Conversion enhancement of exothermic reversible reactions in unsteady-state ring reactor

Original
Conversion enhancement of exothermic reversible reactions in unsteady-state ring reactor / Fissore, Davide; Barresi, Antonello; Velardi, Salvatore; Vanni, Marco. - ELETTRONICO. - (2002), pp. paper #58/1-/8. (Intervento presentato al convegno 17th International Symposium on Chemical Reaction Engineering tenutosi a Hong Kong, China nel August 25-28).

Availability:
This version is available at: 11583/1522893 since: 2017-08-29T14:47:57Z

Publisher:
The Hong Kong University of Science and Technology

Published
DOI:

ISCRE 17

17th International Symposium on
Chemical Reaction Engineering

Chemical Reaction Engineering: Challenges and Opportunities in a Global Environment

August 25-28, 2002
Hong Kong Convention and Exhibition Centre
Hong Kong, China

Organized by
The Hong Kong University of Science and Technology

CONVERSION ENHANCEMENT OF EXOTHERMIC REACTIONS IN UNSTEADY-STATE RING REACTOR NETWORK

D. FISSORE, A.A. BARRESI, S. VELARDI AND M. VANNI

PAPER #0508

WEB EDITION: ***http://www.ceng.ust.hk/iscre17/manu/postpaper.asp***

Conversion Enhancement of Exothermic Reactions in Unsteady-state Ring Reactor Network

Davide FISSORE*, Antonello A. BARRESI, Salvatore VELARDI, Marco VANNI

Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino,
Corso Duca degli Abruzzi 24, 10129 Torino, Italy.

Keywords: combustion, chemical reactors, reaction engineering, moving bed, forced unsteady-state reactors, exothermic reversible reactions.

Abstract

The ring reactor network, which consists of a closed sequence of two or more catalytic fixed bed reactors, with periodical variation of the feed position, has been considered by means of numerical simulation. The methanol synthesis and the production of syngas have been simulated in order to demonstrate that the temperature profile of such a reactor can generally enhance the conversion for exothermic equilibrium-limited reactions of great industrial interest. The VOC combustion has also been simulated in order to point out the possibility of exploiting the thermal storage capacity of the catalyst, which can act as a regenerative heat exchanger.

1. Introduction

Forced unsteady-state catalytic reactors have received much attention in recent years, as concerns both industrial applications and scientific investigation and have been proposed both for endothermal and exothermal processes, for irreversible and equilibrium reactions. Increased conversion, improved selectivity, reduced catalyst deactivation and autothermal behaviour are the main goals of such a mode of reactor operation.

Dynamic operation can be obtained with a periodic reversal of the flow in the reactor; extensive investigations about the reverse-flow reactor, including both numerical simulations and experimental works, have been performed in the past twenty years and have been reviewed by Boreskov & Matros (1983) and Matros (1996). Two are the main advantages of this reactor configuration: first, the possibility of exploiting the thermal storage capacity of the catalyst bed, which acts as a regenerative heat exchanger, thus allowing, for example, auto-thermal behaviour when lean VOC mixtures are burnt; second, an approach toward optimum temperature distribution, which makes possible the creation of favourable thermodynamic conditions for exothermic equilibrium-limited reactions. Vanden Bussche et al. (1993) showed that the application of reverse flow operation to methanol synthesis can be economically attractive compared to steady state technology; nevertheless, reverse flow reactor presents the problem of wash-out, i.e. the drop in product concentration upon flow reversal, due to the removal of unconverted gas immediately after the change of the inlet section. De Groote & Froment (1996) and Gosiewski (1999, 2000) showed the feasibility of the synthesis gas production in a reverse-flow reactor, pointing out the influence of the main operative parameters on the methane conversion and product selectivity.

The reactor network has been recently investigated for lean VOC mixtures combustion (Brinkmann et al., 1999); autothermal behaviour with a nearly uniform catalyst exploitation due to the constant flow direction is an advantage of this configuration. The results suggest that the reactors network can be a suitable alternative to reverse-flow operation as it can reduce the emissions of unburned gas at every switch (Barresi & Vanni, 1999, 2002).

The aim of this work is to study the performance of this device from the point of view of the enhancement of the conversion of exothermic reversible reactions, as in the methanol synthesis and in the partial oxidation of methane to synthesis gas. These two reactions have been considered for their industrial interest, and because they are representative of different thermal behaviours: methanol synthesis is an example of exothermal process, while the overall process of syngas production is weakly exothermal, due to the simultaneous occurring of the high exothermal methane combustion and of the endothermal reforming reactions. The combustion of VOC mixtures has also been considered, pointing out the influence of the concentration on the stability of the reactor.

---

* Corresponding author. Tel. +39-011-5644695, Fax: +39-011-5644699, E-mail: fissore@athena.polito.it

2. The model

A one-dimensional heterogeneous model has been considered; pressure loss inside the network of reactors is neglected and adiabatic operation is considered. Plug flow condition is assumed for the gas phase with dispersive transport of mass and energy. The transient term is taken into account in the gas phase equations and in the energy equation for the solid phase, while the solid catalytic surface is considered in pseudo-steady state condition. Thus, the dynamics of the process can be described by the following set of algebraic-differential equations:

Continuity equation for the gas phase:

$$\frac{\partial c_g}{\partial t} + \frac{\partial}{\partial x} c_g u_g = \sum_{i=1}^{n_r} \frac{k_{g,i} a_v}{\varepsilon} (y_{s,i} - y_{g,i}) \tag{1}$$

Continuity equation for component *j* in the gas phase:

$$\frac{\partial y_{g,j}}{\partial t} = D_{eff} \frac{\partial^2 y_{g,j}}{\partial x^2} - u_g \frac{\partial y_{g,j}}{\partial x} + \frac{k_{g,j} a_v}{c_g \varepsilon} \left(y_{s,j} - y_{g,j} \right) - y_{g,j} \sum_{i=1}^{n_r} \frac{k_{g,i} a_v}{c_g \varepsilon} \left(y_{s,i} - y_{g,i} \right) \tag{2}$$

Energy balance for the gas phase:

$$\frac{\partial T_g}{\partial t} = \frac{k_{eff}}{\varrho c_{p,g}} \frac{\partial^2 T_g}{\partial x^2} - u_g \frac{\partial T_g}{\partial x} + \frac{h a_v}{\varrho c_{p,g} \varepsilon} (T_s - T_g) \tag{3}$$

Mass balance for the solid phase:

$$k_{g,j} a_v \left(y_{s,j} - y_{g,j} \right) = [\varrho_s (1 - \varepsilon)] \sum_{k=1}^{N_R} \nu_{j,k} R'_k \tag{4}$$

Energy balance for the solid phase:

$$\frac{\partial T_s}{\partial t} = \frac{\lambda_s}{\varrho_s c_{p,s}} \frac{\partial^2 T_s}{\partial x^2} - \frac{h a_v}{\varrho_s c_{p,s} (1 - \varepsilon)} (T_s - T_g) + \frac{1}{c_{p,s}} \sum_{i=1}^{n_r} \left(\sum_{k=1}^{N_R} \nu_{i,k} R'_k \right) (-\Delta \tilde{H}_{f,i}) \tag{5}$$

Further details about the model and the correlations used for the evaluation of transport coefficients and other parameters can be found elsewhere (van de Beld, 1995). Danckwerts' boundary conditions are assumed for the gas phase in each reactor and the continuity of gas temperature and concentration profiles is imposed between the reactors of the network. In the following we refer to *L* as to the total length of the network and to *l* as to the length of a single reactor of the sequence. The origin of the *x*-axis corresponds with the inlet section to the network; consequently it moves from the first reactor of the sequence to the second one when switching time is reached. At this time the boundary conditions are switched as well in order to simulate the variation of the inlet position.

The methane combustion has been simulated with the same kinetic model used by Barresi & Vanni (2002); for the methanol synthesis the kinetic model by Graaf, Stamhuis & Beenackers (1988) and for the partial oxidation of methane to synthesis gas the kinetic model by Gosiewski et al. (1999) have been used.

The PDE system (1)-(5) has been solved by discretising the domain of the spatial variable *x* thus obtaining a DAE system; for the algebraic part, given by the mass balances (4) for the solid phase, the non-linear equations solver HYBRID1 from FORTRAN package MINPACK has been used, while the routine LSODE from ODEPACK library has been implemented in order to solve the differential part of the system.

3. Results

3.1 *Methanol synthesis*

The reactor network may lead to obtain an optimum temperature distribution, which makes possible the creation of favourable thermodynamic conditions for exothermic equilibrium-limited reactions; as an example we have simulated the methanol synthesis in such a configuration, proving that in certain conditions the yield and selectivity of the process can be higher than in the reverse-flow operation and in the traditional multi-bed reactors with inter-refrigeration (the average carbon conversion is 58% against 30-40% of the other devices). The operating conditions are the same considered by Vanden Bussche et al. (1993) for the methanol synthesis in the reverse-flow reactor.

Figure 1 shows the influence of the switching time on the outlet conversion in the two and in the three reactors network for different inlet temperatures and constant total length. In the network of three reactors two relatively limited ranges of t_c exist in which the system can operate adiabatically; better performances compared to the high t_c range can be obtained at low t_c. This is related to the particular morphology of the temperature profiles along the reactors that are obtained for low t_c, as it is shown in Figure 2 (left hand side) for different t_c values. In the second and third reactor of the sequence the heat waves initially have a negative slope; so the results of the switching strategy is analogous to an intermediate cooling, which allows for a further increase of conversion by shifting the reaction far from equilibrium. For very low t_c (curve 1a and 2a) the cooling effect is small and it is vanished by the subsequent increase of temperature; for higher t_c values (curve 3a) the initial sections of the second and third beds show a deeper temperature drop which allows for a continuously increasing conversion inside the system.

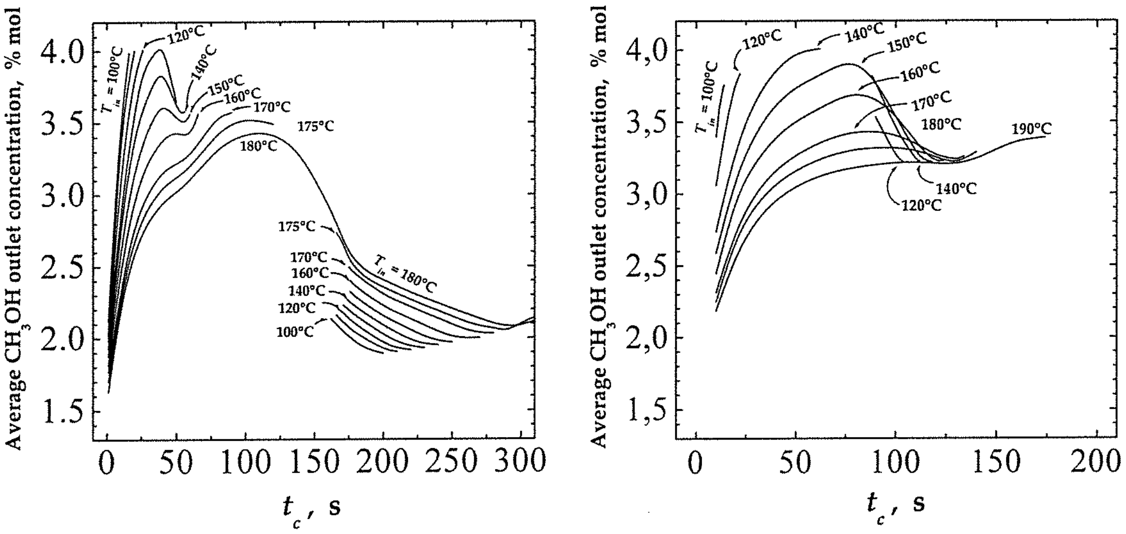

Figure 1. Influence of the switching time t_c on the average methanol outlet concentration in the network of three reactors (left graph) and in the network of two reactors (right graph), $v_g = 0.02$ m s^{-1}.

In the three reactors network, at high t_c, the average methanol concentration increases with the inlet temperature before a maximum is reached; by operating at low t_c the performances of the network become worse when increasing the inlet temperature because the effect of intermediate cooling is reduced and the temperature level of the catalytic bed is increased. The best choice of operating parameters corresponds to t_c = 40 s and T_{in} = 130 °C, when the temperature profile approximates the curve corresponding to the maximum methanol generation, as it is shown in Figure 2 (right hand side).

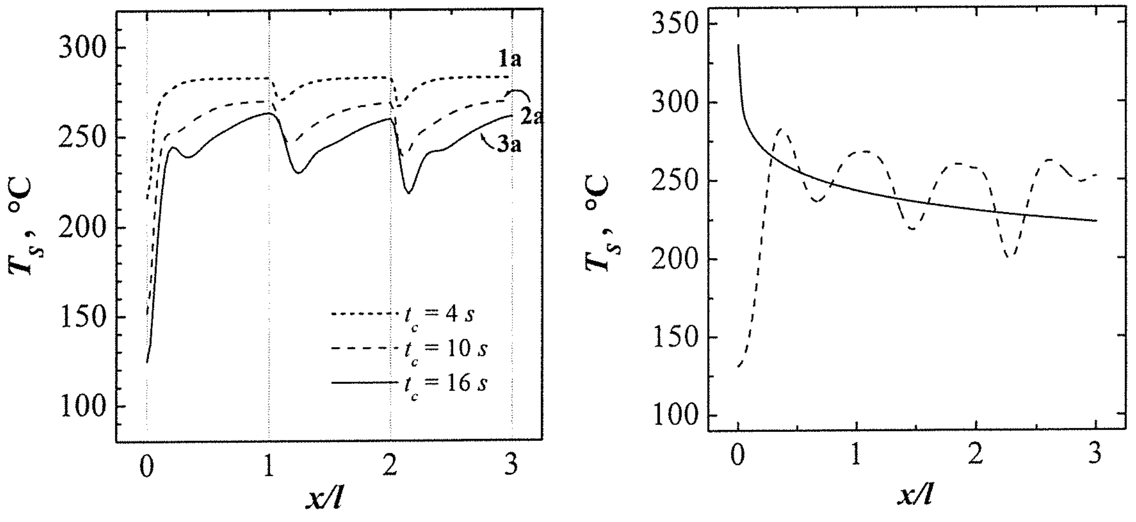

Figure 2. On the left: influence of the switching time t_c on the temperature profiles of the catalyst along the three reactors network. Low t_c operating range. Profiles taken at the end of the cycle. T_{in} = 100 °C, v_g = 0.02 m s^{-1}. On the right: comparison between the solid temperature profile in the case of maximum CH$_3$OH generation (continuous line) and in the optimal network configuration corresponding to t_c = 40 s and T_{in} = 130 °C (dashed line).

The behaviour of the network of two reactors is similar; also in this configuration there are two ranges of t_c in which the operation is stable and the influence of the switching time and of the inlet temperature on the performance of the system is similar, even if the CH_3OH conversion is slightly lower.

3.2 *Syngas production*

As the unsteady-state catalytic reactors seem to be the ideal solution for weakly exothermal processes, we have considered the feasibility of the production of synthesis gas by partial oxidation of methane (POM) in the ring reactor: despite the strongly exothermal methane combustion reaction, the whole process of the conversion of methane to synthesis gas is only weakly exothermal due to the simultaneous occurring of endothermal reactions:

$$CH_4 + 0.5O_2 \rightarrow 2H_2 + CO \qquad \Delta H_r = -21.8 \text{ kJ/mol}$$

This alternative mode of reactor operation may lead to lower manufacturing costs than the unidirectional fixed bed reactor, as external heat exchangers are no longer required: the cold feed is progressively heated by the pre-heated bed and, at a certain depth, the exothermic combustion reaction takes off, leading to a temperature rise in the bed; the maximum temperature of the catalyst that is obtained can lead to catalyst sintering or melting; as a consequence a large amount of steam is required in the feed to avoid excessive temperature increase. Methane is then reformed by carbon dioxide and water and finally the composition of the syngas is governed by the water-gas shift reaction. An example of the temperature profile which are established after the transient period is shown in Figure 3: after a transient, a cyclic-steady state is reached, in which the outlet gas average composition and temperature do not change any more; particularly important are the intermediate coolings in order to shift the syngas conversion towards higher values. The change of the feed position makes it possible to avoid any pre-heating of the inlet gases, as a consequence of the storage of the heat of reaction inside the bed. The influence of the switching time on the performance of the network of three reactors is shown in Figure 4; the results obtained in a reverse flow reactor with the same total length are shown for comparison. We can observe that the CH_4 conversion is almost complete and that high values of CO selectivity are obtained. Contrary to the behaviour of the rector network used for methanol synthesis, only one range of switching times that allow stable operation appears in this process; similar is the stability range of the reverse-flow reactor. At high t_c values the methane conversion and CO and CO_2 selectivity obtained are the same in the two devices and t_c slightly influences the

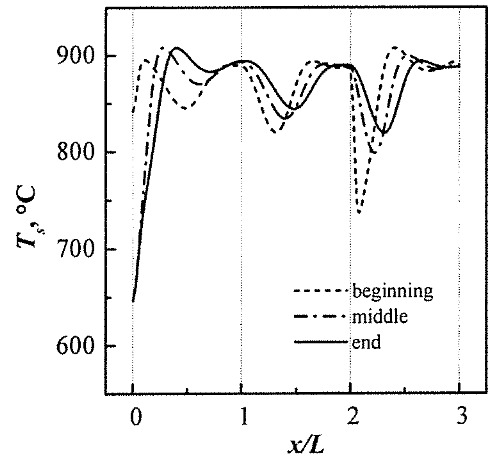

Figure 3. Temperature profile in the network of reactors for syngas production during the cycle, after the cyclic-steady state has been reached. $H_2O/CH_4 = 1.6$, $CH_4/O_2 = 2$, $t_c = 50$ s, $v_g = 0.25$ m s^{-1}.

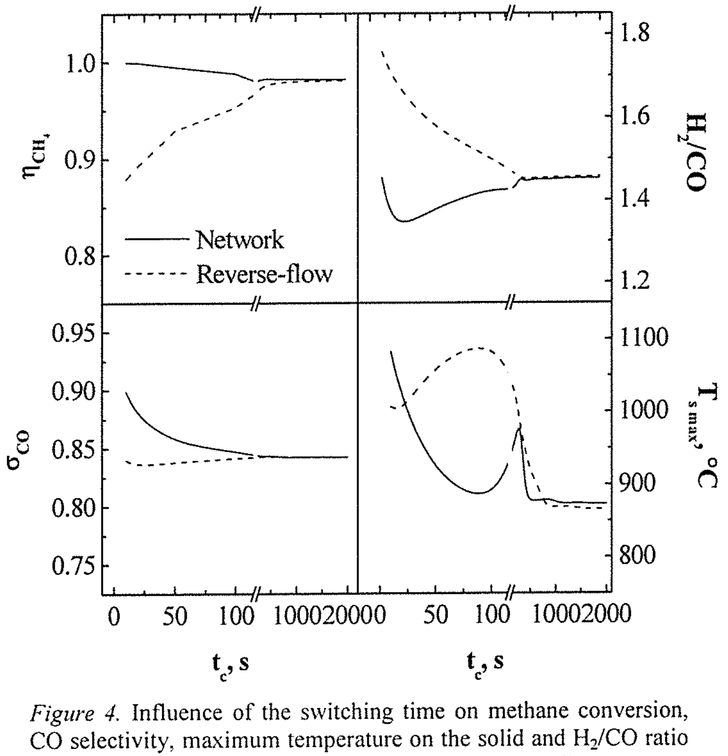

Figure 4. Influence of the switching time on methane conversion, CO selectivity, maximum temperature on the solid and H_2/CO ratio in the three reactors network and in the reverse-flow reactor. $H_2O/CH_4 = 1.6$, $CH_4/O_2 = 2$, $v_g = 0.25$ m s^{-1}.

performance, as a consequence of the lower influence of intermediate cooling; at low t_c the switching time has a stronger influence on conversion and selectivity values: the reactor network shows higher methane conversion and lower H_2/CO ratio and maximum temperature on the solid in comparison to the reverse-flow reactor.

The influence of the inlet gas velocity on the performance of the two devices is similar both for the ring reactor and for the reverse-flow reactor, as it is shown in Figure 5, except for the maximum temperature of the solid which is strongly increased in the reverse-flow reactor. The higher the inlet flow rate, the higher methane conversion and CO selectivity.

Finally the influence of the CH_4/O_2 ratio has been considered, both for the reverse-flow reactor and for the three reactors network. If we increase the CH_4/O_2 ratio methane conversion is reduced because of the lack of reactant; as a consequence of the smaller amount of heat generated by methane combustion, the maximum temperature of the solid decreases. The H_2/CO ratio is increased when we increase the CH_4/O_2 ratio because of the lowering of the CO selectivity.

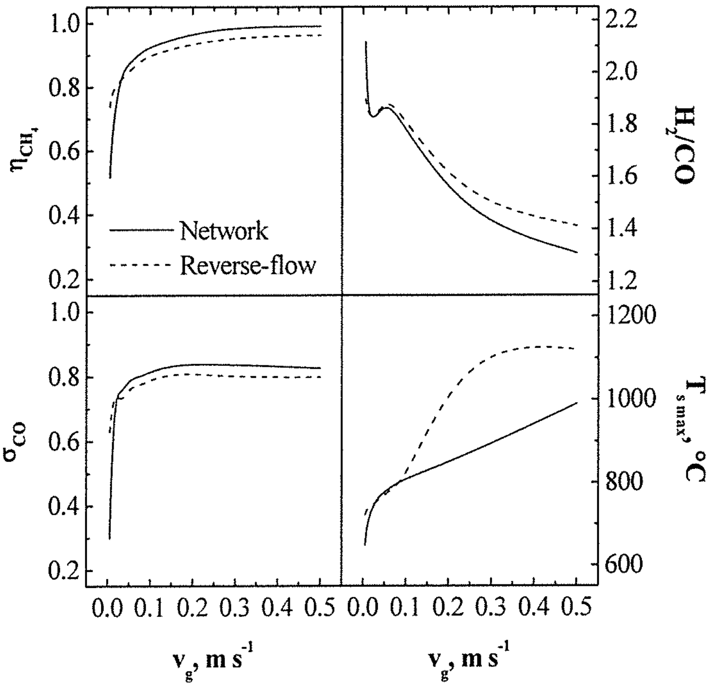

Figure 5. Influence of the inlet gas velocity on methane conversion, CO selectivity, maximum temperature on the solid and H_2/CO ratio in the three reactors network and in the reverse-flow reactor. $H_2O/CH_4 = 1.6$, $CH_4/O_2 = 2$, $t_c = 40$ s.

As it is evident from Figures 3-6 the H_2/CO ratio can be changed by varying the main operative parameters and can be tailored to the value required for processes such as the production of methanol, the Fischer-Tropsch synthesis or the oxosynthesis.

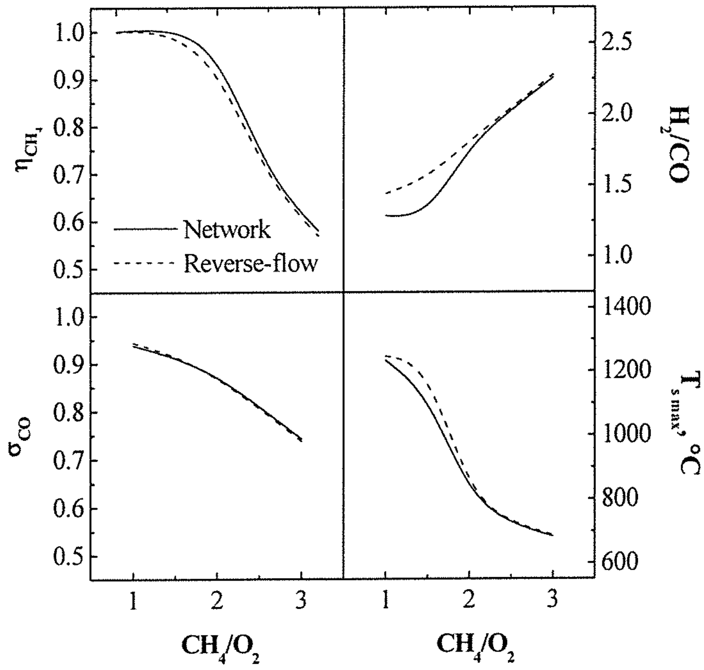

Figure 6. Influence of the CH_4/O_2 ratio on methane conversion, CO selectivity, maximum temperature on the solid and H_2/CO ratio in the three reactors network and in the reverse-flow reactor. $H_2O/CH_4 = 1.6$, $t_c = 40$ s, $v_g = 0.25$ m s^{-1}

3.3 *Network of unsteady state VOC combustors*

The heat storage effect has also been pointed out in the reactor network when lean VOC mixtures are burnt: the reactor network can operate autothermally without external pre-heating of the gases, but the bed must be pre-heated above the ignition temperature before start-up. Depending on the VOC load in the feed and on the switching time, either extinction or a state of periodical operation is reached (Barresi & Vanni, 2002). Rich VOC mixtures have been simulated in this work in order to investigate the influence of the organic load on the stability of the reactor network.

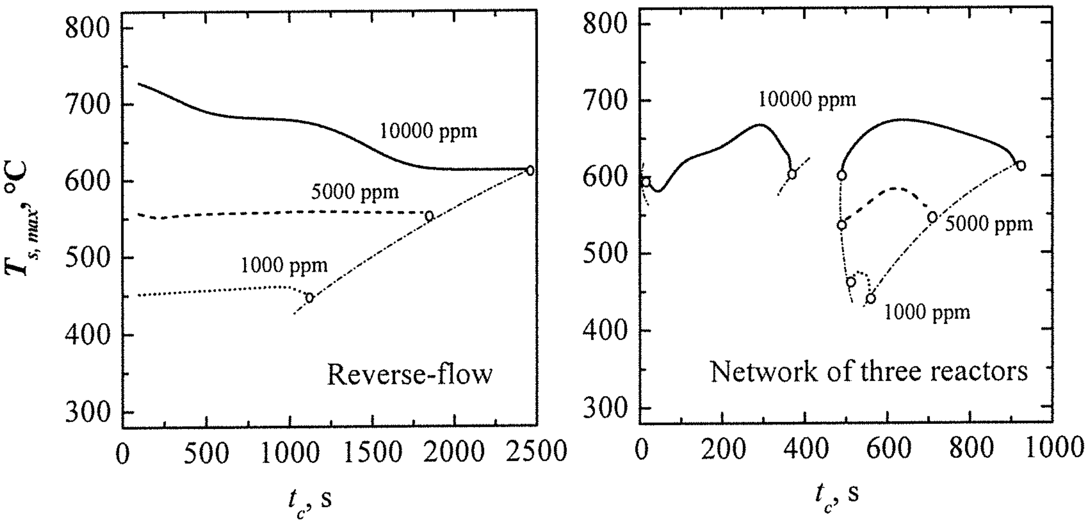

Figure 7. Comparison between the maximum temperature of the solid both for the reverse-flow reactor and for the network of three reactors for different inlet concentrations and switching times.
$v_g = 0.1$ m s^{-1}, $L = 0.3$ m, $\rho_s = 1000$ kg m^{-3}, $c_{p,s} = 1000$ J kg^{-1} K^{-1}.

Figure 7 shows the maximum temperature of the solid as a function of the switching time in a three reactor network; the results obtained in the reverse-flow reactor, with the same total length, are also shown for comparison. The circles in Figure 7 delimit the stability range: the stability behaviour of the network of reactors when VOC combustion and methanol synthesis take place are similar; complex dynamic behaviours may arise as a consequence of the change of the feed position. The reactor network has a narrower stability range than the reverse-flow reactor: the VOC conversion quickly decreases for values of t_c slightly lower or higher than those leading to autothermal behaviour; this because in the network of combustors the proper switching period is closely related to the velocity of the heat front: if the period is too long, the first section is cooled too much, and the gas do not reach the catalyst at the required temperature, while if it is too short, there is no time to accumulate enough heat in the second reactor before switching, and the system gradually extinguishes. In the case of the reverse-flow reactor stable operation is possible even for very low t_c values, while, if the cycle time is too high, the heat front is removed from the reactor and no autothermal operation can be obtained. Figure 7 also shows the effect of the switching period on the maximum temperature of the solid: t_c slightly influences the maximum temperature in the reverse-flow reactor, except for very high inlet concentration, where the higher the switching time, the lower the maximum temperature because the amount of heat which is kept inside the reactor decreases. If we increase the inlet concentration the maximum temperature increases both in the reverse-flow and in the reactor network because of the higher amount of heat generated; as a consequence, the range of switching time which makes stable operation possible is enlarged and in the case of the reactor network a second stability range appears at high inlet VOC concentration.

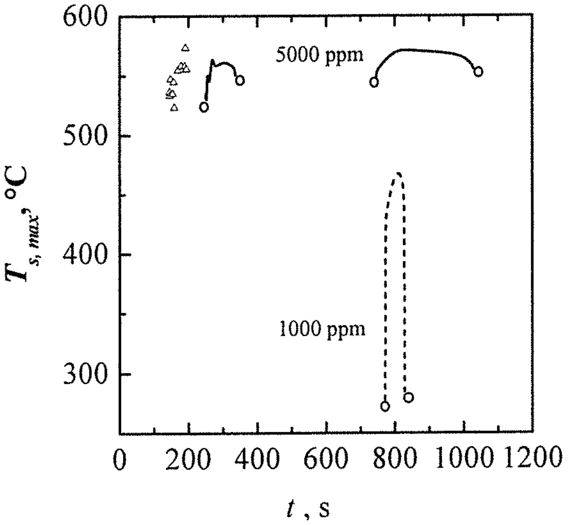

Figure 8. Maximum temperature of the solid in the network of two reactors for different inlet concentrations and switching times.

Figure 8 shows the analogous results for the network of two reactors: it appears that if we reduce the number of reactors, with constant total length, the stability limits become slightly wider. If we increase the organic load, a second stability window appears at 5000 ppm, while in the three reactors network a higher concentration is required to obtain this second stability window. Stable operation can be obtained for an inlet concentration of 5000 ppm also for low switching times: the triangles plotted in Figure 8 show some values of the maximum temperature that can be obtained in this region.

4. Conclusions

The reactor network with periodical variation of the feed position has been considered by means of numerical simulation. The methanol synthesis and the production of syngas have been simulated in order to demonstrate that the temperature distribution obtained in this reactor can enhance the conversion for exothermic equilibrium-limited reactions.

The results of the simulations have shown that higher values of yield and selectivity may be obtained in the reactor network in comparison to the reverse-flow reactor for both the process considered; in the case of syngas production not only higher values of methane conversion and product selectivity can be obtained, but the H_2/CO ratio can be changed by varying the main operating parameters and can be tailored to the value required for processes such as the production of methanol, the Fischer-Tropsch synthesis or the oxosynthesis.

Complex dynamic behaviour appear in the reactor network in the range of parameters of industrial interest when methanol synthesis is considered, while the behaviour of the device is similar to the reverse-flow reactor in the case of syngas production. The combustion of lean VOC mixtures has also been simulated for rich VOC mixtures, showing that also in this process the same complex behaviours may arise; it is a consequence of the strategy of changing of the feed position and not of the complex kinetic mechanism.

Notation

a_v	external particle surface area per unit volume of reactor, m^{-1}
c	molar concentration, mol m^{-3}
c_p	specific heat at constant pressure, J $kg^{-1}K^{-1}$
D_{eff}	effective mass dispersion coefficient, m^2s^{-1}
$\Delta\tilde{H}_f$	molar enthalpy of formation, J mol^{-1}
h	gas-solid heat transfer coefficient, J $m^{-2}K^{-1}s^{-1}$
k_{eff}	effective heat dispersion coefficient, J $m^{-1}K^{-1}s^{-1}$
k_g	gas-solid mass transfer coefficient, mol $m^{-2}s^{-1}$
L	total network length, m
l	single reactor length, m
N_R	number of reactions
n_r	number of components in the mixture
R'	reaction rate, mol $s^{-1}kg^{-1}$
T	temperature, K
t	time coordinate, s
t_c	switching time, s
u	interstitial velocity, m s^{-1}
v	surface velocity, m s^{-1}
x	axial reactor coordinate, m
y	molar fraction

Greeks

ε	void fraction of the catalytic bed
η	conversion
λ	thermal conductivity of the bed, J $m^{-1}K^{-1}s^{-1}$
$\nu_{\varphi\kappa}$	stoichiometric coefficient of component *j* in reaction *k*
ρ	density, kg m^{-3}
σ	selectivity

Subscripts and superscripts

g	gas phase
s	solid phase or solid surface
in	inlet value

References

Barresi, A. A., Vanni, M., Brinkmann, M. & Baldi G. (1999). Control of an autothermal network of nonstationary catalytic reactors. AIChE Journal, 45(7), 1597-1602.

Barresi, A.A., & Vanni, M. (2002). Dynamics and control of forced unsteady-state catalytic combustors, in "Nonlinear dynamics and control in process engineering – Recent advances" (G. Continillo, S. Crescitelli & M. Giona, Eds.). Springer Verlag, pp 73-88.

Boreskov, G. C. & Matros, Y. S. (1983). Unsteady-state performance of heterogeneous catalytic reactions. Catalysis Reviews-Science and Engineering, 25(4), 551-590.

Brinkmann, M., Barresi, A.A., Vanni, M., & Baldi, G. (1999). Unsteady state treatment of very lean waste gases in a network of catalytic burners. Catalysis Today, 47(1-4), 263-277.

De Groote, A. M. & Froment, G. F. (1996). Synthesis gas production from natural gas in a fixed bed reactor with reversed flow. Canadian Journal of Chemical Engineering, 74, 735-742.

Graaf, G.H., Stamhuis, E.J., & Beenackers, A.A.C.M. (1988). Kinetics of low-pressure methanol synthesis. Chemical Engineering Science, 43(12), 3185-3195.

Gosiewski, K., Bartmann, U., Moszczynski, M., & Mleczko, L. (1999). Effect of the intraparticle mass transport limitation on temperature profiles and catalytic performance of the reverse-flow reactor for the partial oxidation of methane to synthesis gas. Chemical Engineering Science, 54(20), 4589-4602.

Gosiewski, K. (2000). Mathematical simulations of reactors for catalytic conversion of methane to syngas with forced concentration cycling. Chemical Engineering and Processing, 39, 459-469.

Matros, Y. S. (1996). Forced unsteady-state processes in heterogeneous catalytic reactors. Canadian Journal of Chemical Engineering, 74, 566-579.

van de Beld, L. (1995). Air purification by catalytic oxidation in an adiabatic packed bed reactor with periodic flow reversal. Ph.D. thesis, University of Twente, Enschede, the Netherlands.

Vanden Bussche, K.M., Neophytides, S.N., Zolotarskii, I.A., & Froment, G.F. (1993). Modelling and simulation of the reversed flow operation of a fixed-bed reactor for methanol synthesis. Chemical Engineering Science, 48(19), 3335-3345.