the switching moments. At these moments, in the void spaces of the cooled feeding bed remains a small amount of gas containing untransformed reactant, as shown in figure 5 (curve corresponding to t=0). After the gas flow is restarted, this reactant stored in the void spaces will be displaced and contacted with the catalyst zone of the same bed, being partially transformed if the temperature of catalyst is sufficiently elevated, or, alternatively, not transformed. In the conditions analyzed in this work, as the feeding bed is fully cooled at the end of a stage, the transformation of the reactant stored in the voids of this bed does not occur, this being purged out from the system. The phenomenon can be observed in figure 5A, where it is shown the stored reactant migration towards the reactor exit, the entire amount being removed after approximately 3 s. This is a small disadvantage common also for the reverse flow operation of fixed beds. In the figure 4B is depicted the time variation of dimensionless hydrocarbon concentration at the outlet of the network. The time intervals corresponding to maximum hydrocarbon concentrations at network exit appear in this figure as isolated points, due to the tightness of the purging intervals. The time evolution of the hydrocarbon fraction at the outlet of the network presents an "U" shape, due to the removal of different amounts of hydrocarbon reacted inside the network, depending on the high-temperature front position.

Due to reactant purges appearing after feed point switches, it is advantageous to keep the switching time at maximum possible values. This is favoring also the conservation of the equipment (particularly the valves). Figure 6 shows that the maximum temperature achieved in the bed and the outlet reactant conversion are depending on the switching time, the dependence presenting a maximum. This is explained mainly by the extension of the overlapping region between the high temperature front

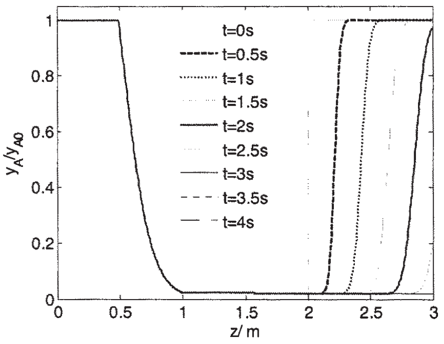

Fig. 5A. Hydrocarbon fraction along the networks beds at different moments of time

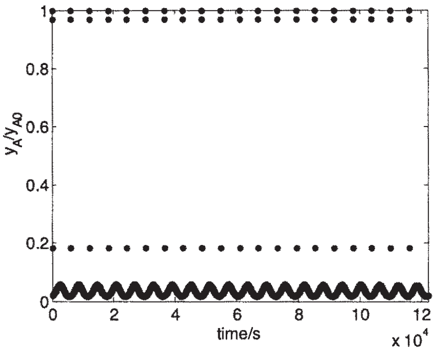

Fig. 5B. Hydrocarbon fraction at network exit after feed point shifting

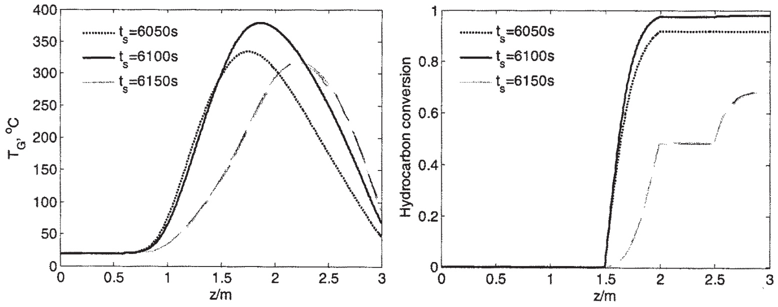

Fig. 6. Influence of the switching time on final gas temperature and hydrocarbon conversion profiles along the three beds network ($t=t_s$)

and the catalyst zones. From figure 6 it can be observed also that, in the working conditions, there is a trend of rising the gas temperature at the reactor outlet with the increase of switching time.

Working parameters influence on process performance

As known, the process operation in applications at commercial scale is affected by perturbations in input variables. In the case of residual gas treatment by catalytic combustion, the most important are the perturbations in feed composition and gas flow rate. The calculated effects of variations in these parameters are presented in figure 7 and 8. In figure 7 are presented the influences of a 10% variation in feed concentration, on temperature and concentration profiles along the beds network. As seen, increasing the feed concentration, the hydrocarbon conversion increases as well (fig. 7A), due to the increase of the bed temperature (fig. 7B), the system stability being conserved. However, when the feed concentration is decreased by 10%, the pseudo-steady state is no more achieved, the process being extinguished. This occurs because the amount of fed reactant is not sufficient to release the required quantity of heat in order to maintain the bed temperature profile at the necessary level. Note that in figure 7 are given the profiles after a switching time insuring the stabilization of the process at the nominal conditions (100 stages of 6100 s). Regarding the influence of gas flow rate, it was found that a variation of only 3% in the gas feed velocity (feed rate) in respect with the nominal value lead to process extinguishment and the pseudo-steady state cannot be achieved in absence of a control strategy, due to the high process sensitivity to this kind of perturbations.

In order to evaluate the influence of the initial solid beds temperature on the process behavior, there were calculated the influences of 10% variations around the nominal value. The results are evidencing that the initial temperature of the solid bed does not influence significantly the pseudo-steady state temperature and conversion profiles, providing that it is sufficiently high to insure the reaction start-up.

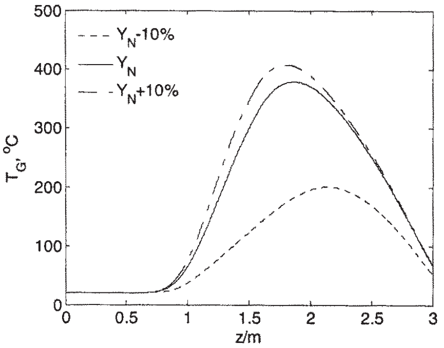

Fig. 7A. Dependence of the pseudosteady state temperature profile on the organic load in the network of three beds

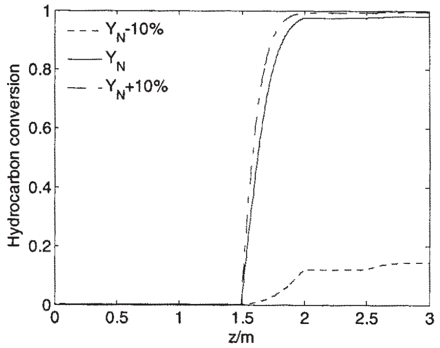

Fig. 7B. Dependence of the pseudosteady state conversion profile on the organic load in the network of three beds

Sensitivity analysis

Among the parameters involved in the process model used in this analysis, usually the highest uncertainty is specific for those describing the gas-solid mass and heat transfer kinetics, as well as those characterizing the heat and mass transport intensity by axial dispersion. Our calculations indicate that, among these parameters, the strongest influence have the heat transfer coefficient and the coefficient of heat transport in solid phase by axial conduction. In figures 8A and 8B are depicted the influences of a 10% variation in the two parameters on temperature profiles along the network beds. From figure 8A it can be seen that the effect of heat transfer coefficient

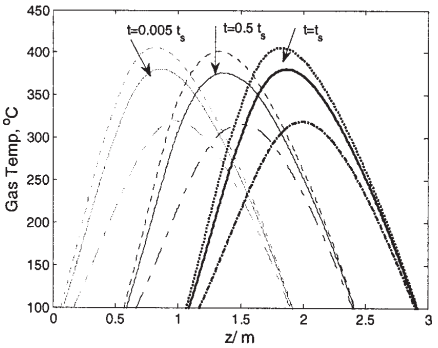

Fig. 8A. Temperature sensitivity with respect to gas-solid heat transfer coefficient (solid lines- nominal value; dashed lines-90% of nominal value; dotted line-110% of nominal value)

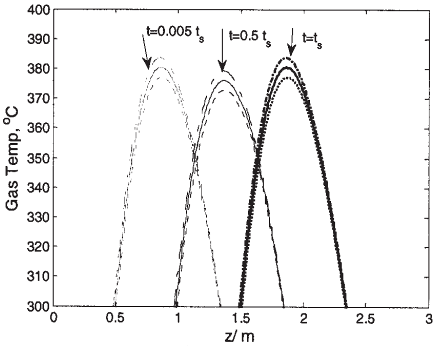

Fig. 8B. Temperature sensitivity with respect to axial heat conduction coefficient in solid phase (solid lines- nominal value; dashed lines-90% of nominal value)

on temperature along the bed is a positive one. By increasing the heat transfer coefficient there are improved both the gas heating on the first bed and the solid heating on the last bed of the reactor. Temperature profiles for variations of axial heat conduction coefficient in solid phase are shown in figure 8B. As observed, the sensitivity in respect with the axial heat conduction coefficient is lower than that in respect with solid-gas heat transfer coefficient. From these results it can be inferred that a 10% uncertainty in the value of the solid-gas heat transfer coefficient (which is a realistic hypothesis for values obtained from published correlations) leads to an uncertainty in the maximum of temperature along the beds of over 60°C. In the same time, an equivalent uncertainty of 10% in the value of axial heat conduction coefficient in solid phase has as consequence an uncertainty in the maximum temperature of approximately 4°C.

Similar evaluations for uncertainties of 5 % in the values of the two parameters indicated possible errors in the maximum temperature of roughly 14 and 2°C respectively. The influences of the other model parameters being much more lower, these will not be presented. This study is evidencing that the coefficients of heat and mass transport by axial dispersion in gas phase have a small influence on temperature and conversion evolutions and consequently, the corresponding mechanisms can be neglected in the design process models.

Conclusions

The operation of a series of catalytic reactors with periodical shift of the feed point is a technique that permits auto-thermal operation, even for very low feed concentration of reactant, a feature that makes it very attractive for gas cleaning by catalytic combustion. An important characteristic of these systems in practical applications is the duration between two successive feed point switches, insuring process stabilization in time. The results evidenced that, for a given set of working conditions, this duration can vary only in a narrow interval and this interval is unique for given operation conditions. The simulation results evidenced strong influences of the gas feed rate and feed composition on temperature and conversion profiles along the network. Also, it was found that the highest sensitivity of the temperature and VOCs conversion appear in respect with the gas-solid heat transfer coefficient and axial heat transport conduction in solid phase respectively. The errors in the calculation of temperature profile due to the uncertainties in the gas-solid heat transfer coefficient evaluation could be important. Our results shown that, a 10 % uncertainty in the value of gas-solid heat transfer coefficient corresponds to a variation in the maximum temperature of approximately 60°C.

Nomenclature

a_v – specific interfacial surface area (m^{-1});
C_{AS} – VOC concentration at external surface of catalyst pellet (kmol m^{-3});
c_p – specific heat (J kg^{-1}K^{-1});
C_t - molar density (total molar concentration) of the gas (kmol m^{-3});
Δ_L - mass transport coefficient by axial dispersion (m^2 s^{-1});
DH_{RA}- reaction enthalpy (J kmol^{-1});
k_G - gas-solid mass transfer coefficient (m s^{-1});
R –radius of the spherical catalyst pellet (m);
r_A- VOC combustion rate (kmol m^{-3}s^{-1});
$\overline{r}_A$ - average combustion rate in the catalyst pellet (kmol m^{-3}s^{-1});
T- temperature (K);
u – superficial velocity of the gas (m s^{-1});
ρ - density (kg m^{-3});
Y_A- molar fraction of hydrocarbon (-);

Greek letters

α - gas-solid heat transfer coefficient (J m^{-2}s^{-1}K^{-1});
ε - void fraction of the bed (-);
λ_{LG} –gas phase heat transport coefficient by axial dispersion (J m^{-1}s^{-1}K^{-1});
λ_{LS} – effective thermal conductivity of the packed bed (J m^{-1}s^{-1}K^{-1});
η_i – internal effectiveness factor.

Subscripts

cat- catalyst
G- gas phase;
S- solid phase.

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